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DR-0492-8

DOE/FC/10157-1600
(DE84016077)

MEASUREMENT AND PREDICTION OF AROMATIC SOLUTE
DISTRIBUTION COEFFICIENTS FOR AQUEOUS-ORGANIC
SOLVENT SYSTEMS

Final Report

By
James R. Campbell
Richard G. Luthy

June 1984
Date Revised

Work Performed Under Contract No. AC18-80FC10157

For
Morgantown Energy Technology Center
Grand Forks, North Dakota

By
Carnegie-Mellon University
Pittsburgh, Pennsylvania

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Richard G. Luthy

Submitted December 1983
(Revised June 1984)

Work Performed Under Contract No. DE18-80FC10157-79

Prepared for
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ABSTRACT

Experimental and modeling activities were performed to assess techniques for measurement and prediction of distribution coefficients for aromatic solutes between water and immiscible organic solvents. Experiments were performed to measure distribution coefficients in both clean water and wastewater systems, and to assess treatment of a wastewater by solvent extraction. The theoretical portions of this investigation were directed towards development of techniques for prediction of solute-solvent/water distribution coefficients.

Experiments were performed to assess treatment of a phenolic-laden coal conversion wastewater by solvent extraction. The results showed that solvent extraction for recovery of phenolic material offered several wastewater processing advantages including: elimination of the need for dilution prior to biological treatment, provision for lower final effluent organic loading in comparison with non-solvent extracted wastewater, and removal of most identifiable non-phenolic wastewater organic components including those associated with the suspended phase.

Distribution coefficients were measured in clean water and wastewater systems for aromatic solutes of varying functionality (e.g. phenol, naphthalene, naphthol, pyridine, and aniline) with different solvent types (e.g. diisopropyl ether, methylisobutyl ketone, n-butyl acetate, and toluene). It was found that distribution coefficients for these compounds in clean water systems were not statistically different from distribution coefficients determined in a complex coal conversion process wastewater.

These and other aromatic solute distribution coefficient data were employed for evaluation of modeling techniques for prediction of solute-solvent/water distribution coefficients. Eight solvents were selected in order to represent various chemical classes: toluene and benzene (aromatics), hexane and heptane (alkanes), n-octanol (alcohols), n-butyl acetate (esters), diisopropyl ether (ethers), and methylisobutyl ketone (ketones). The aromatic solutes included: nonpolar compounds such as benzene, toluene and naphthalene, phenolic compounds such as phenol, cresol and catechol, nitrogenous aromatics such as aniline, pyridine and aminonaphthalene, and other aromatic solutes such as naphthol, quinolinol and halogenated compounds.

It was shown that a regular solution theory model was appropriate only for systems which did not include hydrogen bonding. This restricted the utility of the regular solution approach, as the experimental data with polar aromatic solutes

demonstrated that hydrogen bond formation was the dominant chemical interaction governing successful partitioning between water and solvent for the systems considered in this investigation. It was demonstrated that linear free energy relationships offered an acceptable method for predicting distribution coefficients by correlation with a reference solvent/water system (e.g. octanol/water). The procedure was appropriate for comparison of compatible hydrogen bonding solute-solvent/water systems. However, the approach was limited because estimation of distribution coefficients for particular solute-solvent pairs required a correlation based on data for similar solutes and that particular solvent.

Solute distribution coefficients were estimated by a group contribution technique (UNIFAC model) using interaction parameters derived from both a vapor-liquid equilibria data base and a liquid-liquid equilibria data base. The prediction was performed for situations in which both solvent phase and aqueous phase activity coefficients were estimated, and cases where an estimate of the solvent phase activity coefficient was taken with an experimental value of the aqueous phase activity coefficient. It was demonstrated that distribution coefficients could, in many cases, be estimated within a factor of two by use of experimental values of the aqueous phase activity coefficient with the solvent phase activity coefficient calculated by use of the vapor-liquid equilibria data base. This degree of accuracy was considered reasonable in recognition that distribution coefficients for the range of solvents and solutes considered in this investigation varied over approximately six orders of magnitude. The technique was shown to be useful for solvent screening purposes as well as for evaluating the relative partitioning of various compounds between water and a given solvent. The methodology was considered to be utilitarian in view of the availability of experimental values of aqueous phase activity coefficients for aromatic solutes. The UNIFAC approach is applicable to many solute-solvent systems, however, group interaction parameters are not available for certain functional groups. In these situations the linear free energy approach is recommended.

The results of this study are useful for evaluation of solvent extraction systems for industrial wastewater treatment. The results are also useful for assessing the fate of contaminants in the environment by estimation of various physical and chemical properties which may be correlated with distribution coefficients. The methodology lends itself towards developing improved procedures for prediction of Henry's Law constants, soil adsorption coefficients, and solubility of hydrophobic solutes in miscible water/solvent mixtures.

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Chapter 1

SOLVENT EXTRACTION AND DISTRIBUTION COEFFICIENTS

1.1. Introduction

This report presents the findings of an investigation which examined techniques for measurement and prediction of distribution coefficients for aromatic solutes. Environmental engineers are interested in solute-solvent distribution coefficients for design and evaluation of solvent extraction systems for wastewater treatment as well as for assessing the fate of contaminants in the environment.

The aromatic solutes of interest in this study include those commonly found in wastewaters from coal gasification and liquefaction facilities, coke and iron manufacturing plants, and petrochemical and petroleum refining operations. These aromatic compounds include: non-polar solutes such as benzene, toluene, and naphthalene; phenolic molecules such as phenol, cresol, and catechol; nitrogenous aromatics such as aniline, pyridine, and aminonaphthalene; and other aromatic solutes representing different types of functionality such as naphthol, quinolinol and halogenated compounds. The solvents employed in this investigation were chosen in order to represent various chemical classes: toluene and benzene (aromatics); hexane, heptane, and tetradecane (alkanes); octanol (alcohols); n-butyl acetate (esters); diisopropyl ether (ethers) and methylisobutyl ketone (ketones). Selection of each particular solvent was guided by the desire to evaluate solvents which are used commercially for extraction of aromatic solutes from wastewaters, and for which sufficient data were available for modeling purposes.

This investigation does not attempt to justify the inclusion of a solvent extraction process in a particular wastewater treatment train; nor does this report evaluate the economics of solvent extraction. Rather, the information presented here serves as an aid to engineers and designers who are concerned with evaluation of wastewater treatment alternatives or who are concerned with predicting the fate of aromatic solutes during solvent extraction processing. However, information presented in Chapter Six of this report shows that treatment of phenolic wastewaters by solvent extraction offers various advantages. With respect to treatment of coal gasification and liquefaction process wastewaters these advantages are qualitatively summarized below (Campbell et al., 1981):

1. Solvent extraction removes most base and neutral fraction solutes. This is significant because many of the toxic or hazardous organic contaminants in coal conversion wastewaters are found in these fractions.
2. Recovered material may be combusted and used as an energy source to drive the extraction process. Properly designed combusters would destroy hazardous organic compounds. Alternatively, recovered material may be processed to provide chemical by-products.
3. Removal of hazardous organic contaminants by solvent extraction would reduce or eliminate problems with disposal of hazardous organic sludges formed as a result of wastewater treatment and reuse.
4. Solvent extraction would reduce or eliminate problems with carry over of volatile aromatics during sour water treatment.
5. Solvent extraction removes creosotes, thus it is likely that most "tar acids" would be removed. This may be particularly important in treatment of coal liquefaction wastewater where it is believed that tar acids must be removed prior to biological oxidation (Drummond et al., 1981).
6. Solvent extraction can eliminate the need for dilution prior to biological oxidation. Various studies have shown that dilution may be required for biological treatment of heavily contaminated gasification or liquefaction process condensates (Luthy, 1981; Drummond et al., 1981). Work performed as part of this investigation has shown that dilution was not necessary when treating solvent extracted coal gasification condensate.
7. Pretreatment by solvent extraction results in lower mass loading of residual organic material (i.e. TOC, COD, and color) in treated

wastewater following biological oxidation. Since solvent extraction can eliminate the need for dilution water as well as result in lower loadings of residual organics, it should benefit any additional treatment required prior to wastewater reuse or discharge.

In recent years researchers have shown that distribution coefficients are also useful for providing correlations with various physical and chemical properties of aromatic compounds. Noteworthy among these activities are correlations with octanol-water partition coefficients (K_{ow}) for calculating environmental parameters such as: bioaccumulation, sorption on soil, and volatilization to the atmosphere from soil or water (Arbuckle, 1983; Lyman et al., 1982, Hansch and Leo, 1979; Mackay and Patterson, 1981 and 1982). Hence, activities aimed at measurement and prediction of distribution coefficients are of interest to both the environmental engineering and environmental science communities.

1.2. The Solvent Extraction Process

Solvent extraction as applied to wastewater treatment involves the selective removal of organic pollutants from water by contact with an immiscible liquid solvent. Figure 1-1 (Earhart et al., 1977) shows that a typical solvent extraction system involves three basic unit operations. The first is the the extractor where water and organic solvent are mixed and separated in order that solute molecules (pollutants) can be removed from the aqueous phase. The second operation involves solvent regeneration where contaminated solvent is purified for recycle to the extractor. The third operation involves recovery of residual dissolved solvent from the wastewater. This step is important because solvent losses increase the operating costs of the extraction process and because residual solvent may also be considered as a pollutant.

Solvent recovery is normally accomplished by steam or vacuum stripping, although recovery by secondary solvent extraction may be used. Solvent regeneration may be accomplished by distillation, evaporation or secondary solvent extraction (Kiezyk and Mackay, 1971; Earhart et al., 1977). Extractors may

be classified as either stage contactors such as mixer-settlers, or as differential contact extractors such as rotary disk contactors. The latter type are most commonly used for wastewater treatment (Perry and Chilton, 1973, section 21). Extraction equipment and design procedures are described by Treybal (1963) and by Perry and Chilton (1973).

A critical element in the design of solvent extraction systems is selection of the appropriate solvent (Kiezyk and Mackay, 1971; Treybal, 1963; Perry and Chilton, 1973). This decision is influenced by several solvent properties which include: high solute distribution coefficient, low aqueous solubility, and various physical properties which influence extraction efficiency and ease of solvent recovery and regeneration (Treybal, 1980). While solvent physical properties and aqueous solubilities are available for most solvents, solute distribution coefficients are not commonly available. Hence, distribution coefficients must often be measured experimentally or estimated from thermodynamic considerations or empirical correlations.

It is apparent that solute distribution coefficients are most accurately obtained by experimental measurement. However, this task can become quite costly and time consuming as there are literally thousands of solvents and solvent mixtures from which to choose. Hence, it is advantageous to estimate solute distribution coefficients for solvent selection or solvent screening purposes. The remainder of this report addresses issues which are important to measurement and prediction of distribution coefficients for aromatic solutes.

1.3. The Distribution Coefficient

When an aqueous solution is mixed with an immiscible solvent and allowed to come to equilibrium, the solutes contained in the water distribute themselves in relation to their solubilities in the two solvents. For low to moderate solute concentrations, the widely accepted definition of the distribution coefficient is (Sawyer and McCarty, 1978; Abrams and Prausnitz, 1975a; Kiezyk and Mackay, 1971; Leo et al., 1971),

Figure 1-1: Schematic of a Typical Solvent Extraction System with a Volatile Solvent

Source: Earhart et al., 1977

$$K_D = C_s / C_w \quad (1-1)$$

where C_s and C_w refer to the solute concentration (mg/l or mol/l) in the organic solvent and water phases, respectively. Since concentrations are expressed on a unit volume basis the value of K_D is independent of the ratio of solvent volume (v_s) to water volume (v_w). However, in determining the distribution of a given mass of solute between the solvent and water phases, the relative phase volumes must be specified. For example, in laboratory experiments in which clean solvent is used to extract solute from water, the distribution coefficient may be calculated as:

$$K_D = \frac{(C_o - C_f) v_w}{C_f v_s} \quad (1-2)$$

where C_o is the initial concentration of solute in water prior to contact with solvent and C_f is the concentration of solute in water after extraction. The fraction of solute remaining in the water phase after successive extractions with equal volumes of clean solvent is

$$C_f / C_o = [v_w / (K_D v_s + v_w)]^n \quad (1-3)$$

where n is the number of successive extractions with clean solvent (Sawyer and McCarty, 1978; Treybal, 1963).

The distribution coefficient may also be defined on a thermodynamic basis by recognizing that at equilibrium the solute chemical potential must be equal in each phase,

$$\mu_s = \mu_w \quad (1-4)$$

where the subscript s and w refer to the solvent and aqueous phases, respectively.

This relationship may also be expressed in terms of fugacities (Prausnitz, 1969; Kiezyk and Mackay; 1973, Atkins, 1978),

$$f_s = f_w \quad (1-5)$$

The fugacity in turn can be expressed as (Prausnitz, 1969; Kiezyk and Mackay, 1973),

$$f_s = x_s \gamma_s f_r = x_w \gamma_w f_r = f_w \quad (1-6)$$

where x is the solute mole fraction, γ is the associated mole fraction activity coefficient, and f_r is the standard state fugacity. By taking the standard state to be a liquid of pure solute (Raoult's Law convention for activity coefficients), the equilibrium condition may be expressed as,

$$x_s \gamma_s^* = x_w \gamma_w^* \quad (1-7)$$

where γ^* are the activity coefficients in the solvent and water phase at equilibrium. These activity coefficients (γ^*) are not necessarily equal to those in the pure solvents (γ). At equilibrium, each solvent phase may dissolve a sufficient amount of the other solvent to affect changes in the chemical nature of that phase (Chiou et al., 1982).

In order to obtain the distribution coefficient in terms of activity coefficients we make the assumption that as infinite dilution is approached each solute mole fraction is equal to the product of the solute molar concentration (C) and the equilibrium molar volume (V^*) of each phase (Cratin, 1968),

$$x = C V^* \quad (\text{mol/l}) (\text{l/mol}) \quad (1-8)$$

substituting equations (1-7) and (1-8) into equation (1-1) and rearranging, the thermodynamic expression for the distribution coefficient is obtained (Chiou et al., 1982).

$$K_D = C_s / C_w = (\gamma_w^{*,\infty} / \gamma_s^{*,\infty}) (V_w^* / V_s^*) \quad (1-9)$$

where γ^{∞} values refer to infinite dilution mole fraction activity coefficients.

For water-solvent systems which are slightly miscible, pure component properties are not necessarily equal to equilibrium properties (Leo and Hansch,

1971). Banerjee et al., (1980) and Chiou et al., (1982) have addressed the effect of mutual phase saturation on activity coefficients and suggest that it is an important consideration only when the solutes of interest are very insoluble in water. Banerjee et al., (1980) found no measurable difference between solute behavior in octanol-saturated water and distilled water for the following compounds, with the indicated mole fraction aqueous solubilities (x_w): 1,2-dichlorobenzene ($x_w = 1.8 \times 10^{-5}$); 1,2,3,5-tetrachlorobenzene ($x_w = 3.4 \times 10^{-7}$); and a pesticide called RDX ($x_w = 4.8 \times 10^{-6}$). Chiou et al., (1982) found a measurable difference in the behavior of hexachlorobenzene ($x_w = 4.9 \times 10^{-8}$) and DDT ($x_w = 3.3 \times 10^{-9}$). Hence, it appears that mutual phase saturation becomes an important consideration for solutes with mole fraction solubilities less than about 10^{-7} . The solutes of interest in this study all have mole fraction aqueous solubilities greater than 10^{-6} (Tsonopoulos and Prausnitz, 1971). The effect of mutual phase saturation on solvent molar volume appears to have little influence as it is commonly ignored (Mackay and Patterson, 1981; Mackay, 1977, Arbuckle, 1983; Abrams and Prausnitz, 1975a). Furthermore, experimentally determined partial molar volumes and mutual phase saturated activity coefficients are not easily found nor are these effects easily accounted for by modeling techniques. Hence, mutual phase saturation effects were not considered in this investigation. We should note, however, that mutual phase saturation may become an important consideration if we are interested in single and double ring aromatic solutes with multiple hydrophobic substitutions (e.g. hexachlorobenzene) or in condensed polycyclic aromatic hydrocarbons other than naphthalene and its derivatives (e.g. anthracene, pyrene, chrysene), or solvent systems which are miscible to a greater degree. These restrictions are not particularly significant for solvent extraction treatment of wastewaters in that process design is typically dictated by recovery of the more soluble solutes. Furthermore, highly miscible solvents are not generally used for wastewater treatment because of the increased problems related to high levels of residual solvent in the treated wastewater and difficulty with solvent recovery.

In the discussion which follows, experimentally measured distribution

coefficients refer to equation (1-1) and K_D values which are estimated by thermodynamic modeling techniques utilize the widely accepted definition of K_D expressed in terms of infinite dilution solute mole fraction activity coefficients (γ^∞) and pure solvent molar volumes (V) (Arbuckle, 1983; Chiou et al., 1982; Mackay, 1977; Leo et al., 1971),

$$K_D = (\gamma_w^\infty / \gamma_s^\infty) (V_w / V_s) \quad (1-10)$$

Infinite dilution solute mole fraction activity coefficients can range from greater than zero to infinity and represent deviations of the system from ideality. Activity coefficients which are greater than one refer to systems with positive deviations from ideal behavior. Physically this refers to segregated systems where solvent and solute molecules prefer to interact with molecules of their own kind (Atkins, 1978; Prausnitz, 1969). Activity coefficients which are less than one refer to systems with negative deviations from ideal behavior. Physically this refers to integrated systems where solute and solvent molecules prefer to interact with molecules of the other component. Hydrogen bonded solute-solvent pairs are a good example of systems which show negative deviations from ideality (Atkins, 1978; Prausnitz, 1969; Pimentel and McClellan, 1960).

1.4. Overview

This introduction has defined the meaning and significance of the solute distribution coefficient. The remaining chapters of this report address issues important to experimental measurement and model estimation of K_D values. Chapter Two presents a qualitative review of the molecular interactions which are important to solute partitioning between aqueous and organic phases. This review is not intended to provide a detailed, quantified description of molecular interactions, rather its purpose is to introduce several concepts which will be used to help explain the experimental observations of Chapter Three and to help understand the fundamental assumptions and applicability of the distribution coefficient models described in Chapters Four and Five. In Chapter Six we will

discuss the results of two treatability studies which were conducted to evaluate solvent extraction processing of coal gasification wastewater. The results from the treatability studies provided motivation for studying techniques for measurement and prediction of aromatic solute distribution coefficients.

Chapter 2

MOLECULAR FORCES OF ATTRACTION

2.1. Introduction

In a typical solvent extraction system solute mass is partitioned between two immiscible liquid phases. This division, or phase equilibria, is governed by the relative magnitude of the intermolecular energy of attraction occurring between the solute and each solvent phase. As the attractive energy between solute and solvent molecules increases there is a greater tendency for the solute to concentrate in that phase (Karger et al., 1973). It follows, then, that interpretation of experimental solvent extraction data and assessment of distribution coefficient models will be facilitated by an understanding of the predominant features of molecular interactions important to fluid phase equilibria.

The following discussion will consider molecular forces of attraction as being of two types, physical or chemical. Physical, or van der Waals, forces occur between all molecular types and may be further divided into three categories: electrostatic, dispersion and induction. Dispersion forces exist between any adjacent pair of atoms or molecules. The attraction between a non-polar and a polar molecule results from both dispersion and induction energies. When two polar molecules come into contact in solution all three physical forces are important (Hirschfelder et al., 1954).

Chemical forces occur when the electron clouds of adjacent molecules overlap, hence these forces are the very nature of chemical bonding. The discussion of chemical forces in this chapter will be confined to the weakest

and most commonly encountered chemical effect in solution, hydrogen bonding. It will be shown that hydrogen bond interactions include electrostatic and dispersion energy contributions; although because of the close approach of the molecules involved in hydrogen bonding these energies do not follow the traditional van der Waals expressions. Because hydrogen bonding includes both "physical" and "chemical" terms it is a very dominant solution effect. As shown in Chapter Three, the formation of a hydrogen bond between a solute-solvent pair can change the value of the distribution coefficient by an order of magnitude or more.

It should be noted that accurate estimates of interaction energies are restricted to very few physical systems. Therefore, the discussion that follows serves to illustrate the parameters and mechanisms that control molecular interactions and phase equilibria rather than to provide a rigorous quantified description of these forces. The information presented in this discussion will be used qualitatively in Chapters Three, Four, and Five to aid interpretation of experimentally determined solute distribution coefficients and to provide a framework for assessing distribution coefficient models which estimate solute activity coefficients from molecular interactions.

2.2. Electrostatic Forces

Electrostatic interactions that are important in nonelectrolyte solutions result from permanently uneven spatial distribution of electrons around the nuclei of polar molecules. This uneven distribution of electrons causes different areas of the molecule to have equal and opposite charges, with the overall molecular charge remaining neutral. The number of such charge concentrations and the distance between them causes electric moments (e.g. dipoles) to be formed (Prausnitz, 1969; Hirschfelder et al., 1954; Rowlinson, 1969).

The potential energy arising from contact between two molecules with permanent dipoles may be obtained by considering the coulombic forces acting

between the dipoles. This energy is dependent upon the distance separating the molecules and on the relative orientations of the dipoles (Prausnitz, 1969). For a given value of molecular separation there are relative orientations for which the potential energy is a maximum or a minimum, and from a statistical viewpoint the molecules spend more time in those orientations for which the potential energy is small (Hirschfelder et al., 1959). However, this preferred orientation is disrupted by thermal agitation. As the temperature of the system increases, the orientation becomes more and more random until at very high temperatures the attractive potential energy averages to zero (Atkins, 1978).

The average electrostatic potential energy (PE_e , kcal/mole) occurring between two dipoles 1 and 2, at a fixed separation in a gas, can be found by averaging over all orientations using a Boltzman distribution (Atkins, 1978):

$$PE_e = -[(2 u_1^2 u_2^2)/(48(\pi E_o)^2 r^6 kT)] \quad (2-1)$$

where: u = dipole moment expressed in Debye (10^{-18} esu-cm)

k = Boltzman constant (kcal/ $^{\circ}$ K)

t = absolute temperature ($^{\circ}$ K)

r = separation distance (cm)

E_o = vacuum permittivity (esu²/kcal-cm)

Equation (2-1) shows the significant factors which affect dipole-dipole interactions: the dipole moment of molecules 1 and 2, the temperature, and the inverse of the sixth power of separation distance.

Equation (2-1) is not a rigorous representation of dipolar attraction in liquids because the orientation of molecules in liquids are dependent upon molecular shapes and do not strictly follow the Boltzman distribution of dipole orientations derived for gases (Karger et al., 1973; Hildebrand and Scott, 1950). For the liquid case it has been suggested that PE_e is proportional to $u_1 u_2$ rather than the square of this quantity (Karger et al., 1973). In addition, single polar

groups of adjacent molecules are in such close proximity in liquids that the molecules tend to interact via individual bond dipoles (Karger et al., 1973 and 1976). Hence, the overall dipole moment is not always a useful measure of the tendency of a molecule to interact with other polar molecules (Karger et al., 1973; Hildebrand and Scott, 1950). One should also consider molecular size and shape and location of the polar groups within molecules (Hildebrand and Scott, 1950).

As an example of the magnitude of electrostatic energies, the attractive potential between two molecules at 3 nm separation (as in a liquid) and having dipole moments of 1 Debye is about 0.3 kcal/mole, for dipole moments of 2 Debye the energy increases to 1.3 kcal/mole (Atkins, 1978). Tables of experimental dipole moments found in McClellan (1963) show that most aromatic molecules have dipole moments in the range of 0-2 Debyes.

2.3. Dispersion Forces

London was the first researcher to understand the "nonpolar" attractive potentials acting between two molecules. He surmised that if an instantaneous photograph of a molecule A were taken it would show that, at any given instant, the electrons are pulled slightly in one direction while the nucleus is pulled in the opposite direction, causing a temporary dipole moment. This instantaneous dipole moment then induces a dipole in an adjacent molecule B. The induced dipole in B then interacts with the instantaneous dipole in A to produce an energy of attraction between the two. Although the magnitude and direction of the dipole moment in molecule A changes very rapidly, the induced dipole in B follows it so that the attractive energy does not average to zero (Hirschfelder et al., 1954; Atkins, 1978).

Dispersion forces act between all neighboring molecules or atoms. However, the description of these forces depends upon the nature of the molecules involved. If the force field surrounding the molecule is symmetric, the energy of dispersion is independent of orientation and proportional to the

inverse sixth power of separation distance. For asymmetric molecules the dispersion energy is dependent upon the relative orientation of the two molecules. In addition, as two asymmetric molecules come into closer contact the dispersion energy becomes proportional to a higher power of separation distance (Hirschfelder et al., 1954).

London derived the dispersive potential energy of attraction (PE_d , kcal/mole) between two simple, spherically symmetric gaseous molecules 1 and 2 as (Atkins, 1978):

$$PE_d = -3/2 (\alpha_1 \alpha_2 / r^6) [(I_1 I_2) / (I_1 + I_2)] \quad (2-2)$$

where: α = polarizability (cm^3)

I = ionization potential (kcal/mole)

r = separation distance (cm)

This shows that dispersion forces, unlike electrostatic interactions, are independent of temperature. Even though the molecules rotate more rapidly at higher temperatures the induced dipole still lies in the direction of the field inducing it, therefore PE_d is not averaged to zero by thermal motion (Atkins, 1978). Equation (2-2) also shows that dispersive forces are dependent upon the first ionization potential and the polarizability, being more sensitive to the latter (Prausnitz, 1969; Karger et al., 1973).

The first ionization potential may be defined as the work required to remove one electron from an uncharged molecule (Prausnitz, 1969). Ionization potentials and interatomic distances do not vary greatly among organic compounds, therefore a reasonable approximation is (Karger et al., 1973):

$$I_1 + I_2 = 2 (I_1 I_2)^{0.5} \quad (2-3)$$

and

$$r = r_1 + r_2 = 2(r_1 r_2)^{0.5} \quad (2-4)$$

Substitution of equations (2-3) and (2-4) into (2-2) yields

$$PE_d = -3/8 [(I_1 \alpha_1 / r_1^6)^{0.5} (I_2 \alpha_2 / r_2^6)^{0.5}] \quad (2-5)$$

Equation (2-5) shows that the dispersive potential energy of interaction between two molecules 1 and 2 is equal to the geometric mean of the interaction potential of the separate pairs 11 and 22 (Karger et al., 1973). The significance of geometric mean interaction energies will be discussed when the concept of regular solutions is examined in Chapters Four and Five.

The other molecular property which influences the dispersive attraction between two molecules is polarizability. Polarizability is defined as the ease with which the electrons of a molecule can be displaced by an electric field. Small molecules with few electrons generally have low polarizabilities. Larger molecules have less control over the electrons and generally have higher polarizabilities (Atkins, 1978).

The orientational dependence of dispersion forces results from the polarizability of an individual bond being different in the parallel and perpendicular directions. Because the polarizability of a molecule is the sum of the polarizabilities of its bonds, measured values of molecular polarizability may differ for the x, y and z directions. For perfectly symmetric molecules (e.g. carbon tetrachloride) the differences in parallel and perpendicular bond polarizabilities cancel, leaving the overall molecule without a directional dependence. However, when the molecule is asymmetric (e.g. as for many aromatic compounds), there is no overall cancellation and the molecule has a polarizability that is dependent upon the orientation of the applied field (Hirschfelder et al., 1954).

As an example of the magnitude of dispersion forces, the attractive energy between two methane molecules at 3 nm separation is about 1.1 kcal/mole (Atkins, 1978). Tables of experimentally determined ionization potentials and polarizabilities may be found in Landolt-Bornstein (1951) pages 359 to 368 and 510 to 513, respectively.

2.4. Induction Forces

Induction forces result from the interaction of the electric field produced by a polar molecule A and the polarizability of another molecule B, which may or may not be polar. The permanent dipole present in A induces a dipole in B which then interacts with the polarity of A to produce an attractive force. If molecule B also has a permanent dipole then it induces an electric moment in A which adds to the attractive energy. The magnitude of the inductive energy is small when compared to the potential energy due to electrostatic and dispersion forces (Prausnitz, 1965). Hence, solutions of nonpolar molecules with polar molecules having dipole moments of 1 Debye or less can often be described with neglect of induction forces (Hildebrand and Scott, 1950).

The average inductive potential energy (PE_i) between two molecules 1 and 2 was first calculated by Debye and is usually associated with his name. For polar molecules, in the gas phase, the general Debye formula is (Atkins, 1978):

$$PE_i = -(u_1^2 \alpha_2 + u_2^2 \alpha_1) / (2 \pi \epsilon_0 r^6) \quad (2-6)$$

where: u = dipole moment expressed in Debye (10^{-18} esu-cm)

α = polarizability (cm^3)

r = separation distance (cm)

ϵ_0 = vacuum permittivity ($\text{esu}^2/\text{kcal-cm}$)

Equation (2-6) shows that inductive forces are independent of temperature and are inversely proportional to the sixth power of separation distance. It should also be noted that for asymmetric molecules the magnitude of the inductive energy is dependent on the relative orientation of the two molecules due to the directional properties of molecular polarizability.

As an example of the magnitude of induction forces, the attractive energy at 3 nm between benzene and a polar molecule with a dipole moment of 1 Debye is about 0.2 kcal/mole (Atkins, 1978).

2.5. Comparison of Physical Attractive Forces

The strength of the combined van der Waals attractive forces lies in the range of 2 to 10 kcal/mole (Vinogradov and Linnell, 1971). Some comments on their relative importance may be derived from Prausnitz (1969).

1. The contribution due to inductive forces is small, even for strongly polar molecules
2. Dispersion forces dominate the attractive potential for nonpolar and slightly polar molecules.
3. Polar forces do not become important until the dipole moment of the molecules is greater than about 1 Debye unit.
4. While dipole-dipole interactions dominate the attractive potential for very polar molecules, the dispersive attraction between those compounds is not negligible.

2.6. Hydrogen Bonding

2.6.1. Definition of the Hydrogen Bond

While there is no universally accepted definition of the hydrogen bond (H-bond), there are certain criteria which can help to identify its existence and understand its significance. H-bond interactions involve two functional groups in the same or different molecules. One group serves as a proton donor, an acidic group termed A-H, and the other as proton acceptor, a basic group B. An H-bond is generally shown schematically as A-H---B. Pimentel and McClellan (1960) suggest that an H-bond exists between the groups A-H and B when: (a) there is evidence of bond formation (association), and (b) there is evidence that the association between the two groups specifically involves the hydrogen atom already bonded to A. It is specifically criterion (b) that differentiates the H-bond from other types of associative interaction (Pimentel and McClellan, 1960). It is interesting to note that both A and B are electronegative groups, most commonly O, N, S, C or halogen atoms. The difference is that the A group is already chemically bonded to hydrogen while the lone electron pair of B just shares the single hydrogen proton. The pi-electron orbitals of unsaturated

molecules can also serve as a proton acceptor. Hence, in general terms, an H-bond can be characterized as a proton shared by two lone electron pairs.

Theory and experiment have shown some additional phenomena which help to characterize H-bonding (Vinogradov and Linnell, 1971; Schuster, 1976):

1. Formation of an H-bond causes A---B bond length contraction. The molecules forming H-bonds come closer together than the sum of their van der Waals radii. Therefore, the electron distributions of the molecules overlap.
2. As a consequence of the close approach of the electronegative atoms A and B, the length of the A-H bond is somewhat increased. The A-H bond is thereby weakened but not broken. Breaking this bond would result in an acid-base reaction with proton transfer. The properties of the acceptor group are also affected.
3. Electron densities at the protons involved in H-bonds are decreased.
4. H-bonding increases the polarity of the molecules involved. The dipole moment of an H-bonded complex is larger than the vectorial sum of the monomer moments.

As a chemical entity, the H-bond resembles both chemical bonding and physical interactions. H-bonds lead to the formation of molecular aggregates which in many respects conform to the criteria of chemical bonds, especially covalent bonds. However, H-bonds differ from chemical bonds in that H-bonded systems exist in a state of dynamic equilibrium where many H-bonds are being formed and broken at any one instant. This dynamic character is not present at normal temperatures in systems with the usual chemical bonds: covalent, ionic and metallic. This difference is borne out by the disparity of the bond strengths; ordinary chemical bonds have strengths on the order of 50-200 kcal/mole while normal H-bond energies vary from 2 to 10 kcal/mole (Pimentel and McClellan, 1960 and Vinogradov and Linnell, 1971):

H-bond energy is derived from several contributions which include electrostatic and dispersive terms, hence formation of an H-bond encompasses the physical attractive energies. However, because an H-bonded complex involves a greater degree of molecular orientation and a closer approach of molecular centers, the contributions due to electrostatic and dispersive energies

do not strictly follow the form of the equations (2-1) and (2-2) (Coulson, 1959 and Bratoz, 1967). In addition, formation of an H-bond normally evolves heat while physical attractive forces cause a small amount of heat to be absorbed (Prausnitz, 1969).

2.6.2. Hydrogen Bond Models

Attempts at modeling the strength and geometry of H-bond interactions are faced with the problem that H-bonding is a complicated superposition of several interactive energies (Schuster, 1976):

1. electrostatic energy
2. charge transfer energy (covalent contribution)
3. repulsive energy
4. dispersive energy

A straight forward application of simple models to describe each of these energy components is not strictly correct. The electrostatic component is not directly correlated with dipole moments (Coulson, 1959 and Bratoz, 1967). The atoms in question are much too close together for the customary analysis of dispersion forces to apply (Coulson, 1959). The charge transfer energy involved in H-bonding differs from traditional charge transfer in that as the H-bond gets stronger the amount of charge transfer does not increase as it does in normal charge transfer complexes (Kollman and Allen, 1972). Hence, H-bond energies can not be described by simple expressions as was the case for the physical intermolecular forces. Accurate descriptions of H-bond energy can be computed from sophisticated techniques based on molecular orbital theory or perturbation techniques. Description of even the simplest of these methods is, however, beyond the scope of this discussion; the interested reader is referred to the reviews of Bratoz (1967), Kollman and Allen (1972), Joesten and Schaad (1974) and Schuster (1976). For the purpose of this study, it is more useful to understand what groups can form H-bonds in order that experimental distribution coefficient data and partitioning models can be interpreted.

2.6.3. Classification of Donor and Acceptor Molecules

Following the notation of Pimentel and McClellan (1960) one can refer to proton acceptors as B-type molecules and proton donors as A-type molecules. Molecules that possess both donor and acceptor functional groups are termed AB-type, and compounds exhibiting poor or no hydrogen bonding characteristics are classified as N-type. Hence, H-bonding can occur when A- and B-type, A- and AB-type, B- and AB-type or AB-and AB-type molecules are mixed together. H-bonding does not occur between solute and solvent molecules when two B-type or two A-type molecules are mixed together, or when one or both components are N-type.

This scheme is complicated somewhat by the behavior of AB-type molecules. These compounds can self-associate to form dimers, trimers, etc. or form H-bonds within a single molecule. The latter is termed intramolecular H-bonding. Intramolecular H-bonded compounds are of particular interest because they may not behave like AB species; despite their having both acidic and basic groups, they tend to behave as N- or B-class molecules (Pimentel and McClellan, 1960). The self-associating tendency of AB-class molecules, both polymer and intramolecular types, may be disrupted when these molecules are mixed with a strong donor or acceptor molecule. In this case, H-bonding between the two different molecules can occur and displace the self-associated H-bond. Table 2-1 lists typical molecules which fit each classification.

2.7. Summary

The preceding discussion has provided a brief review of four intermolecular attractive forces that are important to partitioning systems. Physical intermolecular forces, including electrostatic, dispersion and induction energies, show a dependence on the reciprocal sixth power of separation distance and can be described by considering the physical properties of the separate molecules. Hydrogen bond interactions are more difficult to describe and must be evaluated for each separate molecular pair.

While H-bond and physical forces are of approximately equal interaction energy, being in the range of 2 to 10 kcal/mole, it will be shown that H-bond forces have a more dominant effect on partitioning systems of interest in this study. It will be shown that formation of an H-bond between a particular solute and an organic solvent can increase the distribution coefficient for that solute by an order of magnitude over the K_D value for a non-hydrogen bonded solute-organic solvent system.

Table 2-1: Classification of Molecular Hydrogen Bond Types ⁽¹⁾

<u>Type</u>	<u>Description</u>	<u>Examples</u>
A	molecules with one or more proton donor groups (acids) and no acceptor groups	haloforms, highly halogenated compounds, oximes, acetylenes
B	molecules with one or more proton acceptor groups (bases) and no donor groups	ketones, ethers, esters, olefins, aromatics, tertiary amines, pyridines, aldehydes, amides, nitriles, isonitriles
AB	molecules with both donor and acceptor groups	alcohols, water, phenols, inorganic and carboxylic acids, primary and secondary amines
N	molecules with neither donor nor acceptor groups	saturated hydrocarbons, carbon tetrachloride, carbon disulfide

1) Data Source: Pimentel and McClellan (1960).

Chapter 3

EXPERIMENTAL MEASUREMENT OF DISTRIBUTION COEFFICIENTS

3.1. Introduction

The experimental portion of this study included measurement of distribution coefficients for several aromatic solutes which are common to condensate wastewaters formed during the production of synthetic fuels in coal liquefaction and low-temperature coal gasification. It has been shown that phenol and its derivatives, including cresols and xylenols comprise the largest mass fraction of organic material in condensate water from low-temperature gasification processes. Dihydric phenols, hydantoins, nitrogenous aromatics and derivatives of naphthalene have also been identified (Mohr and King, 1982; Luthy et al., 1983, and Stamoudis and Luthy, 1980).

This chapter describes techniques used for measurement of distribution coefficients for phenolic, naphthalenic, and nitrogenous organic solutes between water and several organic solvents. In these studies phenol and naphthol were selected as representative acid-fraction solutes. Aniline and pyridine were chosen as representative nitrogen-containing aromatic solutes. The interest in nitrogen aromatics is also motivated by a report that aminopolynuclear aromatics were identified as the most mutagenic fraction in a variety of synthetic fuel wastewaters (Guerin et al., 1980). Naphthalene was selected as a representative neutral fraction aromatic hydrocarbon solute. Five solvents were used in these tests, methylisobutyl ketone (MIBK), diisopropylether (DIPE), n-butyl acetate (NBA), toluene, and tetradecane. These compounds are representative of major classes of organic solvents: ketones, ethers, esters, aromatic hydrocarbons and alkanes, respectively. MIBK is reportedly used in a

licensed phenol extraction process (Greminger and King, 1979), while DIPE is employed in the Lurgi Phenol-Solvan process. NBA shows a relatively high distribution coefficient for phenol, and it has been proposed for use in dual-solvent extraction systems (Earhart et al., 1977). Toluene is a component of coal-derived light oil, which was widely used at one time for extraction of phenolics from coke plant ammonia liquor. Tetradecane was included in this study because it simulates the nature of crude oil and related compounds which are sometimes used in petroleum refining operations for extraction of phenol from water or for washing phenol from refinery products. Solvent extraction tests were performed with these solvents and solutes in single and multiple solute clean water systems, as well as in actual wastewater to investigate potential synergistic/antagonistic effects due to H-bond formation between solutes.

An analysis of the H-bonding character of these molecules according to the classification scheme presented in Chapter Two gives the following: phenol, naphthol and aniline are AB-type solutes while pyridine, MIBK, NBA and DIPE are B-type molecules. Naphthalene and toluene show weak proton acceptor characteristics (B-type) because they are unsaturated molecules. The saturated character of the C-H bonds of tetradecane classifies it as N-type.

With the above classification scheme, one would expect that phenol, naphthol and aniline should be able to form stronger hydrogen bonds with the solvents NBA, MIBK and DIPE, weaker H-bonds with toluene, and no H-bonds with tetradecane. Pyridine and naphthalene are not expected to form H-bonds of significant strength with any of those solvents. Antagonistic/synergistic solute effects may occur as a result of H-bond formation between pyridine, phenol, naphthol or aniline. The AB-character of phenol, aniline and naphthol can also lead to self association. The formation of hydrogen bonds between these compounds and water can also have an effect on the value of the distribution coefficient. Because water displays strong AB-type character, formation of strong H-bonds could be expected with phenol, aniline, naphthol

and pyridine. The poor H-bonding character of naphthalene does not allow for formation of strong H-bonds with water.

3.2. Materials and Methods

3.2.1. Reagents and Glassware

All reagents were of ACS certified or technical grade and were used without further purification. To ensure against contamination, all glassware was cleaned with acid, rinsed with acetone, rinsed twice with distilled water and heated to dryness in an oven. All clean water samples were buffered with 0.1N sodium bicarbonate to pH 8.4; thus, pH was not a variable in these experiments. The pH condition was chosen because wastewaters from some coal gasification processes have been shown to have pH values in this range (Luthy, 1981).

A raw coal gasification condensate water was obtained from the slagging fixed-bed gasifier at the Grand Forks Energy Technology Center during steady state operation (run RA-92) with lignite coal. To prevent sample degradation, the wastewater was stored in a freezer or refrigerator in full containers in the absence of oxygen. Prior to use in extraction experiments the wastewater was vacuum filtered through 0.45 μm glass fiber filters to remove residual emulsified tar and particulates. This wastewater was buffered at pH 8.3 by high levels of dissolved ammonia and carbon dioxide, thus pH conditions were similar in both wastewater and clean water extraction tests.

The magnitude of K_D is reduced for ionizable solutes as pH approaches $\text{p}K_a$ for the solute. Greminger et al., (1982) discuss the effect of pH on the extraction of phenolics from water. They have shown that the relation between pH and K_D for phenolics is given by

$$K_D(\text{ionized}) = K_D / ((K_a / [\text{H}^+]) + 1) \quad (3-1)$$

where K_D is the distribution coefficient for the unionized solute and K_a is the acidic dissociation constant. For phenol ($\text{p}K_a = 9.98$) the value of K_D is lowered by about 2% at pH 8.3, which is within the experimental accuracy of these tests.

3.2.2. Extraction Experiments

Distribution coefficients for aniline, pyridine, and phenol were determined by batch extraction at ambient laboratory temperatures ($23^{\circ}\text{C} \pm 2^{\circ}\text{C}$) using glass separatory funnels. Duplicate tests were performed at solvent-to-water ratios of 0.2, 0.4, 0.6, 0.8 and 1.0. Water and solvent were mixed by conducting 50 sample inversions in approximately 90 seconds. This was followed by 30 minutes of separation after which the aqueous phase was placed in a tapered volumetric flask for further analysis. It was found in initial screening studies that the sample inversion and separation procedure provided sufficient contact time for equilibrium. Other workers (Leo et al., 1971) have also reported equilibrium to be achieved rapidly when extracting solutes from water to solvent.

Because naphthalene and naphthol have lower aqueous solubilities, a different technique was used to determine distribution coefficients for these solutes. Batch extractions were conducted in specially constructed Erlenmeyer flasks at ambient laboratory temperatures in the absence of light with no head space. The flasks were fitted with septum ports at the base in order that aqueous phase samples could be withdrawn for HPLC analysis. Teflon lined screw caps were fitted to the top of the flasks to prevent loss of solvent and solute by volatilization. Different quantities of naphthalene or naphthol (1 to 15 grams) were dissolved in 250 ml of solvent and then added to 800 ml of buffered distilled water in the extraction flasks. The solutions were then mixed on a magnetic stirrer for 24 hours, as screening tests had shown that 24 hours were required for equilibrium to be achieved under conditions in which solute was extracted from solvent to water. This was followed by 90 minutes of separation after which an aqueous sample was withdrawn with a microliter syringe for immediate analysis.

3.2.3. Analysis

Aqueous samples of aniline, phenol, and pyridine were analyzed on a temperature programmable Varian 3700 gas chromatograph equipped with a flame ionization detector. Aniline and pyridine analyses were performed with a glass column (1.8m x 2 mm i.d.) packed with a silicone phase on a support deactivated for basic compounds (Supelco, Cat. No. 1-1896). Phenol was analyzed on a Tenax-GC glass column (1.8 m x 2 mm, Supelco, 1-3671).

Naphthalene and naphthol determinations were accomplished with a Perkin-Elmer Series 3 high pressure liquid chromatograph using a constant flow gradient pumping system with acetonitrile and water, and a reverse phase column (Supelcosil LC-PAH, 4.6 mm x 250 mm). Quantification was accomplished with a fluorescence detector set at an excitation wavelength of 280 nm and an emission wave length of 340 nm.

3.3. Experimental Results

3.3.1. Single Solute Systems

Initial tests were conducted with single-solute, clean water solutions of aniline or pyridine using each of the five solvents and with naphthalene and naphthol using DIPE, MIBK and NRA. Approximately one hundred and seventy individual experiments were performed to determine single solute, clean water distribution coefficients. These were followed by additional tests to assess the effect of solute concentration on K_D for selected systems, as well as tests to compare single solute, clean water values of K_D with those observed in multiple solute, wastewater systems. Table 3-1 summarizes the results of the single solute, clean water tests for the systems considered. Each reported value of K_D for aniline and pyridine represents the mean of twelve experimental values, K_D values for naphthalene and naphthol are the average of from eight to twelve determinations. Standard deviation (S.D.), relative standard deviation (R.S.D., %) and, range (lowest-highest experimental value) are also included in Table 3-1.

Table 3-1: Distribution Coefficients for Single Solute Systems

Solute	Solvent	K_D (mg/l/mg/l)*		RANGE
		MEAN	S.D.	
ANILINE	DIPE	7.6 ± 0.4	5.3	6.9 - 8.2
	MIBK	31.4 ± 1.4	4.5	28.9 - 33.5
	NBA	23.1 ± 1.5	6.4	20.8 - 25.3
	Tetradecane	0.74 ± 0.07	9.4	0.67 - 0.88
	Toluene	8.4 ± 0.4	5.2	7.6 - 9.1
PYRIDINE	DIPE	1.34 ± 0.10	7.7	1.21 - 1.51
	MIBK	2.9 ± 0.14	4.8	2.7 - 3.2
	NBA	2.3 ± 0.2	6.7	2.5 - 3.0
	Tetradecane	0.46 ± 0.05	10.0	0.41 - 0.56
	Toluene	2.5 ± 0.2	6.1	2.3 - 2.8
NAPHTHALENE	DIPE	3534 ± 577	16.3	2670 - 4446
	MIBK	5076 ± 442	8.7	4444 - 5726
	NBA	6398 ± 236	3.7	6226 - 6813
NAPHTHOL	DIPE	740 ± 101	13.6	603 - 893
	MIBK	1370 ± 192	14.0	1123 - 1691
	NBA	1360 ± 160	11.7	1163 - 1559

* Except Relative Standard Deviation,

The relative standard deviation and range data show the reliability of experimental results. It was also noted that the water-solvent ratio did not affect the value of K_D for these systems. The range of K_D values for these solutes did not follow any trend, low to high or high to low, that corresponded to changes in water-solvent ratio.

The relative magnitude of the data shown in Table 3-1 can be explained qualitatively by considering water phase solubility and molecular interactions. The average value of the distribution coefficients for these solutes in all the solvents decrease in the order naphthalene, naphthol, aniline and pyridine. The aqueous solubility of these solutes, at 25°C, increases in the same order; the mole fraction solubility of naphthalene, naphthol and aniline being 4.64×10^{-6} , 5.46×10^{-5} , and 7.32×10^{-3} respectively (Tsonopoulos and Prausnitz, 1971), while pyridine is miscible with water (CRC, 1979). Mackay and Patterson (1981) have also noted that, in general for hydrophobic solutes, the partitioning process is primarily controlled by aqueous solubility.

The differences in the molecular interactions occurring between solute and organic solvent molecules can be used to explain the difference in the magnitude of K_D data for aniline and pyridine. Both aniline and pyridine are single-ring nitrogenous aromatic compounds, however, these molecules exhibit different H-bonding character. While both molecules can H-bond with water, only aniline can form H-bonds with MIBK, NBA, DIPE and toluene. Hence, solute-water interactions are similar but solute-organic solvent interactions are different. The effect of this difference is shown clearly by the K_D values for aniline-MIBK and aniline-NBA systems being an order of magnitude greater than corresponding values for pyridine. For the case in which neither aniline nor pyridine can H-bond with the organic solvent (i.e. tetradecane), the solute-water-organic solvent interactions are similar and the K_D values are nearly equal.

The differences in the molecular interactions occurring between solute and water molecules can be used to explain differences in the magnitude of K_D data for naphthalene and naphthol. Both of these molecules are double-ring aromatic

compounds, but again they exhibit different H-bonding character. Naphthol is capable of forming H-bonds with both water and the polar solvents NBA, MIBK and DIPE, while naphthalene does not form H-bonds of significant strength with any of these compounds. Hence, naphthol shows a greater attraction to the water phase than naphthalene and has K_D values which are an order magnitude lower than corresponding values for naphthalene. In addition, naphthalene shows a greater relative attraction to the organic phase. The interaction between naphthalene and solvent molecules is controlled by dispersion forces. Because the polarizability of water ($15 \times 10^{-25} \text{ cm}^3$) is lower than that of common organic solvents ($100\text{-}150 \times 10^{-25} \text{ cm}^3$, Landolt-Bornstein, 1951, pg. 510-513) the attraction of naphthalene to water is less than that between naphthalene and the organic phase.

Available data on the heat of hydrogen bond formation can be used to help interpret K_D data for aniline. If heat of hydrogen bond formation (ΔH , kcal/mole) is taken as a measure of H-bond strength, then a correlation should exist between ΔH values and K_D . Murthy and Rao (1968) and Joesten and Schaad (1974) have reported ΔH values for a large number of solute-solvent pairs and data for aniline-solvent systems include: NBA, $\Delta H = 2.99$; di-n-propyl ether, $\Delta H = 2.77$; and tetradecane, $\Delta H = 0.0$. No data were given for MIBK, DIPE or toluene, although di-n-propyl ether and DIPE are expected to be similar in H-bonding character. These reported ΔH values follow observed trends of K_D for the aniline-solvent systems: NBA, $K_D = 23.1$; DIPE, $K_D = 7.6$; and tetradecane, $K_D = 0.74$. Hence, distribution coefficients for these aniline-solvent systems increase with increasing heat of H-bond formation.

Since pyridine does not form H-bonds with the organic solvents considered here, and because pyridine has a large dipole moment (2.2 Debye), we would expect that pyridine-organic solvent attractive forces are dominated by electrostatic interactions. The dipole moments of NBA, DIPE, toluene and tetradecane are 1.87, 1.26, 0.43 and 0 Debyes respectively (McClellan, 1963); and Table 3-1 shows distribution coefficients for the corresponding pyridine-solvent

pairs as 2.8, 1.34, 2.5 and 0.46. Hence, except for the anomalous behavior of toluene, an increased value of solvent dipole moment results in an increased value of K_D for the pyridine-solvent systems considered.

3.3.2. Concentration Effects in Single Solute Systems

The magnitude of the distribution coefficient can be affected by solute concentration if the solute can polymerize (Kiezyk and Mackay, 1973; Won, 1974). Won's (1974) experimental work with phenol has shown that in polar organic solvents the distribution coefficient falls with rising solute concentration; the opposite trend prevails when the solvent is a nonpolar hydrocarbon. Kiezyk and Mackay (1971) have shown that, for phenol, the rate of decrease in K_D with increasing solute concentration is greater when diethyl ketone is the extraction solvent than when NBA or DIPE are used. For this reason experiments were performed in this study to determine the effect of pyridine and aniline concentration on the distribution coefficient with MIBK as the extraction solvent. Single solute aqueous concentrations of 500, 2,000, 10,000 and 20,000 mg/l of aniline or pyridine were extracted with MIBK at two volume ratios (0.2 and 0.4); duplicate tests were performed for a total of thirty two individual experiments.

An analysis of variance using the F-test (Bowker and Lieberman, 1972) was performed on the sixteen results for each system. This test compares the means of different sample populations to determine if the means are statistically different. The F-ratios for aniline-MIBK and pyridine-MIBK were 0.19 and 0.66 respectively. The tabulated F-ratios for three degrees of freedom for treatment and twelve degrees of freedom for error were 3.49 and 5.95 at 95% and 99% significance levels, respectively. From this analysis it is clear that solute concentration does not affect the value of the distribution coefficient for aniline or pyridine in MIBK up to concentrations of 20,000 mg/l.

That the K_D value for pyridine does not show a dependence on concentration is not surprising because its B-type H-bonding character does not

allow for formation of self-associative H-bonds. However, the AB-character of aniline suggests that it may self-associate. Lady and Whetsel (1964) have shown that aniline will form self-associative H-bonds in cyclohexane, hence the distribution coefficient for aniline in nonpolar solvents may show a concentration dependence. The fact that the value of K_D for aniline in MIBK does not decrease with increasing aniline concentration suggests that aniline satisfies its H-bonding tendency by forming H-bonds with the strong B-type solvent, MIBK. Murthy and Rao (1968) give a value of ΔH for the aniline dimer as 1.64 kcal/mole, while the ΔH value for aniline and NBA is about 3 kcal/mole. Since esters and ketones demonstrate similar H-bonding strength (Joesten and Schaad, 1974) it would appear that aniline shows a preference toward forming more stable H-bonds with MIBK. This is contrasted to the phenol-MIBK system where a concentration dependence has been observed (Won, 1974). Murthy and Rao (1968) give a ΔH value for the phenol dimer as 5.1 kcal/mole, and an average ΔH value for phenol and three ketones as 4.95 kcal/mole. Hence, self-associative phenol H-bonds and phenol-MIBK H-bonds are approximately equal in strength.

3.3.3. Multiple Solute and Wastewater Systems

Chemical equilibria between two components in solution may often be influenced by the presence of other species. Because a wide range of organic and inorganic compounds will exist in wastewaters, it is of interest to investigate the possibility of antagonistic or synergistic effects on the equilibrium distribution coefficient. To address this issue, K_D 's were experimentally determined in clean water solutions with both aniline and pyridine and in an actual phenolic coal gasification wastewater.

Sixteen individual clean water tests were conducted with initial aniline and pyridine concentrations of 500 mg/l. Duplicate extractions were performed at water-to-solvent ratios of 0.2 and 0.4. These results were then compared statistically with results shown in Table 3-1 by performing a t-test on differently sized populations. The t-tests were performed assuming sample

variances to be equal and also considering them not necessarily equal (i.e. different) using the Smith-Satterthwaite test (Bowker and Lieberman, 1972).

Results of this statistical analysis are shown in Table 3-2. It can be seen that for the NBA, DIPE, and toluene systems there are no apparent antagonistic/synergistic effects; that is, the sample means are not statistically different at the 95% confidence level. The MIBK systems show means that are different. However, because the difference was not significant when variances were assumed equal, and because this small difference in mean values was not observed in tests conducted with the coal gasification wastewater, it is felt that this result is an anomaly. It should be noted that Joesten and Schaad (1974) give the strength of H-bond formation for the aniline-pyridine pair as 3.4 kcal/mole. Hence, these species may form complexes which affect the magnitude of K_D at higher concentrations.

Wastewater tests were conducted with a filtered sample of coal gasification condensate. Because the wastewater had low concentrations of aniline and pyridine (approximately 20 and 40 mg/l, respectively) it was spiked to a measured concentration of 500 and 495 mg/l, respectively. The phenol content after spiking was 2020 mg/l. Duplicate extractions were performed at solvent-water ratios of 0.2 and 0.4 for a total of 24 individual experimental analyses. These results were compared statistically with single solute distribution coefficient data for aniline and pyridine given in Table 3-1. Wastewater samples were also analyzed for phenol content under the same conditions. As there were not adequate experimental results for a statistical comparison, the K_D values reported in the literature for phenol in clean water were used for straight comparison.

Results of the wastewater tests are summarized in Table 3-3. For the aniline and pyridine systems the statistical analysis shows that for all cases except pyridine-toluene, the values of the distribution coefficients are not affected by the presence of other wastewater species. The toluene-pyridine system showed a sharply increased value for the distribution coefficient in the

Table 3-2: Distribution Coefficients for Multiple Solute Systems

Solute	Solvent	K_D (mg/l/mg/l) Mean S.D.	t-Test ^a	
			Variances Equal	Assumed Different
ANILINE	DIPE	7.6 ± 0.3	0.049 N.S. ^b	0.058 N.S.
	MIBK	30.0 ± 0.4	1.97 N.S.	3.15 0.01 ^c
	NBA	23.9 ± 1.5	0.92 N.S.	0.92 N.S.
	Toluene	8.1 ± 0.2	1.17 N.S.	1.64 N.S.
PYRIDINE	DIPE	1.41 ± 0.08	1.21 N.S.	1.38 N.S.
	MIBK	3.03 ± 0.03	1.95 N.S.	3.26 0.01
	NBA	2.9 ± 0.1	1.11 N.S.	1.34 N.S.
	Toluene	2.4 ± 0.1	1.26 N.S.	1.39 N.S.

(a) - Comparison with the experimental values from the single solute tests (see text)

(b) - This mean and that reported in Table 3-1 are not significantly (N.S.) different at the 95% confidence level.

(c) - This mean and that reported in Table 3-1 are significantly different at the 99% confidence level ($\alpha = 0.01$).

wastewater. It was also noted that K_D decreased with an increase in the solvent-wastewater ratio. The values obtained for wastewater K_D 's were 5.2 and 5.4 at the 0.2 ratio, and 4.1 and 4.6 at the 0.4 ratio. This test was repeated under the same conditions and similar results were obtained. To determine if some interaction between pyridine and phenol was responsible for this effect, a synthetic aqueous solution of pyridine and aniline at 500 mg/l each and phenol at 5000 mg/l was prepared and extracted at 0.2 and 0.4 solvent-water ratios. The K_D 's obtained for toluene-pyridine were 3.8 and 4.2 for the higher and lower ratios. Hence, it appears that phenol and pyridine have a synergistic effect on the value of K_D for the toluene-pyridine system.

The distribution coefficients determined for phenol in the wastewater compare favorably with those reported in the literature for phenol in clean water. However, we should note that the K_D for phenol-toluene in the wastewater system (2.5) does show an increase over that for phenol in clean water (2.1). This could be a result of synergistic effects between phenol and pyridine in the toluene-water system. Beychok (1967) notes that an increase in K_D for phenol has been observed in processing of petroleum for gasoline. He attributes the effect to base fraction organic compounds such as pyridine or quinoline present at concentrations greater than about 300 mg/l. Therefore, it appears that phenol and pyridine can form an interactive pair, probably through hydrogen bonding, that results in an increase in their respective K_D 's. Murthy and Rao (1968) show that the phenol-pyridine complex has a ΔH value of 6.5 kcal/mole. This is greater than the values of ΔH given for complex formation between phenol and ketones, esters, ethers and toluene; 4.95, 4.35, 4.30 and 1.33 kcal/mole respectively. Hence, at higher pyridine concentrations and in solvents which show little or no H-bonding character this effect should be more pronounced. It is also noted that the distribution coefficient for phenol decreases in the order MIBK, NBA, DIPE and toluene. This compares with the order of ΔH values given above. Hence, increasing strength of solute-organic solvent interaction results in increased K_D values.

The phenol content of wastewaters is often measured by an analytical procedure involving distillation and color development with 4-aminoantipyrine, 4AAP (APHA, 1980). This procedure is sensitive to the compound phenol as well as ortho- and meta-substituted phenols, with the results reported as "phenolics". For this reason tests were conducted to measure the K_D value for phenolics between wastewater and MIBK, NBA, DIPE and toluene. Replicate tests were performed at water-solvent ratios of 0.2, 0.4, 0.6, 0.8 and 1.0 for a total of forty individual experiments. Results of these tests are shown in Table 3-3. It is interesting to note that the distribution coefficient values for 4AAP phenolics and phenol between wastewater and the four organic solvents are equal. The wastewater employed in measurement of phenolic distribution coefficients was from gasifier run RA-52 with lignite coal, not from run RA-92 as in the other experiments described in this chapter. In general, these two wastewaters had similar compositions as shown in Table 6-2 in Chapter Six. These wastewaters were obtained from the Grand Forks Energy Technology Center's (GFETC) slagging fixed-bed gasifier.

Table 3-3: Distribution Coefficients for Wastewater Systems

		Aniline and Pyridine				
Solute	Solvent	K_D (mg/1/mg/1) ^(a)	Variances Equal	t-Test ^(b)		
		Mean S. D.		Assumed Different		
Aniline	DIPE	7.3 ± 0.3	1.17	N.S.	1.47	N.S.
	MIBK	31.4 ± 1.8	0.01	N.S.	0.01	N.S.
	NBA	23.4 ± 1.4	0.40	N.S.	0.41	N.S.
	TOLUENE	8.4 ± 0.4	0.10	N.S.	0.10	N.S.
Pyridine	DIPE	1.34 ± 0.14	0.03	N.S.	0.02	N.S.
	MIBK	2.9 ± 0.2	0.21	N.S.	0.18	N.S.
	NBA	2.7 ± 0.1	0.42	N.S.	0.51	N.S.
	TOLUENE	4.8 ± 0.6	13.0	0.01	7.70	0.01

Solvent	<u>Phenol</u>	
	K_D (mg/l/mg/l)	Reported K_D ^(c)
	Mean	S. D.
DIPE	30 ± 1.0	29
MIBK	102 ± 4	110
NBA	69 ± 5	71
Toluene	2.5 ± 0.2	2.1

<u>Solvent</u>	<u>Phenolics</u>	
	K_D (mg/l/mg/l)	
	Mean	S. D.
DIPE	29 ± 2.8	
MIBK	106 ± 19	
NBA	75 ± 7.8	
Toluene	2.6 ± 0.32	

Notes:

(a) Initial concentrations were 500, 495, and 2020 mg/l for aniline, pyridine, and phenol respectively

(b) For notation see bottom of Table 3-2

(c) Ref., Medchem Project, 1983

Chapter 4

DISTRIBUTION COEFFICIENT MODELS

4.1. Introduction

When designing or evaluating solvent extraction systems it is often necessary to obtain distribution coefficients for the various solutes. Unfortunately, experimental data for many solute-solvent systems of environmental interest are not available, hence one must rely on liquid phase equilibrium models to estimate K_D values. Because the thermodynamics of nonideal liquid mixtures has not as yet been fundamentally explained, fluid phase equilibrium models are necessarily approximate (Abrams and Prausnitz, 1975b). Theoretical approximations can be made from two points of view; by generalizing gas phase interactions of simple molecules or by assuming that the liquid state is analogous to the solid state (i.e. lattice analogies). Both of these approaches are made tractable by introducing simplifying assumptions concerning the microscopic structure of the system. Empirical approximations can also be made by starting with a macroscopic picture and adding sufficient microscopic detail to make the analysis meaningful (Leffler and Grunwald, 1963). This chapter will highlight the fundamental concepts and describe the mechanics of several distribution coefficient models which start from the approximations described above.

The thermodynamic models examined in this study include regular solutions and UNIFAC. These models estimate distribution coefficients from solute activity coefficients. The regular solution model begins with London's analysis of gas phase dispersion interactions and generalizes it to liquid mixtures. The UNIFAC model starts by assuming that the liquid phase can be

described by a quasi-lattice. UNIFAC offers more flexibility in that it can predict both aqueous and organic phase activity coefficients while regular solutions is limited to the organic phase. A third model, linear free energy analysis, employs the empirical concept that the partitioning process is similar for similar systems. A discussion of the utility and reliability of these models is presented in Chapter Five.

4.2. Regular Solutions

4.2.1. Introduction

The concept of a "regular solution" was first proposed by Hildebrand and Scatchard in the early 1930's as a thermodynamic model for predicting the energy of mixing for binary liquid mixtures. A regular solution may be defined as one which has an ideal entropy of mixing and a real (nonideal) enthalpy of mixing. The advantage of this assumption is that the energy of mixing, and hence activity coefficients, may be computed from enthalpy considerations alone, using only pure component thermal and physical properties (Hildebrand et al., 1970).

Regular solutions is an attractive solution model because of its relative simplicity; in the original formulation no binary data were required. The main disadvantage of this approach is that strict thermodynamic interpretation limits the model to simple, reasonably symmetric, nonpolar molecules. This limitation has been overcome to an extent by introducing adjustable binary parameters to the model. These modifications have extended the range of regular solutions by relaxing the ideal entropy of mixing assumption.

4.2.2. Thermodynamics of Regular Solutions

In Hildebrand's original formulation a regular solution was defined as one involving zero entropy change when a small amount of one of its components was transferred to it from an ideal solution of the same composition, the total volume remaining unchanged (Hildebrand et al., 1970). Scatchard developed this notion into an expression for the Gibbs free energy of mixing by utilizing the concept of cohesive energy density.

$$g^E = (x_1 v_1 + x_2 v_2) (c_{11} + c_{22} - 2c_{12}) \phi_1 \phi_2 \quad (4-1)$$

where:

g^E = excess Gibbs free energy of mixing (cal/g-mole)

x = mole fraction

v = molar volume (cm³/g-mole)

ϕ = volume fraction

c_{11}, c_{22} = pure component cohesive energy density (cal/cm³)

c_{12} = energy density for interaction of unlike species (cal/cm³)

subscript 1 = solvent

subscript 2 = solute

The energy density terms in equation (4-1), c , represent the molecular interactions which occur in solution between the components of a binary mixture. The cohesive energy density of a pure substance (c_{11}, c_{22}) represents the interaction energy that occurs between two molecules of the same species. It is a measure of the energy required to remove a molecule from its own pure liquid and may be expressed as that substance's energy of vaporization (ΔU , cal/g-mole) per molar volume (Hildebrand et al., 1970). The interaction energy

density between unlike components (c_{12}) was assumed to follow a geometric mean, so that

$$c_{12} = (c_{11}c_{22})^{1/2} \quad (4-2)$$

Hildebrand developed Scatchard's cohesive energy density into a more convenient form by defining the solubility parameter (δ) as the square root of the cohesive energy density.

$$\delta = (c)^{1/2} = (\Delta U/V)^{1/2}, (\text{cal/cm}^3)^{1/2} \quad (4-3)$$

Substitution of equation (4-3) into (4-1) yields

$$g^E = (x_1 v_1 + x_2 v_2) (\delta_1^2 + \delta_2^2 - 2\delta_1 \delta_2) \phi_1 \phi_2 \quad (4-4)$$

The infinite dilution solute activity coefficient may be obtained by differentiating equation (4-4) with respect to x_2 as x_2 approaches zero;

$$\ln \gamma_2^\infty = (V_2/RT) [(\delta_1 - \delta_2)^2] \quad (4-5)$$

The use of solubility parameters in equation (4-5) has resulted in regular solution theory being commonly referred to as solubility parameter theory.

It is worthwhile to discuss the two principal assumptions of regular solution theory in more detail. It was shown in Chapter Two that the geometric mean assumption for the interaction energy occurring between unlike molecules holds for molecular pairs which interact primarily through dispersion forces (Karger et al., 1973). The geometric mean rule is also expected to be a good approximation for polar (electrostatic) interactions in that both molecules interact through the same property, i.e. dipole moment (Barton, 1975). The geometric mean rule is less precise when considering forces which are unsymmetric, i.e. the solute and solvent molecules have different roles with respect to chemical interactions. For example, induction forces result from the interaction between the dipole moment of one molecule and the polarizability of

another. Hydrogen bond forces are also unsymmetric in that one molecule acts as proton donor while the other serves as proton acceptor. When considering unsymmetric molecular forces, the interactions between two molecules of the same species are not always the same as those occurring between different solution components. In general, the geometric mean underestimates c_{12} when specific interactions like hydrogen bonding occur between different solution components (Hildebrand et al., 1970).

The other principal assumption of regular solution theory requires that a system have an ideal entropy of mixing with no volume change. Hence, the orientation of molecules in solution must be random and the number of nearest neighbors (coordination number) must be identical in the pure state and in the solution mixture. This assumption is strictly true only for simple, spherically symmetric molecules which interact primarily through dispersion forces. Electrostatic and hydrogen bond interactions may result in specific orientation of molecules, while size differences between molecules can lead to significant volume changes (Hildebrand et al., 1970).

This discussion has shown that solvent-solute systems which include electrostatic and H-bond interactions can violate both of the principal assumptions of regular solution theory. Fortunately the errors which result from violation of these requirements tend to cancel one another when calculating activity coefficients for nonpolar and moderately polar systems (Hildebrand et al., 1970).

4.2.3. Modified Regular Solution Equations

Several researchers have developed regular solution techniques for predicting activity coefficients for systems which include dispersive, dipolar, inductive, and weak hydrogen bond interactions. These applications have grown from Blanks and Prausnitz's (1964) work with polymer solubility, where they developed a two term solubility parameter model. Weimer and Prausnitz (1965) expanded the regular solution expression to more accurately describe mixtures

of polar solvents and nonpolar solutes by dividing the cohesive energy density of a polar solvent (c_{11}) into two parts: one for nonpolar (dispersion) interactions, and one for dipole-dipole effects

$$c_{11} = \Delta U_1/V_1 = (\Delta U_1(\text{nonpolar})/V_1) + (\Delta U_1(\text{polar})/V_1) = \lambda_1^2 + \tau_1^2 \quad (4-6)$$

where λ and τ are defined as the nonpolar and polar solubility parameters, respectively. Weimer and Prausnitz also modified the interaction energy between unlike components (c_{12}) to account for polar solvents by incorporating an empirical correction term, Ψ_{12} (cal/cm³)

$$c_{12} = \lambda_1 \lambda_2 + \Psi_{12} \quad (4-7)$$

Helpinstill and Van Winkle (1968) further modified the expression for excess Gibbs free energy of mixing to account for the interaction between a polar solvent and a polar solute. The solute cohesive energy density was considered in a manner analogous to Weimer and Prausnitz's treatment of polar solvents, where

$$c_{22} = \Delta U_2/V_2 = (\Delta U_2(\text{nonpolar})/V_2) + (\Delta U_2(\text{polar})/V_2) = \lambda_2^2 + \tau_2^2 \quad (4-8)$$

and where the interaction energy term c_{12} was redefined as

$$c_{12} = \lambda_1 \lambda_2 + \tau_1 \tau_2 + \Psi_{12}^* \quad (4-9)$$

Helpinstill and Van Winkle proposed that their approach could be used for all three basic binary systems: nonpolar-nonpolar, nonpolar-polar, and polar-polar.

Weimer and Prausnitz (1965) also modified the regular solution equation (4-5) by incorporating the Flory-Huggins entropy of mixing term

$$RT [x_1 \ln(\phi_1/x_1) + x_2 \ln(\phi_2/x_2)] \quad (4-10)$$

This helps to account for size differences between the solute and solvent

molecules. Helpinstill and Van Winkle suggest that this term is necessary when the molar volumes of the components differ by more than 5 percent.

The resulting modified regular solution equation for computing infinite dilution solute mole fraction activity coefficients may be taken from Helpinstill and Van Winkle;

$$\ln \gamma_s^\infty = (V_2/RT)[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\Psi_{12}] + \ln(V_2/V_1) + 1 - (V_2/V_1) \quad (4-11)$$

where:

γ_s^∞ = mole fraction activity coefficient of solute at infinite dilution in the solvent phase

V = molar volume (cm^3/mole)

λ = nonpolar solubility parameter (cal/cm^3)^{1/2}

τ = polar solubility parameter (cal/cm^3)^{1/2}

Ψ_{12} = empirical correction term (cal/cm^3)

R = universal gas constant ($\text{cal}/\text{K mole}$)

T = absolute temperature (K)

Subscript 1 = solvent

Subscript 2 = solute

4.2.4. Estimation of Parameters

The polar and nonpolar solubility parameters of a substance represent the energy required to remove it from its own pure liquid and may be calculated from enthalpy of vaporization data (ΔH_v , cal/mole) as the potential energy per unit volume (Hildebrand et al., 1970),

$$\lambda^2 + \tau^2 = (\Delta H_v - RT)/V \quad (4-12)$$

In the original modified regular solution models of Weimer and Prausnitz (1965) and Helpinstill and Van Winkle (1968) nonpolar solubility parameters were calculated using the homomorph concept. In this study nonpolar solubility

parameters are calculated from a correlation with refractive index (n) given by Karger et al., (1978),

$$\lambda = 30.7 (n^2 - 1)/(n^2 + 2) \quad (4-13)$$

Polar solubility parameters may thus be calculated from equation (4-12) and (4-13)

$$\tau = [(\Delta H_v - RT)/V - \lambda^2]^{1/2} \quad (4-14)$$

Appendix A lists solubility parameters and molar volumes for the compounds of interest in this study. An example calculation is also provided to illustrate the use of equation (4-11).

The empirical correction term (Ψ_{12}) represents the interaction energy between solute and solvent molecules that is not symmetric. It is intended to account for interactions where the solvent and solute molecules play separate roles. This includes induction effects where the permanent dipole of one molecule acts on the polarizability of the other, and hydrogen bonding forces where one molecule acts as proton donor and the other as proton acceptor. Weimer and Prausnitz (1965) developed one expression for Ψ_{12} based on correlations with solvent polar solubility parameter using experimental data for nonpolar solute-polar solvent pairs. The correction term for aromatic solutes was developed from data for polar solvent-benzene systems for which

$$\Psi_{12} = 0.45 \tau_1^2 \quad (4-15)$$

Helpinstill and Van Winkle (1968) proposed a different correlation for the empirical correction term, referred to as Ψ_{12}^* . They suggest using both solute and solvent polar solubility parameters to estimate the value of the correction term. The authors developed their correlation for aromatic solutes from data for hydrocarbon solute-polar solvent pairs as:

$$\Psi_{12}^* = 0.477 (\tau_1 - \tau_2)^2 \quad (4-16)$$

4.2.5. Expanded Solubility Parameter Treatment

Expanded regular solution models were developed for application in the field of chromatography. They differ from the model of Helsenstill and Van Winkle in that the empirical correction term is replaced by solubility parameters which describe hydrogen bonding and induction interactions.

Tijssen et al., (1976) have described hydrogen bond interactions with solubility parameter terms for the acid and base strengths of solution components. They replace Ψ_{12} in equation (4-11) with the following expression,

$$\Psi_{12} = - (\delta_{a2} - \delta_{a1}) (\delta_{b2} - \delta_{b1}) \quad (4-17)$$

where:

δ_a = proton donor (acid) solubility parameter $(\text{cal/cm}^3)^{1/2}$

δ_b = proton acceptor (base) solubility parameter $(\text{cal/cm}^3)^{1/2}$

1, 2 = solvent and solute respectively

Karger et al., (1976 and 1978) have chosen to express Ψ_{12} in terms of both hydrogen bonding and induction solubility parameters;

$$\Psi_{12} = - [(\delta_{a1} - \delta_{a2}) (\delta_{b2} - \delta_{b1}) + [(\delta_{i1} - \delta_{i2}) (\lambda_1 - \lambda_2)]] \quad (4-18)$$

where δ_a , δ_b and λ are defined as before and δ_i is a solubility parameter which describes the polarizability of a molecule.

A difficulty with the computational methods developed by Tijssen et al. and Karger et al. is that estimation of the additional solubility parameters does not escape empiricism, furthermore the data needed for calculation of acid, base and induction solubility parameters are not readily available (Karger et al., 1978). As part of this investigation calculations were performed with the limited data presented in the papers of Karger and Tijssen. This work showed that, for the

types of solutes and solvents of interest in solvent extraction processing of phenolic wastewaters, the expanded solubility parameter models did not improve upon the results given by equation (4-11). Hence, the models of Karger and Tijssen were not considered for further analysis in this investigation.

4.3. UNIFAC

4.3.1. Introduction

UNIFAC is a group contribution method for predicting activity coefficients in nonelectrolyte liquid mixtures. It is applicable to a wide range of solutions exhibiting either positive or negative deviations from Raoult's law (Fredenslund et al., 1975). UNIFAC is based on Langmuir's group contribution concept which states that a physical property of a compound is the sum of contributions made by the functional groups which comprise that molecule.

The group contribution concept is attractive because, while there are an ever increasingly large number of chemical compounds in existence, the number of functional groups which make up these compounds is much smaller. Hence, it is possible to estimate properties for a very large number of different organic molecules from a small set of functional group properties (Fredenslund et al., 1975). For example, in this work 225 binary system activity coefficients have been estimated using data for only 13 functional groups.

The problem with the group contribution method is that it is necessarily approximate. The behavior of any functional group can not be completely separated from interactions attributable to other groups in the molecule. Fortunately, this error can be reduced by proper choice of functional groups and by applying a correction factor to the calculations.

4.3.2. The Basis of UNIFAC: UNIQUAC and ASOG

UNIFAC was developed in 1975 by Fredenslund and co-workers when they combined two methods for predicting phase equilibria. UNIFAC matches the ideas of the analytical solution of groups (ASOG) model (Wilson and Deal, 1962; Derr and Deal, 1969; Ronc and Ratcliff, 1971) with the calculational procedures of the universal quasi-chemical (UNIQUAC) model of Abrams and Prausnitz (1975b). The name UNIFAC stems from UNIQUAC Functional-group Activity Coefficient.

The solution of groups concept evolved from a series of efforts in the early 1960's which focused on the idea that activity coefficients are dependent upon solute and solvent structure. This dependence was correlated with the number and kind of functional groups which makeup the solution environment (Wilson and Deal, 1962). The ASOG model contains several assumptions which have become the starting point for UNIFAC. The three main assumptions of the ASOG model are (Wilson and Deal, 1962):

1. The activity coefficient of a component is the sum of two contributions. One is associated with differences in molecular size and shape while the other is a function of energy interactions between molecules.
2. The contribution from energy interactions is the sum of the interaction of a particular functional group with the functional groups in the solution, minus the interactions between that functional group and the functional groups in the standard state environment.
3. The individual group contributions in any environment depend upon the functional group concentration and are not a function of the concentration of the molecules themselves.

The second assumption considers that the standard state environment is the pure liquid solute. This provides the boundary condition that as the solution composition approaches pure solute the activity coefficient goes to unity (Ronc and Ratcliff, 1971). This also provides a correction for the fact that functional group properties are not independent of the parent molecule (Fredenslund et al., 1975).

The third assumption probably represents the major contribution of the ASOG method to the development of the group contribution concept. This notion brought forth the idea that existing phase equilibria data could be reduced to yield phase equilibria for systems where no experimental data exist, but which contain the same functional groups (Fredenslund et al., 1975).

The UNIQUAC model is based on Guggenheim's (1952) quasi-chemical lattice theory which considers that a liquid can be represented by a three dimensional lattice of equi-spaced sites, called cells. Each molecule is divided into bonded segments which occupy one cell, the total number of cells being equal to the total number of segments. Abrams and Prausnitz (1975b) generalized this theory for molecules with varying size and shape by postulating that while all segments, by definition, are the same size they differ in their external contact area. For example, in normal pentane the 2 methyl end groups have a larger external area than the 3 methylene groups; in neopentane the central carbon atom has no external contact area at all (Abrams and Prausnitz, 1975b).

The UNIQUAC model computes phase equilibria for any system using only two composition variables and two adjustable parameters per binary. A discussion of these parameters is presented in the next section. When clearly defined simplifications are made, UNIQUAC reduces to nearly all commonly used expressions for the excess Gibbs energy of mixing including the Wilson, NRTL, Van Laar, Margules, Flory-Huggins and Regular Solution equations (Abrams and Prausnitz, 1975b).

4.3.3. UNIFAC Equations

Following Derr and Deal (1969) UNIFAC divides the molecular activity coefficient into two parts: a combinatorial portion (c) which accounts for differences in the size and shape of molecules and a residual portion (R) which takes into account the interaction energy arising between functional groups;

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (4-19)$$

The distinction between the combinatorial and residual portions of γ results from the fact that liquid phase nonidealities caused by steric factors can not be accounted for by group energy interactions (Fredenslund et al., 1977).

The expression for the combinatorial portion of γ is taken directly from UNIQUAC and utilizes only pure component properties. The general form of the expression for the combinatorial portion of γ for multicomponent systems is (Fredenslund et al., 1975):

$$\ln \gamma_i^C = \ln (\phi_i/x_i) + (z/2)q_i \ln (\theta_i/\phi_i) + l_i - (\theta_i/x_i) \sum_j x_j l_j \quad (4-20)$$

where:

$$\phi_i = (r_i x_i) / (\sum_j x_j r_j)$$

ϕ_i = overall lattice segment fraction for component i

$$\theta_i = (q_i x_i) / (\sum_j x_j q_j)$$

θ_i = overall lattice area fraction for component i

$$l_i = (z/2)(r_i - q_i) - (r_i - 1)$$

$$r_i = \sum_k v_k^{(i)} R_k$$

r_i = number of lattice sites occupied by a single molecule i,
(segments per molecule)

$$q_i = \sum_k v_k^{(i)} Q_k$$

q_i = amount of lattice surface area occupied by a single molecule i

x_i = mole fraction of component i

R_k = van der Waals volume of functional group k relative to a
standard lattice segment

Q_k = van der Waals surface area of functional group k relative
to a standard lattice segment

v_k = number of functional groups k in a single molecule i

z = lattice coordination number

The average segment fraction ϕ_i , relates the number (fraction) of total lattice sites that are occupied by a given molecule at a given composition. The average surface area fraction, θ_i , represents the percent (fraction) of lattice surface area occupied by a given molecule at a given composition. The lattice coordination number, z , represents the number of nearest neighbors in a particular lattice configuration. Abrams and Prausnitz arbitrarily set $z = 10$, which is an average of $z = 12$ for a face centered cubic arrangement and $z = 8$ for a body centered cubic configuration. The van der Waals terms will be discussed in the next section. For a binary system with solute (1) at infinite dilution in the solvent (2) the combinatorial portion of the activity coefficient reduces to (Grain, 1982);

$$\ln \gamma_1^{c,00} = \ln (r_1/r_2) + 5q_1 \ln ((q_1 r_2)/(q_2 r_1)) + I_1 - I_2 (r_1/r_2) \quad (4-21)$$

The residual portion of the activity coefficient is derived from ASOG and UNIQUAC. From ASOG:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (4-22)$$

where Γ_k is the functional group residual activity coefficient in the solution mixture, and $\Gamma_k^{(i)}$ is the functional group residual activity coefficient in the standard state environment (i.e. a solution containing only molecules of type i). The standard state term is a correction factor introduced according to the assumptions of ASOG so that the activity coefficient becomes unity as the component mole fraction approaches one. This term also accounts for the fact that the activity coefficient of group k in molecule i depends on the molecule i in which k is situated (Fredenslund et al., 1975).

The functional group activity coefficient, Γ_k , is calculated according to UNIQUAC as

$$\ln \Gamma_k = Q_k [1 - \ln (\sum_m \bar{\theta}_m \Psi_{mk}) - \sum_m ((\bar{\theta}_m \Psi_{km}) / (\sum_n \bar{\theta}_n \Psi_{nm}))] \quad (4-23)$$

where:

$\bar{\theta}_m$ = lattice area fraction for functional group m summed over all different groups

$$\bar{\theta}_m = (\Omega_m X_m) / (\sum_n \Omega_n X_n)$$

X_m = functional group concentration fraction for group m, summed over all different groups

$$X_m = (\sum_j v_m^{(j)} x_j) / (\sum_n \sum_j v_n^{(j)} x_j)$$

Ψ_{mn} = interaction energy between functional groups m and n

$$\Psi_{mn} = \exp(-a_{mn}/T)$$

The other terms remain defined as for the combinatorial portion of the activity coefficient. The group interaction parameter will be discussed in detail in the next section.

For a binary system of solute (1) and solvent (2) molecules the functional group concentration fractions may be more simply expressed as;

$$X_m = [(v_m^{(1)} x_1) + (v_m^{(2)} x_2)] / [x_1 (\sum_m v_m^{(1)}) + x_2 (\sum_m v_m^{(2)})] \quad (4-24)$$

The functional group activity coefficient in the standard state, $\Gamma_k^{(i)}$, is calculated by an equation analogous to (4-23). An example for calculating infinite dilution activity coefficients using the UNIFAC model is presented in Appendix B.

It is noted that the combinatorial portion contains terms which represent molecular properties of the pure component, while the residual portion contains parameters relating to interaction of individual functional groups.

4.3.4. Estimation of UNIFAC Parameters

The UNIFAC method is based on the functional group classifications assigned by Fredenslund and co-workers. At present UNIFAC energy interaction parameters can be derived from two sources: an extensive vapor-liquid equilibria (VLE) data base or the smaller liquid-liquid equilibria (LLE) data base. The functional group parameters based on VLE data are presented by Gmehling et

al., (1982). These authors have distinguished 76 separate sub-groups which are divided among 40 different main-group classifications. The LLE data can be found in Magnussen et al., (1981) and are separated into 57 separate sub-groups which are divided among 32 main group sets.

Functional group sub-sets are divided such that the interaction energy differences between sub-groups is small. An example of the distinction between main- and sub- groups is given by the following: the aliphatic functional groups CH_3 , CH_2 , CH , and C are considered as separate sub-groups but belong to the same main group. The same distinction is made for the aromatic groups ACCH_3 , ACCH_2 , ACCH (Fredenslund et al., 1977 and Gmehling et al., 1982).

The parameters R_k and Q_k are, respectively, the van der Waals volume and area of a functional group k relative to those of the standard lattice segment. The van der Waals terms are obtained from the physical property data given by Bondi (1968). The choice of the standard lattice segment is defined somewhat arbitrarily by Abrams and Prausnitz (1975b) relative to a linear polyethylene molecule. The van der Waals volume and surface area parameters are listed for all 76 VLE sub-groups by Gmehling et al., (1982), the van der Waals terms for the LLE sub-groups are identical to the corresponding VLE values.

The main-group energy interaction parameters Ψ_{mn} represent the difference in the energy of interaction (U) between two functional groups m and n and two groups n .

$$\Psi_{mn} = \exp -((U_{mn} - U_{nn})/RT) = \exp (-a_{mn}/T) \quad (4-25)$$

For a binary system with components 1 and 2 the interaction parameters are given by;

$$\Psi_{12} = \exp - ((U_{12} - U_{22})/RT) = \exp (-a_{12}/T) \quad (4-26)$$

$$\Psi_{21} = \exp - ((U_{21} - U_{11})/RT) = \exp (-a_{21}/T) \quad (4-27)$$

It is noted that $U_{12} = U_{21}$, but a_{12} does not equal a_{21} (Sorensen et al., 1979), also the parameter a_{mn} has units of degrees Kelvin.

To ensure that the a_{mn} parameters are reduced from reliable data, the data are subjected to a consistency test. The consistency check and data reduction schemes are explained in detail by Fredenslund et al., (1977) and Magnussen et al., (1981) and will not be discussed here. We should point out, however, that in reducing equilibria data the order of calculating the a_{mn} parameters is important. For example, if the (COH, CO) group interaction parameters are to be estimated from alcohol-ketone data, it is necessary to first determine the (CH₂, CO) parameters from alkane-ketone data and the (CH₂, COH) parameters from alkane-alcohol data (Fredenslund et al., 1975)

Both the VLE and LLE data apply to non-electrolyte, non-polymeric systems at low to moderate pressures. The VLE data are derived from a broader base and are applicable at system temperatures between 25 and 150°C (Gmehling et al., 1982). The LLE data do not apply to compounds with normal boiling points below 25°C, and can be used for systems in the temperature range 10-40°C. In addition, the LLE data base is dominated by systems containing water and alkanes as one or both components. Hence, this data should be more accurate for predicting activity coefficients in water or alkane solvents.

In discussing the use of the UNIFAC model for predicting distribution coefficients, Fredenslund et al., (1975) note that the infinite dilution region provides an especially severe test because the corresponding activity coefficients are very sensitive to the interaction parameters.

4.4. Linear Free Energy Relationships

4.4.1. Introduction

Linear Free Energy Relationships (LFER) have been widely used to correlate chemical reactions and physical properties of organic molecules, these relationships are particularly common for correlating reactions of aromatic solutes (Wells, 1968; Leffler and Grunwald, 1963). Most commonly, LFER are used to correlate rate or equilibrium constants for one reaction series with those of a second series, provided that both systems are subjected to the same variations in component structure and system conditions (Wells, 1968).

The most valuable feature of LFER is that they permit one to recognize regular patterns of chemical behavior and readily observe deviations from those patterns without an involved analysis (Wells, 1968). The main drawback of this approach is that it has no definite theoretical basis so that LFER are empirically derived. However, while it lies outside the formal structure of thermodynamics, the LFER approach resembles thermodynamic analysis in that the detailed microscopic structure need not be explicitly identified to yield information about microscopic phenomena (Leffler and Grunwald, 1963). For this reason LFER are often referred to as extra thermodynamic relationships.

4.4.2. Correlation of Distribution Coefficients Using LFER

Since distribution coefficients are equilibrium constants it should not be surprising that one can find LFER between partition coefficients measured in different solvent systems (Leo and Hansch, 1971). Collander (1951) was the first to recognize this and he correlated K_D values for a series of alcohol-water systems using the following expression,

$$\log K_{D1} = a + b \log K_{D2} \quad (4-28)$$

where the subscripts refer to systems 1 and 2 and a and b are correlation constants.

Leo and Hansch (1971) noted that while equation (4-28) allows two partitioning systems to be compared, the most useful relationships for studying solute-solvent interaction are obtained if each system is compared to a standard reference system. Leo and Hansch have shown that octanol is a particularly good choice as a reference solvent. Octanol-water partition coefficients (K_{ow}) are available for a wide variety of solutes. Furthermore, a distribution coefficient data bank is maintained by Leo and Hansch (Medchem Project, 1983; also see Hansch and Leo, 1979) which currently lists K_{ow} values for over 8000 organic compounds containing a wide variety of functional groups. Octanol-water partition coefficients are also commonly used in many areas of environmental science including: aqueous solubility (Chiou et al., 1982; Mackay et al., 1980), bio-accumulation (Mackay, 1982; Chiou et al., 1977), sorption on soil (Karickhoff, 1979) and the partitioning process in general (Mackay and Patterson, 1981 and 1982). A review on the use of K_{ow} for estimating chemical properties is provided by Lyman et al., (1982). With the choice of octanol as the standard reference solvent, the basic form of the LFER correlation becomes,

$$\log K_D = a + b \log K_{ow} \quad (4-29)$$

The definition of the LFER concept (Wells, 1968) limits equation (4-29) to systems which are subjected to the same conditions. Leo and Hansch (1971) have shown that better results are obtained when acidic and basic solutes are correlated separately. Further, the evaluation of the LFER approach in this study (Campbell et al., 1983) has shown that the procedure is not expected to work well when the solute set contains molecules which can H-bond with both solvents along with those which can H-bond with only one solvent. The implications of this observation are discussed in more detail in Chapter Five.

4.4.3. LFER Correlation Coefficients

Because LFER correlations are limited to certain types of solutes the correlation coefficients a and b are dependent upon solvent and solute class. For a given solute set we would expect different correlation constants for different solvents. For example, when correlating a given set of phenolic solute data the values of a and b differ for different solvent classes (e.g. ketone vs. aromatic hydrocarbon). Similarly, for a given solvent we would expect different correlation constants for different solute sets. For example, when correlating distribution coefficients for MIBK-solute systems, data from a series of substituted pyridines will not fit the correlation developed for phenolic solutes. Hence, the limitations and boundaries of a particular LFER correlation should be well understood before we attempt to use that equation for prediction of distribution coefficients or for interpretation of the partitioning process.

LFER correlation coefficients can also be used as an indicator of solute-solvent interaction as compared to the standard reference system, octanol. Leo and Hansch (1971) define the slope value (a) obtained in linear free energy analysis as a measure of the solvent systems sensitivity to changes in the "lipophilicity" of the solutes. For example, if the slope is unity then the solvent system reacts to functional group substitution in a series of solutes in a manner similar to octanol. If the slope is greater than one, the solvent is more sensitive than octanol to "lipophilic" substitution on solute molecules. In other words, as a particular solute becomes more hydrophobic by addition of lipophilic ("organic") substituents (e.g. by substitution of methyl groups in the series benzene-methylbenzene-dimethylbenzene) the value of K_D in the solvent rises at a faster rate than it does in octanol ($\Delta K_D / \Delta K_{ow} > 1$). For slopes (a) less than unity, the opposite is true and the relative rate of distribution coefficient increase is lower ($\Delta K_D / \Delta K_{ow} < 1$).

Leo and Hansch (1971) suggest that the intercept values obtained in linear free energy analysis are a measure of the hydrophobicity of a solvent relative to octanol. This follows from the fact that the ordinate intercept represents a

condition where a hypothetical solute is equally distributed between the aqueous and octanol phases ($\log K_{ow} = 0$) with the solute's distribution between the correlating solvent and water being variable. When the intercept is positive ($K_D > 1$), the hypothetical solute prefers the solvent over the aqueous phase, a negative intercept ($K_D < 1$) indicates a preference for water. If the intercept is zero ($K_D = 1$) we expect that the solvent possesses a chemical nature similar to octanol; if the slope also has a value of unity then the solvent possesses properties identical to octanol. It is suggested that if the intercept is positive the solvent is more hydrophilic than octanol while a negative intercept indicates greater hydrophobic character. Leo and Hansch show a strong correlation between intercept values and the solubility of water in solvents to support this hypothesis.

As the preceding discussion suggests, linear free energy analysis provides several uses from a single least squares regression equation. We can predict distribution coefficients for a particular solvent-solute system, we can observe solute properties by noting which correlation equation best represents that solute, and we can observe solvent properties by examining the correlation coefficients.

Chapter 5

ESTIMATION OF DISTRIBUTION COEFFICIENTS AND
EVALUATION OF EQUILIBRIUM MODELS

5.1. Introduction

This chapter evaluates the applicability of the models described in Chapter Four for estimating distribution coefficients for aromatic solutes. Estimated distribution coefficients are compared with experimental K_D values for eight solvent systems: octanol, MIBK, NBA, DIPE, toluene, benzene, hexane and heptane. These compounds are representative of six different organic solvent classes: alcohols, ketones, esters, ethers, aromatic hydrocarbons, and alkanes. Experimental distribution coefficients were obtained from this work as well as from the literature. Other sources include: the Medchem Project (1983), Hansch and Leo (1979), and Greminger and King (1979). The bulk of the data were obtained from the experimental results presented in Chapter Three and from the compilation provided by the Medchem Project.

Distribution coefficients predicted using the regular solution and UNIFAC models are based on the definition of K_D as the ratio of solute infinite dilution activity coefficients described in Chapter One;

$$K_D = (\gamma_w^\infty / \gamma_s^\infty) (V_w / V_s) \quad (5-1)$$

where:

γ_w^∞ = infinite dilution mole fraction activity coefficient of solute
in aqueous phase

γ_s^∞ = infinite dilution mole fraction activity coefficient of solute
in organic solvent phase

V_w = molar volume of water (cm^3/mole)

V_s = molar volume of organic solvent (cm^3/mole)

Analysis of the regular solution model was limited to systems where experimental aqueous phase activity coefficients and experimental distribution coefficients were available. Analysis of the UNIFAC model was limited by availability of functional group interaction parameters and experimental distribution coefficients. The UNIFAC model was examined for two cases, 1) where both aqueous and solvent phase activity coefficients are computed by UNIFAC and 2) where the solvent phase activity coefficient was estimated by UNIFAC and experimental γ_w^∞ values are used. Hence, in the second case the analysis was also limited by the availability of experimental aqueous phase activity coefficients. Analysis of the LFER approach was limited to systems where experimental distribution coefficients are available for the reference system, octanol, and the solvent system being correlated.

It should be reiterated that the purpose of this investigation was to evaluate solvent extraction processing for removal of aromatic solutes from wastewaters. Since it is very likely that design engineers will have experimental distribution coefficients for primary wastewater solutes, modeling techniques will probably be used for assessing the fate of minor and trace contaminants during solvent extraction processing for evaluating changes in process operating conditions. Hence, it is not necessary that a predictive technique provide absolute estimates of distribution coefficients; rather a model should provide a reasonable estimate of K_D so that engineering evaluations can be carried out effectively.

5.2. Regular Solutions

5.2.1. Introduction

The use of the regular solution model for predicting distribution coefficients is examined in this section, data are displayed in Tables 5-1 through 5-8. Two values of predicted K_D are shown, one for each empirical correction term correlation (Ψ_{12} , eqn. 4-15 and Ψ_{12}^* , eqn. 4-16). Error factors are also shown in Tables 5-1 through 5-8. The error factor is defined as the quotient of experimental and predicted distribution coefficients, hence overestimates of K_D have error factors less than one while underestimates have error factors greater than unity. The average error factors shown on each table represent the average of error factors greater than one and the reciprocals of error factors less than one.

It is important to remember that the regular solution approach is not applicable to aqueous systems, therefore aqueous phase activity coefficients must be obtained elsewhere. For the aromatic solutes of interest in this investigation we have obtained experimental γ_w^∞ values from Tsonopoulos and Prausnitz (1971), these are listed in Appendix A. Other tabulations of experimental γ_w^∞ values for aromatics can be found in the papers of Mackay and Shiu (1977) and Pierotti et al., (1959). If experimental aqueous phase activity coefficients are not available they can be estimated from the relatively simple correlation of Pierotti et al., (1959) or by the more complex UNIFAC model.

The regular solution model is easily adapted for computer computation. The Fortran program used in this work and the appropriate solute and solvent input data are presented in Appendix A. It should be noted that the notation used for the empirical correction terms in Tables 5-1 through 5-8 and in Appendix A is different from that of the text; the symbols Ψ_{12} and Ψ_{12}^* are replaced by PSI12 and PSI12*, respectively.

Table 5-1: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and Octanol Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR (1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	29.0	3.80	84.00	7.63	0.35
2-BROMOPHENOL	110.0	13.00	9.80	8.46	11.20
2-CHLOROPHENOL	140.0	10.00	8.30	14.00	17.00
4-CHLOROPHENOL	250.0	12.00	430.00	21.00	0.58
2-HYDROXYPHENOL	8.7	0.08	2.60	109.00	3.35
4-HYDROXYPHENOL	3.9	0.14	0.09	28.00	43.00
2-METHYLPHENOL	87.0	12.00	470.00	7.30	0.19
4-METHYLPHENOL	87.0	15.00	650.00	5.80	0.13
2,4-DIMETHYLPHENOL	200.0	15.00	410.00	13.00	0.49
3,5-DIMETHYLPHENOL	220.0	31.00	2100.00	7.10	0.10
2-NITROPHENOL	100.0	96.00	2500.00	1.04	0.04
ANILINE	7.9	7.10	140.00	1.11	0.06
1-HYDROXYNAPHTHALENE	690.0	190.00	10000.00	3.60	0.07
2-AMINONAPHTHALENE	180.0	51.00	37.00	3.53	4.87
NAPHTHALENE	2000.0	7300.00	500000.00	0.27	0.01
BENZENE	140.0	250.00	1600.00	0.56	0.09
CHLOROBENZENE	450.0	1000.00	13000.00	0.45	0.04
1,2-DICHLOROBENZENE	2400.0	2800.00	2200.00	0.86	1.09
ETHYLBENZENE	1400.0	2600.00	2000.00	0.54	0.70
METHYLBENZENE	540.0	860.00	5400.00	0.63	0.10
1,2-DIMETHYLBENZENE	1300.0	2000.00	1600.00	0.65	0.81
1,4-DIMETHYLBENZENE	1400.0	2300.00	1800.00	0.61	0.78
1,3,5-TRIMETHYLBENZENE	2600.0	4600.00	3400.00	0.57	0.76
AVERAGE ERROR FACTOR (2)				11	14

Table 5-2: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and Diisopropyl Ether Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR (1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	30.0	1.80	0.300	17.00	100.00
2-HYDROXYPHENOL	4.9	0.03	0.010	163.00	490.00
3-HYDROXYPHENOL	2.0	0.01	0.001	200.00	2000.00
4-HYDROXYPHENOL	1.0	0.04	0.001	25.00	1000.00
ANILINE	7.6	3.10	3.300	2.45	2.30
1-HYDROXYNAPHTHALENE	740.0	75.00	100.000	9.87	7.40
2-AMINONAPHTHALENE	140.0	12.00	12.000	12.00	12.00
NAPHTHALENE	3500.0	6600.00	240.000	0.53	15.00
AVERAGE ERROR FACTOR (2,3)				8.4	27

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

(3) COMPUTED WITHOUT ERROR FOR HYDROXYPHENOLS

Table 5-3: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and N-Butyl Acetate Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR (1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	71.0	3.10	37.00	23.00	1.90
2-BROMOPHENOL	290.0	9.10	7.30	32.00	40.00
2-CHLOROPHENOL	220.0	8.50	7.10	26.00	31.00
4-CHLOROPHENOL	320.0	9.20	200.00	35.00	1.60
2-HYDROXYPHENOL	14.0	0.06	1.00	233.00	14.00
4-HYDROXYPHENOL	4.5	0.09	0.02	50.00	225.00
2-METHYLPHENOL	170.0	9.50	230.00	18.00	0.74
4-METHYLPHENOL	200.0	12.00	250.00	17.00	0.90
2,4-DIMETHYLPHENOL	320.0	12.00	230.00	27.00	1.40
3,5-DIMETHYLPHENOL	540.0	24.00	970.00	22.00	0.56
2-NITROPHENOL	200.0	72.00	1300.00	2.78	0.15
ANILINE	23.0	5.40	73.00	4.30	0.32
1-HYDROXYNAPHTHALENE	1360.0	140.00	4800.00	9.70	0.28
2-AMINONAPHTHALENE	520.0	29.00	23.00	18.00	23.00
NAPHTHALENE	6500.0	8800.00	230000.00	0.74	0.03
AVERAGE ERROR FACTOR (2)				20(3)	12(4)

Table 5-4: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and Methylisobutyl Ketone Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	100.0	3.100	280.00	32.00	0.36
2-CHLOROPHENOL	490.0	7.600	5.50	65.00	89.00
2-HYDROXYPHENOL	20.0	0.050	6.90	400.00	2.90
4-HYDROXYPHENOL	10.0	0.100	0.72	100.00	14.00
2,3-DIHYDROXYPHENOL	3.6	0.001	0.03	3600.00	120.00
3-METHYLPHENOL	260.0	10.000	2100.00	26.00	0.12
3,5-DIMETHYLPHENOL	810.0	23.000	5200.00	35.00	0.16
ANILINE	32.0	5.200	230.00	6.15	0.14
1-HYDROXYNAPHTHALENE	1370.0	130.000	20000.00	11.00	0.07
NAPHTHALENE	5100.0	9400.000	5600000.00	0.54	<0.001
AVERAGE ERROR FACTOR (2)				34(5)	29(6)

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

(3) COMPUTED WITHOUT ERROR FOR 2-HYDROXYPHENOL

(4) COMPUTED WITHOUT ERROR FOR 4-HYDROXYPHENOL

(5) COMPUTED WITHOUT ERROR FOR 2-HYDROXYPHENOL AND 2,3-DIHYDROXYPHENOL

(6) COMPUTED WITHOUT ERROR FOR NAPHTHALENE

Table 5-5: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and Toluene Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR (1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	2.00	6.60	0.650	0.30	3.10
2-BROMOPHENOL	41.00	48.00	47.000	0.85	0.87
2-CHLOROPHENOL	23.00	28.00	27.000	0.82	0.85
4-CHLOROPHENOL	12.00	25.00	11.000	0.48	1.09
2-HYDROXYPHENOL	0.05	0.19	0.030	0.26	1.67
4-HYDROXYPHENOL	0.01	0.27	0.001	0.04	10.00
2-METHYLPHENOL	14.00	23.00	11.000	0.61	1.27
4-METHYLPHENOL	11.00	26.00	1.700	0.42	6.50
2,4-DIMETHYLPHENOL	18.00	40.00	50.000	0.45	0.36
3,5-DIMETHYLPHENOL	20.00	74.00	46.000	0.27	0.43
2-NITROPHENOL	190.00	250.00	240.000	0.76	0.79
ANILINE	8.30	17.00	13.000	0.49	0.64
1-HYDROXYNAPHTHALENE	63.00	520.00	490.000	0.12	0.13
2-AMINONAPHTHALENE	230.00	360.00	350.000	0.64	0.66
AVERAGE ERROR FACTOR (2)				4.3	3.1

Table 5-6: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and Benzene Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	2.30	8.00	1.300	0.29	1.77
2-BROMOPHENOL	48.00	61.00	59.000	0.79	0.81
2-CHLOROPHENOL	29.00	34.00	33.000	0.85	0.88
4-CHLOROPHENOL	17.00	32.00	21.000	0.53	0.81
2-HYDROXYPHENOL	0.06	0.25	0.070	0.24	0.86
4-HYDROXYPHENOL	0.01	0.34	0.001	0.03	10.00
2-METHYLPHENOL	14.00	29.00	30.000	0.48	0.47
3-METHYLPHENOL	7.60	31.00	5.400	0.25	1.41
2,4-DIMETHYLPHENOL	22.00	51.00	87.000	0.43	0.25
3,5-DIMETHYLPHENOL	22.00	96.00	93.000	0.23	0.24
2-NITROPHENOL	210.00	320.00	420.000	0.66	0.50
ANILINE	10.00	21.00	22.000	0.48	0.45
1-HYDROXYNAPHTHALENE	78.00	690.00	960.000	0.11	0.08
2-AMINONAPHTHALENE	280.00	450.00	430.000	0.62	0.65
AVERAGE ERROR FACTOR (2)				5.2	3.3

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

Table 5-7: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and Hexane Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR (1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	0.150	2.10	0.620	0.07	0.24
2-BROMOPHENOL	12.000	6.40	6.100	1.88	1.97
2-CHLOROPHENOL	7.100	6.80	6.500	1.04	1.09
4-CHLOROPHENOL	0.560	6.40	6.200	0.09	0.09
2-HYDROXYPHENOL	0.001	0.03	0.020	0.03	0.05
4-HYDROXYPHENOL	0.001	0.05	0.001	0.02	1.00
2-METHYLPHENOL	1.900	6.60	7.400	0.29	0.26
2,4-DIMETHYLPHENOL	2.300	19.00	8.100	0.12	0.29
3,5-DIMETHYLPHENOL	2.300	26.00	16.000	0.09	0.14
2-NITROPHENOL	25.000	48.00	90.000	0.52	0.28
ANILINE	0.910	3.70	5.500	0.25	0.17
1-HYDROXYNAPHTHALENE	3.300	94.00	200.000	0.04	0.02
2-AMINONAPHTHALENE	11.000	16.00	16.000	0.69	0.69
BENZENE	220.000	200.00	360.000	1.10	0.61
CHLOROBENZENE	890.000	680.00	1400.000	1.31	0.64
METHYLBENZENE	740.000	680.00	1300.000	1.09	0.57
1,2-DIMETHYLBENZENE	1300.000	1600.00	1500.000	0.81	0.87
1,4-DIMETHYLBENZENE	520.000	1900.00	1800.000	0.27	0.29
AVERAGE ERROR FACTOR (2)				9.7	6.9

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAIS OF E.F. <1

Table 5-8: Experimental and Predicted Distribution Coefficients For Various Aromatic Solutes Between Water and Heptane Using Regular Solution Theory and Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR (1)	
		PSI12*	PSI12	PSI12*	PSI12
PHENOL	0.130	2.20	0.100	0.06	1.30
2-BROMOPHENOL	11.000	7.80	7.000	1.41	1.57
2-CHLOROPHENOL	7.100	7.70	7.700	0.92	0.92
4-CHLOROPHENOL	0.470	6.60	1.400	0.07	0.34
2-HYDROXYPHENOL	0.001	0.04	0.001	0.03	1.00
4-HYDROXYPHENOL	0.001	0.05	0.001	0.02	1.00
2-METHYLPHENOL	1.600	7.00	1.600	0.23	1.00
4-METHYLPHENOL	0.450	8.20	0.210	0.06	2.14
2,4-DIMETHYLPHENOL	2.300	8.90	7.000	0.26	0.33
3,5-DIMETHYLPHENOL	1.900	17.00	5.300	0.11	0.36
2-NITROPHENOL	25.000	54.00	32.000	0.46	0.76
ANILINE	0.870	4.10	2.000	0.21	0.43
1-HYDROXYNAPHTHALENE	3.600	100.00	53.000	0.04	0.07
NAPHTHALENE	2400.000	6200.00	30.000	0.39	80.00
BENZENE	180.000	210.00	210.000	0.86	0.86
METHYLBENZENE	710.000	710.00	790.000	1.00	0.90
1,2-DIMETHYLBENZENE	2500.000	1800.00	1700.000	1.39	1.47
1,4-DIMETHYLBENZENE	2800.000	2100.00	2000.000	1.33	1.40
AVERAGE ERROR FACTOR (2)				2.1	2.4(3)

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

(3) COMPUTED WITHOUT ERROR FOR NAPHTHALENE

5.2.2. Data Analysis

Data for the polar solvent-aromatic solute systems are shown in Tables 5-1 through 5-4. The data reveal that the regular solution model does not give reliable predictions of K_D for polar solute-polar solvent systems. For example, Ψ_{12}^* estimates of K_D for octanol are predicted within a factor of two for benzene, eight for phenol and twenty eight for 4-hydroxyphenol. This stems from the fact that the regular solution concept excludes systems which include specific interactions, notably hydrogen bonding. Furthermore, there is an inherent error in the model owing to the correlations from which the empirical correction terms were predicted. These correlations are based on data from Deal and Derr (1964) and Pierotti, et al. (1959), which do not include polar solute polar solvent systems.

Tables 5-1 through 5-4 do show that the regular solution model provides reasonable estimates of K_D for nonpolar solute-polar solvent systems when the empirical correction term is correlated with solvent and solute polar solubility parameters, $\Psi_{12}^* = 0.477(\tau_1 - \tau_2)^2$. This is evidenced by K_D estimates for naphthalene in DIPE, NBA and MIBK being within a factor of two of the experimental value. In addition, the average error factor for K_D estimates using Ψ_{12}^* for the 13 nonpolar solutes is 1.7, while the average error factor for all the data in Tables 5-1 through 5-4 is 17 and 22 for K_D estimates using Ψ_{12}^* and Ψ_{12} , respectively.

Data for the nonpolar solvent-aromatic solute systems are presented in Tables 5-5 through 5-8. For these systems it is shown that the regular solution approach provides estimates of K_D which are of much greater accuracy than those for the polar solvent systems. The average error factors for the nonpolar solvent systems are 4 with Ψ_{12} and 7.8 with Ψ_{12}^* . Hence, we can see that range values of K_D can be predicted by the regular solution model for solute-solvent systems that do not interact through hydrogen bonding. This observation is consistent with the assumptions of the regular solution model discussed in Chapter Four.

The data in Tables 5-1 through 5-8 also show that the regular solution model provides better accuracy for estimation of K_D for polar solvent systems when the empirical correction term accounts for the polarity of the solute molecules, i.e. Ψ_{12}^* . Alternatively, better accuracy for estimation of K_D for the nonpolar solvent systems is obtained when the empirical correction term is correlated only with the solvent polar solubility parameter, i.e. Ψ_{12} . This is consistent with the fact that as the limit of infinite dilution is approached, a given solute molecule will interact only with solvent molecules. Hence, the polar solubility parameter of the solute does not reflect a significant contribution to the interaction between a given solute molecule and its nearest neighbors in a nonpolar solvent. Whereas, the interaction between a given solute molecule and its nearest neighbors, at infinite dilution in a polar solvent, would be more dependent upon the solute polar solubility parameter.

An interesting observation can be made by examining the Ψ_{12}^* estimates of K_D in Tables 5-1 through 5-8. For the polar solvent systems, K_D estimates for polar solutes have error factors greater than one and hence are underestimated by the regular solution model. On the other hand, K_D estimates are uniformly overestimated for the nonpolar solutes in Tables 5-1 through 5-4. The Ψ_{12}^* estimates of K_D for the nonpolar solvent systems in Tables 5-5 through 5-8 are also predominantly overestimated. Hence, the regular solution model, with the Ψ_{12}^* correlation, appears to underestimate K_D 's for polar solute-polar solvent systems, while estimates for systems where one or both components is nonpolar are overestimated.

This observation can also be explained in terms of the hydrogen bonding characteristics of the molecules. The polar aromatic solutes considered in Tables 5-1 through 5-8 can be classified as AB-type H-bonding compounds, while the solvents MIBK, NBA and DIPE are proton acceptors and exhibit B-type H-bonding characteristics. Octanol exhibits both proton acceptor and donor properties and is AB-type with respect to H-bonding. For the purposes of this discussion the nonpolar aromatic solutes and the nonpolar solvents can be

considered as exhibiting no significant H-bonding character and are therefore N-type. Hence, we would expect H-bond formation between the polar solutes and octanol, MIBK, NBA and DIPE. We would not expect H-bond formation between the nonpolar solute-polar solvent pairs or between any solute-nonpolar solvent pair. Thus regular solution theory, with Ψ_{12}^* , results in predictions of K_D which are underestimated for systems where solvent and solute molecules interact through H-bonding, and are overestimated for systems where no solvent-solute H-bonding occurs.

5.2.3. Model Applicability

The reliability of regular solution theory estimates of K_D may be evaluated by examining the error factors shown in Tables 5-1 through 5-8. By assuming that the individual error factors are normally distributed, we can compute 95% confidence intervals for the true mean of the error factors using t-statistics. Miller and Freund (1977) note that the normal distribution provides an excellent approximation to the sampling distribution of the mean for sample sizes greater than 30. The sample sizes in this investigation were $n=51$ for polar solvents and $n=63$ for nonpolar solvents. The 95% confidence interval of the true mean of normally distributed error factors is given by (Miller and Freund, 1977)

$$X \pm (t_{.025}) (S/(n)^{1/2}) \quad (5-2)$$

where:

X = average of error factors >1 plus reciprocals of error factors <1

S = standard deviation of sample

n = sample size

$t_{.025}$ = t-statistic for the 95% confidence range and specified n

The 95% confidence intervals for regular solution K_D estimates are given in Table 5-9. We can see that the most accurate predictions are for nonpolar solvent systems with Ψ_{12} . Only in this case does the regular solution model provide semi-qualitative estimates of K_D .

Table 5-9: Confidence Intervals of Error Factors for Regular Solution Theory Distribution Coefficient Estimates Using Experimental Aqueous Phase Activity Coefficients

SOLVENT SYSTEMS	95% CONFIDENCE INTERVALS	
	PSI12*	PSI12
FOUR POLAR SOLVENT SYSTEMS (n=51)	23 - 11	33 - 11
FOUR NONPOLAR SOLVENT SYSTEMS (n=63)	11 - 5.0	5.6 - 2.3
ALL SOLVENT SYSTEMS (n=114)	15 - 8.6	17 - 6.7

Kiezyk and Mackay (1973) have suggested that the regular solution model, with the empirical correction term Ψ_{12} , can be used to screen solvents for extraction of phenol from water. The data shown here suggest that this analysis is not generally applicable for solutes other than phenol. For example, values of K_D predicted using Ψ_{12} show correctly that MIBK and NBA are much better solvents for extraction of phenol than benzene or heptane. On the other hand, the same analysis shows incorrectly that benzene and toluene are better solvents for extraction of 3,5-dimethylphenol than MIBK and NBA. In reality, the K_D values for 3,5-dimethylphenol in those solvents are 22, 20, 810 and 540, respectively. Hence, based on the data considered here, it appears that this screening procedure is applicable for aromatic solutes with one functional group substitution as is demonstrated for phenol, aniline and hydroxynaphthalene, but that the procedure is not applicable for aromatic solutes with more than one substitution such as 3,5-dimethylphenol, 4-methylphenol, 2-chlorophenol, etc.

We should note that some of the error attributed to the regular solution model is a result of inaccuracy in the experimental K_D values. Approximately half of these values were obtained from the Medchem data base. These values represent experimental analyses performed in different laboratories over many years so that we cannot make any general statement as to the accuracy of the experimental K_D 's obtained from the Medchem Project. In addition, distribution coefficients span many orders of magnitude which requires a great deal of flexibility from a model.

We should also mention that since experimentally determined aqueous phase activity coefficients were used to compute regular solution theory estimates of K_D , the results shown in Tables 5-1 through 5-8 probably represent the highest accuracy attainable by this approach (i.e. equation 4-11). We also recognize that while the accuracy of the regular solution model could be improved by developing expressions for the empirical correction term which more accurately reflect the interactions in polar solute-polar solvent systems, the regular solution approach is still likely to be case specific.

5.3. UNIFAC

5.3.1. Introduction

Distribution coefficients computed using UNIFAC estimates of both aqueous and solvent phase activity coefficients are shown in Tables 5-10 through 5-15. Computation of solute infinite dilution mole fraction activity coefficients was facilitated by use of a computer program. The program written for this work is based on the larger, more flexible UNIFAC program developed by Fredenslund et al., (1977). An updated version of the UNIFAC program is also available (Anderson, 1982). The functional group interaction parameters used in this study were obtained from the most recent compilations of Magnussen et al., (1980), and Gmehling et al., (1982). The Fortran programs employed for this study are given in Appendix B. Calculated activity coefficients for the aromatic solute systems considered here are listed in Appendix Tables B-3 and B-4. The accuracy of the computer program was checked with hand calculations for several systems and with some of Arbuckle's (1983) UNIFAC K_D estimates for octanol systems.

The display of data in Tables 5-10 through 5-15 allows for easy comparison of experimental K_D values with UNIFAC estimates. The Tables also show error factors for vapor-liquid equilibria based (VLE) and liquid-liquid equilibria based (LLE) UNIFAC estimates. The error factor is defined as the quotient of the experimental and predicted distribution coefficients so that overestimates have error factors less than one while underestimates have error factors greater than unity.

UNIFAC does not distinguish between isomeric forms of a molecule, thus there is no distinction between ortho (2), meta (3) or para (4) substitution for aromatic compounds. In addition, UNIFAC assumes that the interaction of a particular functional group is independent of the molecule in which it is situated, therefore the model does not account for intramolecular functional group interactions, e.g. intramolecular H-bonding which may occur with ortho (2)

substituted aromatic compounds. Hence, comparisons between experimental and UNIFAC estimated distribution coefficients are made for either meta (3) or para (4) substitution whenever possible.

5.3.2. Data Analysis

Predicted values of distribution coefficients for the polar solvent-aromatic solute systems are shown in Tables 5-10 and 5-11. These results suggest that for polar solvent systems, UNIFAC predictions based on vapor-liquid equilibria (VLE estimates) are more accurate than predictions based on liquid-liquid equilibria (LLE estimates). Results presented in Table 5-12 through 5-15 show that this is also observed for nonpolar solvent systems.

A closer inspection of Tables 5-10 and 5-11 reveals that UNIFAC VLE estimates of K_D for polar solutes are, in general, lower than experimental K_D values, while VLE estimates for the nonpolar solutes are greater than the experimental values of K_D . While the same trend holds for the LLE estimates of the octanol systems, LLE estimates for the MIBK and NBA systems tend to be greater than the experimental K_D values for all the solutes. This is because LLE estimates of solvent phase activity coefficients for polar solutes in MIBK and NBA tend to be extremely low (see Appendix Table R-4), hence K_D values estimated from LLE data are inordinately large. LLE based γ_s^ω values for the MIBK-phenol and MIBK-4-hydroxyphenol systems are lower than an arbitrary limit of 0.001, hence the LLE K_D 's for these systems are given as greater than values in Table 5-11. We should note that the number of distribution coefficients being compared for the solute-solvent systems in Table 5-11 is small because of a lack of experimental K_D data for MIBK, and because of a lack of UNIFAC functional group interaction parameters for ether (DIPE) and ester (NRA) oxygen functional groups.

Comparison of experimental and predicted values of K_n for the nonpolar solvent-aromatic solute systems are shown in Tables 5-12 through 5-15. These data follow certain trends noted for the polar solvent systems: 1) VLE data

Table 5-10: Experimental and Predicted Distribution Coefficients for Aromatic Solutes Between Water and Octanol Using the UNIFAC Model

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		VLE	LLE	VLE	LLE
ANILINE	7.9	9.7	18.00	0.81	0.44
4-NITROANILINE	25.0	3.9	7.10	6.41	3.52
BENZENE	140.0	170.0	260.00	0.82	0.54
CHLOROBENZENE	450.0	1200.0	320.00	0.38	1.41
1,4-DICHLOROBENZENE	2500.0	8000.0	380.00	0.31	6.58
ETHYLBENZENE	1400.0	1900.0	2100.00	0.74	0.67
METHYLBENZENE	540.0	750.0	630.00	0.72	0.86
1,4-DIMETHYLBENZENE	1400.0	3300.0	1500.00	0.42	0.93
1,3,5-TRIMETHYLBENZENE	2600.0	14000.0	3500.00	0.19	0.74
NITROBENZENE	71.0	69.0	120.00	1.03	0.59
NAPHTHALENE	2000.0	4500.0	8200.00	0.44	0.24
2-AMINONAPHTHALENE	180.0	250.0	560.00	0.72	0.32
1-HYDROXYNAPHTHALENE	690.0	325.0	150.00	2.12	4.60
2-HYDROXYQUINOLINE	18.0	18.0	16.00	1.00	1.13
8-HYDROXYQUINOLINE	100.0	18.0	16.00	5.56	6.25
4-METHYL ,8-HYDROXYQUINOLINE	230.0	75.0	37.00	3.07	6.22
PYRIDINE	4.5	3.5	14.00	1.29	0.32
PHENOL	29.0	12.0	4.80	2.42	6.04
4-HYDROXYPHENOL	3.9	0.9	0.09	4.33	43.00
4-METHYLPHENOL	87.0	54.0	11.00	1.61	7.91
3,5-DIMETHYLPHENOL	220.0	240.0	27.00	0.92	8.15
4-NITROPHENOL	81.0	5.0	1.90	16.00	43.00
AVERAGE ERROR FACTOR (2)				3.0	6.8

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

Table 5-11: Experimental and Predicted Distribution Coefficients for Aromatic Solutes Between Water and Three Polar Solvents Using the UNIFAC Model

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		VLE	LLE	VLE	LLE
METHYLISOBUTYL KETONE					
ANILINE	32.0	11.00	1.50	2.91	21.000
NAPHTHALENE	5100.0	15000.00	7600.00	0.34	0.671
1-HYDROXYNAPHTHALENE	1370.0	330.00	460000.00	4.15	0.003
8-HYDROXYQUINOLINE	130.0	3.40	3900.00	38.00	0.033
2-METHYL,8-HYDROXYQUINOLINE	320.0	18.00	9800.00	18.00	0.033
PYRIDINE	2.9	0.84	0.44	3.45	6.600
PHENOL	100.0	8.60	>7700.00	12.00	*****
4-HYDROXYPHENOL	10.0	0.19	>120.00	53.00	*****
3-METHYLPHENOL	260.0	45.00	29000.00	5.78	0.009
3,5-DIMETHYLPHENOL	810.0	240.00	92000.00	3.38	0.009
n-BUTYL ACETATE					
NAPHTHALENE	6500.0	14000.00	31000.00	0.46	0.210
1-HYDROXYNAPHTHALENE	1400.0	370.00	440000.0	3.78	0.001
PHENOL	71.0	9.20	7400.00	7.72	0.009
4-HYDROXYPHENOL	4.5	0.24	110.00	18.75	0.041
4-METHYLPHENOL	200.0	41.00	28000.00	4.88	0.007
3,5-DIMETHYLPHENOL	540.0	180.00	87000.00	3.00	0.006
DIISOPROPYL ETHER					
NAPHTHALENE	3500.0	9600.00	51000.00	0.36	0.069
AVERAGE ERROR FACTOR (2)				11	55(3)

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

(3) COMPUTED WITHOUT DATA FOR 1-HYDROXYNAPHTHALENE IN NBA

Table 5-12: Experimental and Predicted Distribution Coefficients for Aromatic Solutes Between Water and Benzene Using the UNIFAC Model

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		VLE	LLE	VLE	LLE
ANILINE	10.00	6.000	170.000	1.67	0.059
4-NITROANILINE	8.50	5.000	240.000	1.70	0.035
2-AMINONAPHTHALENE	280.00	360.000	10000.000	0.79	0.028
1-HYDROXYNAPHTHALENE	78.00	16.000	145.000	4.88	0.540
8-HYDROXYQUINOLINE	370.00	0.180	11.000	2056.0	34.000
PYRIDINE	2.80	1.200	25.000	2.33	0.111
3,5-DIMETHYLPYRIDINE	32.00	75.000	625.000	0.43	0.051
PHENOL	2.30	0.270	2.300	8.52	1.000
4-HYDROXYPHENOL	0.01	<0.001	0.010	****	1.000
5-METHYL,3-HYDROXYPHENOL	0.03	<0.001	0.031	****	0.969
2,5-DIMETHYL,3-HYDROXYPHENOL	0.27	0.004	0.091	68.00	2.970
AVERAGE ERROR FACTOR (2)				11(3)	14

Table 5-13: Experimental and Predicted Distribution Coefficients for Aromatic Solutes Between Water and Toluene Using the UNIFAC Model

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		VLE	LLE	VLE	LLE
ANILINE	2.00	4.500	73.0	0.44	0.027
4-NITROANILINE	6.00	5.000	170.0	1.20	0.035
2-AMINONAPHTHALENE	230.00	250.000	4100.0	0.92	0.056
1-HYDROXYNAPHTHALENE	63.00	18.000	1200.0	3.50	0.053
8-HYDROXYQUINOLINE	170.00	0.180	46.0	944.00	3.700
2-METHYL,8-HYDROXYQUINOLINE	560.00	0.850	124.0	659.00	4.516
PYRIDINE	2.50	0.860	5.1	2.90	0.492
PHENOL	2.00	0.330	21.0	6.10	0.095
4-HYDROXYPHENOL	0.01	<0.001	1.0	****	0.010
5-METHYL,3-HYDROXYPHENOL	0.03	0.001	2.7	30.00	0.011
2,5-DIMETHYL,3-HYDROXYPHENOL	0.21	0.006	7.4	35.00	0.028
4-METHYLPHENOL	11.00	1.600	58.0	6.88	0.190
3,5-DIMETHYLPHENOL	20.00	7.500	157.0	2.67	0.127
2-NITROPHENOL	190.00	0.360	50.0	528.00	3.800
AVERAGE ERROR FACTOR (2)				9.2(4)	26

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

(3) COMPUTED WITHOUT ERROR FOR 8- HYDROXYQUINOLINE

(4) COMPUTED WITHOUT ERROR FOR SUBSTITUTED QUINOLINES AND 2-NITROPHENOL

Table 5-14: Experimental and Predicted Distribution Coefficients for Aromatic Solutes Between Water and Heptane Using the UNIFAC Model

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		VLE	LLE	VLE	LLE
ANILINE	0.870	0.450	2.200	1.93	0.40
4-NITROANILINE	0.089	0.100	0.200	0.89	0.45
BENZENE	180.000	200.000	300.000	0.90	0.60
METHYLBENZENE	710.000	960.000	830.000	0.74	0.86
1,4-DIMETHYLBENZENE	2800.000	4500.000	2300.000	0.62	1.27
NITROBENZENE	27.000	44.000	27.000	0.61	1.00
NAPHTHALENE	2400.000	6500.000	12000.000	0.37	0.20
1-HYDROXYNAPHTHALENE	3.600	2.400	2.200	1.50	1.64
8-HYDROXYQUINOLINE	22.000	0.017	0.015	1294.0	1467.0
PHENOL	0.130	0.075	0.058	1.73	2.24
4-HYDROXYPHENOL	0.001	<0.001	<0.001	****	****
5-METHYL,3-HYDROXYPHENOL	<0.001	<0.001	<0.001	****	****
2,5-DIMETHYL,3-HYDROXYPHENOL	0.004	0.001	<0.001	4.00	****
4-METHYLPHENOL	0.450	0.350	0.160	1.29	2.81
3,5-DIMETHYLPHENOL	1.900	1.700	0.440	1.12	4.32
2-NITROPHENOL	25.000	0.016	0.005	1563.0	5000.0
AVERAGE ERROR FACTOR (2,3)				1.8	2.4

Table 5-15: Experimental and Predicted Distribution Coefficients for Aromatic Solutes Between Water and Hexane Using the UNIFAC Model

SOLUTE	EXPER	PREDICTED KD'S		ERROR FACTOR(1)	
		VLE	LLE	VLE	LLE
ANILINE	0.910	0.480	2.350	1.90	0.39
4-NITROANILINE	0.240	0.110	0.220	2.18	1.76
BENZENE	220.000	215.000	320.000	1.02	0.69
METHYLBENZENE	740.000	1000.000	890.000	0.74	0.83
1,4-DIMETHYLBENZENE	520.000	5000.000	2500.000	0.10	0.21
NITROBENZENE	30.000	48.000	30.000	0.63	1.00
2-AMINONAPHTHALENE	11.000	23.000	93.000	0.48	0.12
1-HYDROXYNAPHTHALENE	3.300	2.700	2.500	1.22	1.32
8-HYDROXYQUINOLINE	25.000	0.018	0.016	1390.0	1562.0
PHENOL	0.150	0.080	0.061	1.88	2.46
4-HYDROXYPHENOL	0.001	<0.001	<0.001	****	****
5-METHYL,3-HYDROXYPHENOL	<0.001	<0.001	<0.001	****	****
2,5-DIMETHYL,3-HYDROXYPHENOL	0.005	0.001	<0.001	5.00	****
2-METHYLPHENOL	1.900	0.384	0.170	4.95	11.00
3,5-DIMETHYLPHENOL	2.300	1.900	0.480	1.21	4.80
2-NITROPHENOL	25.000	0.018	0.006	1390.0	4167.0
AVERAGE ERROR FACTOR (2,3)				2.9	3.7

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCALLS OF E.F. <1

(3) COMPUTED WITHOUT ERROR FOR 8-HYDROXYQUINOLINE AND 2-NITROPHENOL

generally provide better estimates of K_D than do corresponding LLE data, and 2) VLE predictions for the polar solutes are generally underestimated while VLE predictions for nonpolar solutes are overestimated. The results also show that the accuracy of UNIFAC K_D predictions are better for the heptane and hexane systems than for toluene and benzene systems; particularly for LLE predictions. We should note that the K_D values for some of the hydroxyphenols in Tables 5-12 through 5-15 are less than 0.001; which was chosen as a lower limit for reasons of practical significance.

It is observed from results of the VLE predictions in Tables 5-10 through 5-15 that, in general, 8-hydroxyquinoline (8-HQ) and 2-nitrophenol are responsible for the largest error factors for any given solvent system. This is a result of the failure of UNIFAC to account for intramolecular functional group interaction. Both 8-HQ and 2-nitrophenol are AB-species where the A and B functional groups are situated close enough to one another to form intramolecular H-bonds. The UNIFAC group interaction parameters do not account for this behavior. The effect of intramolecular H-bonding is shown clearly in Table 5-10 where the VLE estimate of K_D for 2-HQ (no intramolecular H-bonding possible) is exact while the VLE estimate of K_D for 8-HQ is low by a factor of 5.6.

Data presented thus far have shown that, in general, UNIFAC estimates of K_D based on VLE data are better than corresponding estimates based on LLE data. This observation can be explained by considering the VLE and LLE group interaction parameters. Data employed in the UNIFAC model are subjected to a consistency test before they are used for extrapolation of interaction parameters. The consistency test for the VLE data has a thermodynamic basis which gives it a strong objective criteria for judgement (Fredenslund et al., 1977), while the consistency check for LLE data does not follow a strict thermodynamic criteria and is therefore somewhat arbitrary (Magnussen et al., 1981). In addition, the VLE based data are reduced in a manner which maximizes accuracy for computation of activity coefficients while LLE data are reduced for prediction of absolute mole fractions. Hence, LLE parameters are

not expected to yield highly accurate solute distribution coefficients at small concentrations (Magnussen et al., 1981).

The data base from which VLE parameters are reduced is also much larger than the LLE data base. Hence, we would expect greater overall accuracy and a wider range of applicability for VLE parameters (Gmehling et al., 1982). The LLE parameters are derived primarily from systems where one or both components are alkanes or water. Therefore, we would expect this data to more accurately represent systems which contain CH_2 , CH_3 or H_2O group interaction terms (Magnussen et al., 1981). Indeed, Tables 5-10, 5-14 and 5-15 show that comparable accuracy is obtained for VLE and LLE predictions for octanol, hexane and heptane systems.

Tables 5-10 through 5-15 also show that VLE estimates of K_D for polar solutes are, in general, lower than experimental K_D values while VLE estimates of K_D for nonpolar solutes are overestimated. Arbuckle's (1983) examination of the UNIFAC model for prediction of K_{ow} values for organic priority pollutants also shows this trend. We can explain this observation by considering the definition of K_D (eqn. 5-1) and by examining UNIFAC estimates of the infinite dilution aqueous phase activity coefficients shown in Table 5-16. Table 5-16 shows that VLE predictions tend to be greater than experimental γ_w^∞ values for nonpolar aromatic solutes and lower than experimental γ_w^∞ values for polar aromatic solutes. This observation in combination with equation (5-1) (overestimates of γ_w^∞ result in overestimates of K_D , etc.) explains the K_D prediction trend. We should also note that γ_w^∞ values predicted using LLE data are more accurate than VLE γ_w^∞ predictions. This is consistent with the fact that the LLE data base is dominated by systems where water is one of the components (Magnussen et al., 1981).

Table 5-16: Infinite Dilution Aqueous Phase Activity Coefficients

SOLUTE	EXPERIMENTAL (1)	UNIFAC ESTIMATES	
		VLE	LLE
BENZENE	2500	2400	2500
CHLOROBENZENE	13000	19000	10000
1,2-DICHLOROBENZENE	56000	170000	28000
ETHYLBENZENE	35000	34000	30000
METHYLBENZENE	9500	12000	7200
1,4-DIMETHYLBENZENE	31000	56000	19000
1,3,5-TRIMETHYLBENZENE	69000	250000	48000
NAPHTHALENE	66000	140000	150000
ANILINE	130	91	577
1-AMINONAPHTHALENE	6400	4000	35000
1-HYDROXYNAPHTHALENE	3500	490	3200
PHENOL	47	11	54
4-HYDROXYPHENOL	4.3	0.11	0.83
4-METHYLPHENOL	190	43	200
3,5-DIMETHYLPHENOL	485	171	640
NITROPHENOL	1900	51	110

(1) DATA SOURCE: TSONOPOULOS AND PRAUSNITZ, 1971

5.3.3. Model Applicability

The following discussion refers only to UNIFAC estimates of K_D based on VLE data because of the greater accuracy obtained with VLE group interaction parameters.

By assuming that the error factors for the K_D estimates are normally distributed we can compute 95% confidence intervals for the true mean of the error factors in Tables 5-10 through 5-15. This analysis parallels the discussion presented in section 5.2.3. The 95% confidence intervals for the average error factors are shown in Table 5-17. We can see that the UNIFAC model provides only semi-qualitatively correct estimates of K_D . Even for the most accurate systems (octanol, hexane and heptane) UNIFAC K_D estimates are not of sufficient accuracy for engineering design of solvent extraction systems. Data in Tables 5-9 and 5-17 show that in comparison with the regular solution approach, the UNIFAC model is more accurate for polar solvent systems, while the regular solution model, using experimental γ_w^∞ values, appears to be more accurate for the nonpolar solvent systems considered here. As discussed later, UNIFAC estimated values of K_D are improved if estimated values of γ_w^∞ are replaced by experimental aqueous phase activity coefficients. Again, we should note that no general statement can be made regarding the accuracy of the experimental distribution coefficients obtained from the Medchem Project. In addition, prediction of distribution coefficients which vary over as many as six orders of magnitude requires a great deal of model flexibility.

Although UNIFAC VLE estimates of K_D provide only semi-qualitative accuracy the results are useful for a relative ranking of K_D values for several solutes being extracted by a particular solvent. For example, estimated K_D values in octanol decrease in the order: naphthalene > methylbenzene > benzene > methylphenol > phenol; solutes in MIBK show the ranking: naphthalene > methylphenol > phenol > aniline > pyridine, etc. UNIFAC also provides a procedure for obtaining a relative ranking of several solvents for extraction of a particular solute. For example, VLE estimates show that octanol, MIBK and NBA

Table 5-17: Confidence Intervals of Error Factors for UNIFAC VLE
Distribution Coefficient Estimates

SOLVENT SYSTEMS	95% CONFIDENCE INTERVALS
OCTANOL (n=22)	4.56 - 1.65
FOUR POLAR SOLVENT SYSTEMS (n=39)	9.83 - 3.35
HEXANE AND HEPTANE (n=24)	3.20 - 1.50
FOUR NONPOLAR SOLVENT SYSTEMS (n=42)	9.28 - 2.05
ALL SOLVENT SYSTEMS (n=81)	8.53 - 3.68

are better solvents for extraction of hydroxynaphthalene than benzene, toluene, hexane or heptane. Likewise, the VLE estimates show correct relative ranking for these solvents and the solutes phenol, 3,5-dimethylphenol and 4-methylphenol. Hence, the UNIFAC model appears to offer greater utility than the regular solution model for screening solvents for extraction of various solutes.

Mukhopadhyay and Dongaonkar (1983) suggest that the accuracy of UNIFAC phase equilibria predictions can be improved by tailoring the functional group interaction parameters to a particular extraction system. This modification will improve model accuracy at the expense of limiting model applicability. Mukhopadhyay and Dongaonkar computed group interaction parameters (a_{mn}) specifically for a petrochemical application pertaining to selective extraction of aromatic hydrocarbons from reformed naphtha using the polar solvent sulfolane. The a_{mn} values were extrapolated from both VLE and LLE data using techniques similar to those described by Fredenslund et al., (1977). However, the values are different from the interaction parameters used in this work, for example the a_{mn} value for ACH-CH₂ interaction was estimated as -54.9 (°K) compared to the VLE estimate of Gmehling et al., (1982), -11.12 (°K), and the LLE estimate of Magnussen et al., (1981), 156.5 (°K).

Mukhopadhyay and Dongaonkar used their specialized parameters to compute phase equilibria composition diagrams for three ternary systems; cyclohexane-benzene-sulfolane, hexane-benzene-sulfolane, and heptane-toluene-sulfolane. Their results compare very favorably with the experimental phase diagrams for these systems. Experimental distribution coefficient data were not available for comparison to Mukhopadhyay and Dongaonkar's predictions, but their values compared favorably with estimates from the more data intensive UNIQUAC and NRTL models. Magnussen et al., (1980) note that, in general, UNIFAC works much better for prediction of phase equilibria diagrams than for prediction of distribution coefficients, especially at low concentrations. Hence, it is not known if the high accuracy obtained for ternary phase diagrams by

modifying the UNIFAC parameters will be obtained for predictions of distribution coefficients at low solute concentrations.

An alternative, more straight forward, technique to improve the accuracy of UNIFAC K_D estimates is to employ experimentally determined aqueous phase activity coefficients. Distribution coefficients computed from experimental values of γ_w^∞ and VLE estimates of γ_s^∞ are shown in Tables 5-18 through 5-21. The results show that the predicted values of K_D are improved over those shown in Tables 5-10 through 5-15, particularly for octanol, MIBK, NBA, benzene, and toluene. Results in Tables 5-18 through 5-21 also show that estimates of K_D based on experimental values of aqueous phase activity coefficients and UNIFAC VLE prediction of solvent phase activity coefficients result in average error factors of approximately 2 for all systems. This is a considerable improvement over regular solution theory and estimates of K_D derived from UNIFAC prediction of both γ_w^∞ and γ_s^∞ . Figure 5-1 provides a graphical representation of the improvement in prediction of K_D values for various solute-octanol-water systems. In Figure 5-1 the logarithm of experimental K_{ow} values are plotted versus the logarithm of K_{ow} values estimated by the regular solution and UNIFAC models. The scatter of the data about the 45° line provides a measure of the accuracy of K_{ow} estimates with each of the models. It is apparent that the most accurate estimates of K_{ow} are obtained when experimental γ_w^∞ values and UNIFAC estimates of solvent phase activity coefficients are used.

Table 5-22 shows 95% confidence intervals for the true mean of the individual error factors shown in Tables 5-18 through 5-21. These data illustrate that this technique is suitable for qualitative prediction of distribution coefficient for various organic solvents and aromatic solutes. Of particular interest is the improvement in the prediction accuracy for the polar solvent systems. Figure 5-2 shows the accuracy of K_D values for NBA and MIBK systems estimated from experimental aqueous phase activity coefficients and UNIFAC estimates of γ_s^∞ .

Table 5-18: UNIFAC VLE Estimates for Octanol Systems Using
Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER.	PREDICTED KD'S	ERROR FACTOR(1)
ANILINE	7.9	14	0.56
BENZENE	140.0	180	0.78
CHLOROBENZENE	450.0	770	0.58
1,2-DICHLOROBENZENE	2400.0	2600	0.92
ETHYLBENZENE	1400.0	1900	0.74
METHYLBENZENE	540.0	590	0.92
1,4-DIMETHYLBENZENE	1400.0	1800	0.78
1,3,5-TRIMETHYLBENZENE	2600.0	3900	0.67
1-HYDROXYNAPHTHALENE	690.0	2300	0.30
2-AMINONAPHTHALENE	180.0	410	0.44
NAPHTHALENE	2000.0	2200	0.91
PHENOL	29.0	53	0.55
4-HYDROXYPHENOL	3.9	35	0.11
4-METHYLPHENOL	87.0	240	0.36
3,5-DIMETHYLPHENOL	220.0	670	0.33
2-NITROPHENOL	100.0	190	0.53
AVERAGE ERROR FACTOR (2)			2.3

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

Table 5-19: UNIFAC VLE Estimates for Three Polar Solvent Systems Using Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S	ERROR FACTOR(1)
METHYLISOBUTYL KETONE			
ANILINE	32.0	16.0	2.00
NAPHTHALENE	5100.0	6900.0	0.74
1-HYDROXYNAPHTHALENE	1370.0	2400.0	0.57
PHENOL	100.0	37.0	2.70
4-HYDROXYPHENOL	10.0	7.6	1.32
3-METHYLPHENOL	260.0	200.0	1.30
3,5-DIMETHYLPHENOL	810.0	670.0	1.21
n-BUTYL ACETATE			
NAPHTHALENE	6500.0	6700.0	0.97
1-HYDROXYNAPHTHALENE	1400.0	2600.0	0.54
PHENOL	71.0	40.0	1.78
4-HYDROXYPHENOL	4.5	9.4	0.48
4-METHYLPHENOL	200.0	180.0	1.11
3,5-DIMETHYLPHENOL	540.0	510.0	1.06
DIISOPROPYL ETHER			
NAPHTHALENE	3500.0	4500.0	0.78
AVERAGE ERROR FACTOR (2)			1.6

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

Table 5-20: UNIFAC VLE Estimates for Benzene and Toluene Systems Using Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S	ERROR FACTOR(1)
BENZENE			
ANILINE	10.0	8.8	1.14
2-AMINONAPHTHALENE	280.0	590.0	0.47
1-HYDROXYNAPHTHALENE	78.0	120.0	0.65
PHENOL	2.3	1.2	1.92
3-METHYLPHENOL	14.0	5.1	2.75
3,5-DIMETHYLPHENOL	22.0	21.0	1.05
2-NITROPHENOL	210.0	8.5	24.71
TOLUENE			
ANILINE	8.30	6.70	1.24
2-AMINONAPHTHALENE	230.00	400.00	0.58
1-HYDROXYNAPHTHALENE	63.00	130.00	0.48
PHENOL	2.00	1.40	1.43
4-HYDROXYPHENOL	0.01	0.01	1.00
4-METHYLPHENOL	11.00	6.90	1.59
3,5-DIMETHYLPHENOL	20.00	21.00	0.95
AVERAGE ERROR FACTOR (2)			3.2
			1.6(3)

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

(3) COMPUTED WITHOUT ERROR FOR 2-NITROPHENOL

Table 5-21: UNIFAC VLE Estimates for Heptane and Hexane Systems Using Experimental Aqueous Phase Activity Coefficients

SOLUTE	EXPER	PREDICTED KD'S	ERROR FACTOR (1)
HEPTANE			
ANILINE	0.87	0.67	1.30
BENZENE	180.00	210.00	0.86
METHYLBENZENE	710.00	750.00	0.95
1,4-DIMETHYLBENZENE	2800.00	2500.00	1.12
NAPHTHALENE	2400.00	3100.00	0.77
1-HYDROXYNAPHTHALENE	3.60	17.00	0.21
PHENOL	0.13	0.32	0.41
4-METHYLPHENOL	0.45	1.60	0.28
3,5-DIMETHYLPHENOL	1.90	4.80	0.40
2-NITROPHENOL	25.00	0.62	40.32
HEXANE			
ANILINE	0.91	0.71	1.28
BENZENE	220.00	220.00	1.00
METHYLBENZENE	740.00	810.00	0.91
1,4-DIMETHYLBENZENE	520.00	2700.00	0.19
2-AMINONAPHTHALENE	11.00	38.00	0.29
1-HYDROXYNAPHTHALENE	3.30	20.00	0.17
PHENOL	0.15	0.34	0.44
2-METHYLPHENOL	1.90	1.40	1.36
3,5-DIMETHYLPHENOL	2.30	5.30	0.43
2-NITROPHENOL	25.00	0.67	37.31
AVERAGE ERROR FACTOR (2)			5.8 2.4(3)

(1) ERROR FACTOR=(EXPERIMENTAL/PREDICTED)

(2) AVERAGE OF E.F. >1 AND RECIPROCAL OF E.F. <1

(3) COMPUTED WITHOUT ERROR FOR 2-NITROPHENOL

Table 5-22: Confidence Intervals of Error Factors for UNIFAC VLE
Distribution Coefficient Estimates Using Experimental
Aqueous Phase Activity Coefficients

SOLVENT SYSTEMS	95% CONFIDENCE INTERVALS
FOUR POLAR SOLVENT SYSTEMS (n=30)	2.73 - 1.16
FOUR NONPOLAR SOLVENT SYSTEMS (n=31)	2.68 - 1.43
ALL SOLVENT SYSTEMS (n=61)	2.47 - 1.53

Figure 5-1: Comparison of Experimental and Estimated Distribution Coefficients for Various Aromatic Solute-Octanol-Water Systems

Figure 5-2: Comparison of Experimental and Estimated Distribution Coefficients for Various Aromatic Solutes in MIBK and NBA Systems

Tables 5-18 through 5-21 show that the UNIFAC trend observed previously for overestimating K_D 's for nonpolar solutes and underestimating K_D 's for polar solutes is not apparent when experimental γ_w^∞ values are used. We should also note that the largest relative errors are still obtained for compounds with intramolecular hydrogen bonds, i.e. 2-nitrophenol, but that the error factor for 2-nitrophenol is reduced for the hexane and heptane systems by a factor of approximately 40. Hence, this suggests that the error introduced in the UNIFAC model by assuming functional group interaction independence has a greater affect on aqueous phase activity coefficients than on solvent phase activity coefficients.

The UNIFAC VLE estimates of K_D with experimental γ_w^∞ values are also useful for a relative ranking of several solutes being extracted by a particular solvent. For example, predicted values of K_D for octanol decrease correctly in the order: 1,3,5-trimethylbenzene > naphthalene > ethylbenzene > 2-aminonaphthalene > benzene > aniline; and predicted values of K_D for MIBK decrease correctly in the order: naphthalene > 1-hydroxynaphthalene > 3,5-dimethylphenol > 3-methylphenol > phenol > aniline > 4-hydroxyphenol, etc. Correct ranking is also provided for the six solutes and NBA. This trend is also evident in general for the other solvent systems.

Except for certain relative errors with respect to octanol, the estimates of K_D obtained with UNIFAC VLE estimates of γ_s^∞ and experimental γ_w^∞ values provide correct relative ranking of the solvents for extraction of a particular solute. For example, predicted values of K_D in Table 5-18 through 5-22 show that for phenol: MIBK $\approx$ NBA > benzene $\approx$ toluene > hexane $\approx$ heptane; for aniline: MIBK > octanol $\approx$ benzene $\approx$ toluene > hexane $\approx$ heptane; for 3,5-dimethylphenol: MIBK > NBA > benzene $\approx$ toluene > hexane $\approx$ heptane; etc. These comparisons show that use of experimental aqueous phase activity coefficients in conjunction with UNIFAC VLE estimates of solvent phase activity coefficients provides a useful method for evaluation of distribution coefficients for aromatic solutes.

5.4. Linear Free Energy Relationships

5.4.1. Introduction

The linear free energy approach of Leo and Hansch (1971) was used to correlate distribution coefficients for aromatic solutes in MIBK, NBA, DIPE, toluene, benzene, hexane and heptane with K_D values for the respective solutes in octanol. These correlations are shown in Figures 5-3 through 5-13. A least squares analysis was used to obtain a best fit straight line for the data, the results are shown on the respective figures. Other statistical data shown include: t-ratios for the coefficients a and b (t-ratio=coef/S.D.), the r-squared values for the equations, the standard deviation of the actual value of $\log K_D$ about the regression line and the number of data points used in the correlation.

The discussion of LFER which follows is separated into two parts; in section 5.4.2 LFER equations are discussed with respect to observation of the chemical properties of solvent and solute molecules, while the discussion in Section 5.4.3 is concerned with use of LFER equations for prediction of distribution coefficients.

5.4.2. LFER Correlation Analysis

A review of Figures 5-3 through 5-13 shows that a strong correlation exists between $\log K_D$ and $\log K_{ow}$ for the systems considered. Excellent correlation is obtained because compatible hydrogen bonding systems are being compared. The procedure is not expected to work well when the solute set contains molecules which can H-bond to both solvents along with those which can H-bond to only one solvent (Leo and Hansch, 1971; Campbell et al., 1983). For a given solvent we expect solute sets with different H-bonding character to fit different correlations, hence there is a dependence of the correlation coefficients, a and b, on the solute set. This is exemplified by the correlations for the nonpolar solvent systems where molecules with predominantly A-type character fit one correlation (Figures 5-6, 5-8, 5-10, and 5-12) and molecules

Figure 5-3: Correlation of Distribution Coefficients for Various AB-type Aromatic Solutes in MIBK-Water and Octanol-Water Systems.

Figure 5-4: Correlation of Distribution Coefficients for Various AB-type Aromatic Solutes in NBA-Water and Octanol-Water Systems.

Figure 5-5: Correlation of Distribution Coefficients for Various AB-type Aromatic Solutes in DIPE-Water and Octanol-Water Systems.

Figure 5-6: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily A-type Character in Toluene-Water and Octanol-Water Systems.

Figure 5-7: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily B-type Character in Toluene-Water and Octanol-Water Systems.

Figure 5-8: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily A-type Character in Benzene-Water and Octanol-Water Systems.

Figure 5-9: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily B-type Character in Benzene-Water and Octanol-Water Systems.

Figure 5-10: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily A-type Character in Hexane-Water and Octanol-Water Systems.

Figure 5-11: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily B-type Character in Hexane-Water and Octanol-Water Systems.

Figure 5-12: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily A-type Character in Heptane-Water and Octanol-Water Systems.

Figure 5-13: Correlation of Distribution Coefficients for Various Aromatic Solutes of Primarily B-type Character in Heptane-Water and Octanol-Water Systems.

with predominantly B-type H-bonding character fit another correlation (Figures 5-7, 5-9, 5-11 and 5-13). Alternatively, for a given solute set, the coefficients a and b are dependent upon the solvent being correlated with octanol. This is evidenced by Figures 5-3 through 5-6 where, for solute sets dominated by AB-type phenolic compounds, different values of a and b are obtained for MIBK, NBA, DIPE and toluene. This is a result of the different H-bonding character of esters, ketones, ethers and aromatic hydrocarbons.

A knowledge of compound structure and use of the solvent selectivity triangle of Snyder (1978) is helpful in understanding differences in solvent character. Snyder gives the relative ranking of decreasing solvent proton acceptor strength as: NBA, MIBK, octanol, DIPE. That NBA and MIBK are listed as having a stronger base strength is consistent with the double bonded structure of the oxygen atom in esters and ketones (Snyder, 1978). Snyder's classification scheme shows that MIBK and NBA have a similar chemical nature, this is also shown in Figures 5-3 and 5-4. Here we can see that the magnitude of the distribution coefficients for the compounds shown are similar in both solvents, and the K_D values are consistently higher than respective K_{ow} 's. The chemical similarity of NBA and MIBK is also reflected by similar values of the slope of the correlation.

The data used in Figures 5-3 and 5-4 are AB-class solutes, except naphthalene and pyridine. Naphthalene was included in these correlations because its distribution coefficient in NBA and MIBK is higher than its K_{ow} value, hence following the trend of the AB-type solutes; and because its attraction to NBA, MIBK and octanol is dominated by nonspecific dispersion forces. Naphthalene does not H-bond to an appreciable extent with these solvents and hence shows similar kinds of attractive energies. Pyridine was not included in these correlations because it can H-bond with octanol but not with NBA and MIBK; note that the K_{ow} value for pyridine is higher than its K_D in either NBA or MIBK. We expect that a separate correlation for B-type solutes (e.g. pyridine) could be made if sufficient data were available. That the ortho

substituted phenolics are shown to behave like AB-type molecules suggests that the H-bonding strength of NBA and MIBK is sufficient to displace the intramolecular H-bonds.

Snyder's selectivity triangle also suggests that DIPE has a chemical nature more like octanol than MIBK or NBA. A comparison of Figures 5-3, 5-4, and 5-5 shows the DIPE correlation to have a steeper slope and a lower intercept value. The parity of K_D and K_{ow} values for aniline, animonaphthalene, phenol, naphthalene and naphthol in Figure 5-5 are evidence of the chemical similarity of DIPE and octanol. Naphthalene was included in the DIPE correlation because it follows the trend of the other data with a K_D value close to its K_{ow} value, and because it does not H-bond with either solvent. Pyridine was not included in the DIPE correlation because it can H-bond with octanol and not with DIPE; note that pyridine has a higher value of K_{ow} than K_D . That pyridine appears to fall on the regression line is fortuitous.

Figures 5-6, 5-7, 5-8, and 5-9 show correlations between K_D and K_{ow} for toluene and benzene with acidic and basic solutes. Figures 5-6 and 5-8 show that the distribution coefficients for the phenolic solutes in toluene and benzene are lower than their respective K_{ow} values as well as being lower than the K_D 's for these solutes in MIBK, NBA or DIPE. This follows from the fact that toluene and benzene do not possess any significant hydrogen bonding character.

Figures 5-7 and 5-9 show correlations for B-type H-bonding solutes with toluene and benzene. It is interesting to note that while the slope values in Figures 5-6 through 5-9 are similar, the intercepts for the B-type correlations are closer to zero than the intercepts of Figures 5-6 and 5-8. Figures 5-7 and 5-9 also show that intramolecularly H-bonded molecules fit the correlation for B-type solutes. This is in agreement with intramolecular H-bonded compounds behaving like N- or B-type molecules and shows that toluene and benzene do not disrupt intramolecular H-bonds.

An interesting observation can be made for aniline and aminonaphthalene.

These amino aromatic compounds fall into the AB-class, but are dominated by B-type H-bonding strength. These solutes can H-bond with NBA, MIBK and DIPE through their A-type character but are correlated with B-type solutes for toluene and benzene. Hence, it is inferred that aniline and aminonaphthalene H-bond with octanol by acting as proton acceptors. These compounds also fit the correlations shown in Figures 5-3, 5-4, and 5-5 where the data is dominated by phenolic solutes. Phenolic solutes are also classified as AB-type molecules, but their H-bonding strength is dominated by A-type character. Therefore, we would expect that phenolics act as proton donors when H-bonding with octanol. Hence, Figures 5-3, 5-4, and 5-5 suggest that even though amino aromatic and phenolic solutes H-bond with octanol through different mechanisms the fact that H-bonding takes place fulfills the requirement for compatible H-bonded systems.

Correlations for the hexane and heptane systems are shown in Figures 5-10 through 5-13. Figures 5-10 and 5-12 show that the K_D values for phenolic solutes in hexane and heptane are lower than their respective K_{ow} values as well as being lower than the K_D 's for these solutes in the other solvents. This is consistent with the N-type H-bonding character of the saturated CH bonds of hexane and heptane. Figures 5-11 and 5-13 show correlations for B-type H-bonding solutes. We can see that both the intercept and slope values are lower for the B-type solute correlations, i.e. slopes are closer to one and intercept closer to zero.

Figures 5-10 through 5-13 show that LFER analysis does not work as well with hexane and heptane systems as it does with the other solvent systems considered here. This is interesting in that hexane and heptane systems were particularly well suited to the regular solution and UNIFAC models. All four of the correlations contain nonpolar aromatic hydrocarbons as well as ortho-substituted phenolics, particularly for the heptane system. It is thought that this is more a failure of LFER to describe these systems than it is a point of significance. It was noted when developing the aromatic solute correlations for hexane and heptane that much of the K_D data did not correlate with

corresponding K_{ow} values. In addition, Leo and Hansch's (1971) LFER correlations with organic acid solutes and 20 widely different solvents showed that heptane systems provided the poorest correlation between K_D and K_{ow} .

Table 5-23 provides a summary of the correlation coefficients obtained in this study. The slope of the correlations for MIBK, NBA, DIPE, toluene and benzene are fairly constant, varying from 0.98 for MIBK to 1.30 for toluene. This indicates that for the range of solutes considered here, MIBK, NBA, DIPE, toluene and benzene react to functional group substitution of aromatic solutes in a similar manner. We should note that the slopes obtained for hexane and heptane systems are different from the other solvents.

The intercept values for the correlations for MIBK, NBA, DIPE, toluene and benzene are shown to vary over a wider range than the slopes for the correlations, i.e. 0.44 for MIBK to -1.51 for the benzene A-type solute correlation. Again it is noted that the intercept values for the hexane and heptane systems are much different than those for the other correlations. We can use the intercept values of the correlations for MIBK, NBA, DIPE, toluene (Figure 5-6), and benzene (Figure 5-8) in combination with Snyder's (1978) selectivity triangle to discuss solvent properties relative to octanol. We should note that the toluene and benzene correlations with A-type solutes are being used so that comparisons can be made between similar solute sets. Hexane and heptane are not included in this discussion because the correlations obtained were poor and because hexane and heptane are not included in Snyder's selectivity triangle.

The correlations presented in Figures 5-3, 5-4, 5-5, 5-6 and 5-8 show NBA and MIBK to have positive intercepts while intercept values for DIPE, toluene, and benzene are negative. Hence, we expect NBA and MIBK to be more hydrophilic and DIPE, toluene and benzene to be less hydrophilic than octanol. Further, it would be expected from the analysis (Leo and Hansch, 1971) that MIBK and NBA should be able to dissolve more water than octanol. However, of the polar solvents considered here, octanol shows the greatest water content

Table 5-23: Summary of LFER Correlation Equations

SOLVENT	SOLUTE CLASS (1)	CORRELATION COEFF.		95% CONF. INTERVAL(2)	RANGE OF LOG KOW
		a	b		
MIBK	A and AB	0.444	0.979	± 0.080	3.3-0.15
NBA	A and AB	0.188	1.06	± 0.061	3.3-0.60
DIPE	A and AB	-0.501	1.22	± 0.156	3.3-0.60
TOLUENE	A	-1.26	1.02	± 0.094	3.1-1.4
TOLUENE	B	-0.348	1.30	± 0.141	2.4-0.65
BENZENE	A	-1.51	1.16	± 0.131	3.1-0.05
BENZENE	B	-0.113	1.02	± 0.109	2.3-0.65
HEXANE	A and N	-5.75	2.95	± 0.392	3.2-0.60
HEXANE	B and N	-1.36	1.41	± 0.173	3.2-0.90
HEPTANE	A and N	-3.58	2.18	± 0.444	3.2-0.04
HEPTANE	B and N	-1.30	1.50	± 0.165	3.3-0.90

(1) ACCORDING TO H-BOND CLASSIFICATION OF PIMENTEL AND MCCLELLAN (1960)

(2) 95% CONFIDENCE INTERVAL OF CALCULATED LOG KD IN LOG UNITS, COMPUTED FROM STANDARD DEVIATIONS OF LOG KD SHOWN ON FIGURES 5-3 THROUGH 5-13.

at saturation (Snyder, 1978) and the lowest water solubility (Earhart et al., 1977; Kiezyk and Mackay, 1971). A polarity index shown by Snyder (1978) does follow the trend of the intercepts, it shows MIBK and NBA to be more "polar" and DIPE, toluene and benzene to be less "polar" than octanol.

We should note that as the solute set changes for a given solvent, the value of the intercept changes. Figures 5-6 and 5-7 show that the intercept for toluene-solute systems changes from -1.26 to 0.348 for acid and base solutes respectively. Hence, one should exercise caution when attempting to characterize solvent properties from linear free energy intercept values.

5.4.3. Model Applicability

In this section we will discuss the use of the LFER correlation equations for predicting K_D values. The LFER equations of Figures 5-3 through 5-13 represent correlation of K_D values for aromatic solutes in a particular solvent with the K_{ow} value for those solutes. The correlation equations are specific to the solvent and solute set being considered, the equations are also strictly applicable only to the range of K_{ow} values used in the original correlation. Hence, one must be aware of the constraints of an LFER equation before it is used for prediction of distribution coefficients. The constraints of the correlation equations developed by this project are shown in Table 5-23. The solute class used to make the correlation is defined according to Pimentel and McClellan's (1960) hydrogen bonding classification (see Table 2-1). The 95% confidence intervals shown in Table 5-23 represent the 95% confidence range of the actual value of $\log K_D$ for a given $\log K_D$ estimate.

An error analysis of LFER estimated K_D values is not particularly significant because all available data were used to make the correlations. Hence, we can not perform an independent check of LFER accuracy. However, by comparing actual K_D values with the 148 predicted K_D values we obtain a 95% confidence interval for the average error factor of 2.63 - 1.69. This is comparable to the error factor range obtained for UNIFAC VLE estimates with

experimental γ_w^∞ values, 2.47 - 1.53. However, the error obtained for LFER estimates of independent K_D values would be expected to be greater than this. We should also note that unlike the UNIFAC model, LFER analysis requires that the user be cognizant of the solute class with respect to H-bonding prior to attempting to predict a value of K_D from correlation with K_{ow} . For example, an estimated K_D value for the phenol-toluene system using the A-type correlation is 1.7, which is very close to the experimental value of 2.0, while inappropriate use of the B-type correlation yields an erroneous value of 36.

5.5. Summary

Four approaches for estimation of aromatic solute distribution coefficients have been evaluated in this chapter. The regular solution model was shown to apply only to systems which do not include hydrogen bonding. The model works fairly well for nonpolar systems showing an error factor range of 5.6 - 2.3 when the empirical correction term is correlated only with the solvent polar solubility parameter (Ψ_{12}). The evaluation presented here suggests that at best the regular solution model can be used for screening of solvents for aromatic solutes with one or less substituted functional group. For example, the model is applicable for screening solvents for phenol or aniline but not for methylphenol. It appears that the regular solution model could be made more accurate by improving the correlations for the empirical correction term, although it is likely that this would require a separate correlation for each solvent system.

The UNIFAC model is not restricted in application to any particular type of solvent-solute system provided that molecules with intramolecular functional group interactions are not included. Our analysis has shown that the UNIFAC model is more accurate than the regular solution model for prediction of K_D values, and it also provides a better approach for solvent screening. It was shown that UNIFAC accuracy can be improved by using experimentally determined aqueous phase activity coefficients in conjunction with predicted

values of solvent phase activity coefficients. Seven different solvent systems were evaluated by this approach, and in most cases it was found that distribution coefficients could be predicted within a factor of approximately two. This is significant in light of the fact that K_D values for the range of solutes and solvents considered in this investigation varied by approximately six orders of magnitude.

The LFER approach was shown to provide strong correlations for the solvent-solute systems considered here. This is because special attention was given to providing correlations between compatible hydrogen bonding systems. It appears, however, that K_D values for alkane solvents do not correlate as well with K_{ow} as those for polar and aromatic solvents. The LFER approach can be used to characterize solvent and solute properties as well as to provide reasonable estimates of K_D values. However, this conclusion needs to be verified by checking the LFER equations with independent data. In addition, LFER correlation equations are specific for each solvent and solute set so that one should be careful when using LFER analysis to estimate distribution coefficients.

It is concluded that the UNIFAC approach with experimental values of aqueous phase activity coefficients is the most desirable method for estimating distribution coefficients for aromatic solutes. The model is not restricted to specific systems as is the case for regular solution theory and LFER analysis. Furthermore, it is expected that the accuracy of the UNIFAC model will improve in the future, as this technique represents the current state-of-the-art for predicting phase equilibrium. Fredenslund and co-workers are currently gathering more VLE and LLE data to improve the functional group interaction parameters. In addition, if a particular extraction system is to be evaluated in great detail, specialized interaction parameters could be estimated as suggested by Mukhopadhyay and Dongaonkar (1983).

Chapter 6

REMOVAL OF ORGANIC CONTAMINANTS FROM WASTEWATER BY SEVERAL UNIT PROCESSES INCLUDING SOLVENT EXTRACTION

6.1. Introduction

This chapter summarizes results of two treatability studies which were designed to evaluate removal of organic pollutants from coal gasification wastewater by several unit processes including solvent extraction. The wastewater used in these studies was obtained from the Grand Forks Energy Technology Center (GFETC) slagging fixed-bed gasifier from runs RA-52 and RA-92 with Indian Head lignite coal. It is envisioned that these wastewater samples are qualitatively similar to quench water that will be produced in a full scale slagging fixed-bed gasifier with lignite coal.

The first study, using wastewater from run RA-52, was designed to evaluate the essential features of proposed wastewater treatment trains for removal of organic and inorganic contaminants from phenolic coal gasification quench condensates. The study focused on evaluation of a treatment train comprised of: 1) solvent extraction with MIBK, 2) ammonia stripping, 3) activated sludge treatment with and without addition of powdered activated carbon (PAC), 4) lime-soda softening, and 5) granular activated carbon adsorption. In addition, this project included detailed organic characterization of run RA-52 wastewater by GC/MS and HPLC after several of the treatment steps. The results of this work have been reported by Luthy et al., (1983).

The second study was performed with run RA-92 quench condensate. This

study did not involve a detailed evaluation of treatment system alternatives, rather, it was designed to: 1) generate a large quantity of biologically treated wastewater for use in another study aimed at evaluating reuse of treated wastewater as makeup to an evaporative cooling tower, and 2) compare activated sludge treatment of coal gasification wastewater pretreated by solvent extraction with MIBK and NBA.

Hicks et al., (1977) have presented design procedures for solvent extraction as applied to the treatment of coal gasification and liquefaction condensates. Several proposed demonstration-scale coal gasification (Milios, 1975; Continental Oil Co., 1978; and Luthy et al., 1980a) and coal liquefaction (Robertaccio and Kaczmarek 1983; and Yen, 1983) facilities have included solvent extraction as an integral part of the wastewaters treatment facilities. Several reports are available on biological treatment of condensates for the new generation of coal conversion processes under development. A discussion of performance data and biological oxidation kinetic values for these processes is presented by Luthy (1981). Relatively few studies have considered biological oxidation of solvent extracted coal conversion condensates (Luthy, 1981; Drummond et al., 1981; Robertaccio and Kaczmarek, 1983; Hung et al. 1982; and Yen, 1983).

6.2. Experimental Design

Figure 6-1 shows a schematic of the experiments conducted in the first study. Analyses were performed on raw wastewater and on sample composites following each treatment step in order to document removal of standard chemical constituents as well as to characterize and assess removal of organic contaminants. High performance liquid chromatography (HPLC) and combined gas chromatography/mass-spectrometry (GC/MS) techniques were employed to follow the removal of organic compounds during treatment. Organic analyses on raw and pretreated samples included characterization of organic constituents common to both suspended and aqueous phases.

The bench-scale solvent extraction procedure used in the first study

Figure 6-1: Experimental Design for Evaluation of Contaminant Removal from a Coal Gasification Wastewater

simulated a staged extraction process by contacting 16 liters of wastewater with fresh solvent (MIBK) in five steps at a solvent-to-water ratio of 1:15 (V_s/V_w). This technique was chosen by experimental design to reduce phenolics to the range of 5 mg/l. Twenty minutes was allowed for each mixing and settling step, after which the solvent was decanted by syphoning.

Ammonia removal was performed in a manner that simulated free- and fixed-leg steam stripping. Solvent extracted wastewater was heated to 85-100°C in a covered container in the presence of a slight nitrogen purge. Ammonia was first stripped without chemical addition to release the fraction of ammonium ion compensated by deprotonated acid species (e.g. dissolved CO_2 and H_2S). Lime slurry was then added to raise sample pH and stripping was continued until $\text{NH}_3\text{-N}$ was reduced to approximately 30 mg/l. Ammonia stripping also effectively removed residual dissolved solvent from the water.

The biological reactors were complete-mix, air activated sludge reactors with internal clarifiers. Mean sludge residence time was controlled at 30 and 20 days for the activated sludge and the PAC-activated sludge reactors, respectively. Amoco PX-21 PAC, having a surface area of about 3000 m^2/g , was added to the PAC-activated sludge reactor on a daily basis to maintain a steady-state PAC concentration of 5000 mg/l in the mixed liquor. Selection of this carbon type and dose was guided by prior PAC-activated sludge studies with nonsolvent extracted GFETC wastewater (Luthy et al., 1981). Nutrient levels of Fe, K, Mg, and P were added to biological reactor influents.

The biological reactors in the first study were operated with a relatively long value of hydraulic retention time consistent with the need to conserve a limited amount of raw wastewater. The reactors were seeded with sludge obtained from a local coke plant and with sludge used in previous biological oxidation studies with phenolic gasification wastewaters. The reactors were acclimated to solvent extracted-ammonia stripped wastewater over a 30 day period. After which, the reactors were managed under steady state conditions for a 60 day balance period. At the end of the 60 day interval, the reactors of

the first study were operated for an additional 10 day period to provide sample composites for organic characterization. During this time influent feed reservoirs, effluent collection vessels, and biological reactors were covered with aluminum foil to prevent external contamination. All glassware was solvent rinsed and acid cleaned prior to use in the experiment.

The experiments performed in the second study used wastewater from run RA-92. The sequence of treatment steps included solvent extraction with NBA, ammonia stripping and activated sludge treatment. No additional unit processes were employed in this work. The bench scale procedures were similar to those of the first study with the following exceptions: 1) solvent extraction was accomplished in a two-stage procedure at a solvent-to-water ratio of 1:6 (V_s/V_w), 2) biological treatment did not include a PAC-activated sludge reactor. The conventional activated sludge reactor was maintained at a mean cell residence of 30 days (consistent with the first study) but the hydraulic retention time was reduced from 12 days to 4 days. This was consistent with the need to generate a large quantity of biological effluent for future use.

6.3. Analytical Procedures

Wet chemical analytical procedures followed those presented in standard methods (APHA, 1980). Biological reactor effluent COD and TOC measurements were performed on filtered samples in order to exclude suspended biomass and PAC. Analysis of solvent extracted samples for TOC, COD, and BOD were performed after gentle heating to expel residual solvent. Removal of residual solvent was ensured by GC analysis.

Determination of eleven polycyclic aromatic hydrocarbons (PAH) was accomplished with a Perkin-Elmer Series 3 high pressure liquid chromatograph using a constant flow gradient pumping system with acetonitrile and water, and a reverse phase column (Supelcosil LC-PAH, 4.6 mm x 250 mm). Quantification was accomplished with a fluorescence detector set an excitation wavelength of 280 nm and an emission wave length of 340 nm.

Aqueous phase samples were defined operationally as being filtered through a 0.45 micron glass fiber filter; material not passing the filter was termed suspended phase. Aqueous and suspended phase samples were extracted for twenty-four hours with the suspended phase samples placed in a pre-cleaned Soxhlet extraction thimble. The presence of phenolics and other hydroxylated aromatic compounds in raw suspended phase samples required alumina column chromatography cleanup prior to analysis (Schiller and Mathiason, 1977). Sample concentration was accomplished by rotary vacuum evaporation (30°C).

GC/MS analyses were performed at Argonne National Laboratory. Suspended and aqueous phase samples were extracted with methylene chloride using soxhlet apparatus for suspended phase samples. Sample extract was fractionated into acid, base, and neutral fractions by means of the extraction scheme shown in Figure 6-2. Sample concentration was performed with Kuderna Danish apparatus. Computer controlled Hewlett-Packard (HP) model 5840 and 5880 GC instruments were used with flexible, fused silica, wall coated (SP2100 methyl silicone) capillary columns (0.31 mm ID). The GC/MS system was an HP model 5984A equipped with an HP model 5840 GC and an HP model 5934A data system. All GC instruments were equipped with the HP Model 1883B Grob-type split/splitless capillary inlet system operated in the splitless mode.

Estimated GC/MS analytical detection limits for the various samples and fractions which were analyzed are reported in Table 6-1. A number of compounds, especially in the raw sample, were not determinable (ND). That is, they were masked in the background of the chromatogram. These compounds would appear later at low levels in treated samples where the general level of contamination was much reduced, and where greater concentration factors could be employed during sample preparation.

Figure 6-2: Extraction Scheme for Analysis of Wastewater Samples

Table 6-1: Estimated Detection Limits for Analysis of Samples by GC/MS

<u>Sample</u>	<u>Phase</u>	<u>Approximate Detection Limit, ug/l</u>		
		<u>Fraction</u>		
		<u>acid</u>	<u>base</u>	<u>neutral</u>
Raw	aqueous	100	3	50
	suspended	50	3	50
Solvent Extracted- Ammonia Stripped	aqueous	1	0.1	5
	suspended	10	0.1	0.1
Biologically Treated	aqueous	0.1	0.1	0.1

6.4. Experimental Results

6.4.1. Pretreatment

During the course of these investigations it was necessary to process several batches of quench water through solvent extraction and ammonia stripping. Wastewater characteristics before and after these treatment steps are summarized in Table 6-2, for both run RA-52 and RA-92 wastewater samples. Raw wastewater averaged about 5500 mg/l phenolics for both samples. The phenol content was measured as 3100 mg/l for run RA-52 and 3000 mg/l for run RA-92, methylphenols (cresols) were measured in RA-52 water as 950 mg/l and 1700 mg/l in RA-92. Analyses of phenol and cresols were performed by GC/MS for run RA-52 water and by GC for RA-92 water. Table 6-2 also shows that the quench waters had high levels of other organic pollutants as evidenced by the COD, TOC and BOD values. It is noted that the quench waters contained comparable levels of phenolics, but that run RA-52 water showed higher levels of other organic material as evidenced by higher values of TOC and COD. Both wastewaters contained high levels of organic-nitrogen, ammonia, thiocyanate, sulfide and alkalinity.

Solvent extraction resulted in over 99% reduction of phenolics from both wastewater samples. Reductions in TOC, COD, and BOD were, respectively, 87, 88 and 89 percent for run RA-52 and 81, 83 and 75 percent for RA-92 wastewater. It is evident that solvent extraction with MIBK or NBA can effectively reduce the concentrations of organic contaminants from a coal conversion process condensate.

Raw wastewater after solvent extraction contained an average total ammonia concentration of 4500 mg/l with alkalinity of 16,500 mg/l as CaCO_3 . Batch stripping studies showed that 80-90% of total ammonia could be removed without the need for addition of lime. During the bench scale tests, lime was added after total ammonia had been reduced to the range of 600-800 mg/l $\text{NH}_3\text{-N}$. Average wastewater characteristics before and after ammonia stripping

Table 6-2

Wastewater Characteristics During Pretreatment (1)
(all units mg/l unless otherwise noted)

Wastewater Parameters	Raw Wastewater		Solvent Extracted		Ammonia Stripped	
	RA-52	RA-92	RA-52	RA-92	RA-52	RA-92
TOC	11,000	6400	2000	1200	1400	1200
COD	32,000	21,000	3900	3500	3000	3400
BOD	26,000	12,000	2900	3000	1800	760
Phenolics	5500	5600	5	35	3	10
Freon Extr.	410	100	***	40	10	5
Org-N	110	70	50	50	30	40
NH3-N	6300	5000	4400	4600	30	65
Thiocyanate	120	85	110	60	100	50
Sulfide	100	190	75	110	<10	<10
Total Sulfur (as S)	380	630	160	530	***	480
Alk(as CaCO3)	21,000	18,000	16,000	17,000	850	570
Calcium Hardness (as CaCO3)	***	***	10	***	740	***
pH (units)	8.6	8.3	8.6	8.3	8.8	8.3
Cond.(umho/cm)	20,000	17,000	19,000	18,000	1500	1300
TDS	***	900	***	700	***	1800

(1) Analyses of solvent extracted samples for TOC, COD, and BOD were performed after gentle heating to expel residual solvent.

are summarized in Table 6-2. The stripping operation reduced ammonia, alkalinity, and sulfide to low levels. TOC analysis show that there was some removal of quench water organic compounds as a result of stripping and liming. The increase in calcium hardness is consistent with addition of lime to release residual ammonia.

6.4.2. Biological Treatment

Average operational and performance data obtained in the first study are summarized in Table 6-3 for activated sludge (AS) and PAC-activated sludge (PAC/AS) treatment of solvent extracted (MIBK)- ammonia stripped wastewater. It was found that solvent extracted wastewater was easier to treat via activated sludge in comparison with wastewater that had not been pretreated for reduction of phenolics. A previous study with GFETC wastewater pretreated only by ammonia stripping had shown that wastewater must be diluted to about 33% strength in order to achieve successful activated sludge treatment (Luthy et al., 1980b).

The biological reactors in the first study were operated under extended aeration conditions with relatively long mean sludge residence times and corresponding low values of BOD and COD removal rates. These conditions produced effluents with low values of BOD. COD removal efficiency for the activated sludge reactor was 55%, which was lower than previously observed values in the range of 75-84% with nonsolvent-extracted GFETC wastewater (Luthy et al., 1980b). This result suggests that solvent extraction yields a product wastewater with a greater proportion of residual material not directly amenable to biological oxidation. However, this did not impair activated sludge treatment.

PAC-activated sludge treatment with 5000 mg/l PAC in the mixed liquor gave better removal efficiencies than activated sludge treatment for TOC, COD, phenolics, organic-N, $\text{NH}_3\text{-N}$, SCN^- , and color. PAC-activated sludge treatment gave a colorless effluent, whereas activated sludge treatment gave a value of

Table 6-3: Average Performance Data for Activated Sludge and PAC-Activated Sludge Treatment of Solvent Extracted-Ammonia Stripped Wastewater

Operating Data		PAC Activated Sludge	Conventional Activated Sludge
Mean Sludge Res. Time, d		20	30
Hydraulic Res. Time, d		11.7	12.6
PAC Conc. in Reactor, mg/L		5000	0
MLSS, mg/L		6470	1620
MLVSS, mg/L		6110	1310
COD Removal Rate, d ⁻¹		--	0.11
BOD Removal Rate, d ⁻¹		--	0.12
SVI, mL/g MLSS		10	65
pH, units		7.3	7.6
Diss. Oxygen, mg/L		>4.0	>4.0
O ₂ Util. Rate, mg O ₂ /mg MLVSS-d		0.02	0.07
Wastewater Characteristics (mg/L unless noted)			
	Influent	Effluent	
TOC	1380	385	580
COD	2980	640	1340
BOD	1820	30	32
Phenolics	3	<0.02	~0.1
Org-N	33	4	10
NH ₃ -N	30	20	84
NO ₃ -N	<5	100	40
SCN ⁻	105	<0.5	4
CN ⁻ TOT	1.5	1.3	1.4
CN ⁻ Amn	~0.1	<0.1	~0.1
SO ₄ ²⁻	--	655	1020
Alk (as CaCO ₃)	850	72	175
Cond (μmho/cm)	1490	2200	2230
Color (Pt-Co units)	700	<20	500
Freon extractable	10	<5	<5

500 Pt-Co units. These effluent color concentrations are significantly lower than those observed in previous activated sludge (Luthy et al., 1980b) and PAC/AS studies (Luthy et al., 1981) with nonextracted wastewater, even considering the one-third strength dilutions employed therein.

Average performance data for activated sludge processing of run RA-92 quench water pretreated by solvent extraction (NBA) and ammonia stripping included: sludge age of 30 days with an average MLVSS of 1600 mg/l, a hydraulic retention time (HRT) of 4.2 days and a COD removal rate 0.30 days^{-1} . Under these conditions wastewater COD was reduced by 63% from an average influent value of 3000 mg/l. This represents a greater reduction of COD with a lower HRT than was obtained with run RA-52 water extracted with MIBK. Hence, it appears that wastewater extracted with NBA may be easier to treat by activated sludge processing than wastewater extracted with MIBK.

Hung et al., (1982) have conducted treatability studies with a GFETC quench condensate similar to the wastewaters used in these studies. Hung et al., evaluated activated sludge treatment of DIPE and MIBK extracted-ammonia stripped wastewater at a sludge age of 10 days and at HRT values of 1,3,5 and 10 days. In all of these experiments wastewater extracted with DIPE showed higher removal efficiencies for TOC, COD and phenolics. Hung suggests that DIPE extracts greater quantities of biologically refractory material than MIBK, thus producing a water more amenable to activated sludge processing. A similar conclusion may be appropriate for biological oxidation of wastewater pretreated by NBA in comparison with MIBK.

6.4.3. Lime-Soda Softening

Lime-soda softening experiments were performed with a composite sample of PAC-activated sludge reactor effluent. Most of the wastewater hardness in PAC-activated sludge effluent existed as noncarbonate hardness and therefore required addition of soda ash. The appropriate lime dose was determined by the amount of stock lime solution required for alkalimetric titration to pH = 10. Soda dose was then computed as:

$$\text{Soda dose} = \text{Initial Ca}^{2+} + \text{Lime dose} - \text{Alkalinity} \quad (6-1)$$

Chemical requirements computed by these techniques were: 720 mg/l lime (as CaCO_3) and 1170 mg/l soda (as CaCO_3). The validity of this procedure was verified by experimental results reported in Table 6-4 where residual Ca^{2+} and Mg^{2+} precipitated to very low levels. Final wastewater hardness was less than 15 mg/l as CaCO_3 .

Table 6-5 reports results of another set of softening experiments in which lime dose was held constant to give a pH of 10 and soda dose was reduced in increments of 10, 20, and 30 percent. These data show that, depending on the specific situation, hardness may be reduced to desired limits by varying soda dose. A soda dose of 850 mg/l as CaCO_3 , gave an 86% reduction in total hardness to 80 mg/l as CaCO_3 with an increase in TDS of only 13%.

Calcium hardness was imparted to the wastewater as a result of liming to remove fixed-ammonia during steam stripping. Had caustic (NaOH) been used instead of lime, residual wastewater hardness would not have been increased. Decisions regarding use of caustic or lime for ammonia stripping are dependent on various factors, including chemical costs, chemical fouling of the ammonia still, and reuse and discharge options for treated water. If treated wastewater is to be reused as cooling tower makeup water, it is probable that caustic is more appropriate for ammonia stripping than lime. This would help to reduce cooling tower side-stream softening costs, and facilitate water reclamation from cooling tower blowdown.

6.4.4. Granular Activated Carbon Adsorption

Granular activated carbon adsorption experiments were performed with a composite sample of activated sludge reactor effluent in order to make qualitative comparisons with effluent from the PAC-activated sludge reactor. These comparisons were made with respect to macro-organic constituents. The tests were conducted with Calgon Filtrasorb 400 having an approximate surface

Table 6-4: Lime-Soda Softening of PAC/AS Effluent

	COD	Alkalinity (mg/L as CaCO ₃)	Ca ²⁺	Mg ²⁺	TDS (mg/L)	Cond. (µmhos/cm)	pH (units)	Turbidity (NTU)
Effluent	685	115	568	5.4	2340	2600	7.7	1.6
Softened Effluent ^a	670	525	11	2.5	3030	3100	10.5	7.0 ^b

^aLime does = 720 mg/L, soda dose = 1173 mg/L, both as CaCO₃

^bAfter settling

Table 6-5: Lime-Soda Softening with Various Soda Doses

Dose		Treated Wastewater Characteristics			
Lime (mg/L as CaCO ₃)	Soda (mg/L as CaCO ₃)	Ca ²⁺ (mg/L as CaCO ₃)	Mg ²⁺ (mg/L as CaCO ₃)	TDS (mg/L)	Cond. (µmhos/cm)
780	1211	12	4.2	3150	3100
780	1090	23	3.3	2900	2850
780	970	58	5.0	2750	2700
780	850	74	5.8	2650	2650

area of $1,100 \text{ m}^2/\text{g}$, effective grain size of about 0.6 mm, and bulk density of 0.4 g/cm^3 . Twenty-four hour TOC and COD batch Freundlich adsorption isotherms are shown in Figure 6-3. These data show that similar adsorption characteristics were obtained with respect to both TOC and COD.

Flow-through column tests were conducted with 35 grams of carbon in a glass column with a carbon bed aspect ratio of 3:1. Figures 6-4 and 6-5 show effluent COD and TOC results, respectively. The column was initially filled with distilled water, and a 50% relative value of conductivity breakthrough occurred at 25 minutes, which corresponded to the desired contact time. Conductivity breakthrough was complete at approximately 1.25 hours. COD or TOC breakthrough was not observed owing to the limited quantity of composite activated sludge effluent sample. At the conclusion of the test effluent COD and TOC values were approximately 30% of influent values. The breakthrough characteristics appear favorable, although this observation is based on an estimated volume of treated water equal to about 44% of that required to obtain saturation.

Table 6-6 shows results of analysis of a composite granular activated carbon treated sample corresponding to the flat portion of the breakthrough curve between 2.0 and 7.5 hours of operation. These data are compared with analyses of AS and PAC-AS effluent. Treatment by AS followed by granular activated carbon adsorption (GAC) removed all residual color, as did PAC-AS. Lower values of COD and TOC resulted from treatment by AS-GAC than PAC-AS.

6.5. Organic Characterization

Figure 6-3: COD and TOC Batch Adsorption Isotherms

Figure 6-4: COD Adsorption Characteristics for Activated Carbon Column Tests

Figure 6-5: TOC Adsorption Characteristics for Activated Carbon Column Tests

Table 6-6: Comparison of Effluent Quality for AS, AS-GAC and PAC/AS Treated Wastewater

<u>Specification</u>	<u>Parameter, mg/l unless noted</u>								
	<u>COD</u>	<u>TOC</u>	<u>BOD</u>	<u>Org-N</u>	<u>Color</u> <u>(Pt-Co units)</u>	<u>SCN⁻</u>	<u>NH₃-N</u>	<u>Conductivity</u> <u>(μmho/cm)</u>	<u>pH</u> <u>(units)</u>
AS Effluent	1975	550	32	10	450	1.6	88	2550	7.3
AS-GAC	315	125	--	1.7	0	1.3	88	2250	8.2
AS-PAC	640	385	30	4	0	<0.5	20	2200	7.4

6.5.1. GC/MS Analysis

A summary of the data from GC/MS analyses of the acid, base, and neutral fractions of the raw RA-52 wastewater sample, and of the samples after the various treatment steps are presented in Table 6-7. Values reported as not detected (NT) refer to detection limits given in Table 6-1, while values reported as not determinable (ND) refer to problems of compound masking and/or sample concentration as discussed previously. Analysis of raw and solvent extracted-ammonia stripped suspended phases refer to measured suspended solid values of 65 and 4 mg/l, respectively. Approximately two hundred and fifty individual organic compounds were identified in this investigation, a listing of these compounds is given in Appendix C.

The filtered water (FW) acid fraction of the raw sample consisted of phenol, hydroxyindans, hydroxyindenes, naphthols, and their alkylated derivatives; phenol and cresols constituted more than 90% of the total acidic components. The acidic components of the suspended solids (SS) phase were similar to the aqueous phase, but their concentration was much less. The difference in the concentration of acidic organics between SS phase and aqueous phase decreased with increasing compound molecular weight and decreasing compound polarity. These data indicate that less polar, higher molecular weight acidic organics were associated with the suspended solids.

The major components of the raw sample base fraction were azabenzenes (pyridines), azanaphthalenes (quinolines), and anilines. Imidazoles or pyrazoles, diazines, thiazoles, azaindanes, and some higher nitrogen-PNAs, such as azabiphenyls, azaacenaphthenes, azafluorenes, azaanthracenes, and azaphenanthrenes, were also present. The proportion of base compounds associated with the SS phase rather than the aqueous phase was also greatest for those species which were relatively higher molecular weight and relatively less polar.

A large variety of neutral organic compounds were present in the raw

Table 6-7: Concentration of Representative Organic Compounds Identified in Run RA-52 Quench Water at Various Stages of Treatment

Peak number	Compound name	Raw water		MIBK-stripped		MIBK-AS	MIBK- PAC/AS
		SS	FW	SS	FW	FW	FW
Acid Fractions							
20	Phenol	15 100	3 080 000	NT	500	10	3
50	Methylphenol	6 300	427 000	NT	100	1	1
80	Methylphenol	16 400	494 000	NT	80	1	1
140	C ₂ -Phenol	8 890	155 000	NT	50	NT	NT
260	Hydroxindan	340	3 820	NT	40	NT	NT
370	1-Napnthol	250	1 150	NT	40	NT	NT
Base Fraction							
10	Pyridine	3.9	14 530	NT	NT	NT	0.1
15	Toluene	NT	77	NT	NT	NT	NT
20	Methylpyridine	12	7 120	NT	1.0	NT	NT
140	Aniline	27	6 500	NT	NT	NT	NT
390	Azanaphthalene	450	500	NT	NT	NT	NT
730	Azatiuorene	20	15	NT	NT	NT	NT
Neutral Fraction							
32	Methylcyclohexane, or C ₂ -cyclopentene	ND	22 750	NT	4230	NT	NT
35	Benzonitrile	ND	2 900	NT	NT	NT	NT
70	Indene	2 300	910	NT	NT	NT	NT
125	C ₂ -Thiazole	ND	ND	NT	31	1.8	2.0
180	Naphthalene	16 300	26 600	NT	NT	NT	NT
330	Indole	150	5 000	NT	NT	NT	NT
360	Biphenyl	1100	ND	NT	NT	NT	NT
460	Acenaphthene	2480	ND	NT	NT	NT	NT
710	Phenanthrene	4680	ND	NT	NT	NT	NT
790	Fluoranthene	1510	ND	NT	NT	NT	NT
810	Pyrene	830	ND	NT	NT	NT	NT

SS, Suspended Solids; FW, Filtered Water; ND, Not Determinable; NT, Not Detected.

sample. The SS phase of the neutral fraction contained representatives of virtually all one-to-four aromatic ring compounds and their alkylated derivatives. Higher molecular weight polynuclear aromatic hydrocarbons (alkylated naphthalenes, biphenyls, and three- and four-ring aromatics) were especially associated with the SS phase. Major components of the aqueous phase neutral fraction were cycloalkanes, cycloalkenes, benzonitrile, acetophenone, indenenes, and naphthalene. The aqueous phase also contained some phenolics which were not completely fractionated to the acid extract.

The experimental results show that extraction with MIBK and ammonia stripping achieved substantial reduction of extractable and chromatographable organic constituents. Acidic components were reduced 85-99.9%, and the most abundant constituents (phenol and cresols) were reduced 99.8-99.9%. The overall reduction of acidic components was 99.6%.

No organic compounds were detected in the SS phase of the MIBK extracted-ammonia stripped samples of acid, base, or neutral fractions. The MIBK aqueous phase base and neutral fractions did show some compounds not determined in the raw sample, particularly imidazole in the base fraction and thiazoles in the neutral fraction. That these compounds were not readily determined in the raw sample was presumably due to their low concentration in that sample.

Except for phenol and cresol, activated sludge treatment of solvent extracted quench water reduced aqueous phase acidic components to levels below detection (less than 0.1 $\mu\text{g/l}$). Activated sludge/powdered activated carbon treatment enhanced removal of phenol and also reduced the concentrations of other acid compounds to levels less than detectable.

None of the organic constituents identified in base or neutral extracts of the raw sample were found in either AS or PAC/AS extracts. Thus, the combination of physicochemical and biological treatment provided excellent removal of all the organics in base and neutral fractions that were readily identifiable in the raw sample extracts.

PAC/AS treatment provided better removal than AS for the imidazoles observed in the MIBK aqueous phase base fraction. Both AS and PAC/AS treatment provided excellent removals for neutral fraction organics. Excepting contamination by plasticizers, the only identifiable neutral fraction organics were several thiazoles present at comparable low levels in either AS or PAC/AS

Data summarized in Table 6-7 show that base and neutral fraction priority organic contaminants (e.g., toluene, naphthalene, acenaphthene, phenanthrene, fluoranthene, and pyrene) are removed to detection limits by pretreatment prior to biological oxidation.

6.5.2. HPLC Analysis

HPLC analyses were performed on liquid and suspended phases of the various samples identified in Figure 6-1. Analyses were performed for eleven polycyclic aromatic hydrocarbons (PAH): NA, naphthalene; ACE, acenaphthene; FLE, fluorene; PH, phenanthrene; AN, anthracene; FLA, fluoranthene; PY, pyrene; CHR, chrysene; BaP, benz(a)pyrene; DBahA, dibenz(ah)anthracene; and BghiP, benz(ghi)perylene. Representative HPLC fluorescence chromatograms are shown in Figure 6-6.

HPLC analysis for the specific PAH confirmed the conclusions derived from the GC/MS results; however, there was some discrepancy in specific concentration values reported for naphthalene in the raw sample, and for estimation of fluoranthene and pyrene associated with raw water suspended solids. The discrepancy with respect to naphthalene probably resulted from the different procedures used to concentrate sample extract, rotary evaporation vs. Kuderna-Danish. HPLC analysis of the raw sample showed that none of the PAH with molecular weights greater than 178 (phenanthrene/anthracene) were detected in the aqueous phase.

Analysis of suspended and aqueous phases following solvent extraction showed no detectable concentrations of the eleven PAHs. Hence, in the process

Figure 6-6: Representative HPLC Fluorescence Chromatogram

of reducing phenolics to the range of several mg/l, solvent extraction effectively removed all eleven PAHs from the water. Additional HPLC analyses following ammonia stripping and activated sludge or PAC-activated sludge processing also showed no PAH in suspended or aqueous phases.

6.6. Summary of Wastewater Treatment

These studies have shown that solvent extraction for phenol recovery offers several wastewater treatment processing advantages. Solvent extracted wastewater did not require dilution prior to biological oxidation, and provided lower effluent COD, TOC and color than non solvent extracted wastewater for both activated sludge and PAC/activated sludge treatment. Especially significant is the observation that most raw wastewater organic contaminants were reduced to detection limits as phenol and cresols were removed to the range of several mg/l by solvent extraction. It also appears that the particular solvent used for extraction can influence the efficiency of downstream activated sludge processing.

Chapter 7

SUMMARY AND CONCLUSIONS

7.1. Introduction

This report summarizes the findings of an investigation which examined techniques for measurement and prediction of distribution coefficients for aromatic solutes. The information which resulted from this project is useful for analysis of solvent extraction systems for wastewater treatment as well as for assessing the fate of contaminants in the environment.

This investigation entailed both theoretical and experimental developments. The experimental portion of the study was primarily directed towards measurement of distribution coefficients for various aromatic solutes in clean water and wastewater systems. Experiments were also performed to evaluate solvent extraction as a unit process for treatment of phenolic coal gasification process condensates. The theoretical portion of this investigation was directed towards evaluation of various techniques for prediction of solute-solvent distribution coefficients. This task represented a significant portion of the overall project effort. The conclusions from the various portions of this project are summarized below.

7.2. Experimental Results

7.2.1. Treatability Studies

The first phase of this investigation included experiments designed to evaluate treatment characteristics of a phenolic coal gasification process wastewater. The major treatment steps evaluated in this portion of the project included solvent extraction with MIBK or NBA, ammonia stripping, and activated sludge processing with and without powdered activated carbon. The results of this work have shown that solvent extraction for phenol recovery offers several wastewater processing advantages for treatment of coal conversion wastewaters. The study showed that solvent extracted wastewater did not require dilution prior to biological treatment and that solvent extraction provided for lower effluent COD, TOC, and color in comparison with non-solvent extracted wastewater. It was also shown that the particular solvent used for extraction can influence the efficiency of downstream activated sludge processing.

Detailed GC/MS analysis of raw and solvent extracted-ammonia stripped wastewater samples showed that solvent extraction for phenol recovery removed most of the raw wastewater organic components, including those associated with the suspended phase. HPLC analysis of selected polycyclic aromatic hydrocarbons confirmed these results. GC/MS analysis of biologically treated wastewater samples showed that the effluent from either activated sludge or activated sludge-powdered activated carbon reactors contained only very low levels of relatively few compounds.

7.2.2. Measurement of Distribution Coefficients

Experimental data for aniline, phenol, and pyridine have shown that distribution coefficients for these compounds in clean water, single solute systems, are not statistically different from those determined in a complex coal conversion wastewater. Hence, this offers the opportunity for simple laboratory experiments to evaluate the partitioning of principal organic solutes during solvent extraction processing of these wastewater systems. This data also

suggest that pure component properties may be used for modeling partitioning behavior. In addition, our analysis of experimentally determined distribution coefficients suggests that hydrogen bond formation is the dominant chemical force governing the partitioning of aromatic solutes between water and the solvents considered in this investigation.

7.3. Modeling Results

Application of equilibrium models for estimating distribution coefficients has resulted in several conclusions. Our analysis has shown that the regular solution concept applies only to systems which do not include hydrogen bonding. Our evaluation of the solute-solvent systems considered here indicates that, at best, the regular solution model is suitable for screening solvents for extraction of aromatic solutes with one or less functional group substitution (e.g. phenol, aniline). The regular solution model was not satisfactory for ranking solvents for extraction of aromatic solutes with more than one functional group substitution (e.g. methylphenol, hydroxyphenol). It appears that the regular solution model could be made more accurate by improving the correlations for the empirical correction term; however, this would not necessarily improve model applicability as correlations would remain empirical and case specific.

Linear Free Energy Relationships (LFER) offer an acceptable method for prediction of distribution coefficients for various solutes and a particular solvent by correlation with octanol-water partition coefficients. It was shown that the procedure holds for comparison of compatible hydrogen bonding solute-solvent systems. The availability of octanol-water partition coefficient data make this approach particularly attractive for engineering analysis and design. LFER analysis is also useful for characterizing solute and solvent chemical properties. It was shown that different slope and intercept values are obtained for different solute-solvent sets. Hence, the approach can not be used to estimate distribution coefficients for a particular solute-solvent pair unless a correlation based on data for similar solutes has been developed for that particular solvent.

The UNIFAC model is clearly the most useful of the techniques examined for prediction of distribution coefficients for aromatic solutes. This approach is not case specific and can be applied for prediction of other environmental parameters (Arbuckle, 1983; Lyman et al., 1992; Fredenslund et al., 1977). Our analysis has shown that distribution coefficients for most of the solute-solvent systems considered here could be predicted within a factor of approximately two when computed using experimental aqueous phase activity coefficients and UNIFAC estimates of the solvent phase activity coefficient based on vapor-liquid equilibria data. This approach offers great utility for solvent screening purposes and for evaluating the relative partitioning of several solutes between water and a particular organic solvent. The approach is applicable to many solute-solvent systems; however, group interaction parameters are not available for certain functional groups. In these cases the LFER approach is recommended for prediction of K_n values.

The UNIFAC model, in conjunction with experimental aqueous phase activity coefficients, is considered to be very useful in light of the availability of experimental aqueous phase activity coefficients for aromatic solutes. Furthermore, estimation of distribution coefficients within a factor of two is judged to be acceptable for initial evaluation and analysis in that distribution coefficients for the range of solutes and solvents considered here varied over approximately six orders of magnitude.

7.4. Future Work

It is recommended that future work with phase partitioning of aromatic solutes be directed towards environmental science applications other than wastewater treatment. For example, part of the environmental engineering community is concerned with hazardous waste management and transport of hazardous materials in the groundwater environment. In this respect, future modeling work could be focused towards improving procedures for prediction of Henry's Law constants and soil adsorption coefficients. Another application of the UNIFAC model would be to assess the effect of enhanced mobility of

solutes in groundwater due to the presence of organic solvents in the aqueous phase. The work performed in this project lends itself to study of these kinds of problems.

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Appendix A

**ESTIMATION OF ACTIVITY COEFFICIENTS
USING REGULAR SOLUTION THEORY**

This Appendix explains the use of the regular solution solubility parameter model for prediction of infinite dilution mole fraction activity coefficients. Pure component data for the solvents and solutes of interest in this study are given in Tables A-1, A-2 and A-3. Table A-4 lists regular solution estimates of the activity coefficients for the 224 solvent-solute systems considered; two values of γ_s^∞ are listed, one for each empirical correction term (Ψ_{12} or Ψ_{12}^*).

The following example gives the step by step procedure used to calculate γ_s^∞ for the system phenol-octanol. This calculation can be easily adapted for computer computation, the Fortran program used in this study is shown in Table A-5.

1. The empirical correction terms are calculated from equations (4-15) and (4-16), where the subscripts 1 and 2 refer to the solvent and solute respectively.

$$\Psi_{12} = 0.45 (\tau_1)^2 = 0.45 (4.90)^2 = 10.80 \text{ (cal/cm}^3)^2$$

$$\Psi_{12}^* = 0.477 (\tau_1 - \tau_2)^2 = 0.477(4.90-5.73)^2 = 0.32 \text{ (cal/cm}^3)^2$$

2. The infinite dilution solute mole fraction activity coefficient is then computed from equation (4-11), with $T = 298^\circ\text{K}$.

$$\begin{aligned} \ln \gamma_s^\infty &= (V_2/RT) [(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2 \Psi_{12}] \\ &\quad + \ln (V_2/V_1) + 1 - (V_2/V_1) \\ \ln \gamma_s^\infty &= (87.8/592.13) [(7.92 - 9.79)^2 + (4.90 - 5.73)^2 - 2\Psi_{12}] \end{aligned}$$

$$+ \ln (87.8/157.5) + 1 - (87.8/157.5)$$

$$\ln \gamma_s^{\infty} = 0.15 \left[4.19 - 2\Psi_{12} \right] - 0.14$$

3. Substituting for Ψ_{12}

$$\gamma_s^{\infty} = 0.064 \quad \text{with } \Psi_{12}$$

$$\gamma_s^{\infty} = 1.43 \quad \text{with } \Psi_{12}^*$$

Table A-1

Solvent Properties

SOLVENT	FORMULA	V(1) (cc/mole)	$\lambda(1,2)$ (cal/cc) ^{1/2}	$T(1,3)$ (cal/cc) ^{1/2}
BENZENE	C6H6	88.9	9.05	1.77
n-BUTYL ACETATE	C6H12O2	132.2	7.44	4.49
DIISOPROPYL ETHER	C6H14O	141.1	6.91	1.78
HEPTANE	C7H16	146.6	7.24	0.95
HEXANE	C6H14	130.5	7.03	2.12
METHYLISOBUTYL KETONE	C6H12O	125.6	7.38	5.81
OCTANOL	C8H18O	157.5	7.92	4.90
TOLUENE	C7H8	106.3	8.97	1.45

(1) DATA SOURCE: CRC (1979), HOY (1970), AND TIMMERMANS (1965)

(2) COMPUTED FROM EQUATION (4-13)

(3) COMPUTED FROM EQUATION (4-14)

Table A-2

Phenolic Solute Properties

SOLUTE	FORMULA	$v(1)$ (cc/mole)	$\lambda(1,2)_{1/2}$ (cal/cc) ^{1/2}	$\tau(1,3)_{1/2}$ (cal/cc) ^{1/2}	χ_w^∞ (4)
PHENOL	C6H6O	87.8	9.79	5.73	47
2-BROMOPHENOL	C6H5BrO	115.9	10.35	0.00	416
2-CHLOROPHENOL	C6H5ClO	101.8	9.82	0.00	188
3-CHLOROPHENOL	C6H5ClO	101.4	9.88	3.84	172
4-CHLOROPHENOL	C6H5ClO	101.6	9.90	4.14	185
2-HYDROXYPHENOL	C6H6O2	95.8	10.56	5.11	1.90
3-HYDROXYPHENOL	C6H6O2	86.6	10.19	8.87	0.61
4-HYDROXYPHENOL	C6H6O2	82.9	10.96	9.94	4.34
2,3-DIHYDROXYPHENOL	C6H6O3	86.8	9.94	8.69	0.02
2-METHYLPHENOL	C7H8O	105.3	9.57	4.61	153
3-METHYLPHENOL	C7H8O	104.6	9.69	5.42	180
4-METHYLPHENOL	C7H8O	106.3	9.50	5.68	191
2,4-DIMETHYLPHENOL	C8H10O	126.6	9.66	2.38	257
3,5-DIMETHYLPHENOL	C8H10O	126.2	9.59	3.53	485
2-NITROPHENOL	C6H5NO2	107.5	10.11	2.93	1934

(1) DATA SOURCE: CRC (1979), HOY (1970), AND TIMMERMANS (1965)

(2) COMPUTED FROM EQUATION (4-13)

(3) COMPUTED FROM EQUATION (4-14)

(4) DATA SOURCE: TSONOPOLOUS AND PRAUSNITZ (1971)

Table A-3

Aromatic Solute Properties

SOLUTE	FORMULA	$v(1)$ (cc/mole)	$\lambda(1,2)$ (cal/cc) ^{1/2}	$\gamma(1,3)$ (cal/cc) ^{1/2}	χ_w^∞ (4)
ANILINE	C6H7N	91.1	10.31	3.37	134
BENZENE	C6H6	88.9	9.05	1.77	2504
CHLOROBENZENE	C6H5CL	101.8	9.39	2.26	12506
1,2-DICHLOROBENZENE	C6H4CL2	112.7	9.80	0.00	56273
ETHYLBENZENE	C8H10	122.5	8.97	0.00	34674
METHYLBENZENE	C7H8	106.3	8.97	1.45	9482
1,2-DIMETHYLBENZENE	C8H10	120.6	9.11	0.00	28900
1,3-DIMETHYLBENZENE	C8H10	122.9	8.99	0.00	31355
1,4-DIMETHYLBENZENE	C8H10	123.3	8.97	0.00	31024
1,3,5-TRIMETHYLBENZENE	C9H12	138.9	9.02	0.00	68782
NAPHTHALENE	C10H8	125.1	7.45	6.18	66025
2-AMINONAPHTHALENE	C10H9N	134.9	11.19	0.00	6437
1-HYDROXYNAPHTHALENE	C10H8O	131.1	9.75	2.95	3520
PYRIDINE (5)	C5H5N	80.6	9.17	5.32	7.1

(1) DATA SOURCE: CRC (1979), HOY (1970), AND TIMMERMANS (1965)

(2) COMPUTED FROM EQUATION (4-13)

(3) COMPUTED FROM EQUATION (4-14)

(4) DATA SOURCE: TSONOPOLOUS AND PRAUSNITZ (1971)

(5) AQUEOUS PHASE ACTIVITY COEFFICIENT COMPUTED BY UNIFAC

Table A-4

Infinite Dilution Activity Coefficients for Various
Aromatic Solutes Using the Regular Solution Model

SOLVENT	SOLUTE	PSI12	PSI12*
OCTANOL	ANILINE	0.110	2.158
OCTANOL	BENZENE	0.180	1.131
OCTANOL	2-BROMOPHENOL	4.867	3.776
OCTANOL	CHLOROBENZENE	0.108	1.410
OCTANOL	2-CHLOROPHENOL	2.586	2.070
OCTANOL	3-CHLOROPHENOL	0.053	1.790
OCTANOL	4-CHLOROPHENOL	0.049	1.810
OCTANOL	2-METHYLPHENOL	0.037	1.521
OCTANOL	3-METHYLPHENOL	0.037	1.619
OCTANOL	4-METHYLPHENOL	0.034	1.469
OCTANOL	2-HYDROXYPHENOL	0.085	2.779
OCTANOL	1,2-DICHLOROBENZENE	2.941	2.298
OCTANOL	ETHYLBENZENE	2.004	1.533
OCTANOL	4-HYDROXYPHENOL	5.237	3.628
OCTANOL	1,3,5-TRIMETHYLBENZENE	2.314	1.708
OCTANOL	NAPHTHALENE	0.015	1.039
OCTANOL	1-HYDROXYNAPHTHALENE	0.040	2.147
OCTANOL	O-NITROPHENOL	0.090	2.312
OCTANOL	PHENOL	0.064	1.432
OCTANOL	2,3-DIHYDROXYPHENOL	0.543	1.729
OCTANOL	PYRIDINE	0.056	1.033
OCTANOL	3-HYDROXYPHENOL	0.779	2.037
OCTANOL	METHYLBENZENE	0.200	1.256
OCTANOL	1,2-DIMETHYLBENZENE	2.105	1.617
OCTANOL	1,3-DIMETHYLBENZENE	2.028	1.550
OCTANOL	1,4-DIMETHYLBENZENE	2.017	1.540
OCTANOL	2,4-DIMETHYLPHENOL	0.072	1.988
OCTANOL	3,5-DIMETHYLPHENOL	0.026	1.803
MIBK	ANILINE	0.084	3.728
MIBK	BENZENE	0.175	1.612
MIBK	2-BROMOPHENOL	10.837	7.586
MIBK	CHLOROBENZENE	0.092	2.167
MIBK	2-CHLOROPHENOL	4.867	3.558
MIBK	3-CHLOROPHENOL	0.031	2.942
MIBK	4-CHLOROPHENOL	0.026	2.975
MIBK	2-METHYLPHENOL	0.019	2.373
MIBK	3-METHYLPHENOL	0.012	2.529
MIBK	4-METHYLPHENOL	0.010	2.211
MIBK	2-HYDROXYPHENOL	0.039	4.980
MIBK	1,2-DICHLOROBENZENE	5.758	4.071
MIBK	ETHYLBENZENE	3.389	2.325
MIBK	4-HYDROXYPHENOL	0.864	6.220
MIBK	1,3,5-TRIMETHYLBENZENE	4.124	2.690
MIBK	NAPHTHALENE	0.002	1.002
MIBK	1-HYDROXYNAPHTHALENE	0.025	3.763
MIBK	O-NITROPHENOL	0.069	4.096
MIBK	PHENOL	0.024	2.171
MIBK	2,3-DIHYDROXYPHENOL	0.097	2.600

Table A-4 Continued

SOLVENT	SOLUTE	PSI12	PSI12*
MIBK	PYRIDINE	0.024	1.422
MIBK	3-HYDROXYPHENOL	0.138	3.177
MIBK	METHYLBENZENE	0.202	1.817
MIBK	1,2-DIMETHYLBENZENE	3.653	2.521
MIBK	1,3-DIMETHYLBENZENE	3.448	2.362
MIBK	1,4-DIMETHYLBENZENE	3.416	2.338
MIBK	2,4-DIMETHYLPHENOL	0.057	3.409
MIBK	3,5-DIMETHYLPHENOL	0.013	2.978
NBA	ANILINE	0.249	3.367
NBA	BENZENE	0.274	1.449
NBA	2-BROMOPHENOL	7.712	6.233
NBA	CHLOROBENZENE	0.194	1.937
NBA	2-CHLOROPHENOL	3.627	3.008
NBA	3-CHLOROPHENOL	0.129	2.691
NBA	4-CHLOROPHENOL	0.124	2.737
NBA	2-METHYLPHENOL	0.091	2.191
NBA	3-METHYLPHENOL	0.113	2.400
NBA	4-METHYLPHENOL	0.104	2.119
NBA	2-HYDROXYPHENOL	0.261	4.620
NBA	1,2-DICHLOROBENZENE	4.183	3.400
NBA	ETHYLBENZENE	2.455	1.960
NBA	4-HYDROXYPHENOL	25.985	6.242
NBA	1,3,5-TRIMETHYLBENZENE	2.877	2.229
NBA	NAPHTHALENE	0.040	1.027
NBA	1-HYDROXYNAPHTHALENE	0.099	3.337
NBA	O-NITROPHENOL	0.207	3.647
NBA	PHENOL	0.175	2.071
NBA	2,3-DIHYDROXYPHENOL	2.148	2.605
NBA	PYRIDINE	0.126	1.359
NBA	3-HYDROXYPHENOL	3.253	3.178
NBA	METHYLBENZENE	0.301	1.607
NBA	1,2-DIMETHYLBENZENE	2.649	2.122
NBA	1,3-DIMETHYLBENZENE	2.494	1.990
NBA	1,4-DIMETHYLBENZENE	2.471	1.970
NBA	2,4-DIMETHYLPHENOL	0.154	2.992
NBA	3,5-DIMETHYLPHENOL	0.068	2.698

Table A-4 Continued

SOLVENT	SOLUTE	PSI12	PSI12*
DIPE	ANILINE	5.180	5.542
DIPE	BENZENE	1.182	1.813
DIPE	2-BROMOPHENOL	10.580	10.232
DIPE	CHLOROBENZENE	1.748	2.748
DIPE	2-CHLOROPHENOL	4.313	4.188
DIPE	3-CHLOROPHENOL	5.469	4.456
DIPE	4-CHLOROPHENOL	7.035	4.612
DIPE	2-METHYLPHENOL	4.932	3.523
DIPE	3-METHYLPHENOL	23.567	4.185
DIPE	4-METHYLPHENOL	29.506	3.642
DIPE	2-HYDROXYPHENOL	30.578	8.764
DIPE	1,2-DICHLOROBENZENE	5.082	4.919
DIPE	ETHYLBENZENE	2.543	2.455
DIPE	4-HYDROXYPHENOL	65808.685	13.525
DIPE	1,3,5-TRIMETHYLBENZENE	3.059	2.938
DIPE	NAPHTHALENE	34.490	1.275
DIPE	1-HYDROXYNAPHTHALENE	4.281	6.027
DIPE	O-NITROPHENOL	4.697	6.267
DIPE	PHENOL	19.855	3.337
DIPE	2,3-DIHYDROXYPHENOL	2495.569	4.787
DIPE	PYRIDINE	6.558	1.901
DIPE	3-HYDROXYPHENOL	4456.412	6.103
DIPE	METHYLBENZENE	1.262	2.066
DIPE	1,2-DIMETHYLBENZENE	2.824	2.727
DIPE	1,3-DIMETHYLBENZENE	2.596	2.506
DIPE	1,4-DIMETHYLBENZENE	2.561	2.472
DIPE	2,4-DIMETHYLPHENOL	2.939	5.023
DIPE	3,5-DIMETHYLPHENOL	4.802	4.731
BENZENE	ANILINE	1.336	1.399
BENZENE	BENZENE	0.655	1.000
BENZENE	2-BROMOPHENOL	1.424	1.378
BENZENE	CHLOROBENZENE	0.649	1.012
BENZENE	2-CHLOROPHENOL	1.157	1.124
BENZENE	3-CHLOROPHENOL	1.433	1.153
BENZENE	4-CHLOROPHENOL	1.812	1.172
BENZENE	2-METHYLPHENOL	1.527	1.077
BENZENE	3-METHYLPHENOL	6.772	1.181
BENZENE	4-METHYLPHENOL	9.551	1.157
BENZENE	2-HYDROXYPHENOL	5.550	1.566
BENZENE	1,2-DICHLOROBENZENE	1.146	1.110
BENZENE	ETHYLBENZENE	1.009	0.974
BENZENE	4-HYDROXYPHENOL	12759.399	2.554
BENZENE	1,3,5-TRIMETHYLBENZENE	0.958	0.921
BENZENE	NAPHTHALENE	53.860	1.942
BENZENE	1-HYDROXYNAPHTHALENE	0.746	1.037
BENZENE	O-NITROPHENOL	0.921	1.216
BENZENE	PHENOL	7.234	1.197
BENZENE	2,3-DIHYDROXYPHENOL	827.869	1.550
BENZENE	PYRIDINE	3.775	1.079
BENZENE	3-HYDROXYPHENOL	1269.530	1.697
BENZENE	METHYLBENZENE	0.604	0.985
BENZENE	1,2-DIMETHYLBENZENE	1.013	0.979
BENZENE	1,3-DIMETHYLBENZENE	1.007	0.972
BENZENE	1,4-DIMETHYLBENZENE	1.007	0.972
BENZENE	2,4-DIMETHYLPHENOL	0.598	1.013
BENZENE	3,5-DIMETHYLPHENOL	1.054	1.024

Table A-4 Continued

SOLVENT	SOLUTE	PSI12	PSI12*
TOLUENE	ANILINE	1.717	1.338
TOLUENE	BENZENE	0.754	0.987
TOLUENE	2-BROMOPHENOL	1.507	1.474
TOLUENE	CHLOROBENZENE	0.833	1.035
TOLUENE	2-CHLOROPHENOL	1.173	1.150
TOLUENE	3-CHLOROPHENOL	2.213	1.204
TOLUENE	4-CHLOROPHENOL	2.897	1.227
TOLUENE	2-METHYLPHENOL	2.441	1.125
TOLUENE	3-METHYLPHENOL	12.681	1.245
TOLUENE	4-METHYLPHENOL	18.568	1.219
TOLUENE	2-HYDROXYPHENOL	9.620	1.654
TOLUENE	1,2-DICHLOROBENZENE	1.184	1.159
TOLUENE	ETHYLBENZENE	1.033	1.009
TOLUENE	4-HYDROXYPHENOL	31174.578	2.690
TOLUENE	1,3,5-TRIMETHYLBENZENE	1.011	0.984
TOLUENE	NAPHTHALENE	121.356	1.996
TOLUENE	1-HYDROXYNAPHTHALENE	1.209	1.143
TOLUENE	O-NITROPHENOL	1.336	1.289
TOLUENE	PHENOL	12.274	1.219
TOLUENE	2,3-DIHYDROXYPHENOL	1847.336	1.603
TOLUENE	PYRIDINE	5.758	1.066
TOLUENE	3-HYDROXYPHENOL	2891.333	1.765
TOLUENE	METHYLBENZENE	0.712	1.000
TOLUENE	1,2-DIMETHYLBENZENE	1.039	1.015
TOLUENE	1,3-DIMETHYLBENZENE	1.033	1.009
TOLUENE	1,4-DIMETHYLBENZENE	1.033	1.009
TOLUENE	2,4-DIMETHYLPHENOL	0.875	1.099
TOLUENE	3,5-DIMETHYLPHENOL	1.795	1.115
SOLVENT	SOLUTE	PSI12	PSI12*
HEPTANE	ANILINE	8.397	4.029
HEPTANE	BENZENE	1.439	1.476
HEPTANE	2-BROMOPHENOL	6.582	6.519
HEPTANE	CHLOROBENZENE	2.436	2.114
HEPTANE	2-CHLOROPHENOL	3.005	2.980
HEPTANE	3-CHLOROPHENOL	11.281	3.315
HEPTANE	4-CHLOROPHENOL	15.794	3.435
HEPTANE	2-METHYLPHENOL	11.424	2.698
HEPTANE	3-METHYLPHENOL	80.903	3.225
HEPTANE	4-METHYLPHENOL	114.278	2.871
HEPTANE	2-HYDROXYPHENOL	79.094	6.248
HEPTANE	1,2-DICHLOROBENZENE	3.429	3.397

Table A-4 Continued

SOLVENT	SOLUTE	PSI12	PSI12*
HEPTANE	ETHYLBENZENE	1.863	1.845
HEPTANE	4-HYDROXYPHENOL	440987.449	10.187
HEPTANE	1,3,5-TRIMETHYLBENZENE	2.144	2.119
HEPTANE	NAPHTHALENE	270.942	1.301
HEPTANE	1-HYDROXYNAPHTHALENE	8.114	4.174
HEPTANE	O-NITROPHENOL	7.502	4.410
HEPTANE	PHENOL	59.623	2.659
HEPTANE	2,3-DIHYDROXYPHENOL	14919.714	3.879
HEPTANE	PYRIDINE	17.226	1.613
HEPTANE	3-HYDROXYPHENOL	27054.709	4.839
HEPTANE	METHYLBENZENE	1.476	1.636
HEPTANE	1,2-DIMETHYLBENZENE	2.039	2.019
HEPTANE	1,3-DIMETHYLBENZENE	1.895	1.876
HEPTANE	1,4-DIMETHYLBENZENE	1.873	1.854
HEPTANE	2,4-DIMETHYLPHENOL	4.503	3.530
HEPTANE	3,5-DIMETHYLPHENOL	11.142	3.425
SOLVENT	SOLUTE	PSI12	PSI12*
HEXANE	ANILINE	3.371	4.993
HEXANE	BENZENE	0.959	1.730
HEXANE	2-BROMOPHENOL	9.370	8.936
HEXANE	CHLOROBENZENE	1.267	2.531
HEXANE	2-CHLOROPHENOL	4.000	3.837
HEXANE	3-CHLOROPHENOL	3.238	3.992
HEXANE	4-CHLOROPHENOL	4.014	4.120
HEXANE	2-METHYLPHENOL	2.833	3.172
HEXANE	3-METHYLPHENOL	11.417	3.725
HEXANE	4-METHYLPHENOL	13.781	3.253
HEXANE	2-HYDROXYPHENOL	15.854	7.678
HEXANE	1,2-DICHLOROBENZENE	4.641	4.432
HEXANE	ETHYLBENZENE	2.385	2.268
HEXANE	4-HYDROXYPHENOL	23472.595	11.774
HEXANE	1,3,5-TRIMETHYLBENZENE	2.806	2.651
HEXANE	NAPHTHALENE	14.339	1.217
HEXANE	1-HYDROXYNAPHTHALENE	2.446	5.177
HEXANE	O-NITROPHENOL	2.971	5.525
HEXANE	PHENOL	10.584	3.053
HEXANE	2,3-DIHYDROXYPHENOL	991.866	4.301
HEXANE	PYRIDINE	3.921	1.800
HEXANE	3-HYDROXYPHENOL	1728.584	5.432
HEXANE	METHYLBENZENE	1.010	1.934
HEXANE	1,2-DIMETHYLBENZENE	2.636	2.509
HEXANE	1,3-DIMETHYLBENZENE	2.431	2.312
HEXANE	1,4-DIMETHYLBENZENE	2.400	2.281
HEXANE	2,4-DIMETHYLPHENOL	1.873	4.386
HEXANE	3,5-DIMETHYLPHENOL	2.605	4.117

Table A-5

Fortran File Solute.For

```

C*****C
C  THIS FORTRAN PROGRAM CALCULATES INFINITE DILUTION MOLE FRACTION  C
C  ACTIVITY COEFFICIENTS BASED ON THE REGULAR SOLUTION MODEL.      C
C  PURE COMPONENT SOLUTE DATA IS STORED IN THE INPUT FILE SOLUTE.DAT.C
C  PURE COMPONENT SOLVENT DATA IS INPUTTED AT THE TERMINAL WHEN THE C
C  COMPUTER PROMPTS YOU TO DO SO. CALCULATED VALUES OF ACTIVITY    C
C  AND DISTRIBUTION COEFFICIENTS ARE LISTED IN THE OUTPUT FILE      C
C  SOLUTE.OUT.                                                       C
C*****C

      DIMENSION SOLUTE(28,2),A2(28),T2(28),V2(28),GW(28)
      DOUBLE PRECISION SOLVNT,SOLUTE
      OPEN (UNIT=51,DEVICE='DSK',FILE='SOLUTE.DAT')
      OPEN (UNIT=52,DEVICE='DSK',FILE='SOLUTE.OUT')
      DO 10 I=1,28
      READ (51,8) (SOLUTE(I,II),II=1,2)
8      FORMAT (2A10)
      READ (51,*) A2(I),T2(I),V2(I),GW(I)
10     CONTINUE

      WRITE (5,9)
      FORMAT (' INPUT SOLVNT NAME')
      READ (5,1) SOLVNT
1      FORMAT (A10)
      WRITE (5,3)
      FORMAT (' INPUT PARAMETERS A1,T1,V1')
      READ (5,*) A1,T1,V1

      WRITE (52,5)
      DO 2 I=1,28
      N=1
17     CORR=2*(0.477*((T1-T2(I))**2))
      GO TO 20
20     CORR=2*(0.45*(T1)**2)
30     DISP=(A1-A2(I))**2
      DIPL=(T1-T2(I))**2
      FHEM=ALOG(V2(I)/V1)+1-(V2(I)/V1)
      GS=EXP((V2(I)/592.42)*(DISP+DIPL-CORR)+FHEM)
      DK=(18/V1)*(GW(I)/GS)
      WRITE (52,4) (SOLUTE(I,II),II=1,2),GS,DK
5      FORMAT (1X,T5,'SOLVENT',T20,'SOLUTE',T43,'GS',T55,'DK'/)
4      FORMAT (1X,T5,A10,T41,2A10,T48,F15.5,T55,F20.5)
      N=N+1
      IF (N.EQ.2) GO TO 20
2      CONTINUE
      WRITE (5,6)
6      FORMAT (' DO YOU HAVE MORE TO BE CALCULATED, IF "YES", TYPE 1,
1IF "NO", TYPE 0')
      READ (5,*) IND
      IF (IND.EQ.0) STOP
      GO TO 7
      END

```

Appendix B

ESTIMATION OF ACTIVITY COEFFICIENTS USING UNIFAC

This Appendix explains the use of the UNIFAC group contribution model for prediction of infinite dilution solute mole fraction activity coefficients. Some of the functional group data used as input parameters in the UNIFAC model are shown in the example calculation. The complete listing of the available functional group data is provided in the original references (Gmehling et al., 1982 and Magnussen et al., 1981). Calculation of activity coefficients from the UNIFAC model is facilitated by use of the computer. Programs may be written by referring to the UNIFAC equations in Chapter Four or by adapting the Fortran programs given by Fredenslund et al., (1977). Tables B-3 and B-4 list the combinatorial and residual contributions and the total infinite dilution activity coefficients for the 225 binary systems using VLE and LLE data, respectively. Group interaction parameters are not available for many of the DIPE and NBA systems, therefore residual portions of the activity coefficient could not be calculated. Tables B-5 through B-12 show the Fortran programs used in this study for calculation of activity coefficients.

The following example shows how to calculate an infinite dilution activity coefficient for the binary system phenol (1) - octanol (2) using the VLE data base of Gmehling et al., (1982). Additional examples are given by Grain (1982).

1. The formula for phenol is C_6H_6O and it may be divided into the following functional groups; 5-ACH and 1-ACOH.
2. The formula for octanol is $C_8H_{18}O$ and it may be divided into the following functional groups; 1-CH₃, 7-CH₂ and 1-OH.
3. Table B-1 lists values of the sub-group parameters which are used to calculate the combinatorial portion of the activity coefficient;

Table B-1
Functional Group Parameters

Group	Main-Group No.	Sub-Group No.	v_k	R_k	Q_k
CH ₂	1	2	7	0.6744	0.540
CH ₂ ²	1	1	1	0.9011	0.848
OH ³	5	15	1	1.000	1.200
ACH	3	10	5	0.5313	0.400
ACOH	8	18	1	0.8952	0.680

4. From equation (4-21)

$$\ln \gamma_1^{c,\infty} = \ln (r_1/r_2) + 5q_1 \ln (q_1 r_2 / q_2 r_1) + I_1 - (r_1/r_2)(I_2)$$

$$r_1 = \sum_k v_k^{(1)} R_k = (5)(0.5313) + (1)(0.8952) = 3.5517$$

$$r_2 = (7)(0.6744) + (1)(0.9011) + (1)(1.0) = 6.6219$$

$$q_1 = \sum_k v_k^{(1)} Q_k = (5)(0.4) + (1)(0.68) = 2.68$$

$$q_2 = (7)(0.54) + (1)(0.848) + (1)(1.2) = 5.828$$

$$I_1 = 5(r_1 - q_1) - (r_1 - 1) = 5(3.5517 - 2.68) - (3.5517 - 1) = 1.807$$

$$I_2 = 5(6.6219 - 5.828) - (5.6219) = -1.652$$

$$\begin{aligned} \ln \gamma_1^{c,\infty} &= \ln (3.5517/6.6219) + 5(2.68) \ln [((2.68)(6.6219))/((5.828)(3.5517))] \\ &\quad + 1.807 + (1.652)((3.5517)/(6.6219)) \end{aligned}$$

$$\ln \gamma_1^{c,\infty} = 0.008$$

5. Table B-2 lists the group interaction parameters which are used to calculate the residual portion of the infinite dilution activity coefficient for phenol (1) in octanol (2). Note that CH₃ and CH₂ are members of the same main group.

Table B-2
Group Interaction Parameters

Main Group	1 CH ₂ ,CH ₃	3 ACH	5 OH	8 ACOH
1-CH ₂ ,CH ₃	0	61.13	986.5	1333
3-ACH	-11.12	0	636.1	1329
5-OH	156.4	89.60	0	-259.7
8-ACOH	275.8	25.34	-451.6	0

6. Compute the functional group interaction energies, where m refers to main group by row and n to main group by column to identify UNIFAC interaction parameter a_{mn} .

$$\Psi_{mn} = \exp(-a_{mn}/T), \quad T = 298^\circ\text{K}$$

$$\Psi_{1,1} = \Psi_{3,3} = \Psi_{5,5} = \Psi_{8,8} = 1.0$$

$$\Psi_{1,3} = 0.815$$

$$\Psi_{3,1} = 1.261$$

$$\Psi_{1,5} = 0.037$$

$$\Psi_{3,5} = 0.118$$

$$\Psi_{1,8} = 0.011$$

$$\Psi_{3,8} = 0.012$$

$$\Psi_{5,1} = 0.592$$

$$\Psi_{8,1} = 0.396$$

$$\Psi_{5,3} = 0.740$$

$$\Psi_{8,3} = 0.818$$

$$\Psi_{5,8} = 2.390$$

$$\Psi_{8,5} = 4.551$$

7. Compute functional group concentration fractions, X , and functional group lattice area fractions, θ

- (i) For pure phenol, X is computed by reference to subgroup numbers 10 and 18.

$$X_k^{(1)} = \frac{v_k}{\sum v_k}$$

$$X_{10}^{(1)} = 5/6 \text{ and } X_{18}^{(1)} = 1/6$$

$$\bar{\theta}_k^{(1)} = Q_k X_k^{(1)} / \sum Q_k X_k^{(1)}$$

$$\bar{\theta}_{10}^{(1)} = (0.4)(5/6) / [(0.4)(5/6) + (0.68)(1/6)] = 0.746$$

$$\bar{\theta}_{18}^{(1)} = 1 - \bar{\theta}_{10}^{(1)} = 0.254$$

(ii) For phenol at infinite dilution in octanol (i.e. pure octanol) and referring to sub group numbers

$$\bar{\theta}_{10} = \bar{\theta}_{18} = 0$$

$$X_1 = X_{15} = 1/9 \text{ and } X_2 = 7/9$$

$$\bar{\theta}_1 = 0.146$$

$$\bar{\theta}_2 = 0.648$$

$$\bar{\theta}_{15} = 0.206$$

8. Compute the residual portion of the activity coefficient for the functional groups ACH and ACOH in pure phenol ($\ln \Gamma_k^{(1)}$) and in the solvent mixture ($\ln \Gamma_k$) according to equation (4-23):

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \bar{\theta}_m \Psi_{mk} \right) - \sum_m \left[(\bar{\theta}_m \Psi_{mk}) / \left(\sum_n \bar{\theta}_n \Psi_{nm} \right) \right] \right]$$

- (i) For pure phenol, ($\ln \Gamma_k^{(1)}$), define (referring to sub-group nos.):

$$\text{Den } 1^{(1)} = (\bar{\theta}_{10}) (\Psi_{10,10}) + (\bar{\theta}_{18}) (\Psi_{18,10})$$

$$\text{Den } 2^{(1)} = (\bar{\theta}_{10}) (\Psi_{10,18}) + (\bar{\theta}_{18}) (\Psi_{18,18})$$

$$\begin{aligned} \ln \Gamma_{10}^{(1)} &= Q_{10} \left[1 - \ln (\text{Den } 1^{(1)}) - \frac{(\bar{\theta}_{10}) (\Psi_{10,10})}{\text{Den } 1^{(1)}} - \frac{(\bar{\theta}_{18}) (\Psi_{18,10})}{\text{Den } 2^{(1)}} \right] \\ &= 0.099 \end{aligned}$$

$$\begin{aligned} \ln \Gamma_{18}^{(1)} &= Q_{18} \left[1 - \ln (\text{Den } 2^{(1)}) - \frac{(\bar{\theta}_{10}) (\Psi_{18,10})}{\text{Den } 1^{(1)}} - \frac{(\bar{\theta}_{18}) (\Psi_{18,18})}{\text{Den } 2^{(1)}} \right] \\ &= 0.456 \end{aligned}$$

(ii) For phenol at infinite dilution in octanol, $(\ln \Gamma_k)$, define:

$$\text{Den 1} = (\bar{\theta}_{15}) (\Psi_{15,15}) + (\bar{\theta}_1) (\Psi_{1,15}) + (\bar{\theta}_2) (\Psi_{2,15})$$

$$\text{Den 2} = (\bar{\theta}_{15}) (\Psi_{15,1}) + (\bar{\theta}_1) (\Psi_{1,1}) + (\bar{\theta}_2) (\Psi_{2,1})$$

$$\text{Den 3} = (\bar{\theta}_{15}) (\Psi_{15,2}) + (\bar{\theta}_1) (\Psi_{1,2}) + (\bar{\theta}_2) (\Psi_{2,2})$$

$$\begin{aligned} \ln \Gamma_{10} &= Q_{10} \left[1 - \ln [(\bar{\theta}_{15}) (\Psi_{15,10}) + (\bar{\theta}_1) (\Psi_{1,10}) + (\bar{\theta}_2) (\Psi_{2,10})] \right. \\ &\quad \left. - \frac{(\bar{\theta}_{15}) (\Psi_{10,15})}{\text{Den 1}} - \frac{(\bar{\theta}_1) (\Psi_{10,1})}{\text{Den 2}} - \frac{(\bar{\theta}_2) (\Psi_{10,2})}{\text{Den 3}} \right] \\ &= 0.008 \end{aligned}$$

$$\begin{aligned} \ln \Gamma_{18} &= Q_{18} \left[1 - \ln [(\bar{\theta}_{15}) (\Psi_{15,18}) + (\bar{\theta}_1) (\Psi_{1,18}) + (\bar{\theta}_2) (\Psi_{2,18})] \right. \\ &\quad \left. - \frac{(\bar{\theta}_{15}) (\Psi_{18,15})}{\text{Den 1}} - \frac{(\bar{\theta}_1) (\Psi_{18,1})}{\text{Den 2}} - \frac{(\bar{\theta}_2) (\Psi_{18,2})}{\text{Den 3}} \right] \\ &= -1.792 \end{aligned}$$

9. Compute the residual portion of the infinite dilution activity coefficient from equation (4-22):

$$\ln \gamma_1^{R,\infty} = \sum_k V_k^{(1)} (\ln \Gamma_k - \ln \Gamma_k^{(1)})$$

$$\ln \gamma_1^{R,\infty} = 5 (0.088 - 0.099) + 1 (-1.792 - 0.456)$$

$$\ln \gamma_1^{R,\infty} = -2.303$$

10. Compute the infinite dilution mole fraction activity for phenol in octanol from equation (4-19):

$$\ln \gamma_1^{\infty} = \ln \gamma_1^{c,\infty} + \ln \gamma_1^{R,\infty}$$

$$\ln \gamma_1^{\infty} = 0.008 + -2.303 = -2.295$$

$$\gamma_1^{\infty} = 0.101$$

Table B-3

Infinite Dilution Activity Coefficients For Various Aromatic Solutes
Predicted by the UNIFAC Model Using VLE Data

SOLVENT	SOLUTE	COMB	RES	GAMMA
OCTANOL	ANILINE	0.027	0.040	1.069
OCTANOL	NITROANILINE	0.125	1.450	4.831
OCTANOL	BENZENE	-0.058	0.528	1.600
OCTANOL	CHLOROBENZENE	0.078	0.543	1.861
OCTANOL	DICHLOROBENZENE	0.188	0.718	2.474
OCTANOL	ETHYLBENZENE	0.128	0.610	2.092
OCTANOL	METHYLBENZENE	0.063	0.547	1.840
OCTANOL	DIMETHYLBENZENE	0.148	0.536	1.982
OCTANOL	TRIMETHYLBENZENE	0.208	0.507	2.044
OCTANOL	NITROBENZENE	0.070	1.641	5.534
OCTANOL	NAPHTHALENE	0.512	0.756	3.554
OCTANOL	AMINONAPHTHALENE	0.531	0.056	1.799
OCTANOL	HYDROXYNAPHTHALENE	0.533	-2.292	0.172
OCTANOL	HYDROXYQUINOLINE	0.706	-1.905	0.301
OCTANOL	METHYLHYDROXYQUINOLINE	0.727	-2.248	0.218
OCTANOL	PYRIDINE	0.037	-1.507	0.230
OCTANOL	DIMETHYLPYRIDINE	0.249	-1.093	0.430
OCTANOL	PHENOL	0.008	-2.303	0.101
OCTANOL	HYDROXYPHENOL	0.063	-4.334	0.014
OCTANOL	METHYLHYDROXYPHENOL	0.149	-4.766	0.010
OCTANOL	DIMETHYLHYDROXYPHENOL	0.209	-5.094	0.008
OCTANOL	METHYLPHENOL	0.109	-2.505	0.091
OCTANOL	DIMETHYLPHENOL	0.181	-2.668	0.083
OCTANOL	NITROPHENOL	0.114	0.049	1.177
OCTANOL	TRINITROPHENOL	0.219	4.969	179.110
MIBK	ANILINE	0.143	0.010	1.165
MIBK	NITROANILINE	0.192	-0.401	0.811
MIBK	BENZENE	0.087	-0.174	0.917
MIBK	CHLOROBENZENE	0.190	-0.002	1.207
MIBK	DICHLOROBENZENE	0.266	0.330	1.815
MIBK	ETHYLBENZENE	0.196	-0.137	1.016
MIBK	METHYLBENZENE	0.168	-0.306	0.871
MIBK	DIMETHYLBENZENE	0.213	-0.468	0.775
MIBK	TRIMETHYLBENZENE	0.233	-0.648	0.660
MIBK	NITROBENZENE	0.166	-0.882	0.489
MIBK	NAPHTHALENE	0.566	-0.250	1.372
MIBK	AMINONAPHTHALENE	0.556	-0.278	1.322
MIBK	HYDROXYNAPHTHALENE	0.567	-2.118	0.212
MIBK	HYDROXYQUINOLINE	0.753	-0.095	1.931
MIBK	METHYLHYDROXYQUINOLINE	0.734	-0.589	1.156
MIBK	PYRIDINE	0.195	-0.012	1.201
MIBK	DIMETHYLPYRIDINE	0.326	0.045	1.449
MIBK	PHENOL	0.133	-1.825	0.184
MIBK	HYDROXYPHENOL	0.169	-2.676	0.082
MIBK	METHYLHYDROXYPHENOL	0.214	-3.259	0.048
MIBK	DIMETHYLHYDROXYPHENOL	0.235	-3.738	0.030
MIBK	METHYLPHENOL	0.195	-2.178	0.138
MIBK	DIMETHYLPHENOL	0.227	-2.492	0.104
MIBK	NITROPHENOL	0.190	-1.294	0.332
MIBK	TRINITROPHENOL	0.198	-0.016	1.200

Table B-3 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
NBA	ANILINE	0.108	*****	*****
NBA	NITROANILINE	0.151	*****	*****
NBA	BENZENE	0.055	-0.138	0.920
NBA	CHLOROBENZENE	0.149	-0.316	0.846
NBA	DICHLOROBENZENE	0.218	-0.334	0.890
NBA	ETHYLBENZENE	0.154	-0.005	1.161
NBA	METHYLBENZENE	0.130	-0.094	1.037
NBA	DIMETHYLBENZENE	0.169	-0.080	1.093
NBA	TRIMETHYLBENZENE	0.183	-0.084	1.104
NBA	NITROBENZENE	0.129	*****	*****
NBA	NAPHTHALENE	0.491	-0.198	1.340
NBA	AMINONAPHTHALENE	0.478	*****	*****
NBA	HYDROXYNAPHTHALENE	0.490	-2.192	0.182
NBA	HYDROXYQUINOLINE	0.666	*****	*****
NBA	METHYLHYDROXYQUINOLINE	0.641	*****	*****
NBA	PYRIDINE	0.153	*****	*****
NBA	DIMETHYLPYRIDINE	0.273	*****	*****
NBA	PHENOL	0.098	-1.915	0.163
NBA	HYDROXYPHENOL	0.131	-2.892	0.063
NBA	METHYLHYDROXYPHENOL	0.170	-3.299	0.044
NBA	DIMETHYLHYDROXYPHENOL	0.185	-3.602	0.033
NBA	METHYLPHENOL	0.154	-2.092	0.144
NBA	DIMETHYLPHENOL	0.179	-2.230	0.129
NBA	NITROPHENOL	0.149	*****	*****
NBA	TRINITROPHENOL	0.145	*****	*****

SOLVENT	SOLUTE	COMB	RES	GAMMA
DIPE	ANILINE	0.095	*****	*****
DIPE	NITROANILINE	0.132	*****	*****
DIPE	BENZENE	0.046	0.114	1.174
DIPE	CHLOROBENZENE	0.134	*****	*****
DIPE	DICHLOROBENZENE	0.196	*****	*****
DIPE	ETHYLBENZENE	0.135	0.070	1.228
DIPE	METHYLBENZENE	0.115	0.128	1.275
DIPE	DIMETHYLBENZENE	0.149	0.112	1.298
DIPE	TRIMETHYLBENZENE	0.158	0.078	1.266
DIPE	NITROBENZENE	0.114	*****	*****
DIPE	NAPHTHALENE	0.454	0.164	1.855
DIPE	AMINONAPHTHALENE	0.438	*****	*****
DIPE	HYDROXYNAPHTHALENE	0.450	*****	*****
DIPE	HYDROXYQUINOLINE	0.622	*****	*****
DIPE	METHYLHYDROXYQUINOLINE	0.592	*****	*****
DIPE	PYRIDINE	0.140	*****	*****
DIPE	DIMETHYLPYRIDINE	0.248	*****	*****
DIPE	PHENOL	0.086	*****	*****
DIPE	HYDROXYPHENOL	0.116	*****	*****
DIPE	METHYLHYDROXYPHENOL	0.150	*****	*****
DIPE	DIMETHYLHYDROXYPHENOL	0.159	*****	*****
DIPE	METHYLPHENOL	0.136	*****	*****
DIPE	DIMETHYLPHENOL	0.157	*****	*****
DIPE	NITROPHENOL	0.132	*****	*****
DIPE	TRINITROPHENOL	0.116	*****	*****

Table B-3 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
BENZENE	ANILINE	-0.012	1.138	3.083
BENZENE	NITROANILINE	-0.075	1.973	6.673
BENZENE	BENZENE	0.000	0.000	1.000
BENZENE	CHLOROBENZENE	-0.016	0.364	1.416
BENZENE	DICHLOROBENZENE	-0.059	0.888	2.291
BENZENE	ETHYLBENZENE	-0.074	-0.049	0.884
BENZENE	METHYLBENZENE	-0.023	-0.029	0.949
BENZENE	DIMETHYLBENZENE	-0.081	-0.088	0.845
BENZENE	TRIMETHYLBENZENE	-0.165	-0.165	0.719
BENZENE	NITROBENZENE	-0.032	0.538	1.659
BENZENE	NAPHTHALENE	-0.050	0.000	0.951
BENZENE	AMINONAPHTHALENE	-0.129	0.926	2.219
BENZENE	HYDROXYNAPHTHALENE	-0.101	1.895	6.013
BENZENE	HYDROXYQUINOLINE	-0.002	3.927	50.653
BENZENE	METHYLHYDROXYQUINOLINE	-0.124	3.536	30.326
BENZENE	PYRIDINE	0.022	0.182	1.226
BENZENE	DIMETHYLPYRIDINE	-0.054	-0.104	0.854
BENZENE	PHENOL	-0.006	2.112	8.215
BENZENE	HYDROXYPHENOL	-0.023	5.024	148.562
BENZENE	METHYLHYDROXYPHENOL	-0.081	4.544	86.747
BENZENE	DIMETHYLHYDROXYPHENOL	-0.164	4.168	54.817
BENZENE	METHYLPHENOL	-0.048	1.862	6.135
BENZENE	DIMETHYLPHENOL	-0.120	1.651	4.623
BENZENE	NITROPHENOL	-0.060	3.889	46.016
BENZENE	TRINITROPHENOL	-0.276	7.659	1608.408

SOLVENT	SOLUTE	COMB	RES	GAMMA
TOLUENE	ANILINE	-0.001	1.226	3.404
TOLUENE	NITROANILINE	-0.013	1.723	5.529
TOLUENE	BENZENE	-0.020	-0.018	0.963
TOLUENE	CHLOROBENZENE	0.001	-0.041	0.961
TOLUENE	DICHLOROBENZENE	-0.004	0.096	1.096
TOLUENE	ETHYLBENZENE	-0.013	0.005	0.992
TOLUENE	METHYLBENZENE	0.000	0.000	1.000
TOLUENE	DIMETHYLBENZENE	-0.016	-0.012	0.972
TOLUENE	TRIMETHYLBENZENE	-0.056	-0.042	0.907
TOLUENE	NITROBENZENE	0.000	0.182	1.200
TOLUENE	NAPHTHALENE	0.043	-0.026	1.017
TOLUENE	AMINONAPHTHALENE	-0.005	1.006	2.721
TOLUENE	HYDROXYNAPHTHALENE	0.013	1.519	4.627
TOLUENE	HYDROXYQUINOLINE	0.105	3.670	43.598
TOLUENE	METHYLHYDROXYQUINOLINE	0.026	3.326	28.560
TOLUENE	PYRIDINE	-0.005	0.325	1.377
TOLUENE	DIMETHYLPYRIDINE	0.004	0.077	1.084
TOLUENE	PHENOL	-0.005	1.744	5.692
TOLUENE	HYDROXYPHENOL	0.000	4.306	74.143
TOLUENE	METHYLHYDROXYPHENOL	-0.015	3.873	47.371
TOLUENE	DIMETHYLHYDROXYPHENOL	-0.056	3.544	32.720
TOLUENE	METHYLPHENOL	-0.004	1.541	4.651
TOLUENE	DIMETHYLPHENOL	-0.033	1.377	3.834
TOLUENE	NITROPHENOL	-0.008	3.183	23.927
TOLUENE	TRINITROPHENOL	-0.120	6.277	472.010

Table B-3 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
HEXANE	ANILINE	0.094	3.161	25.920
HEXANE	NITROANILINE	0.119	5.218	207.888
HEXANE	BENZENE	0.052	0.402	1.575
HEXANE	CHLOROBENZENE	0.130	0.601	2.077
HEXANE	DICHLOROBENZENE	0.183	0.960	3.136
HEXANE	ETHYLBENZENE	0.122	0.298	1.522
HEXANE	METHYLBENZENE	0.111	0.372	1.621
HEXANE	DIMETHYLBENZENE	0.135	0.312	1.564
HEXANE	TRIMETHYLBENZENE	0.133	0.234	1.443
HEXANE	NITROBENZENE	0.108	2.162	9.679
HEXANE	NAPHTHALENE	0.425	0.550	2.651
HEXANE	AMINONAPHTHALENE	0.401	2.748	23.313
HEXANE	HYDROXYNAPHTHALENE	0.416	2.792	24.730
HEXANE	HYDROXYQUINOLINE	0.586	5.276	351.426
HEXANE	METHYLHYDROXYQUINOLINE	0.545	4.884	227.921
HEXANE	PYRIDINE	0.144	1.181	3.762
HEXANE	DIMETHYLPYRIDINE	0.232	0.562	2.212
HEXANE	PHENOL	0.087	2.861	19.068
HEXANE	HYDROXYPHENOL	0.112	6.120	508.772
HEXANE	METHYLHYDROXYPHENOL	0.136	5.639	322.144
HEXANE	DIMETHYLHYDROXYPHENOL	0.135	5.262	220.743
HEXANE	METHYLPHENOL	0.127	2.610	15.441
HEXANE	DIMETHYLPHENOL	0.137	2.398	12.616
HEXANE	NITROPHENOL	0.121	5.860	395.836
HEXANE	TRINITROPHENOL	0.081	12.074	190042.0

SOLVENT	SOLUTE	COMB	RES	GAMMA
HEPTANE	ANILINE	0.047	3.161	24.730
HEPTANE	NITROANILINE	0.095	5.218	202.958
HEPTANE	BENZENE	-0.009	0.402	1.481
HEPTANE	CHLOROBENZENE	0.084	0.601	1.984
HEPTANE	DICHLOROBENZENE	0.150	0.960	3.034
HEPTANE	ETHYLBENZENE	0.098	0.298	1.486
HEPTANE	METHYLBENZENE	0.069	0.372	1.554
HEPTANE	DIMETHYLBENZENE	0.111	0.312	1.527
HEPTANE	TRIMETHYLBENZENE	0.128	0.234	1.436
HEPTANE	NITROBENZENE	0.070	2.162	9.318
HEPTANE	NAPHTHALENE	0.395	0.576	2.641
HEPTANE	AMINONAPHTHALENE	0.385	3.123	33.381
HEPTANE	HYDROXYNAPHTHALENE	0.395	2.818	24.854
HEPTANE	HYDROXYQUINOLINE	0.554	5.276	340.359
HEPTANE	METHYLHYDROXYQUINOLINE	0.532	4.884	224.977
HEPTANE	PYRIDINE	0.072	1.181	3.501
HEPTANE	DIMETHYLPYRIDINE	0.198	0.562	2.138
HEPTANE	PHENOL	0.035	2.861	18.102
HEPTANE	HYDROXYPHENOL	0.070	6.120	487.846
HEPTANE	METHYLHYDROXYPHENOL	0.112	5.639	314.505
HEPTANE	DIMETHYLHYDROXYPHENOL	0.130	5.262	219.642
HEPTANE	METHYLPHENOL	0.094	2.610	14.939
HEPTANE	DIMETHYLPHENOL	0.123	2.398	12.441
HEPTANE	NITROPHENOL	0.093	5.860	384.906
HEPTANE	TRINITROPHENOL	0.100	12.074	193690.0

Table B-3 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
WATER	ANILINE	2.736	1.774	91
WATER	NITROANILINE	2.925	2.171	164
WATER	BENZENE	2.588	5.208	2431
WATER	CHLOROBENZENE	2.929	6.932	19168
WATER	DICHLOROBENZENE	3.243	8.816	172646
WATER	ETHYLBENZENE	2.943	7.495	34132
WATER	METHYLBENZENE	2.824	6.578	12112
WATER	DIMETHYLBENZENE	3.024	7.918	56500
WATER	TRIMETHYLBENZENE	3.199	9.240	252458
WATER	NITROBENZENE	2.808	5.308	3348
WATER	NAPHTHALENE	4.385	7.464	139944
WATER	AMINONAPHTHALENE	4.467	3.818	3964
WATER	HYDROXYNAPHTHALENE	4.467	1.724	488
WATER	HYDROXYQUINOLINE	4.997	-1.169	46
WATER	METHYLHYDROXYQUINOLINE	5.133	-0.161	144
WATER	PYRIDINE	3.041	-1.087	7
WATER	DIMETHYLPYRIDINE	3.482	2.279	318
WATER	PHENOL	2.714	-0.315	11
WATER	HYDROXYPHENOL	2.830	-5.038	0.110
WATER	METHYLHYDROXYPHENOL	3.031	-4.119	0.337
WATER	DIMETHYLHYDROXYPHENOL	3.206	-3.096	1.116
WATER	METHYLPHENOL	2.931	0.834	43
WATER	DIMETHYLPHENOL	3.118	2.022	171
WATER	NITROPHENOL	2.912	1.024	51
WATER	TRINITROPHENOL	3.200	3.918	1234

Table B-4

Infinite Dilution Activity Coefficients For Various Aromatic Solutes
Predicted by the UNIFAC Model Using LLE Data

SOLVENT	SOLUTE	COMB	RES	GAMMA
OCTANOL	ANILINE	0.027	1.276	3.680
OCTANOL	NITROANILINE	0.125	1.095	3.387
OCTANOL	BENZENE	-0.058	0.168	1.116
OCTANOL	CHLOROBENZENE	0.078	1.227	3.688
OCTANOL	DICHLOROBENZENE	0.188	1.968	8.637
OCTANOL	ETHYLBENZENE	0.128	0.328	1.578
OCTANOL	METHYLBENZENE	0.063	0.217	1.323
OCTANOL	DIMETHYLBENZENE	0.148	0.236	1.468
OCTANOL	TRIMETHYLBENZENE	0.208	0.237	1.560
OCTANOL	NITROBENZENE	0.070	1.151	3.391
OCTANOL	NAPHTHALENE	0.512	0.240	2.121
OCTANOL	AMINONAPHTHALENE	0.531	1.432	7.121
OCTANOL	HYDROXYNAPHTHALENE	0.533	0.359	2.440
OCTANOL	HYDROXYQUINOLINE	0.706	-2.332	0.197
OCTANOL	METHYLHYDROXYQUINOLINE	0.727	-2.293	0.209
OCTANOL	PYRIDINE	0.037	-6.904	0.001
OCTANOL	DIMETHYLPYRIDINE	0.249	-3.431	0.042
OCTANOL	PHENOL	0.008	0.245	1.288
OCTANOL	HYDROXYPHENOL	0.063	0.008	1.074
OCTANOL	METHYLHYDROXYPHENOL	0.149	0.454	1.828
OCTANOL	DIMETHYLHYDROXYPHENOL	0.209	0.798	2.737
OCTANOL	METHYLPHENOL	0.109	0.594	2.020
OCTANOL	DIMETHYLPHENOL	0.181	0.815	2.707
OCTANOL	NITROPHENOL	0.114	1.791	6.719
OCTANOL	TRINITROPHENOL	0.219	3.856	58.850
MIBK	ANILINE	0.143	3.859	54.707
MIBK	NITROANILINE	0.192	2.667	17.444
MIBK	BENZENE	0.087	0.342	1.536
MIBK	CHLOROBENZENE	0.190	4.253	85.030
MIBK	DICHLOROBENZENE	0.266	7.846	3334.240
MIBK	ETHYLBENZENE	0.196	0.604	2.226
MIBK	METHYLBENZENE	0.168	0.459	1.872
MIBK	DIMETHYLBENZENE	0.213	0.546	2.136
MIBK	TRIMETHYLBENZENE	0.233	0.615	2.335
MIBK	NITROBENZENE	0.166	0.454	1.859
MIBK	NAPHTHALENE	0.566	0.490	2.875
MIBK	AMINONAPHTHALENE	0.556	4.091	104.272
MIBK	HYDROXYNAPHTHALENE	0.567	-7.644	0.001
MIBK	HYDROXYQUINOLINE	0.753	-7.915	0.001
MIBK	METHYLHYDROXYQUINOLINE	0.734	-7.808	0.001
MIBK	PYRIDINE	0.195	-3.429	0.039
MIBK	DIMETHYLPYRIDINE	0.326	-0.747	0.656
MIBK	PHENOL	0.133	-7.834	<0.001
MIBK	HYDROXYPHENOL	0.169	-16.324	<0.001
MIBK	METHYLHYDROXYPHENOL	0.214	-15.810	<0.001
MIBK	DIMETHYLHYDROXYPHENOL	0.235	-15.398	<0.001
MIBK	METHYLPHENOL	0.195	-7.417	0.001
MIBK	DIMETHYLPHENOL	0.227	-7.128	0.001
MIBK	NITROPHENOL	0.190	-7.299	0.001
MIBK	TRINITROPHENOL	0.198	-7.256	0.001

Table B-4 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
NBA	ANILINE	0.108	*****	*****
NBA	NITROANILINE	0.151	*****	*****
NBA	BENZENE	0.055	-0.618	0.569
NBA	CHLOROBENZENE	0.149	1.902	7.776
NBA	DICHLOROBENZENE	0.218	4.104	75.339
NBA	ETHYLBENZENE	0.154	-0.231	0.926
NBA	METHYLBENZENE	0.130	-0.178	0.953
NBA	DIMETHYLBENZENE	0.169	0.232	1.493
NBA	TRIMETHYLBENZENE	0.183	0.624	2.241
NBA	NITROBENZENE	0.129	*****	*****
NBA	NAPHTHALENE	0.491	-0.886	0.674
NBA	AMINONAPHTHALENE	0.478	*****	*****
NBA	HYDROXYNAPHTHALENE	0.490	-13.302	<0.001
NBA	HYDROXYQUINOLINE	0.666	*****	*****
NBA	METHYLHYDROXYQUINOLINE	0.641	*****	*****
NBA	PYRIDINE	0.153	*****	*****
NBA	DIMETHYLPYRIDINE	0.273	*****	*****
NBA	PHENOL	0.098	-13.076	<0.001
NBA	HYDROXYPHENOL	0.131	-25.848	<0.001
NBA	METHYLHYDROXYPHENOL	0.170	-25.011	<0.001
NBA	DIMETHYLHYDROXYPHENOL	0.185	-24.276	<0.001
NBA	METHYLPHENOL	0.154	-12.336	<0.001
NBA	DIMETHYLPHENOL	0.179	-11.724	<0.001
NBA	NITROPHENOL	0.149	*****	*****
NBA	TRINITROPHENOL	0.145	*****	*****

SOLVENT	SOLUTE	COMB	RES	GAMMA
DIPE	ANILINE	0.095	*****	*****
DIPE	NITROANILINE	0.132	*****	*****
DIPE	BENZENE	0.046	-0.996	0.387
DIPE	CHLOROBENZENE	0.134	*****	*****
DIPE	DICHLOROBENZENE	0.196	*****	*****
DIPE	ETHYLBENZENE	0.135	-0.937	0.448
DIPE	METHYLBENZENE	0.115	-1.079	0.381
DIPE	DIMETHYLBENZENE	0.149	-1.192	0.352
DIPE	TRIMETHYLBENZENE	0.158	-1.323	0.312
DIPE	NITROBENZENE	0.114	*****	*****
DIPE	NAPHTHALENE	0.454	-1.428	0.378
DIPE	AMINONAPHTHALENE	0.438	*****	*****
DIPE	HYDROXYNAPHTHALENE	0.450	*****	*****
DIPE	HYDROXYQUINOLINE	0.622	*****	*****
DIPE	METHYLHYDROXYQUINOLINE	0.592	*****	*****
DIPE	PYRIDINE	0.140	*****	*****
DIPE	DIMETHYLPYRIDINE	0.248	*****	*****
DIPE	PHENOL	0.086	*****	*****
DIPE	HYDROXYPHENOL	0.116	*****	*****
DIPE	METHYLHYDROXYPHENOL	0.150	*****	*****
DIPE	DIMETHYLHYDROXYPHENOL	0.159	*****	*****
DIPE	METHYLPHENOL	0.136	*****	*****
DIPE	DIMETHYLPHENOL	0.157	*****	*****
DIPE	NITROPHENOL	0.132	*****	*****
DIPE	TRINITROPHENOL	0.116	*****	*****

Table B-4 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
BENZENE	ANILINE	-0.012	-0.339	0.704
BENZENE	NITROANILINE	-0.075	-1.647	0.179
BENZENE	BENZENE	0.000	0.000	1.000
BENZENE	CHLOROBENZENE	-0.016	-0.137	0.858
BENZENE	DICHLOROBENZENE	-0.059	-0.592	0.522
BENZENE	ETHYLBENZENE	-0.074	0.037	0.964
BENZENE	METHYLBENZENE	-0.023	-0.029	0.949
BENZENE	DIMETHYLBENZENE	-0.081	-0.088	0.845
BENZENE	TRIMETHYLBENZENE	-0.165	-0.165	0.719
BENZENE	NITROBENZENE	-0.032	-0.004	0.965
BENZENE	NAPHTHALENE	-0.050	0.000	0.951
BENZENE	AMINONAPHTHALENE	-0.129	-0.255	0.681
BENZENE	HYDROXYNAPHTHALENE	-0.101	1.600	4.477
BENZENE	HYDROXYQUINOLINE	-0.002	-0.657	0.517
BENZENE	METHYLHYDROXYQUINOLINE	-0.124	-0.696	0.440
BENZENE	PYRIDINE	0.022	-6.488	0.001
BENZENE	DIMETHYLPYRIDINE	-0.054	-3.281	0.036
BENZENE	PHENOL	-0.006	1.558	4.721
BENZENE	HYDROXYPHENOL	-0.023	2.802	16.103
BENZENE	METHYLHYDROXYPHENOL	-0.081	3.170	21.955
BENZENE	DIMETHYLHYDROXYPHENOL	-0.164	3.436	26.364
BENZENE	METHYLPHENOL	-0.048	1.829	5.936
BENZENE	DIMETHYLPHENOL	-0.120	1.972	6.373
BENZENE	NITROPHENOL	-0.060	1.977	6.801
BENZENE	TRINITROPHENOL	-0.276	1.788	4.536

SOLVENT	SOLUTE	COMB	RES	GAMMA
TOLUENE	ANILINE	-0.001	0.287	1.331
TOLUENE	NITROANILINE	-0.013	-1.555	0.208
TOLUENE	BENZENE	-0.020	-0.018	0.963
TOLUENE	CHLOROBENZENE	0.001	-0.275	0.760
TOLUENE	DICHLOROBENZENE	-0.004	-0.850	0.426
TOLUENE	ETHYLBENZENE	-0.013	-0.020	0.968
TOLUENE	METHYLBENZENE	0.000	0.000	1.000
TOLUENE	DIMETHYLBENZENE	-0.016	-0.012	0.972
TOLUENE	TRIMETHYLBENZENE	-0.056	-0.042	0.907
TOLUENE	NITROBENZENE	0.000	-0.556	0.573
TOLUENE	NAPHTHALENE	0.043	-0.026	1.017
TOLUENE	AMINONAPHTHALENE	-0.005	0.363	1.430
TOLUENE	HYDROXYNAPHTHALENE	0.013	-0.806	0.452
TOLUENE	HYDROXYQUINOLINE	0.105	-2.413	0.099
TOLUENE	METHYLHYDROXYQUINOLINE	0.026	-2.405	0.093
TOLUENE	PYRIDINE	-0.005	-5.622	0.004
TOLUENE	DIMETHYLPYRIDINE	0.004	-2.791	0.062
TOLUENE	PHENOL	-0.005	-0.840	0.430
TOLUENE	HYDROXYPHENOL	0.000	-1.976	0.139
TOLUENE	METHYLHYDROXYPHENOL	-0.015	-1.561	0.207
TOLUENE	DIMETHYLHYDROXYPHENOL	-0.056	-1.248	0.271
TOLUENE	METHYLPHENOL	-0.004	-0.522	0.591
TOLUENE	DIMETHYLPHENOL	-0.033	-0.332	0.694
TOLUENE	NITROPHENOL	-0.008	-0.955	0.382
TOLUENE	TRINITROPHENOL	-0.120	-2.212	0.097

Table B-4 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
HEXANE	ANILINE	0.094	3.429	33.886
HEXANE	NITROANILINE	0.119	4.787	135.098
HEXANE	BENZENE	0.052	0.054	1.112
HEXANE	CHLOROBENZENE	0.130	4.045	65.040
HEXANE	DICHLOROBENZENE	0.183	7.718	2699.981
HEXANE	ETHYLBENZENE	0.122	0.025	1.158
HEXANE	METHYLBENZENE	0.111	0.001	1.119
HEXANE	DIMETHYLBENZENE	0.135	-0.082	1.054
HEXANE	TRIMETHYLBENZENE	0.133	-0.183	0.951
HEXANE	NITROBENZENE	0.108	2.716	16.844
HEXANE	NAPHTHALENE	0.425	0.078	1.654
HEXANE	AMINONAPHTHALENE	0.401	3.537	51.316
HEXANE	HYDROXYNAPHTHALENE	0.416	4.776	179.828
HEXANE	HYDROXYQUINOLINE	0.586	4.841	227.466
HEXANE	METHYLHYDROXYQUINOLINE	0.545	4.778	204.998
HEXANE	PYRIDINE	0.144	-3.271	0.044
HEXANE	DIMETHYLPYRIDINE	0.232	-1.011	0.459
HEXANE	PHENOL	0.087	4.710	121.146
HEXANE	HYDROXYPHENOL	0.112	9.052	9547.169
HEXANE	METHYLHYDROXYPHENOL	0.136	9.396	13794.15
HEXANE	DIMETHYLHYDROXYPHENOL	0.135	9.638	17553.35
HEXANE	METHYLPHENOL	0.127	4.957	161.418
HEXANE	DIMETHYLPHENOL	0.137	5.076	183.644
HEXANE	NITROPHENOL	0.121	7.795	2740.786
HEXANE	TRINITROPHENOL	0.081	12.938	450899.6

SOLVENT	SOLUTE	COMB	RES	GAMMA
HEPTANE	ANILINE	0.047	3.429	32.330
HEPTANE	NITROANILINE	0.095	4.787	131.894
HEPTANE	BENZENE	-0.009	0.054	1.046
HEPTANE	CHLOROBENZENE	0.084	4.045	62.116
HEPTANE	DICHLOROBENZENE	0.150	7.718	2612.336
HEPTANE	ETHYLBENZENE	0.098	0.011	1.114
HEPTANE	METHYLBENZENE	0.069	0.001	1.073
HEPTANE	DIMETHYLBENZENE	0.111	-0.082	1.029
HEPTANE	TRIMETHYLBENZENE	0.128	-0.183	0.946
HEPTANE	NITROBENZENE	0.070	2.716	16.216
HEPTANE	NAPHTHALENE	0.395	0.078	1.605
HEPTANE	AMINONAPHTHALENE	0.385	3.537	50.501
HEPTANE	HYDROXYNAPHTHALENE	0.395	4.776	176.091
HEPTANE	HYDROXYQUINOLINE	0.554	4.841	220.302
HEPTANE	METHYLHYDROXYQUINOLINE	0.532	4.778	202.350
HEPTANE	PYRIDINE	0.072	-3.271	0.041
HEPTANE	DIMETHYLPYRIDINE	0.198	-1.011	0.440
HEPTANE	PHENOL	0.035	4.710	115.008
HEPTANE	HYDROXYPHENOL	0.070	9.052	9154.492
HEPTANE	METHYLHYDROXYPHENOL	0.112	9.396	13467.03
HEPTANE	DIMETHYLHYDROXYPHENOL	0.130	9.638	17465.80
HEPTANE	METHYLPHENOL	0.094	4.957	156.179
HEPTANE	DIMETHYLPHENOL	0.123	5.076	181.091
HEPTANE	NITROPHENOL	0.093	7.795	2665.108
HEPTANE	TRINITROPHENOL	0.100	12.938	459548.6

Table B-4 Continued

SOLVENT	SOLUTE	COMB	RES	GAMMA
WATER	ANILINE	2.736	3.622	577
WATER	NITROANILINE	2.925	2.425	211
WATER	BENZENE	2.588	5.268	2581
WATER	CHLOROBENZENE	2.929	6.299	10178
WATER	DICHLOROBENZENE	3.243	7.012	28424
WATER	ETHYLBENZENE	2.943	7.353	29614
WATER	METHYLBENZENE	2.824	6.064	7244
WATER	DIMETHYLBENZENE	3.024	6.830	19035
WATER	TRIMETHYLBENZENE	3.199	7.578	47906
WATER	NITROBENZENE	2.808	5.375	3580
WATER	NAPHTHALENE	4.385	7.550	152512
WATER	AMINONAPHTHALENE	4.467	5.988	34718
WATER	HYDROXYNAPHTHALENE	4.467	3.607	3210
WATER	HYDROXYQUINOLINE	4.997	-1.706	27
WATER	METHYLHYDROXYQUINOLINE	5.133	-0.920	68
WATER	PYRIDINE	3.041	-5.151	0.121
WATER	DIMETHYLPYRIDINE	3.482	1.229	111
WATER	PHENOL	2.714	1.283	54
WATER	HYDROXYPHENOL	2.830	-3.016	0.831
WATER	METHYLHYDROXYPHENOL	3.031	-1.823	3.347
WATER	DIMETHYLHYDROXYPHENOL	3.206	-0.732	11.870
WATER	METHYLPHENOL	2.931	2.379	202
WATER	DIMETHYLPHENOL	3.118	3.347	642
WATER	NITROPHENOL	2.912	1.813	113
WATER	TRINITROPHENOL	3.200	1.846	155

Table B-5

Fortran File Resid.For

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C*****C
C THIS FORTRAN FILE CALCULATES THE RESIDUAL PORTION OF THE INFINITE C
C DILUTION ACTIVITY COEFFICIENT FOR A GIVEN SOLUTE AND SOLVENT PAIR C
C USING THE UNIFAC GROUP CONTRIBUTION METHOD. THE PROGRAM IS SET UP C
C TO HANDLE SOLUTES AND SOLVENTS WITH THREE OR LESS DIFFERENT FUNC- C
C TIONAL GROUPS. THE INPUT FILES RESID.INLLE AND .INVLE CONTAIN C
C SOLUTE DATA: V1,V2,V3 ARE THE NUMBER OF SUCH COMPONENTS IN THE C
C SOLUTE MOLECULE, B1,B2,B3 ARE THE SOLUTE FUNCTIONAL GROUP GAMMA C
C VALUES COMPUTED IN LAMBUT.FOR. THE INPUT FILES RES.INLLE AND C
C .INVLE CONTAIN GAMMA VALUES FOR SOLUTE COMPONENTS AT INFINITE C
C DILUTION IN THE SOLVENT PHASE, B4,B5,B6, COMPUTED IN LAMBVN.FOR. C
C SOLUTES WITH LESS THAN THREE COMPONENTS ASSUME ZERO FOR ANY C
C MISSING B OR V VALUE. C
C*****C

      DIMENSION SOLUTE(24),V1(24),B1(24),V2(24),B2(24),
      *V3(24),B3(24),SOLVNT(24,9),B4(24,9),B5(24,9),B6(24,9)
      DOUBLE PRECISION SOLVNT, SOLUTE, RESD(24,9)
      OPEN (UNIT=61, DEVICE='DSK', FILE='RESID.INLLE')
      OPEN (UNIT=62, DEVICE='DSK', FILE='RESID.OUTLLE')

      DO 30 I=1,24
      READ (61,5) SOLUTE(I)
      READ (61,*) V1(I),B1(I),V2(I),B2(I),V3(I),B3(I)
30  CONTINUE
      CLOSE (UNIT=61, DEVICE='DSK', FILE='RESID.INLLE')
      OPEN (UNIT=63, DEVICE='DSK', FILE='RES.INLLE')

      DO 40 J=1,9
      DO 45 K=1,24
      READ (63,5) SOLVNT(K,J)
      READ (63,*) B4(K,J),B5(K,J),B6(K,J)

      RESD(K,J)=(V1(K)*(B4(K,J)-B1(K)))+(V2(K)*(B5(K,J)-B2(K)))+
      *(V3(K)*(B6(K,J)-B3(K)))

      WRITE (62,2) SOLVNT(K,J), SOLUTE(K), RESD(K,J)
2  FORMAT (1X,T5,A10,T20,A10,T40,F7.3)
5  FORMAT (A10)
45 CONTINUE
40 CONTINUE
      STOP
      END

```

Table B-6

Fortran File Lambvn.For

```

C*****C
C THIS IS A FORTRAN PROGRAM WHICH CALCULATES GAMMA VALUES FOR FUNC- C
C TIONAL GROUPS AT INFINITE DILUTION IN A GIVEN SOLVENT. THE PROGRAM C
C IS SET UP TO HANDLE SOLVENTS WITH THREE OR LESS FUNCTIONAL GROUPS C
C AND AS MANY INDIVIDUAL SOLUTE FUNCTIONAL GROUPS AS YOU WANT. DATA C
C FOR SOLVENTS OF INTEREST ARE READ FROM THE INPUT FILE LAMBVN.INLLE C
C OR .INVLE IN THE FIRST DO LOOP. THE DATA SYMBOLS ARE DEFINED AS C
C FOLLOWS: T1,T2,T3 ARE SURFACE AREA FRACTION PARAMETERS FOR SOLVENT C
C FUNCTIONAL GROUPS, P11 THROUGH P33 ARE SOLVENT FUNCTIONAL GROUP C
C INTERACTION PARAMETERS (PSI NM VALUES). DATA FOR SOLUTE FUNCTIONALC
C GROUPS ARE READ FROM THE FILES FUNC GP.INLLE OR .INVLE DEPENDING C
C ON WHETHER YOU DESIRE LIQUID-LIQUID EQ. DATA OR VAPOR-LIQUID EQ. C
C DATA. THE DATA SYMBOLS ARE EXPLAINED AS FOLLOWS: Q VALUES ARE C
C THE SURFACE AREA PARAMETERS FOR SOLUTE FUNCTIONAL GROUPS AND C
C P1F THROUGH PF3 ARE THE INTERACTION TERMS FOR A GIVEN SOLUTE C
C FUNCTIONAL GROUP AND THE FUNCTIONAL GROUPS OF THE SOLVENT (PSI NM).C
C MISSING TERMS ARE INPUTED AS ZEROES. C
C*****C

```

```

      DIMENSION SOLVNT(9),T1(9),T2(9),T3(9),P11(9),P12(9),
      *P13(9),P21(9),P22(9),P23(9),P31(9),P32(9),
      *P33(9),DEN1(9),DEN2(9),DEN3(9),
      *FUNC GP(9,13),Q(9,13),P1F(9,13),P2F(9,13),P3F(9,13),
      *PF1(9,13),PF2(9,13),PF3(9,13)
      DOUBLE PRECISION SOLVNT,FUNC GP,LAMBF(9,13)
      OPEN (UNIT=34, DEVICE='DSK', FILE='LAMBVN.INLLE')
      OPEN (UNIT=35, DEVICE='DSK', FILE='LAMBVN.OUTLLE')

      DO 30 I=1,9
      READ (34,1) SOLVNT(I)
1    FORMAT (A10)
      READ (34,*) T1(I),T2(I),T3(I),P11(I),P12(I),P13(I),
      *P21(I),P22(I),P23(I),P31(I),P32(I),P33(I)
      DEN1(I)=(T1(I)*P11(I))+(T2(I)*P21(I))+(T3(I)*P31(I))
      DEN2(I)=(T1(I)*P12(I))+(T2(I)*P22(I))+(T3(I)*P32(I))
      DEN3(I)=(T1(I)*P13(I))+(T2(I)*P23(I))+(T3(I)*P33(I))
30   CONTINUE
      CLOSE (UNIT=34, DEVICE='DSK', FILE='LAMBVN.INLLE')
      OPEN (UNIT=36, DEVICE='DSK', FILE='FUNC GP.INLLE')

```

Table B-6 Continued

```

DO 45 K=1,9
DO 40 J=1,13
READ (36,1) FUNC GP(K,J)
READ (36,*) Q(K,J),P1F(K,J),P2F(K,J),P3F(K,J),PF1(K,J),
*PF2(K,J),PF3(K,J)
IF(DEN1(K).EQ.0)GO TO 61
TEM1=((T1(K)*PF1(K,J))/DEN1(K))
GO TO 64
61 TEM1=0.0
64 IF(DEN2(K).EQ.0)GO TO 62
TEM2=((T2(K)*PF2(K,J))/DEN2(K))
GO TO 65
62 TEM2=0.0
65 IF(DEN3(K).EQ.0)GO TO 63
TEM3=((T3(K)*PF3(K,J))/DEN3(K))
GO TO 66
63 TEM3=0.0
66 TEM4=((T1(K)*P1F(K,J))+(T2(K)*P2F(K,J))+(T3(K)*P3F(K,J)))
IF(TEM4.EQ.0.0)GO TO 67
TEM5=ALOG(TEM4)
GO TO 68
67 TEM5=0.0
68 LAMBF(K,J)=Q(K,J)*(1-TEM5-TEM1-TEM2-TEM3)
WRITE(35,3) SOLVNT(K),FUNC GP(K,J),LAMBF(K,J)
3 FORMAT (1X,T5,A10,T20,A10,T40,F10.3)
40 CONTINUE
45 CONTINUE
STOP
END

```

Table B-7

Output File Lambvn.Outvle

GAMMA VALUES FOR FUNCTIONAL GROUPS AT INFINITE DILUTION IN
THE SOLVENT PHASE USING VAPOR-LIQUID EQUILIBRIA DATA

SOLVENT	FUNCTIONAL GROUP	GAMMA
OCTANOL	CH	0.043
OCTANOL	CH2	0.102
OCTANOL	CH3	0.160
OCTANOL	AC	0.026
OCTANOL	ACH	0.088
OCTANOL	ACCH2	0.042
OCTANOL	ACCH3	0.062
OCTANOL	ACOH	-1.792
OCTANOL	ACNH2	1.017
OCTANOL	C5H3N	-1.107
OCTANOL	C5H5N	-1.507
OCTANOL	ACCL	0.235
OCTANOL	ACNO2	2.487
MIBK	CH	0.048
MIBK	CH2	0.115
MIBK	CH3	0.180
MIBK	AC	-0.009
MIBK	ACH	-0.029
MIBK	ACCH2	-0.140
MIBK	ACCH3	-0.206
MIBK	ACOH	-0.729
MIBK	ACNH2	1.572
MIBK	C5H3N	-0.009
MIBK	C5H5N	-0.012
MIBK	ACCL	0.275
MIBK	ACNO2	0.549
NBA	CH	0.043
NBA	CH2	0.101
NBA	CH3	0.158
NBA	AC	-0.007
NBA	ACH	-0.023
NBA	ACCH2	-0.016
NBA	ACCH3	-0.024
NBA	ACOH	-0.849
NBA	ACNH2	*****
NBA	C5H3N	*****
NBA	C5H5N	*****
NBA	ACCL	-0.069
NBA	ACNO2	*****

Table B-7 Continued

DIPE	CH	0.004
DIPE	CH2	0.010
DIPE	CH3	0.015
DIPE	AC	0.006
DIPE	ACH	0.019
DIPE	ACCH2	-0.008
DIPE	ACCH3	-0.012
DIPE	ACOH	*****
DIPE	ACNH2	*****
DIPE	C5H3N	*****
DIPE	C5H5N	*****
DIPE	ACCL	*****
DIPE	ACNO2	*****
TOLUENE	CH	0.019
TOLUENE	CH2	0.046
TOLUENE	CH3	0.072
TOLUENE	AC	-0.001
TOLUENE	ACH	-0.003
TOLUENE	ACCH2	-0.020
TOLUENE	ACCH3	-0.030
TOLUENE	ACOH	2.710
TOLUENE	ACNH2	2.658
TOLUENE	C5H3N	0.239
TOLUENE	C5H5N	0.325
TOLUENE	ACCL	0.106
TOLUENE	ACNO2	1.483
HEXANE	CH	0.000
HEXANE	CH2	0.000
HEXANE	CH3	0.000
HEXANE	AC	0.007
HEXANE	ACH	0.067
HEXANE	ACCH2	-0.005
HEXANE	ACCH3	-0.008
HEXANE	ACOH	3.477
HEXANE	ACNH2	4.243
HEXANE	C5H3N	0.868
HEXANE	C5H5N	1.181
HEXANE	ACCL	0.398
HEXANE	ACNO2	3.113

Table B-7 Continued

HEPTANE	CH	0.000
HEPTANE	CH2	0.000
HEPTANE	CH3	0.000
HEPTANE	AC	0.020
HEPTANE	ACH	0.067
HEPTANE	ACCH2	-0.005
HEPTANE	ACCH3	-0.008
HEPTANE	ACOH	3.477
HEPTANE	ACNH2	4.243
HEPTANE	C5H3N	0.868
HEPTANE	C5H5N	1.181
HEPTANE	ACCL	0.398
HEPTANE	ACNO2	3.113
WATER	CH	0.455
WATER	CH2	1.078
WATER	CH3	1.692
WATER	AC	0.260
WATER	ACH	0.868
WATER	ACCH2	1.495
WATER	ACCH3	2.193
WATER	ACOH	-3.704
WATER	ACNH2	-1.149
WATER	C5H3N	-0.799
WATER	C5H5N	-1.087
WATER	ACCL	2.724
WATER	ACNO2	2.254
BENZENE	CH	0.034
BENZENE	CH2	0.080
BENZENE	CH3	0.034
BENZENE	AC	0.000
BENZENE	ACH	0.000
BENZENE	ACCH2	-0.051
BENZENE	ACCH3	-0.074
BENZENE	ACOH	3.063
BENZENE	ACNH2	2.555
BENZENE	C5H3N	0.134
BENZENE	C5H5N	0.182
BENZENE	ACCL	0.496
BENZENE	ACNO2	1.824

Table B-8

Output File Lambvn.Outlle

GAMMA VALUES FOR FUNCTIONAL GROUPS AT INFINITE DILUTION IN
THE SOLVENT PHASE USING LIQUID-LIQUID EQUILIBRIA DATA

SOLVENT	FUNCTIONAL GROUP	GAMMA
OCTANOL	CH	0.034
OCTANOL	CH2	0.080
OCTANOL	CH3	0.125
OCTANOL	AC	0.008
OCTANOL	ACH	0.028
OCTANOL	ACCH2	0.022
OCTANOL	ACCH3	0.032
OCTANOL	ACOH	-0.346
OCTANOL	ACNH2	0.594
OCTANOL	C5H3N	-5.074
OCTANOL	C5H5N	-6.904
OCTANOL	ACCL	-0.481
OCTANOL	ACNO2	1.140
MIBK	CH	0.051
MIBK	CH2	0.121
MIBK	CH3	0.190
MIBK	AC	0.017
MIBK	ACH	0.057
MIBK	ACCH2	0.088
MIBK	ACCH3	0.129
MIBK	ACOH	-8.570
MIBK	ACNH2	3.032
MIBK	C5H3N	-2.520
MIBK	C5H5N	-3.429
MIBK	ACCL	2.400
MIBK	ACNO2	0.158
NBA	CH	0.012
NBA	CH2	0.028
NBA	CH3	0.044
NBA	AC	-0.031
NBA	ACH	-0.103
NBA	ACCH2	0.199
NBA	ACCH3	0.292
NBA	ACOH	-13.012
NBA	ACNH2	*****
NBA	C5H3N	*****
NBA	C5H5N	*****
NBA	ACCL	0.849
NBA	ACNO2	*****

Table B-8 Continued

DIPE	CH	0.014
DIPE	CH2	0.034
DIPE	CH3	0.053
DIPE	AC	-0.050
DIPE	ACH	-0.166
DIPE	ACCH2	-0.201
DIPE	ACCH3	-0.294
DIPE	ACOH	*****
DIPE	ACNH2	*****
DIPE	C5H3N	*****
DIPE	C5H5N	*****
DIPE	ACCL	*****
DIPE	ACNO2	*****
TOLUENE	CH	-0.007
TOLUENE	CH2	-0.017
TOLUENE	CH3	-0.026
TOLUENE	AC	-0.001
TOLUENE	ACH	-0.003
TOLUENE	ACCH2	-0.020
TOLUENE	ACCH3	-0.030
TOLUENE	ACOH	-1.276
TOLUENE	ACNH2	-0.240
TOLUENE	C5H3N	-4.132
TOLUENE	C5H5N	-5.622
TOLUENE	ACCL	-1.828
TOLUENE	ACNO2	-0.552
HEXANE	CH	0.000
HEXANE	CH2	0.000
HEXANE	CH3	0.000
HEXANE	AC	0.003
HEXANE	ACH	0.009
HEXANE	ACCH2	-0.061
HEXANE	ACCH3	-0.089
HEXANE	ACOH	4.214
HEXANE	ACNH2	2.842
HEXANE	C5H3N	-2.404
HEXANE	C5H5N	-3.271
HEXANE	ACCL	2.432
HEXANE	ACNO2	2.660

Table B-8 Continued

HEPTANE	CH	0.000
HEPTANE	CH2	0.000
HEPTANE	CH3	0.000
HEPTANE	AC	0.003
HEPTANE	ACH	0.009
HEPTANE	ACCH2	-0.075
HEPTANE	ACCH3	-0.089
HEPTANE	ACOH	4.214
HEPTANE	ACNH2	2.842
HEPTANE	C5H3N	-2.404
HEPTANE	C5H5N	-3.271
HEPTANE	ACCL	2.432
HEPTANE	ACNO2	2.660
WATER	CH	0.487
WATER	CH2	1.153
WATER	CH3	1.811
WATER	AC	0.263
WATER	ACH	0.878
WATER	ACCH2	1.111
WATER	ACCH3	1.629
WATER	ACOH	-3.558
WATER	ACNH2	-1.310
WATER	C5H3N	-3.786
WATER	C5H5N	-5.151
WATER	ACCL	0.341
WATER	ACNO2	0.974
BENZENE	CH	0.013
BENZENE	CH2	0.030
BENZENE	CH3	0.047
BENZENE	AC	0.000
BENZENE	ACH	0.000
BENZENE	ACCH2	-0.051
BENZENE	ACCH3	-0.074
BENZENE	ACOH	1.107
BENZENE	ACNH2	-0.881
BENZENE	C5H3N	-4.768
BENZENE	C5H5N	-6.488
BENZENE	ACCL	-1.705
BENZENE	ACNO2	-0.015

Table B-9

Fortran File Lambut.For

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C*****C
C  THIS IS A FORTRAN PROGRAM WHICH CALCULATES GAMMA VALUES FOR      C
C  SOLUTE FUNCTIONAL GROUPS IN THE PURE SOLUTE. IT IS SET UP        C
C  TO HANDLE SOLUTES WITH THREE OR LESS FUNCTIONAL GROUPS. THE     C
C  CALCULATIONS ARE MADE WITH DATA FROM THE INPUT FILE LAMBUT.INVLE C
C  OR .INLLE DEPENDING ON WHETHER YOU WISH TO USE VAPOR-LIQUID DATA C
C  OR LIQUID-LIQUID DATA. THE DATA SYMBOLS ARE EXPLAINED AS      C
C  FOLLOWS: Q1,Q2,Q3 VALUES ARE FUNCTIONAL GROUP SURFACE AREA PARA- C
C  METERS, T1,T2,T3 VALUES ARE GROUP SURFACE AREA FRACTION PARAMETERS C
C  P11 THROUGH P33 VALUES ARE THE GROUP INTERACTION TERMS REFERED  C
C  TO AS PSI NM PARAMETERS. FURTHER EXPLANATION OF THESE TERMS IS C
C  PROVIDED IN THE TEXT. FOR SOLUTES WITH LESS THAN THREE FUNC-   C
C  TIONAL GROUPS, MISSING VALUES ARE INPUTED AS ZEROES.          C
C*****C

      DIMENSION SOLUTE(24,5),Q1(24),Q2(24),Q3(24),T1(24),T2(24),
*      T3(24),P11(24),P12(24),P13(24),P21(24),P22(24),P23(24),
*      P31(24),P32(24),P33(24),DEN1(24),DEN2(24),DEN3(24)
      INTEGER SOLUTE
      DOUBLE PRECISION LAMB1(24),LAMB2(24),LAMB3(24)
      OPEN (UNIT=21, DEVICE='DSK', FILE='LAMBUT.INVLE')
      OPEN (UNIT=25, DEVICE='DSK', FILE='LAMBUT.OUTVLE')

      DO 10 I=1,24
      READ (21,1) (SOLUTE(I,J),J=1,5)
1      FORMAT(5A5)
      READ (21,*) Q1(I),Q2(I),Q3(I),T1(I),T2(I),T3(I),P11(I),
*      P12(I),P13(I),P21(I),P22(I),P23(I),P31(I),P32(I),P33(I)
10     CONTINUE
      WRITE (25,2)
2      FORMAT(/1X,T1,'SOLUTE',T31,'LAMB1',T51,'LAMB2',T71,'LAMB3'/)

      DO 20 I=1,24
      DEN1(I)=(T1(I)*P11(I))+(T2(I)*P21(I))+(T3(I)*P31(I))
      DEN2(I)=(T1(I)*P12(I))+(T2(I)*P22(I))+(T3(I)*P32(I))
      DEN3(I)=(T1(I)*P13(I))+(T2(I)*P23(I))+(T3(I)*P33(I))
      IF(DEN1(I).EQ.O.)DEN1(I)=1.0E-10
      IF(DEN2(I).EQ.O.)DEN2(I)=1.0E-10
      IF(DEN3(I).EQ.O.)DEN3(I)=1.0E-10
      LAMB1(I)=Q1(I)*(1-ALOG(DEN1(I))-((T1(I)*P11(I))/DEN1(I))-
*      ((T2(I)*P12(I))/DEN2(I))-((T3(I)*P13(I))/DEN3(I)))

      LAMB2(I)=Q2(I)*(1-ALOG(DEN2(I))-((T1(I)*P21(I))/DEN1(I))-
*      ((T2(I)*P22(I))/DEN2(I))-((T3(I)*P23(I))/DEN3(I)))

      LAMB3(I)=Q3(I)*(1-ALOG(DEN3(I))-((T1(I)*P31(I))/DEN1(I))-
*      ((T2(I)*P32(I))/DEN2(I))-((T3(I)*P33(I))/DEN3(I)))

      WRITE (25,3) (SOLUTE(I,J),J=1,5),LAMB1(I),LAMB2(I),LAMB3(I)
3      FORMAT (1X,T1,5A5,T30,F6.3,T50,F6.3,T70,F6.3)
20     CONTINUE
      STOP
      END

```

Table B-10

Output File Lambut.Outvle

GAMMA VALUES FOR SOLUTE FUNCTIONAL GROUPS IN THE PURE
SOLUTE BASED ON VAPOR-LIQUID EQUILIBRIA DATA

GAMMA VALUES

SOLUTE

BENZENE	0.000	ACH	*****	*****
PYRIDINE	0.000	C5H5N	*****	*****
DIMETHYLPYRIDINE	0.099	CH3	0.108	C5H3N *****
ANILINE	0.902	ACNH2	0.103	ACH *****
NITROBENZENE	0.941	ACNO2	0.069	ACH *****
CHLOROBENZENE	0.017	ACCL	0.023	ACH *****
DICHLOROBENZENE	-0.006	ACCL	0.029	ACH *****
MEHTYLBENZENE	-0.030	ACCH3	-0.003	ACH *****
DIMETHYLBENZENE	-0.012	ACCH3	-0.009	ACH *****
TRIMETHYLBENZENE	-0.005	ACCH3	-0.014	ACH *****
PHENOL	0.456	ACOH	0.099	ACH *****
HYDROXYPHENOL	0.179	ACOH	0.186	ACH *****
NAPHTHALENE	0.000	AC	0.000	ACH *****
HYDROXYNAPHTHALENE	0.636	ACOH	0.021	AC 0.070 ACH
AMINONAPHTHALENE	1.136	ACNH2	0.019	AC 0.065 ACH
ETHYLBENZENE	0.056	CH3	-0.044	ACCH2 0.004 ACH
NITROPHENOL	0.385	ACNO2	-0.155	ACOH 0.192 ACH
METHYLPHENOL	0.213	ACCH3	0.666	ACOH 0.062 ACH
DIMETHYLPHENOL	0.162	ACCH3	0.817	ACOH 0.041 ACH
TRINITROPHENOL	0.156	ACNO2	-0.600	ACOH 0.504 ACH
NITROANILINE	0.885	ACNO2	0.713	ACNH2 0.202 ACH
METHYLHYDROXYPHENOL	0.467	ACCH3	0.333	ACOH 0.125 ACH
DIMETHYLHYDROXYPHENOL	0.357	ACCH3	0.458	ACOH 0.090 ACH
HYDROXYQUINOLINE	-0.596	ACOH	-0.557	C5H3N 0.141 ACH

Table B-11

Output File Lambut.Outlle

GAMMA VALUES FOR SOLUTE FUNCTIONAL GROUPS IN THE PURE
SOLUTE BASED ON LIQUID-LIQUID EQUILIBRIA DATA

		GAMMA VALUES	
SOLUTE			
BENZENE	0.000 ACH	*****	*****
PYRIDINE	0.000 C5H5N	*****	*****
DIMETHYLPYRIDINE	-0.281 CH3	-0.831 C5H3N	*****
ANILINE	-0.337 ACNH2	0.041 ACH	*****
NITROBENZENE	-0.006 ACNO2	-0.001 ACH	*****
CHLOROBENZENE	-1.443 ACCL	-0.025 ACH	*****
DICHLOROBENZENE	-1.183 ACCL	-0.113 ACH	*****
METHYLBENZENE	-0.030 ACCH3	-0.003 ACH	*****
DIMETHYLBENZENE	-0.012 ACCH3	-0.009 ACH	*****
TRIMETHYLBENZENE	-0.005 ACCH3	-0.014 ACH	*****
PHENOL	-0.316 ACOH	-0.027 ACH	*****
HYDROXYPHENOL	-0.116 ACOH	-0.089 ACH	*****
NAPHTHALENE	0.000 AC	0.000 ACH	*****
HYDROXYNAPHTHALENE	-0.433 ACOH	-0.002 AC	-0.008 ACH
AMINONAPHTHALENE	-0.444 ACNH2	-0.007 AC	-0.024 ACH
ETHYLBENZENE	0.002 CH3	-0.048 ACCH2	0.001 ACH
NITROPHENOL	-0.093 ACNO2	-0.520 ACOH	-0.068 ACH
METHYLPHENOL	-0.289 ACCH3	-0.427 ACOH	-0.020 ACH
DIMETHYLPHENOL	-0.195 ACCH3	-0.569 ACOH	-0.018 ACH
TRINITROPHENOL	0.012 ACNO2	-0.566 ACOH	-0.098 ACH
NITROANILINE	-0.069 ACNO2	0.456 ACNH2	0.091 ACH
METHYLHYDROXYPHENOL	-0.454 ACCH3	-0.180 ACOH	-0.072 ACH
DIMETHYLHYDROXYPHENOL	-0.357 ACCH3	-0.266 ACOH	-0.062 ACH
HYDROXYQUINOLINE	-0.293 ACOH	-1.640 C5H3N	-0.357 ACH

Table B-12

Fortran File Comb.For

```

C*****C
C THIS IS A FORTRAN PROGRAM THAT CALCULATES THE COMBINATORIAL C
C PORTION OF THE INFINITE DILUTION ACTIVITY COEFFICIENT BY THE C
C UNIFAC GROUP CONTRIBUTION METHOD. REFER TO THE TEXT FOR DETAILS.C
C THE COMPUTATION IS DONE FOR SOLUTES LISTED IN INPUT FILE C
C COMB.IN. THIS FILE CONTAINS SOLUTE NAMES AS WELL AS R AND Q C
C VALUES. SOLVENTS OF INTEREST AND THEIR RESPECTIVE R AND Q C
C VALUES ARE INPUTED AT THE TERMINAL. C
C*****C

      DIMENSION SOLUTE(25,5),R1(25),Q1(25),COMB(25),F1(25)
      INTEGER SOLUTE
      LOGICAL DEBUG
      DOUBLE PRECISION SOLVNT
      DATA DEBUG/.FALSE./
      OPEN (UNIT=11, DEVICE='DSK', FILE='COMB.IN')
      OPEN (UNIT=12, DEVICE='DSK', FILE='COMB.OUT')
      DO 10 I=1,25
      READ (11,8) (SOLUTE(I,J),J=1,5)
8      FORMAT (5A5)
      READ (11,*) R1(I), Q1(I)
      IF(DEBUG) WRITE(5,1047) (SOLUTE(I,J),J=1,5),R1(I),Q1(I)
1047  FORMAT(' ',5A5,10X,F6.3,2X,F6.3)
10      CONTINUE
7      WRITE (5,9)
9      FORMAT (1X,'INPUT SOLVNT NAME')
      READ(5,1) SOLVNT
1      FORMAT (A10)
      WRITE (5,3)
3      FORMAT (1X,'INPUT SOLVNT PARAMETERS R2,Q2')
      READ (5,*) R2,Q2
      WRITE (12,5)
      DO 2 I=1,25
      F1(I)=5*(R1(I)-Q1(I))-(R1(I)-1)
      F2=5*(R2-Q2)-(R2-1)
      COMB(I)=ALOG(R1(I)/R2)+5*Q1(I)*ALOG((Q1(I)*R2)/(Q2*R1(I)))+F1(I)
      *-F2*(R1(I)/R2)
      WRITE (12,4) SOLVNT, (SOLUTE(I,J),J=1,5), COMB(I)
5      FORMAT (///1X,T5,'SOLVNT',T20,'SOLUTE',T48,'COMB'/)
4      FORMAT (1X,T5,A10,T20,5A5,T47,F6.3)
2      CONTINUE
      WRITE(5,6)
6      FORMAT (1X,'MORE TO BE CALCULATED, IF "YES", TYPE 1, IF "NO",
      *TYPE 0')
      READ (5,*) IND
      IF (IND.EQ.0) STOP
      GO TO 7
      END

```

Appendix C

GC/MS DATA

Data from GC/MS analyses of the acid, base and neutral fractions of raw RA-52 quench condensate and samples of RA-52 wastewater after various treatment steps are presented in this Appendix. Tables C-1, C-2, and C-3 contain compound concentration data ($\mu\text{g/l}$) and cumulative percent removals after each treatment step for the acid, base, and neutral fractions, respectively. Data is reported for filtered water (FW) and suspended solids (SS) for raw wastewater and solvent extracted-ammonia stripped water (MIBK); and for filtered water for activated sludge (MIBK-AS) and activated sludge-powdered activated carbon effluent (MIBK-AS/PAC).

Values reported as not detected (NT) refer to detection limits given in Table 6-1 in Chapter Six, while values reported as not determinable (ND) relate to problems of compound masking and/or sample concentration as discussed in Chapter Six. Analysis of raw and solvent extracted ammonia stripped suspended phases refer to measured suspended solids values of 65 and 4 mg/l, respectively.

Table C-1

Concentration of Organics, ug/l, Identified in the
Acid Fraction of Run RA-52 Quench Condensate

Peak Number	Retention Time	Compound Name	Run		MIBK			MIBK-AS		MIBK-AS/PAC	
			SS	FW	SS	FW	% Removal	FW	% Removal	FW	% Removal
20	32.5	Phenol	15,100	3,080,000	NT	500	99.8	10	99.99	3	99.99
30	36.6	Methylphenol	6,300	427,000	NT	100	99.9	1	99.99	1	99.99
80	39.0	Methylphenol	16,400	494,000	NT	80	99.9	1	99.99	1	99.99
100	41.9	Ethylphenol	960	18,700	NT	30	99.8	NT	100	NT	100
110	42.4	C ₂ -Phenol	5,370	85,800	NT	50	99.9	NT	100	NT	100
140	44.7	C ₂ -Phenol	8,890	155,000	NT	50	99.9	NT	100	NT	100
160	46.3	C ₂ -Phenol	1,130	28,800	NT	40	99.8	NT	100	NT	100
170	47.3	C ₃ -Phenol	270	1,110	NT	30	97.2	NT	100	NT	100
180	47.5	C ₃ -Phenol	160	780	NT	20	97.4	NT	100	NT	100
190	48.0	C ₃ -Phenol	770	3,650	NT	30	99.2	NT	100	NT	100
210	49.8	C ₃ -Phenol	400	5,100	NT	30	99.4	NT	100	NT	100
220	50.2	C ₃ -Phenol	1,500	7,900	NT	60	99.2	NT	100	NT	100
230	51.4	C ₃ -Phenol	190	2,140	NT	20	99.1	NT	100	NT	100
250	53.6	C ₄ -Phenol	280	3,300	NT	40	98.8	NT	100	NT	100
260	55.1	Hydroxyindan	340	3,870	NT	40	98.9	NT	100	NT	100
270	55.4	C ₄ -Phenol and Hydroxyindan	250	2,140	NT	30	98.6	NT	100	NT	100
280	56.3	Methyl-Hydroxyindan and C ₄ -Phenol	230	2,170	NT	30	98.6	NT	100	NT	100
300	58.8	Methyl-Hydroxyindan	100	750	NT	30	88.0	NT	100	NT	100
310	61.3	Methyl-Hydroxyindan and Methyl-Hydroxyindene	110	300	NT	40	86.7	NT	100	NT	100
320	62.7	C ₂ -Hydroxyindan and Methyl-Hydroxyindene	100	780	NT	40	85.7	NT	100	NT	100
330	64	Hydroxybiphenyl and C ₂ -Hydroxyindan	120	320	NT	40	87.5	NT	100	NT	100
340	65.1	C ₂ -Hydroxyindan	80	200	NT	30	85.0	NT	100	NT	100
350	65.9	C ₃ -Hydroxyindan	60	150	NT	20	86.7	NT	100	NT	100
360	66.8	2-Naphthol	110	520	NT	20	96.2	NT	100	NT	100
370	67.7	1-Naphthol	250	1,150	NT	40	96.5	NT	100	NT	100
400	72.9	Methylnaphthol	190	300	NT	20	93.3	NT	100	NT	100
410	74.0	Methylnaphthol	100	300	NT	20	93.3	NT	100	NT	100
420	76.8	C ₂ -Naphthol	90	200	NT	20	90.0	NT	100	NT	100
440	79.1	C ₂ -Naphthol	80	200	NT	20	90.0	NT	100	NT	100

SS, Suspended Solids; FW, Filtered Water; ND, Not Determinable; NT, Not Detected.

Table C-2

Concentration of Organics, ug/l, Identified in the
Base Fraction of Run RA-52 Quench Condensate

Peak Number	Retention Time	Compound Name	Raw		MIRK			MIRK-AS		MIRK-AS/PAC	
			SS	FW	SS	FW	% Removal	FW	% Removal	FW	% Removal
10	11.0	Pyridine	3.9	14,530	NT	NT	100	NT	100	0.1	100
15	12.1	Toluene	NT	77	NT	NT	100	NT	100	NT	100
17	12.3	Methyl-Piperidine	NT	ND	NT	NT	100	5.0	ND	2.3	ND
20	13.3	Methylpyridine	12	7,120	NT	1.0	99.00	NT	100	NT	100
22	13.6	Methyl-imidazole	NT	45	NT	25	44	25	44	1.7	96
38	15.9	Imidazolidinone	NT	ND	NT	7.6	99.8	3.1	ND	1.3	ND
40	16.0	Methylpyridine	37	4,480	NT	NT	100	NT	100	NT	100
44	16.3	C ₂ -imidazole or C ₂ -Pyrazole	NT	ND	NT	1.4	ND	5.8	ND	0.5	ND
50	17.7	C ₂ -Pyridine	19	1,530	NT	NT	100	NT	100	NT	100
54	18.4	C ₂ -Dihydroimidazole	NT	ND	NT	7.1	ND	4.0	ND	0.2	ND
55	18.5	C ₂ -imidazole or C ₂ -Pyrazole	3.0	460	NT	NT	100	NT	100	NT	100
60	19.0	C ₂ -Pyridine	4.0	280	NT	NT	100	NT	100	NT	100
68	20.7	C ₂ -imidazole or C ₂ -Pyrazole	NT	ND	NT	8.6	ND	9.5	ND	0.9	ND
70	20.9	C ₂ -Pyridine	67	1,160	NT	NT	100	NT	100	NT	100
80	21.7	C ₂ -Pyridine	22	370	NT	NT	100	NT	100	NT	100
90	22.7	C ₂ -Pyridine	11	80	NT	NT	100	NT	100	NT	100
100	23.3	C ₂ -imidazole	NT	410	NT	240	41	8.3	98	2.4	99.4
105	23.7	C ₃ -Pyridine and Aniline	6.7	70	NT	NT	100	NT	100	NT	100
110	24.3	C ₂ -Pyridine	10	840	NT	NT	100	NT	100	NT	100
120	24.6	C ₂ -Pyridine	11	62	NT	NT	100	NT	100	NT	100
125	25.0	C ₂ -imidazole or C ₃ -Pyrazole	NT	ND	NT	NT	ND	14	ND	.2	ND
130	25.8	C ₂ -Pyridine	44	250	NT	NT	100	NT	100	NT	100
140	26.2	Aniline	27	6,500	NT	NT	100	NT	100	NT	100
150	26.9	C ₃ -Pyridine	39	150	NT	NT	100	NT	100	NT	100
152	27.1	Indoline	NT	ND	NT	5.7	ND	NT	ND	0.1	ND
160	27.5	C ₃ -Pyridine	12	70	NT	NT	100	NT	100	NT	100
168	27.6	Methylimidazole	NT	ND	NT	8.5	ND	NT	ND	NT	ND
170	28.4	C ₃ -Pyridine	10	50	NT	NT	100	NT	100	NT	100
180	28.7	C ₃ -Pyridine	14	36	NT	NT	100	NT	100	NT	100
182	28.8	C ₂ -Diazine	NT	ND	NT	4.1	ND	NT	ND	0.4	ND
190	29.6	C ₄ -Pyridine	NT	ND	NT	NT	100	NT	100	NT	100

Table C-2 Continued

Peak Number	Retention Time	Compound Name	Raw		SS	MIBK		I Removal	MIBK-AS		I Removal	MIBK-AS/PAC	
			SS	FW		SS	FW		FW	I Removal		FW	I Removal
195	30.0	Dimethyl-Isothiazole	NT	ND	NT	4.0	ND	NT	5.1	ND	0.6	ND	ND
200	30.5	C ₃ -Pyridine	26	70	NT	NT	100	NT	NT	100	NT	NT	100
208	31.1	C ₁₀ H ₂₁ N (Olefinic amine)	NT	ND	NT	6.3	ND	NT	NT	ND	0.2	NT	ND
210	31.3	C ₃ -Pyridine	33	70	NT	NT	100	NT	NT	100	NT	NT	100
215	31.8	C ₂ -Thiazole	NT	ND	NT	14	ND	NT	NT	ND	.2	NT	ND
220	31.9	C ₄ -Pyridine	27	850	NT	NT	100	NT	NT	100	NT	NT	100
230	32.3	C ₄ -Pyridine	14	310	NT	NT	100	NT	NT	100	NT	NT	100
240	33.2	C ₄ -Pyridine	40	610	NT	NT	100	NT	NT	100	NT	NT	100
250	33.7	C ₄ -Pyridine	11	60	NT	NT	100	NT	NT	100	NT	NT	100
270	34.7	C ₄ -Pyridine and Diazalindene	17	32	NT	NT	100	NT	NT	100	NT	NT	100
285	35.3	C ₁₁ H ₂₃ N (Olefinic amine)	NT	ND	NT	5.7	ND	NT	NT	ND	NT	NT	ND
290	36.2	C ₅ -Pyridine and C ₄ -Pyridine	25	32	NT	NT	100	NT	NT	100	NT	NT	100
310	37.2	C ₄ -Pyridine	28	21	NT	NT	100	NT	NT	100	NT	NT	100
320	37.8	C ₄ -Pyridine	15	95	NT	11	90	NT	NT	100	NT	NT	100
322	38.0	C ₂ -Triazine	NT	ND	NT	21	ND	NT	NT	ND	0.5	NT	ND
330	38.1	C ₅ -Pyridine	16	70	NT	NT	100	NT	NT	100	NT	NT	100
340	38.3	C ₅ -Pyridine and C ₄ -Pyridine	7.0	35	NT	NT	100	NT	NT	100	NT	NT	100
342	38.4	C ₂ -Aniline	NT	60	NT	NT	100	NT	NT	100	NT	NT	100
350	38.8	C ₅ -Pyridine and C ₂ -Aniline	16	70	NT	NT	100	NT	NT	100	NT	NT	100
352	38.8	C ₂ -Aniline	NT	85	NT	NT	100	NT	NT	100	NT	NT	100
360	39.6	C ₅ -Pyridine and Methyl-Azaindan	16	40	NT	NT	100	NT	NT	100	NT	NT	100
362	39.7	C ₂ -Aniline	NT	29	NT	NT	100	NT	NT	100	NT	NT	100
370	41.2	C ₅ -Pyridine and Methyl-Azaindan	10	31	NT	NT	100	NT	NT	100	NT	NT	100
380	42.3	Methyl-Azaindan	9.3	13	NT	NT	100	NT	NT	100	NT	NT	100
390	44.0	Azanaphthalene	450	500	NT	NT	100	NT	NT	100	NT	NT	100
398	45.1	C ₅ -Pyridine	17	53	NT	NT	100	NT	NT	100	NT	NT	100
400	45.3	Azanaphthalene	160	150	NT	NT	100	NT	NT	100	NT	NT	100
420	46.8	C ₂ -Azaindan	13	ND	NT	NT	100	NT	NT	100	NT	NT	100
425	48.3	Dimethyl-Diazaindan	17	15	NT	NT	100	NT	NT	100	NT	NT	100
430	48.9	Methyl-Azanaphthalene	160	105	NT	NT	100	NT	NT	100	NT	NT	100
435	49.2	Dimethyl-Diazaindan	NT	29	NT	NT	100	NT	NT	100	NT	NT	100
440	49.4	Methyl-Azanaphthalene	42	12	NT	NT	100	NT	NT	100	NT	NT	100
460	50.4	Methyl-Azanaphthalene	64	35	NT	NT	100	NT	NT	100	NT	NT	100

Table C-2 Continued

Peak Number	Retention Time	Compound Name	Raw		SS	MIBK		I Removal	MIBK-AS		MIBK-AS/PAC	
			SS	FW		FW	I Removal		FW	I Removal	FW	I Removal
470	50.8	Methyl-Azanaphthalene	2C	13	NT	NT	100	NT	100	NT	100	100
480	51.2	Methyl-Azanaphthalene	3C	36	NT	NT	100	NT	100	NT	100	100
490	52.0	Methyl-Azanaphthalene	12C	31	NT	NT	100	NT	100	NT	100	100
500	52.4	Methyl-Azanaphthalene	5B	25	NT	NT	100	NT	100	NT	100	100
510	53.2	Methyl-Azanaphthalene	24	50	NT	NT	100	NT	100	NT	100	100
520	53.7	C ₂ -Azanaphthalene	9C	50	NT	NT	100	NT	100	NT	100	100
530	54.7	C ₂ -Azanaphthalene	1E	23	NT	NT	100	NT	100	NT	100	100
540	55.4	C ₂ -Azanaphthalene	3B	37	NT	NT	100	NT	100	NT	100	100
545	56.1	C ₃ -Diazindan	NT	65	NT	NT	100	NT	100	NT	100	100
550	56.6	C ₂ -Azanaphthalene	6C	ND	NT	NT	100	NT	100	NT	100	100
560	57.0	C ₂ -Azanaphthalene	13	26	NT	NT	100	NT	100	NT	100	100
570	57.9	C ₂ -Azanaphthalene	64	ND	NT	NT	100	NT	100	NT	100	100
580	58.7	C ₂ -Azanaphthalene and Azabiphenyl	65	6	NT	NT	100	NT	100	NT	100	100
590	59.8	C ₂ -Azanaphthalene and Azabiphenyl	1E	5	NT	NT	100	NT	100	NT	100	100
600	60.7	C ₂ -Azanaphthalene and Azanaphthalene	3C	10	NT	NT	100	NT	100	NT	100	100
630	62.7	C ₂ -Azanaphthalene and C ₃ -Azanaphthalene and Methylbiphenyl	3B	5	NT	NT	100	NT	100	NT	100	100
640	63.0	C ₂ -Azanaphthalene and C ₂ -Azanaphthalene	11	ND	ND	NT	100	NT	100	NT	100	100
650	63.9	C ₂ -Azanaphthalene and Azacenaphthene and Methyl-Azabiphenyl and C ₂ -Azabiphenyl	13	9	NT	NT	100	NT	100	NT	100	100
690	66.0	Methyl-Azacenaphthene	20	11	NT	NT	100	NT	100	NT	100	100
710	67.8	C ₃ -Azanaphthalene and C ₄ -Azanaphthalene and Methyl-Azacenaphthene	10	5	NT	NT	100	NT	100	NT	100	100
730	69.7	Azafluorene	20	15	NT	NT	100	NT	100	NT	100	100
800	77.7	Azaphenanthrene	B.7	5	NT	NT	100	NT	100	NT	100	100
810	79.9	Azaanthracene	16	5	NT	NT	100	NT	100	NT	100	100

SS, Suspended Solids; FW, Filtered Water; ND, Not Determinable; FI, Not Detected.

Table C-3

Concentration of Organics, ug/l, Identified in the
Neutral Fraction of Run RA-52 Quench Condensate

Peak Number	Retention Time	Compound Name	Raw		SS	MIBK		Removal	MIBK-AS		MIBK-AS/PAC	
			SS	FW		SS	FW		FW	% Removal	FW	% Removal
20	17.7	C ₂ -Benzene	365	ND	NT	NT		100	NT	100	NT	100
21	17.9	Methylcyclohexene or C ₂ -Cyclopentene	ND	2220	NT		36	99.5	NT	100	NT	100
32	19.4	Methylcyclohexene or C ₂ -Cyclopentene	ND	22250	NT		4230	81	NT	100	NT	100
35	21.0	Benzonitrile	ND	2900	NT	NT		100	NT	100	NT	100
36	21.2	C ₈ -Alkane	NT	ND	NT		440	ND	NT	100	NT	100
38	21.6	Methylcyclohexene or C ₂ -Cyclopentene	ND	3130	NT	ND		100	NT	100	NT	100
39	22.1	Methylcyclohexene or C ₂ -Cyclopentene	ND	850	NT		71	92	NT	100	NT	100
40	26.9	C ₃ -Benzene and Indan	330	ND	NT	NT		100	NT	100	NT	100
42	27.2	C ₂ -Cyclohexene and C ₃ -Cyclopentene	ND	1160	NT		67	94	NT	100	NT	100
48	28.1	Methylthiazole	ND	ND	NT		15	ND	NT	100	NT	100
50	29.0	C ₃ -Benzene and C ₂ -Cyclohexene or C ₃ -Cyclopentene	1130	8770	NT		87	99	NT	100	NT	100
55	29.8	C ₂ -Thiazole	ND	ND	NT	ND		ND	3.1	ND	3.0	ND
70	30.4	Indene	2300	910	NT	NT		100	NT	100	NT	100
78	31.9	C ₂ -Thiazole	ND	ND	NT		22	ND	.6	93	.7	93
80	32.3	C ₃ -Benzene	860	ND	NT	NT		100	NT	100	NT	100
82	32.6	Acetophenone	ND	3583	NT	NT		100	NT	100	NT	100
92	33.2	C ₃ -Cyclohexene or C ₄ -Cyclopentene	ND	1540	NT		65	96	NT	100	NT	100
95	34.2	C ₂ -Thiazole	ND	ND	NT		30	ND	NT	100	NT	100
96	34.5	C ₂ -Thiazole	ND	ND	NT		40	ND	NT	100	NT	100
100	34.6	Methylindan	290	ND	NT	NT		100	NT	100	NT	100
110	34.8	Methylindan	165	ND	NT	NT		100	NT	100	NT	100
115	35.0	Cresol	ND	5520	NT	NT		100	NT	100	NT	100
120	35.3	Methylindan	470	ND	NT	NT		100	NT	100	NT	100
125	35.5	C ₃ -Thiazole	ND	ND	NT		31	ND	1.8	94	2.0	94
130	35.6	Methylindan	590	ND	NT	NT		100	NT	100	NT	100
135	35.8	C ₃ -Thiazole	ND	ND	NT		30	ND	2.5	92	2.1	93
140	36.3	C ₃ -Cyclohexadiene or C ₄ -Cyclopentadiene	ND	1000	NT	NT		100	NT	100	NT	100

Table C-3 Continued

Peak Number	Retention Time	Compound Name	Raw		SS	MIBK		I Removal	MIBK-AS		I Removal	MIBK-AS/PAC	
			SS	FW		SS	FW		FW	I Removal		FW	I Removal
145	16.4	C ₃ -Thiazole	ND	ND	NT	27	ND	1.3	93	1.6	94		
150	16.5	Cresol	ND	1180	NT	NT	100	NT	100	NT	100		
160	18.5	Methylindene and Dihydronaphthalene	1220	ND	NT	NT	100	NT	100	NT	100		
170	18.8	Dihydronaphthalene	1390	ND	NT	NT	100	NT	100	NT	100		
172	19.2	C ₃ -Thiazole	ND	ND	NT	15	ND	NT	100	NT	100		
175	19.1	C ₂ -Phenol	ND	4580	NT	NT	100	NT	100	NT	100		
180	19.8	Naphthalene	16300	26600	NT	NT	100	NT	100	NT	100		
185	19.9	C ₃ -Thiazole	ND	ND	NT	17	ND	NT	100	NT	100		
189	12.8	C ₂ -Phenol	ND	6140	NT	NT	100	NT	100	NT	100		
190	12.9	C ₂ -Indan	570	-	NT	NT	100	NT	100	NT	100		
191	13.0	C ₂ -Phenol	ND	7850	NT	NT	100	NT	100	NT	100		
199	13.4	C ₂ -Phenol	ND	1600	NT	NT	100	NT	100	NT	100		
200	13.5	C ₂ -Indan	1450	ND	NT	NT	100	NT	100	NT	100		
210	13.7	C ₂ -Indan and C ₂ -Azaindan	450	ND	NT	NT	100	NT	100	NT	100		
225	14.6	C ₂ -Phenol	ND	2670	NT	NT	100	NT	100	NT	100		
242	15.1	C ₃ -Phenol	ND	1190	NT	NT	100	NT	100	NT	100		
248	15.5	C ₃ -Phenol	ND	710	NT	NT	100	NT	100	NT	100		
250	16.1	C ₂ -Indene	290	ND	NT	NT	100	NT	100	NT	100		
251	16.2	C ₃ -Phenol	ND	3320	NT	NT	100	NT	100	NT	100		
260	16.2	C ₂ -Indene	360	ND	NT	NT	100	NT	100	NT	100		
262	16.4	C ₃ -Phenol	ND	1450	NT	NT	100	NT	100	NT	100		
270	16.7	C ₂ -Indene	880	ND	NT	NT	100	NT	100	NT	100		
278	16.9	C ₃ -Phenol	ND	8100	NT	NT	100	NT	100	NT	100		
280	17.0	C ₂ -Indene	120	ND	NT	NT	100	NT	100	NT	100		
285	17.2	C ₃ -Phenol	ND	2700	NT	NT	100	NT	100	NT	100		
290	17.7	Hexahydronaphthalene	610	ND	NT	NT	100	NT	100	NT	100		
295	18.1	C ₃ -Phenol	ND	2100	NT	NT	100	NT	100	NT	100		
300	18.5	2-Methylnaphthalene	6300	ND	NT	NT	100	NT	100	NT	100		
302	19.0	C ₃ -Phenol	ND	7300	NT	NT	100	NT	100	NT	100		
308	19.3	C ₃ -Phenol	ND	2900	NT	NT	100	NT	100	NT	100		
310	19.4	1-Methylnaphthalene	3530	ND	NT	NT	100	NT	100	NT	100		

Table C-3 Continued

Peak Number	Retention Time	Compound Name	Raw		MIBK			MIBK-AS		MIBK-AS/PAC	
			SS	FW	SS	FW	% Removal	FW	% Removal	FW	% Removal
323	50.0	C ₃ -Indan	750	ND	NT	NT	100	NT	100	NT	100
339	51.0	Indole	150	5000	NT	NT	100	NT	100	NT	100
349	51.2	C ₃ -Indan	570	ND	NT	NT	100	NT	100	NT	100
345	51.4	C ₃ -Phenol	ND	1220	NT	NT	100	NT	100	NT	100
355	51.8	C ₄ -Phenol	ND	600	NT	NT	100	NT	100	NT	100
360	52.9	C ₁₃ -Alkane and C ₄ -Indan	2340	ND	NT	NT	100	NT	100	NT	100
370	53.2	C ₁₃ -Alkane	350	ND	NT	NT	100	NT	100	NT	100
380	54.0	Biphenyl	1100	ND	NT	NT	100	NT	100	NT	100
390	54.9	C ₂ -Naphthalene	700	ND	NT	NT	100	NT	100	NT	100
400	55.8	C ₂ -Naphthalene	1900	ND	NT	NT	100	NT	100	NT	100
405	56.3	Methylindole	ND	570	NT	NT	100	NT	100	NT	100
410	56.8	C ₂ -Naphthalene	4200	ND	NT	NT	100	NT	100	NT	100
420	57.8	C ₁₃ -Alkane	500	ND	NT	NT	100	NT	100	NT	100
430	58.2	Acenaphthalene	4930	ND	NT	NT	100	NT	100	NT	100
440	58.7	C ₂ -Naphthalene	780	ND	NT	NT	100	NT	100	NT	100
450	59.0	C ₂ -Naphthalene	280	ND	NT	NT	100	NT	100	NT	100
460	60.1	Acenaphthene	2480	ND	NT	NT	100	NT	100	NT	100
470	60.8	Methylbiphenyl	1000	ND	NT	NT	100	NT	100	NT	100
480	61.3	Methylbiphenyl	690	ND	NT	NT	100	NT	100	NT	100
490	61.6	Methylbiphenol	320	ND	NT	NT	100	NT	100	NT	100
500	62.5	Dibenzofuran	3340	ND	NT	NT	100	NT	100	NT	100
510	63.0	C ₄ -Decalin and BHT (antioxidant)	2910	NT	NT	NT	100	NT	100	NT	100
520	63.7	C ₃ -Naphthalene	820	ND	NT	NT	100	NT	100	NT	100
530	64.5	C ₃ -Naphthalene	570	ND	NT	NT	100	NT	100	NT	100
540	65.5	C ₃ -Naphthalene	650	ND	NT	NT	100	NT	100	NT	100
550	66.4	Benzoindene	5000	ND	NT	NT	100	NT	100	NT	100
552	66.6	Plasticizer (Phthalate)	ND	ND	NT	NT	ND	6.7	ND	2.6	ND
560	66.8	C ₄ -Naphthalene	2100	ND	NT	NT	100	NT	100	NT	100
570	67.3	Methylacenaphthene	600	ND	NT	NT	100	NT	100	NT	100
580	67.7	Methylacenaphthene and C ₂ -Biphenyl	750	ND	NT	NT	100	NT	100	NT	100
590	68.2	Benzoindene	300	ND	NT	NT	100	NT	100	NT	100

Table C-3 Continued

Peak Number	Retention Time	Compound Name	Raw		MIBK			MIBK-AS		MIBK-AS/FAC	
			SS	FW	SS	FW	I Removal	FW	I Removal	FW	I Removal
600	68.8	Fluorene and C ₂ -Biphenyl	1700	ND	NT	NT	100	NT	100	NT	100
610	69.6	C ₂ -Biphenyl	1700	ND	NT	NT	100	NT	100	NT	100
620	78.0	C ₂ -Biphenyl and C ₆ -Naphthalene	310	ND	NT	NT	100	NT	100	NT	100
630	70.7	C ₂ -Biphenyl and C ₆ -Naphthalene	380	ND	NT	NT	100	NT	100	NT	100
640	71.5	C ₄ -Naphthalene and C ₇ -Biphenyl	140	ND	NT	NT	100	NT	100	NT	100
650	72.2	C ₅ -Naphthalene	530	ND	NT	NT	100	NT	100	NT	100
660	71.0	Methylfluorene	1120	ND	NT	NT	100	NT	100	NT	100
670	71.4	Methylfluorene	540	ND	NT	NT	100	NT	100	NT	100
680	73.9	Methylfluorene	630	ND	NT	NT	100	NT	100	NT	100
690	74.4	C ₂ -Acenaphthene	220	ND	NT	NT	100	NT	100	NT	100
700	75.2	C ₃ -Biphenyl	750	ND	NT	NT	100	NT	100	NT	100
710	71.2	Phenanthrene	4680	ND	NT	NT	100	NT	100	NT	100
720	71.7	C ₃ -Biphenyl and Anthracene	1160	ND	NT	NT	100	NT	100	NT	100
728	82.4	Plasticizer (Phthalate)	ND	ND	NT	NT	ND	NT	ND	12	ND
740	83.6	Methylphenanthrene	410	ND	NT	NT	100	NT	100	NT	100
750	84.2	Methylanthracene	790	ND	NT	NT	100	NT	100	NT	100
760	84.7	Methylphenanthrene and/or Methylanthracene	180	ND	NT	NT	100	NT	100	NT	100
770	81.0	Phenylanthracene	210	ND	NT	NT	100	NT	100	NT	100
780	59.6	C ₂ -Phenanthrene or C ₇ -Anthracene	210	ND	NT	NT	100	NT	100	NT	100
790	51.2	Fluoranthene	1510	ND	NT	NT	100	NT	100	NT	100
810	91.5	Pyrene	830	ND	NT	NT	100	NT	100	NT	100
820	94.1	Methyl-Phenylanthracene	250	ND	NT	NT	100	NT	100	NT	100

SS, Suspended Solids; FW, Filtered Water; ND, Not Determinable; NT, Not Detected.