**THERMODYNAMIC AND RHEOLOGICAL
PROPERTIES OF SOLID-LIQUID SYSTEMS
IN COAL PROCESSING**

**Final Technical Report
June 30, 1995**

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**Prepared for
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Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania 15236**

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The work on viscosity of coal model compounds and coal derived liquids was mostly performed by the graduate student Mr. Mohandas Palakkal. Work on liquid state equation of state for coal model compounds, and predictive models for vapor pressure and saturated liquid volumes was done by graduate student Mr. Jinsong Wang. The work was supervised and directed by the Principal Investigator, V. N. Kabadi. The project also benefitted from the assistance of two undergraduate students, Ms. Angelia Charles and Ms. Ronica Sibert. In all, four manuscripts have been submitted for publication.

1. M. Palakkal and V. N. Kabadi, "Viscosity of Coal Derived Liquids 1. A Group Contribution Method for Pure Model Compound Liquids, " accepted by Energy & Fuels.
2. V.N. Kabadi and M. Palakkal, "Viscosity of Coal Derived Liquids 2. Application of the Model to Coal Liquid Fractions," submitted to Energy & Fuels.
3. J. Wang and V. N. Kabadi, "A Predictive Vapor Pressure Correlation for Organic Liquids," Fluid Phase Equilibria, in Review.
4. J. Wang and V. N. Kabadi, "Generalized Method for Prediction of Saturated Liquid Volumes Using Modified Rackett Equation and Van der Waals Volumes," accepted by AIChE Journal.

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ABSTRACT

The work on this project was initiated on September 1, 1991. The project consisted of two different tasks: 1. Development of a model to compute viscosities of coal derived liquids, and 2. Investigate new models for estimation of thermodynamic properties of solid and liquid compounds of the type that exist in coal, or are encountered during coal processing.

As for task 1, a model for viscosity computation of coal model compound liquids and coal derived liquids has been developed. The detailed model is presented in this report. Two papers, the first describing the pure liquid model and the second one discussing the application to coal derived liquids, are expected to be published in Energy & Fuels shortly.

Marginal progress is reported on task 2. Literature review for this work included compilation of a number of data sets, critical investigation of data measurement techniques available in the literature, investigation of models for liquid and solid phase thermodynamic computations. During the preliminary stages it was discovered that for development of a liquid or solid state equation of state, accurate predictive models for a number of saturation properties, such as, liquid and solid vapor pressures, saturated liquid and solid volumes, heat capacities of liquids and solids at saturation, etc. Most the remaining time on this task was spent in developing predictive correlations for vapor pressures and saturated liquid volumes of organic liquids in general and coal model liquids in particular. All these developments are discussed in this report. Some recommendations for future direction of research in this area are also listed.

PROJECT OBJECTIVES AND SCOPE

The objective of this project is to develop a model for solid-liquid equilibria and a model for viscosities of the products of coal liquefaction processes. The same characterization procedure and representation by continuous distributions as used in our previous work on vapor-liquid equilibria and excess enthalpies of coal liquids will be used. Models when fully developed will give the solid-liquid phase equilibrium properties and viscosities as functions of temperature and pressure for known molecular weight distribution and structural characterization of the coal liquid. To accomplish this well, the project requires three tasks:

- (1) Solid-Liquid phase equilibrium model development: This will require data compilations for vapor pressure of solids and available single and multi-component solid-liquid phase equilibrium data. Model development will include models for thermodynamics of solids such as in coal products, thermodynamics of defined solid-liquid systems and finally application to complex coal derived products.
- (2) Experimental Viscosity Measurements: A viscometer will be purchased to measure viscosities of coal liquids and slurries at different temperatures and pressures. The data will be used in conjunction with literature data for viscosity model development.
- (3) Viscosity Model Development: Viscosity model development will require collection of physical property data for model compounds to estimate the model parameters. Both group contribution and corresponding states methods will be used to account of the effect of pressure and temperature on the liquid viscosity. The model will then be extended to coal liquid fractions. The experimentally measured viscosity data will be used to evaluate the model and recommend modifications.

TECHNICAL HIGHLIGHTS AND MILESTONES

I. SUMMARY OF ACCOMPLISHMENTS

This project consisted of two different tasks: 1. Development of a model to compute viscosities of coal derived liquids, and 2. Investigate new models for estimation of thermodynamic properties of solid and liquid compounds of the type that exist in coal, or are encountered during coal processing.

As for task 1, a model for viscosity computation of coal model compound liquids and coal derived liquids has been developed. The detailed model is presented in section II of this report. Two papers, the first describing the pure liquid model and the second one discussing the application to coal derived liquids, are expected to be published in Energy & Fuels shortly.

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II. VISCOSITY OF COAL DERIVED LIQUIDS

The work area began with considerable efforts to compile a databank of viscosity of pure and binary mixtures of coal model compound liquids. A compound by compound listing of the data sets of pure component data and binary mixture data are given in Table 1 of the two manuscripts submitted to Energy & Fuels, and which are included in full in this report in sub-sections 1 and 2 below. One of the initial objectives of this project was to undertake viscosity data measurements for pure components, mixtures as well as coal derived liquids. However, upon research, it was observed that sufficient experimental data were available in the literature, so that data measurements were not necessary.

All the details of the model development are given in the two manuscripts included below. The general conclusion of this work was that a new model for viscosity computation of coal derived liquids was successfully developed. This is first such model that is developed particularly for the type of molecular structures that exist in coal derived liquids., and therefore the model estimates viscosities of homogeneous coal derived liquids quite accurately.

1. A Group Contribution Method for Pure Model Compound Liquids

Viscosity of Coal Derived Liquids

1. A Group Contribution Method for Pure Model Compound Liquids

by

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ABSTRACT

Viscosity of coal derived liquids is an important property useful in the design of coal liquefaction processes as well as for understanding the flow characteristics of coal liquids. A new model for the prediction of viscosity of coal liquid model compounds has been developed. The model uses Andrade equation with the constants A and B given by a well defined group contribution method. The group contribution method uses the group definitions, group parameters and procedure for property calculation, such that all the heteroatom functionalities and some significant molecular structures prevalent in coal derived liquids are included. The model was tested using experimental data from literature and the average error was determined to be 11.55%. Two of the prominent liquid viscosity models available in the literature were also evaluated using the same experimental data set of coal model compounds. These models could not be applied to all the compounds, as some model parameters were not available. Both the models resulted in errors a few percent higher than obtained from our model, indicating that for coal model compounds the correlation developed here is more widely applicable and more accurate than any other model in the literature. Future efforts will include extension of the correlation to mixtures of coal model compounds and description of a procedure to compute viscosities of appropriately characterized coal derived liquids.

Introduction

Viscosity of coal liquids is an important property essential for the design of coal liquefaction processes, as well as for understanding of the flow characteristics of coal liquids through conduits. With the increasing importance of synthetic fuels as a source for energy, there is a need for a reliable and accurate predictive method for coal liquid viscosity. Currently such a method is not available in the literature. Correlations presently available are too general to apply to coal liquids with sufficient degree of accuracy.

Although, a large amount of literature is available on theoretical advances in understanding of rheological behavior of fluids, most practical methods for prediction of viscosity of complex fluids are empirical or semi-empirical in nature. A brief review of these methods is presented here. Viscosity correlations may be classified as corresponding states methods, group contribution methods or other mostly empirical methods using regressed compound specific constants.

Although, the principle of corresponding states fundamentally applies to equilibrium thermodynamic properties of fluids, attempts have been made to extend its application for viscosity calculations¹⁻⁶. This is generally done by defining a reducing parameter for viscosity as the critical viscosity, and correlating the reduced viscosity with reduced temperature using other parameters such as acentric factor, boiling point and molecular weight. Some corresponding states methods are also available that increase the accuracy by using one or two reference fluids⁷⁻⁹. A number of these methods perform very well for viscosity of pure liquids when accurate information on critical properties is available.

Group contribution methods, on the other hand use certain basic functionalities or

groups as the building blocks for the molecules and the overall molecular property is obtained as a function of parameters (or group contributions) assigned to individual groups. Methods of Van Velzen et al¹⁰, Wu¹¹ and Allan et al¹² are some of the best group contribution methods for liquid viscosities. Of these, the Van Velzen method has the most potential for application to coal liquids, as it incorporates detailed molecular functionalities and structures. However, it uses the carbon chain length as its main parameter and so is not very suitable for aromatic liquids.

In conjunction with the above methods, studies are available in the literature where experimental liquid viscosities are correlated using various empirical mathematical expressions^{13, 14}. Of these, the simplest and most practical form is the Andrade equation¹³ given below.

$$\log \eta = A + \frac{B}{T} \quad (1)$$

where η is viscosity in centipoise

T is temperature in °K

and A and B are regressed constants

It is well documented in the literature that the Andrade equation fits experimental liquid viscosity data well¹⁴. In fact, the correlation of Van Velzen et al¹⁰ uses this equation as the basis and defines group contribution methods for evaluation of A and B. Development of a similar method for coal liquid model compounds and for coal derived liquids is quite feasible and would be very desirable. This is exactly the objective of the current study.

Some methods are available in the literature for viscosity prediction of undefined

mixtures of complex fluids such as petroleum fractions¹⁵⁻²⁵. These methods either use broad characterization parameters such as Watson characterization factor, API gravity, molecular weight, refractive index etc. or define the mixture as a pseudo pure component and use a corresponding states method developed for pure liquids. Although quite adequate for petroleum fractions such methods are not sufficiently accurate for coal derived liquids because of the presence of fused aromatic ring structures and heteroatom functionalities²⁶.

Based on the above review, it was determined that an accurate method for viscosity prediction of coal liquid model compounds and coal derived liquids is currently not available. The approach of Van Velzen et al¹⁰, i.e. using the Andrade equation¹³ with a group contribution method for constants A and B, was judged most attractive for development of a new correlation. However, the new correlation would use the aromatic ring as the building block as compared to the alkyl chain length used in the Van Velzen correlation. In this work, such a correlation for pure coal liquid model compounds has been developed. The development of the model and the results of comparison with experimental data are discussed in the following sections.

Model Development

As a first step towards the development of a model, the experimental viscosity data for 136 model compounds were compiled. The data set contains 2397 data points for compounds in the temperature range $0.35 < T_R < 0.70$ at atmospheric pressure. The compounds may be classified into various homologous series such as alkanes, alkybenzenes, fused multi-ring aromatics, cyclopentanes, cyclohexanes, phenols, amines, thiophenes, pyridines, and other ring compounds. The compounds, the temperature range of data and the data sources are listed in Table 1.

Before undertaking the development of a new correlation, two of the widely used models for liquid viscosities were considered; the group contribution method of Van Velzen et al.¹⁰ and the corresponding states correlation of Przezdziecki et al.⁶. It was soon observed that neither of these methods could be applied to all coal compounds because of the lack of parameters. The Van Velzen model is designed for compounds with variable alkyl chain lengths and parameters have not been developed for a number of very common structures in coal liquids, such as, fused multi-ring aromatics, pyridines, thiophenes, etc. Przezdziecki model, on the other hand requires critical properties which are not available for a number of heavy model compounds. To predict viscosities of coal model compounds a correlation is necessary that will include all the functionalities and structures prevalent in coal derived liquids. The task of development of such a correlation was therefore undertaken.

Using the pure liquid databank for each compound constants A and B in equation 1

were regressed, and the nature of the regression fit was analysed. Not surprisingly, the data fitted the equation satisfactorily with errors less than 3% for all the compounds in the databank. It was therefore, felt that the Andrade equation is quite adequate as the basis for the new model. Further efforts were then focused on the development of a relation between molecular structure and the Andrade constants A and B. Equation 1 and a group contribution method for calculating the constants A and B, would then be a complete model for viscosity of the model compound liquids.

A careful analysis of the trends and patterns in the values of A and B was next undertaken. The trends were analysed for each homologous series of compounds. Some of the trends were very apparent and obvious, while others were more subtle. It was observed that the trends in the values of constant B for each homologous series were easier to analyse. In order to make the method accurate, it was decided to obtain a model for the constant B first, then re-regress the entire data to obtain new values of A, next to analyse the trends and patterns in the values of A for each homologous series and finally developing a model for the constant A. This method reduced the chance of propagation of errors from the model for B to the model for A. In developing these models for A and B, basic functionalites or groups constituting coal liquids were defined and the objective was to obtain expressions for A and B as functions of parameters assigned to the individual groups and to the molecular structures that these groups may form.

The simplest group contribution method is one that involves obtaining the property for a compound by simply adding all the group contributions of individual groups constituting the molecule. For most properties, however, it is generally observed that group

contributions are not simply additive and other parameters have to be introduced for better accuracy. For viscosity in particular it was observed that not only is this true but also the structure of the molecule plays a significant role. The model developed here hence involves individual group contributions, non-additivity parameters and molecular structural parameters. Before presenting the group contribution model for constants A and B, some observations made in the trends of A and B and some preliminary work leading to the final model are listed below.

1. Intercepts A are negative and slopes B are positive for all compounds.
2. B and absolute values of A generally increase with molecular weight within a class of compounds. However, the curves are non-linear with the values increasing almost linearly at lower molecular weights and tapering off almost asymptotically at higher molecular weights.
3. The above trend was found to be true for fused ring aromatics and other fused ring compounds. The non-additivity of the group contributions was described by a damping factor as a function of number of rings. Additionally, group contribution of each ring was also found to depend on the configurations of the ring in the overall molecular structure. In other words, how many and which sides of a ring are fused with other rings, affected the group contribution of that ring. Consequently, the method for fused ring structures includes primary ring contributions for each ring type, multipliers that depend on ring configuration and an overall parameter that depends on the total number of rings in the fused ring structure.
4. It was observed that the alkyl chains attached to ring structures, except the first

methyl group (α - group) could be treated as methyl groups in paraffins. To draw an equivalence between the two families of compounds, viscosity plots for a number of compounds in the two families are shown in Figure 1. It is easily observed that pairs of lines corresponding to toluene and heptane, propylbenzene and nonane, hexylbenzene and dodecane, run almost parallel. Also intercepts corresponding to the pairs of compounds, toluene and butane, propylbenzene and hexane, hexylbenzene and nonane, are almost equivalent. It, therefore, seems that the slope B of an alkylbenzene is equivalent to that of a paraffin with the same carbon number, and the intercept A of an alkylbenzene is equivalent to that of a paraffin with carbon number three less than that of the alkylbenzene. For a comprehensive model for alkylbenzenes, it was hence necessary to develop a model for paraffins.

Viscosity data of 19 n-alkanes (567 data points) between C_1 to C_{43} were regressed using equation 1 and the error in the fit was determined to be less than 3%. The constants A and B were analysed to identify the trends and patterns. It was observed that the constants A and B were exponential functions of the number of carbon atoms in the n-Alkanes. The following model emerged as an accurate representation of the Andrade constants A_{par} and B_{par}

$$A_{par} = 10[0.5246 + 0.1657e^{-0.2083n_c} - 1] \quad (2)$$

$$B_{par} = 2392.82 [1 - e^{-0.08n_c}] \quad (3)$$

where n_c is the number of carbon atoms in the paraffin.

For any paraffin, therefore, if the number of carbon atoms in the molecule are known, equations 2 and 3 combined with equation 1 can predict the viscosity at a particular temperature. The average error in the predicted values of viscosity using the above model was found to be 7.45% . Percentage errors reported throughout this work are calculated as absolute errors normalized by the experimental values and reported on a percentage basis.

To obtain a model for the group contributions of the alkyl chains, first the group contributions of the α -alkyl group were regressed from the experimental data for toluene, xylenes, methyl naphthalenes, etc. For the rest of the methyl groups in the alkyl chains a procedure was then developed that utilizes the equivalence in slopes and intercepts observed in Figure 1, and is described below.

Let n_t be the sum of all the ring carbon atoms and the alkyl chain carbon atoms in the molecule. Let n_r be the sum of all the ring carbon atoms and the carbon atoms in α -alkyl groups. Then $(\Delta A)_{alk}$ and $(\Delta B)_{alk}$ are contributions to intercept and slope of $(n_t - n_r)$ alkyl groups in the molecule and are given as

$$(\Delta A)_{alk} = (A_{par})_{n_c=n_t-3} - (A_{par})_{n_c=n_r-3} \quad (4)$$

$$(\Delta B)_{alk} = (B_{par})_{n_c=n_t} - (B_{par})_{n_c=n_r} \quad (5)$$

where A_{par} and B_{par} are given by equations 2 and 3. This procedure, although developed only from data on single ring alkylbenzenes, can be applied to all model compounds with alkyl chains, and was found to perform satisfactorily when eval-

uated with limited experimental data available for multi-ring compounds with alkyl chains and ring compounds with alkyl chains and other side attachments such as hydroxyl and amine groups.

5. The attachments to the rings considered are hydroxyl, amine, α -alkyl, N-alkyl and O-alkyl groups. The last two groups are the alkyl groups substituting the hydrogens in the amine and the hydroxyl groups which are attached to the rings. The contributions corresponding to these groups were obtained as accurately and extensively as the limited experimental data would permit.

From all the above considerations the overall model for A and B was developed and may be given in compact form as follows:

$$A = 10 \left[\left(\sum_i \Delta A_i \theta_i \right)_{ring} (N^{**})^{0.467} + \sum_i \Delta A_i n_i^{\alpha i} - 1 \right] + \Delta A_{alk} \quad (6)$$

$$B = \left(\sum_i \Delta B_i \phi_i \right)_{ring} (N^*)^{-0.5} + \sum_i \Delta B_i n_i^{\beta i} + \Delta B_{alk} \quad (7)$$

In both the above expressions (equations 6 and 7), the first summation is over group contributions of various ring structures. Types of ring groups considered are aromatic (ar), cyclopentane (cp), cyclohexane (ch), pyridine (py), thiophene (th), cyclopentene (cpe), cyclohexene (che), pyrrole (pyr), furan (fu) and tetrahydrofuran (thf). Primary contributions of each of these rings (ΔA_i and ΔB_i) are given in Table 2. θ_i and ϕ_i represent multiplication factors to the primary group contributions corresponding to the way ring i is attached to other rings in a composite fused ring structure. Factors θ_i and ϕ_i for various

ring configurations are given in Table 3. Let N_t be the total number of rings in the molecule,

$$\text{For } N_t = 1, \quad N^* = 1, \quad N^{**} = 1 \quad (8)$$

For $N_t > 1$,

$$N^* = (N_{ar} + N_{cp} + 1.9N_{ch} + 0.68N_{py} + 2.8N_{th} + 0.75N_{cpe} + N_{che} + N_{pyr} + N_{fu} + N_{thf}) \quad (9)$$

$$N^{**} = (N_{ar} + 0.75N_{cp} + 1.33N_{ch} + 0.8N_{py} + 2.4N_{th} + N_{cpe} + N_{che} + N_{pyr} + N_{fu} + N_{thf}) \quad (10)$$

The contributions corresponding to phenyl linkages as in biphenyl and terphenyl must be added in the summations over the ring contributions.

For both A and B, the second summation is over all the other non-ring groups in Table 2. Here, n_i represents number of groups of type i , and α_i and β_i are exponents which are all unity except for the $-OH$ group for which $\alpha_i = 0.1$ and $\beta_i = 0.5$. Finally the last terms in equation 6 and 7 i.e. ΔA_{alk} and ΔB_{alk} are obtained from equations 2 to 5 as described before. The viscosity of a compound at a particular temperature is, therefore, calculated using equation 1 where the constants A and B are calculated using equations 6 and 7. The procedure to calculate the viscosity of a model compound with an illustration is given in the appendix.

Results and Discussion

The viscosity model described in the last section was evaluated with the available data on model compound liquids. The model compounds were classified into a few homologous series for the sake of model performance evaluation. The results are given in Table 1 which lists average percent errors for each compound, for each homologous series and for the whole data set. An overall error of 11.55% for a total of 2397 data points indicates a fairly accurate model. A few mostly high molecular weight compounds exhibited large error in excess of 40%. Data for these compounds came from a single source with A and B evaluated from a handful of data points. The accuracy of these data sets would be somewhat in question. Nevertheless these compounds are included in our overall error calculation. Table 1 also shows compound by compound error analysis for the correlations of Van Velzen et al¹⁰ and Przewdziecki et al⁶. The overall errors for these two methods are 17.34% and 28.99% respectively. For these compounds, therefore, our model performs significantly better than these two widely used literature models. More importantly, neither of the two models could be applied to all the coal model compounds in our data set. Of the total of 136 compounds and 2397 data points, error analysis of Van Velzen method includes 89 compounds and 1773 data points and that of Przewdziecki method includes only 68 compounds and 1688 data points. The comparisons of Table 1 indicate that a correlation has been successfully developed that is more accurate and applies more widely to liquids of coal model compounds than any other method available in the literature.

Our model errors could have been further reduced by more detailed group descriptions. A few significant simplifications in the model are 1. The group attachments

are not classified according to the type of ring they are attached to. 2. The group attachments are not classified according to their position of attachment to a ring, such as, ortho, meta, or para. 3. Stereo-isomers, cis, trans and gauche are considered equivalent. Although, a more detailed group description to include above classifications is possible and would have somewhat reduced the overall errors reported here it was not attempted for two reasons, 1. Not enough data were available to allow for such detailed group description and 2. One of the objectives of this work is to apply this model to coal derived liquids. Some methods are available in the literature for characterization of coal derived liquids by molecular weight distribution and composition of heteroatom functionalities²⁵⁻²⁸. However, it is almost impossible to characterize coal liquids in such details as to describe the group attachments by above classifications. From this perspective, such an effort would not be very meaningful. Particularly in the case of phenols and amines with alkyl chain attachments, it was observed that ortho, meta and para descriptions are important and the errors could have been reduced by assigning different contributions corresponding to these structures.

In summary, a group contribution model for liquid viscosity of coal model compounds has been developed. The model requires only the functional group characterization of the molecule and no other adjustable parameters are used. The model is easy to use and results in accurate predictions. As a part of the overall model, an accurate method for viscosity of liquid alkanes is also provided. Future work will include application of the correlation to mixtures of model compounds and evaluation with limited viscosity data available for coal derived liquids.

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Appendix

Stepwise Procedure for Viscosity Calculation:

Step 1 : Identify the class of compound (ring or straight chain structure)

- For straight chain compounds, use equations 2 and 3 to calculate A and B respectively
- For compounds with ring structure, follow steps 2 thro' 6

Step 2 : a) Calculate the total number of rings

- Use equations 8-10 to calculate N^* and N^{**} respectively

Step 3 : Analysis of ring configurations and calculation of their contributions to A and B

- Read ΔA_i and ΔB_i from table 2 for the rings
- Read θ_i and ϕ_i from table 3 for the rings
- Calculate $(\sum \Delta A_i \theta_i)_{\text{ring}}$ and $(\sum \Delta B_i \phi_i)_{\text{ring}}$ by multiplying the corresponding values of ΔA_i by θ_i as well as ΔB_i by ϕ_i and obtaining their respective sums

Step 4 : a) Calculate the number ($=n_i$) of each of the non-ring functional groups ($-\text{NH}_2$, $-\text{OH}$, biphenyl bridge, α -alkyl, N-alkyl and o-alkyl groups)

- Obtain the value of ΔA_i , ΔB_i for the non-ring groups from table 2
- Calculate $\sum \Delta A_i n_i^{\alpha_i}$ and $\sum \Delta B_i n_i^{\beta_i}$; $\alpha_i = 0.1$, $\beta_i = 0.5$ for -OH group and $\alpha_i = 1$, $\beta_i = 1$ for all other groups.

Step 5 : To calculate $(\Delta A)_{\text{alk}}$ and $(\Delta B)_{\text{alk}}$

- Calculate n_t = sum of all the ring carbon atoms and the alkyl carbon atoms in the molecule
- Calculate n_r = sum of all the ring carbon atoms and the α -alkyl carbons.
- Calculate $(A_{\text{par}})_{n_{\text{cent}}-3}$, $(A_{\text{par}})_{n_{\text{cent}}-3}$, $(B_{\text{par}})_{n_{\text{cent}}}$, $(B_{\text{par}})_{n_{\text{cent}}}$ using equations 2 and 3
- Calculate $(\Delta A)_{\text{alk}}$ and $(\Delta B)_{\text{alk}}$ using equations 4 and 5 respectively.

Step 6 : a) Calculate A and B using equations 6 and 7 respectively

- Calculate the dynamic viscosity η (in centipoise) of the compound at absolute temperature $T(^{\circ}\text{K})$ using equation 1.

Example:

Compound : 1-Butyl Naphthalene

Required to calculate viscosity at 50 °C

Step 1: Identify class of compound (= ring)

Step 2: Total number of rings = 2

Type of ring = aromatic

$$N^* = 2$$

$$N^{**} = 2 \quad (\text{From equations 8 - 10})$$

Step 3: Analysis of ring configurations and calculation of their contributions to A and B

From tables 2 and 3

ΔA_i	0.6122	0.6122
θ_i	0.3375	0.3375
ΔB_i	1000	1000
ϕ_i	1.06	1.06
$\Delta A_i \theta_i$	0.20661	0.20661
$\Delta B_i \phi_i$	1060	1060

$$\therefore (\Sigma \Delta A_i \theta_i)_{\text{ring}} = 0.41322 \quad (\Sigma \Delta B_i \phi_i)_{\text{ring}} = 2120$$

Step 4: Non-ring functional groups include only one α -alkyl group. Using Table 2,
 $n_i=1$, $\alpha_i = 1$, $\beta_i = 1$, $\therefore \Delta A_i = -0.015$, $\Delta B_i = 47$ (One α -alkyl group)

$$\Delta A_i n_i^{\alpha_i} = -0.015 \quad \Delta B_i n_i^{\beta_i} = 47$$

$$\therefore \Sigma \Delta A_i n_i^{\alpha_i} = -0.015 \quad \Sigma \Delta B_i n_i^{\beta_i} = 47$$

Step 5: To calculate $(\Delta A)_{\text{alk}}$ and $(\Delta B)_{\text{alk}}$

$$n_t = 14 \quad n_r = 11$$

Using equations 2,3,4 and 5,

$$(A_{\text{par}})_{\text{acut-3}} = -4.58642$$

$$(A_{\text{par}})_{\text{acut-3}} = -4.44094$$

$$(B_{\text{par}})_{\text{acut}} = 1612.09$$

$$(B_{\text{par}})_{\text{acut}} = 1400.32$$

$$\therefore (\Delta A)_{\text{alk}} = -0.14548$$

$$\therefore (\Delta B)_{\text{alk}} = 211.8$$

Step 6 : To calculate A and B

Using equations 6 and 7

$$\begin{aligned} A &= 10 [0.41322 (2)^{0.467} - 0.015 - 1] - 0.14548 \\ &= -4.58382 \end{aligned}$$

$$\begin{aligned} B &= 2120(2)^{-0.5} + 211.8 + 47 \\ &= 1757.8 \end{aligned}$$

Using equation 1

$$\therefore \eta \text{ at } 323.15^\circ\text{K} = e^{A+B/T} = 2.353 \text{ cp}$$

From literature, experimental value = 2.00 cp

$$\text{Error} = 17.68\%$$

Table 1
Comparison of the model with experimental data and other models from literature

Compound	no. pts.	Temp. range C	% error Our Model	% error Van Velzen	% error Przedziecki- Sridhar	Data References
Alkanes:						
Methane	10	-180 to -162	41.50	120.41	7.00	44
Ethane	16	-160 to -105	6.79	14.79	9.71	44
Propane	21	-73 to -40	6.58	11.24	21.08	44
n-Butane	9	-74 to 0.0	6.02	9.79	6.86	44
n-Pentane	28	-132 to 32	4.63	5.12	20.36	44
n-Hexane	62	-95 to 70	4.99	3.19	9.30	36,40,44
n-Heptane	64	-90 to 100	3.99	5.27	18.16	36,44,45
n-Octane	69	-55 to 125	2.56	2.46	18.49	36,44
n-Nonane	12	10 to 100	2.31	1.29	29.46	44
n-Decane	21	-33 to 100	3.99	5.43		44
n-Undecane	9	0 to 100	2.66	1.93	40.23	44
n-Dodecane	72	-10 to 215	2.80	2.81	38.14	36,44
n-Tridecane	7	10 to 100	2.82	2.15	47.97	44
n-Tetradecane	24	4.5 to 100	5.29	5.46	46.35	44
n-Hexadecane	52	0 to 250	3.63	3.44		44
n-Eikosane	3	100 to 210	66.49	67.13		44
n-Tetracosane	33	50 to 306	4.09	1.84		44
n-Pentatriacontane	28	80 to 306	22.59	26.77		44
n-Tritetrakontane	27	90 to 306	36.99	64.00		44
Average Error	567,567,403*		7.10	13.74	22.89	
Alkylbenzenes:						
Benzene	75	9 to 80	3.69	23.84	6.90	31,32,33,35,36,37 40,44,45,47
Toluene	67	-10 to 182.5	7.864	10.62	19.93	33,34,36,37,39,44
O-Xylene	50	-20 to 141.14	18.73	15.02	3.55	33,36,37,44
m-Xylene	40	0 to 135	2.58	5.63	2.58	33,36,37,44
p-Xylene	45	10 to 135.21	1.60	3.92	44.76	32,33,36,39,44
Ethylbenzene	42	0.28 to 132	15.41	2.93	22.66	33,36,37,39,44
Styrene	24	0 to 145	7.23	9.05	6.89	33,36
n-Propylbenzene	12	0 to 40	15.14	1.52	38.23	33,37,44
Isopropylbenzene (cumene)	20	0 to 80	7.23	5.69	31.02	33,36,37,44
p-Ethyltoluene	6	20 to 80	23.32	3.96	24.97	33,37,38
n-Butylbenzene	9	9.85 to 80	6.80	3.13	40.56	37,44
p-Diethylbenzene	2	25 to 60	16.62	12.52	15.20	33
1-Methyl 2-Propylbenzene	1	25	9.73	12.05	33.41	38
1-Methyl 4-Propylbenzene	2	30 to 40	14.28	7.94		37
1-Methyl 2-Isopropylbenzene	1	25	9.73	12.05	41.56	37
1-Methyl 4-Isopropylbenzene	1	30	14.05	22.68	29.45	37
m-Isopropyltoluene	4	25 to 80	13.09	6.81	39.15	38
1,3,5-Trimethylbenzene (mesitylene)	11	20 to 100	13.40		4.66	36,44
1,2,4-Trimethylbenzene	5	25 to 30	30.52		21.23	33,36,37,44
n-Hexylbenzene	5	-20 to 140	6.03	10.79		44
n-Nonylbenzene	4	0 to 150	6.64	9.83		44
1,2-Dimethyl 4-Heptylbenzene	4	50 to 150	34.47			44
n-Octadecylbenzene	4	50 to 150	6.53	6.26		44
1,4-Dimethyl 2-Decylbenzene	3	100 to 150	28.09			44
1,3,5-Trimethyl 2-Decylbenzene	4	50 to 150	47.53			44
1,4-Dinonylbenzene	4	50 to 150	18.36	4.59		44
1,2,4-Trihexylbenzene	4	50 to 150	29.35			44
1,2-Dimethyl-4-Hexadecylbenzene	3	100 to 150	33.22			44
Average error	454,420,417*		10.61	10.56	17.72	

Table 1(Cont'd)						
Compound	no. pts.	Temp.range C	% error Our Model	% error Van Velzen	% error Przedziecki- Sridhar	Data References
Fused/multi ring aromatics:						
Napthalene	16	80 to 100	0.65		20.70	33,36,37,44
1-Methyl Napthalene	61	5 to 230	17.00		10.09	33,34,36,37
2-Methyl Napthalene	22	20 to 230	2.35		9.38	33,34,36,37
2,3-Dimethylnapthalene	11	105 to 150	20.60			33,36
1-Butyl Napthalene	1	50	17.65			37
2,6-Dimethylnapthalene	11	112 to 160	13.63			33,36
Tetrafin	42	0 to 185	7.75		38.29	33,34,37,44
Chrysene	4	50 to 427	17.19			33,36
Anthracene	10	222 to 300	3.55			33,36
Fluorene	12	113 to 202	6.97			33,36
Phenanthrene	14	98 to 315	3.16			33,36
Fluoranthene	8	110 to 179	5.96			33,36
Acenaphthene	11	92 to 140	1.30			33,36
Indan	11	20 to 100	12.56		38.08	33,36,37,44
Pyrene	10	152 to 233	1.34			33,36
Biphenyl	22	70 to 256	11.08	1.52	2.46	33,37,44
cis-Decalin	30	-30 to 180	45.89		71.13	33,44
Trans-Decalin	30	-30 to 180	20.67		53.69	33,44
Average error	326,22,234*		13.82	1.52	29.82	
Cyclopentanes:						
Cyclopentane	19	0 to 50	1.49	32.13	33.05	33,37,44
Methylcyclopentane	15	0 to 80	11.68	22.29	42.48	33,37,44
Ethylcyclopentane	4	5 to 70	15.68	20.35	45.31	37,38
n-Propylcyclopentane	16	-20 to 100	7.69	6.38	39.68	38,44
n-Butylcyclopentane	10	15 to 100	14.32	10.59		38,47
n-Pentylcyclopentane	3	-20 to 40	22.23	19.68		38
n-Hexylcyclopentane	4	-20 to 40	25.61	20.50		38
1,2-Dimethylcyclopentane (cis)	2	15 to 30	37.63	30.66	37.99	37
1,2-Dimethylcyclopentane(trans)	2	15 to 30	15.12	5.63	37.30	37
1,3-Dimethylcyclopentane	2	5 to 30	7.34	2.69		37
Average error	77,77,58*		10.67	18.87	38.48	
Cyclohexanes:						
Cyclohexane	61	0 to 83.7	15.08	34.06	24.28	32,33,36,37,44,45,46,47
Methylcyclohexane	53	-25 to 100	11.05	8.14	46.60	33,36,37,44
Ethylcyclohexane	25	0 to 100	14.97	2.15	46.83	37,44,47
1,1-Dimethylcyclohexane	7	15 to 50	11.98	13.97	37.85	33,37
1,2-Dimethylcyclohexane(cis)	2	15 to 30	23.82	23.42	52.00	37
1,2-Dimethylcyclohexane(trans)	2	15 to 30	2.98	3.47	47.59	37
1,3-Dimethylcyclohexane(cis)	12	0 to 40	4.02	3.34	51.64	33,44
1,3-Dimethylcyclohexane(trans)	12	0 to 40	32.15	31.35	30.34	33,44
1,4-Dimethylcyclohexane(cis)	12	0 to 40	4.76	5.15	38.33	33,44
1,4-Dimethylcyclohexane(trans)	9	0 to 40	18.17	17.78	40.22	33,44
n-Propylcyclohexane	18	0 to -110	20.64	4.86	59.00	33,44
n-Butylcyclohexane	8	0 to 100	17.42	3.60		33,44
Isobutylcyclohexane	5	0 to 100	18.94	7.33		44
Isopropylcyclohexane	3	0 to 40	17.40	4.65		44
1,1,3-Trimethylcyclohexane	3	0 to 40	5.95	20.07		44
n-Nonylcyclohexane	4	50 to 150	17.61	41.41		44
1,4-Dihexylcyclohexane	4	50 to 150	30.78	10.24		44
1,4-Dimethyl-2-Decylcyclohexane	4	50 to 150	38.97	5.92		44
1,3,5-Trimethyl-2-Decylcyclohexane	4	50 to 150	49.70	8.54		44
n-Octadecylcyclohexane	5	80 to 150	26.01	14.77		44
Average error	253,253,213*		15.92	15.49	39.69	

Table 1(Cont'd)						
Compound	no. pts.	Temp. range C	% error Our Model	% error Van Velzen	% error Przedziecki-Sridhar	Data References
Phenols:						
Phenol	45	45 to 183	7.38	14.37	44.77	33,34,36,38,44
o-Cresol	34	25 to 190	14.07	23.95	40.97	33,36,38,41,44
m-Cresol	32	25 to 199.7	21.22	30.07	55.72	33,36,38,41,44
p-Cresol	25	40 to 199.7	24.64	36.85	52.45	33,36,44
2,5-Xylenol	16	80 to 200	10.59	36.15	6.41	33,38,42
3,4-Xylenol	16	80 to 200	39.95	60.58	37.94	33,42,38
3,5-Xylenol	16	75 to 200	26.74	52.04		33,42,38
Resorcinol (m-Dihydroxybenzene)	25	131 to 276	30.72	89.60		33,36,44
o-Dihydroxybenzene	11	121 to 245	32.30	64.80		44
1-Naphthol	12	95 to 140	8.14			44
Guaiaacol	3	30 to 184	5.87	169.52		33
Average error	235,223,168*		19.49	41.19	42.93	
Amines:						
Aniline	64	-5 to 184.45	10.49	17.51	53.57	33,36,44
o-Toluidine	35	15 to 198.7	7.83	18.12		33,36,38,44
m-Toluidine	39	0 to 198.7	12.79	9.83		33,36,38,44
p-Toluidine	30	39.2 to 200	12.86	7.77		33,36,44
p-Ethylaniline	3	20 to 60	37.90	9.48		38
p-Butylaniline	13	20 to 239.5	62.57	11.09		38,44
N-ethylaniline	3	0 to 70	8.72	15.33		44
Average error	187,187,64*		14.88	13.85	53.57	
Pyridines:						
Pyridine	31	0 to 110	6.13		35.76	36,44
2,4-Lutidine	4	20 to 60	7.47			33,36
2,6-Lutidine	5	20 to 60	6.22			33,36
Lepidine	3	20 to 60	22.13			36
Quinoline	33	0 to 190	8.22			33,34,36,44
Isoquinoline	27	20 to 200	6.29			33,36,44
2-Picoline	23	0 to 80	22.58		37.80	36,44
Quinaldine	3	20 to 60	8.39			36
2-Methyquinoline	1	20	4.04			33
4-Methyquinoline	1	20	34.49			33
6-Methyquinoline	1	20	7.51			33
8-Methyquinoline	1	20	7.93			33
3-Picoline	8	0 to 80	10.51			34
Average error	141,0,54*		10.22	0	36.63	
Thiophenes:						
Thiophene	24	0 to 82.53	0.96			33,35,44,47
Thionaphthene	2	35 to 40	7.54			36
3-Methylthiophene	8	0 to 30	3.05			33,38,44
2-Methylthiophene	3	20 to 25	6.84			33
Average error	37,0,24*		2.25	0	10.81	
Other ring compounds						
Furan	11	0 to 40	0.09		31.72	43,47
Tetrahydrofuran	42	-70 to 100	1.35		33.92	43,44
Cyclopentane	5	13 to 30	9.88			33,37,44
Pyrrole	25	-20 to 70	3.30			33,36,44
Cyclohexene	13	13 to 60	3.10			33,37,44
Phenyl ether	24	30 to 210	15.35	55.45		33,34
Average error	120,24,53		4.99	55.45	33.46	
Overall average error	2397,1773,1688*		11.55	17.34	28.99	

Table 2
Primary Groups And Their Contributions

Groups		ΔA	ΔB
benzene	0.6122	1000
cyclohexane	0.4903	1435
cyclohexene	0.5684	1140
pyridene	0.6100	1140
cyclopentane	0.5934	965
thiophene	0.5934	1068
cyclopentene	0.4772	1240
tetrahydrofuran	0.6203	900
furan	0.5962	900
pyrrole	0.4618	1675
biphenyl bridge	-0.841	400
hydroxyl	-0.2756	1541
amine	-0.1622	1030
α -alkyl	-0.0150	47
N-alkyl	-0.0696	0.0
o-alkyl	0.10023	-966

attached to a ring
attached to nitrogen
attached to oxygen

Table 3

Group Multipliers θ_i and ϕ_i for Various Ring Configurations [†]

Sub-Group	Multipliers for $\Delta A, \theta_i$	Multipliers for $\Delta B, \phi_i$
1.000	1.00
0.3375	1.06
-0.0666	0.76
-0.1413	1.23
0.1746	1.15
0.0309	1.365
-0.229	1.40
-0.563	1.59
0.00	1.80

[†] These multipliers are common to all the different types of rings in the same configuration (See Table 2)

Figure Caption

1. Comparison of liquid viscosity data of alkanes and alkybenzenes. Alkanes in increasing order of slopes are n-butane, n-hexane, n-heptane, n-nonane, and n-dodecane. Alkylbenzenes in increasing order of slopes are toluene, n-propylbenzene and n-hexylbenzene.

2. Application of the Model to Coal Liquid Fractions

Viscosity of Coal Derived Liquids

2. Application of the Model to Coal Liquid Fractions

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ABSTRACT

The group contribution viscosity model for pure coal model liquids described in reference 1 has been successfully extended to binary liquid mixtures of coal model compounds, and a procedure has been developed to use the model for computation of viscosities of coal derived liquids. It is shown that simple mixing rules, or even a pseudo-pure component model are adequate to estimate mixture viscosity within reasonable accuracy for these compounds. For application of the model to coal derived liquids, a data set on SRC-II coal liquid cuts available in the literature has been used. Sufficient chemical analysis data were available for these cuts to make the application of our model possible. The computational procedure involved transformation of the analytical data into functional group characterization of the coal liquid. Central to this procedure was the definition of types and distributions of various ring structures in multi-ring compounds. When compared to limited studies available in the literature, this model predicts viscosities of coal liquids with better accuracy. Overall, this is the first viscosity model that has been developed for the type of structures that exist in coal derived liquids, and provides a reasonably accurate procedure for computation of viscosities of narrow boiling coal liquid cuts, a property that is necessary in designing efficient coal liquefaction processes.

Introduction

The objective of this work was to develop a correlation for the viscosity of coal liquids characterized by atomic and molecular compositions which are easily measurable by available analytical techniques. In the first paper (reference 1), a group contribution method for viscosity of pure aromatic hydrocarbons was presented. Groups were defined to include maximum number of structures that occur in coal derived liquids.

The next step is to extend this correlation to mixtures using suitable mixing rules. It was with this purpose in view that a binary viscosity databank (2213 data points, 66 binary systems) was compiled. If sufficiently accurate mixing rules are obtained for binary mixtures of coal liquid model compounds, efforts could be made to extend the model to compute viscosities of coal derived liquids.

Almost all the models for mixture viscosities available in the literature involve first obtaining the pure component viscosities and then computing the mixture viscosity using a mixing rule. Two mixing rules which have found most extensive usage are the Kendall-Monroe mixing rule² (equation 1) and the Grunberg-Nissan mixing rule³ (equation 2).

$$\eta_m = \left(\sum x_i \eta_i^{1/3} \right)^3 \quad (1)$$

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \sum_{i \neq j} x_i x_j G_{ij} \quad (2)$$

The Kendall-Monroe mixing rule is purely empirical and is found to work well for most simple liquid mixtures. The binary interaction parameter G_{ij} in the Grunberg-Nissan mix-

ing rule, on the other hand, has some physical basis in that it is supposed to be proportional to W/RT , where W is the interchange energy arising from the fact that, although the molecules of the two components of a regular solution are interchangeable as far as size and shape are concerned, there is an increase in the lattice energy equal to $2W$ when a molecule of component i is introduced into the lattice of component j .

It appears from a study of the literature on binary liquid viscosities that no other single model for mixture viscosity has been more extensively tested than the Grunberg and Nissan method. The method was applied to various liquid mixtures by various researchers. The mixtures tested included benzene, cyclohexane, cis-decalin, trans-decalin, toluene, p-Xylene, n-alkanes, halogenated benzenes, etc. among other compounds, and binary parameters G_{ij} are available for these compounds. Furthermore, Isdale et al.⁴ have proposed a group contribution method to estimate the binary interaction parameter at 298 K. The group contributions for typical hydrocarbon groups are available.^{4,5} However, these groups do not include a number of structures characteristic of coal derived liquids, such as, multi-ring structures, pyridines, thiophenes, etc. Furthermore, G_{ij} is found in a number of cases to be a function of both concentration and temperature. For application of the Grunberg-Nissan mixing rule to mixtures of coal model compounds, it would be necessary to develop binary interaction parameters for a number of additional groups, and also determine the temperature dependence of these parameters. Such a development would require considerably more data than what is currently available in the literature, and hence was not attempted.

In addition to the Kendall-Monroe mixing rule, two other methods were attempted. The first one is the quadratic mean mixing rule (equation 3) which has been very successful in relating liquid and vapor mixture thermodynamic properties to pure components using cubic equations of state. The quadratic mean mixing rule can be further extended by incorporating a binary interaction parameter k_{ij} . Such a development would require a large amount of data, and the process would be similar to development of G_{ij} of the Grunberg-Nissan method. This was, therefore, not attempted.

$$\eta_M = \sum \sum x_i x_j (\eta_i \eta_j)^{1/2} \quad (3)$$

The other method evaluated here, involves treating the mixture as a pseudo pure component. In this approach, the constants A and B for the pure components are calculated using our pure component model (reference 1), the constants A and B for the mixture are then obtained as a sum of the component A's and B's weighted by the mole fractions of the components, and finally viscosity is calculated from the Andrade equation on which our model is based.

$$\ln(\eta_M) = A_M + B_M/T \quad (4)$$

$$A_M = \sum A_i x_i \quad (5)$$

$$B_M = \sum B_i x_i \quad (6)$$

The application of the model for computation of viscosity of coal derived liquid is a two step process. The first step involves using the measured analytical data on coal liquid to obtain as much information as possible on the types and amounts of components and functionalities present in the liquid, the second step then uses this information to generate

parameters in our pure and mixture models to compute the viscosity of the coal derived liquid. A data set that allows us to test this approach, is fortunately available in the literature.⁶ Very few studies attempting to estimate viscosities of coal derived liquids are available in the literature.^{7,8} Two of the methods that have been used include a liquid viscosity correlation developed for petroleum fractions by Abbott et al,⁹ and a pseudo-component corresponding states correlation originally developed by Abbott and Kaufmann.¹⁰ Both these methods suffer from the limitation that they do not relate viscosity to the multi-ring structures and heteroatom functionalities so characteristic of coal derived liquids, unlike our model which is specifically developed for coal liquids. In what follows, we discuss the results for defined binary mixtures and next for coal derived liquids.

Comparison of Mixing Rules for Binary Systems

A databank of binary viscosities of coal model compounds was compiled. The binary systems and the literature sources are listed in Table 1. It is observed that the data set is limited especially with respect to systems containing multi-ring (four and higher) aromatics and lack of high temperature data. Table 1 also gives the results of comparison of various mixing rules with experimental data. These errors (and others in this work) are presented as percent average absolute deviations (AAD) defined as absolute deviation of the calculated value from the experimental data normalized by the experimental value. The two columns corresponding to each of the two mixing rules, Kendall- Monroe and

quadratic mean, correspond to using experimental values for the pure component viscosities and pure component viscosities calculated from our model (reference 1). The first column for each of the mixing rules, therefore, represents a true test of the accuracy of the mixing rule. The two mixing rules are very comparable with the Kendall-Monroe somewhat better giving an average percent error of 11.72. This is an excellent result considering that significant amount of viscosity data is reported to have uncertainties in the range of 5 to 10 %. Using our model to compute viscosities of pur components increases the errors by a few percent to 19.31% and 19.39% for the two mixing rules. Even so, these results are quite satisfactory and indicate that development of more sophisticated model for these mixtures is not warranted. The pseudo pure component method discussed before was also evaluated. Overall percent AAD of 19.76 shows that even this method is quite acceptable to calculate viscosities of coal model compound mixtures. In fact, this is the method we have used in our computation of viscosity of coal derived liquids as will be seen in the next section. The general conclusion of this study is that both the mixing rules evaluated here as well as the pseudo pure component method are quite acceptable to attempt extending the viscosity model for computation of viscosities of coal derived liquids.

Application to Coal Derived Liquids

For extension of our model to compute viscosities of coal derived liquids, data would be necessary that would allow representation of the coal liquid by average molecules of known functional groups. The analytical data that would be necessary may be listed as: average molecular weight or molecular weight distribution; C,H,N,O,S elemental

analysis; distribution by mass of hydrocarbon types, i.e. saturates, aromatics, olefins, etc.; in high molecular weight liquids, distribution of various types of ring structures; functionality types and distribution of various functionalities containing heteroatoms. Two viscosity data sets are currently available in the literature. Hwang et al.⁷ made extensive measurements over a range of temperatures and pressures on liquids produced with the Exxon Donor Solvent (EDS) process from Illinois and Wyoming coals. The second data set is of Gray et al.⁶ who made viscosity measurements on SRC-II liquids over a range of temperatures but at relatively low pressures. For the EDS liquids, sufficient amount of analytical data are not available in the literature, hence application of our model to these liquids was not possible. On the other hand, Gray et al.⁶ have reported average molecular weights, elemental analysis, and relative composition of saturates, aromatics and olefins, amongst other properties. These data are sufficient to allow computation of viscosities of these liquids using our model. However, in a number of areas the data were not detailed enough, thereby requiring a number of assumptions to convert the quantitative data into parameters necessary in our model. These assumptions are listed below:

1. For each SRC-II cut, only the average molecular weight is available. In the absence of a measured molecular weight distribution, two approaches were possible. First one would involve assuming a molecular weight distribution and using the method of Gaussian quadratures to approximate the distribution by a number of discrete components. The viscosity calculation would then reduce to that of a known multi-component mixture. This approach would be analogous to the continuous thermodynamics approach¹¹ that has been applied for thermodynamic property compu-

tation of Wilsonville and H-Coal liquids.¹² The second and a lot simpler approach is to consider each SRC-II cut to be a pseudopure component represented by an average molecule with the known molecular weight. It was shown in the last section that the pseudo pure component method works almost as well as the simple mixing rules for the coal model compound binary mixtures. This method was therefore selected.

2. The hydrocarbon saturates were assumed to be paraffins and naphthenes (cyclohexanes) in the ratio of 1.5:1 by mass. Although, this is an arbitrary choice, it was necessary to quantify the group composition of the coal liquid, and a sensitivity analysis showed that the final results are not very sensitive to the exact magnitude of this ratio.
3. All nitrogen was assumed to be in pyridines, all sulfur in thiophenes and all oxygen in phenols and alcohols. Although no direct data on these liquids are available to justify this, White et al.¹² observed this to be true for similar coal derived liquids.
4. For higher molecular weight coal liquids, which are largely made of multi-ring structures, The distribution of various types of ring structures is necessary for computation of viscosity. It was clearly observed from the analysis of viscosity data of pure aromatic hydrocarbons¹ that even for compounds of similar molecular weights viscosity is very sensitive to the different types of fused ring structures in multi-ring compounds. Some of the possible structures in three to five ring aromatics are listed below:

Three-ring: anthracene, phenanthrene

Four-ring: naphthacene, benzanthracene, chrysene, pyrene, triphenylene

Five-ring: pentacene, benzo-pyrene, perylene, dibenzanthracene (various isomers)

Data on distribution of such structures are not available for the SRC-II cuts, and moreover such data are not easily measured. Some assumption therefore was needed to quantify the group composition of the coal liquids. In each ring category, all configurations were considered equally probable. Based on this, some rounded-off numbers representing distribution of various types of fused rings in each ring category were obtained. These are listed in Table 2. These numbers allow conversion of data on composition of one, two three, four and five ring aromatics in the liquid to corresponding composition of the fused aromatic groups necessary in the computation of the model parameters.

Using the available analytical data and with the above assumptions, the following stepwise procedure was devised to compute the viscosities of the SRC-II cuts.

Step 1: Use the elemental analysis, the composition of aromatics, the composition of saturates, and assumptions 2 and 3 above to calculate the mass of aromatic, paraffin, naphthene (cyclohexane), pyridine, thiophene and hydroxyl groups in one mole of the liquid. For this calculation, pyridine and thiophene are considered to be C_5H_5N and C_4H_4S respectively. The results of this calculation for all 15 SRC-II cuts are listed in Table 3.

Step 2: Assuming each ring structure to consist of a single ring and using molecular weights of 78, 84, 79 and 84 for aromatic, cyclohexane, pyridine and thiophene

respectively, calculate the number of each ring per mole of the liquid. Sum all the rings. If the sum is less than one, the liquid must be treated as a mixture of ring compounds and paraffin (our model equations are not valid when N^* or N^{**} is less than one, see reference 1). This is the case for SRC-II cuts 1 through 4. Proceed to step 3a. If the sum is greater than one, proceed to step 3b.

Step 3a: For this case the coal liquid is defined as a mixture of two components each with its average molecule consisting of the functional groups as defined in our model. The first component is made of single ring compounds with α -alkyl groups ($-\text{CH}_2$) added so that the molecular weight of each of the ring compounds is equivalent to that of the coal liquid. The average molecule is made of fractional aromatic, cyclohexane, pyridine and thiophene rings and α -alkyl groups, normalized so that the molecular weight is equal to that of that cut. This procedure results in the sum of all the rings to be exactly equal to one. All the remaining paraffinic groups and the hydroxyl groups then are considered to constitute the second component. Again these are normalized so that the molecular weight of this average molecule is equal to that of the coal liquid. The mole fractions of the two components and the group compositions of the average molecules are listed in Table 4.

Step 4a: For each cut, calculate A and B for each component using our pure component model (reference 1), and then obtain A_M and B_M from equations 5 and 6. For cuts 1 through 4, A_M and B_M are listed in Table 6. Viscosity of the liquid (in centipoise or milliPascal-seconds) is then given by equation 4.

Step 3b: For cuts 5 through 16, each SRC-II cut is considered a pseudo pure component

defined by a single average molecule. Following is the procedure used to determine the group composition of the average molecule. For each cut, the ring components i.e. aromatic, naphthene (cyclohexane), pyridine and thiophene are considered mixtures of compounds made of n and $(n+1)$ fused rings, where $n=1$, for cuts 5,6,7; $n=2$ for cuts 8,9,10; $n=3$, for cuts 11,15; and $n=4$, for cuts 12,13,16. The ratios of the four types of rings relative to each other are determined using the molecular weight of a single unfused ring of each type and the mass compositions of Table 3. If M_A is the aromatic mass per mole of the SRC-II cut (from Table 3), X_A is the fraction of the total number of rings that are aromatic, W_n and W_{n+1} are the molecular weights of the average fused ring aromatic compounds with n and $(n+1)$ rings respectively (these are calculated from the group compositions of Table 2), then N_n which represents the molar composition of the aromatic compound with n fused rings in one mole of the average molecule, is given by the following mass balance:

$$N_n W_n + (X_A - N_n) W_{n+1} = M_A \quad (7)$$

$(X_A - N_n)$ gives the molar composition of the compound with $(n+1)$ fused rings. The molar compositions of n and $(n+1)$ ring fused aromatics are then converted to the compositions of various types of fused aromatic rings using the group distribution information of Table 2. This calculation is repeated for naphthenes (cyclohexanes), pyridines and thiophenes. Table 5 gives the molar group compositions (per mole of the liquid) of the average molecules of the SRC-II cuts 5 through 16. To save space, only the molar compositions of the n and $(n+1)$ fused ring comp-

onents are reported. The group compositions corresponding to these can be easily calculated using Table 2.

Step 4b: From the group distributions of the average molecules (Table 5), use the model (procedure described in reference 1) to compute A_M and B_M . These values for cuts 5 through 16 are listed in Table 6. Viscosity of these liquids can then be calculated from equation 4.

Results and Discussion

Viscosities of the fifteen SRC-II cuts were calculated at the temperatures of experimental measurements of Gray et al.⁶ and percent absolute average deviations (AAD) and biases for each cut were determined. These are listed in Table 6. An overall result of 25 % AAD for the 15 cuts ranging in molecular weights from 85 to 243, represents good agreement between the model and the experimental data. An overall bias of +12.79% shows that the model does not consistently overpredict or underpredict the data. It was observed that the model results are very sensitive to the molecular weights of the cuts used in the calculations. Uncertainties in the molecular weights reported by Gray et al.⁶ may be responsible for extreme biases observed for some of the cuts. To further investigate the temperature dependence of viscosity as predicted by the model with experimental data, Figure 1 shows plots of natural logarithm of viscosity versus reciprocal temperature for five cuts 2,5,9,11 and 16 varying in molecular weight from 95 to 243. Model results obviously show straight lines, the experimental data on the other hand is more or less linear at lower molecular weights, but exhibits increasing nonlinearity as molecular weight

increases. Data for cuts 11 and 16 are very nonlinear and not much improvement of model results is possible even if one obtains the best fit lines by least squares regression. Such distinct nonlinearity was not observed in pure component viscosity data.¹ Whether this is an artefact of treating a complex multi-component mixture such as a coal liquid as a pseudo pure component, or this is because of multiple phases that exist in high molecular weight coal liquids¹³ needs to be further investigated.

Tsonopoulos et al.⁸ have computed viscosities of these same 15 SRC-II cuts using two different methods: the petroleum fraction correlation of Abbott et al.⁹ and the defined compound correlation originally developed by Abbott and Kaufmann¹⁰ which is a pseudo-component corresponding states correlation. The AAD and biases for these two methods are also given in Table 6. The results indicate that our model is definitely superior to the other two. Whereas the "petroleum"-fraction correlation works well for the low molecular weight cuts, it totally falls apart for the very high molecular weight cuts 11 to 16. In contrast, no such trend with molecular weight is observed for the defined compound correlation, which gave an overall percent AAD of 34.30; but average bias of -34.30% indicates consistent underprediction for this method. The reason for this is not quite clear. The above two methods are based on characterization parameters, such as, mid boiling point, specific gravity, critical properties and acentric factor. For complex mixtures such as coal derived liquids, the critical properties and acentric factors are not well defined, and they have to be estimated from molecular structures or from other parameters like refractive index, specific gravity, boiling point, etc. Even the best estimation procedures can result in considerable errors for all these properties, but especially in prediction of acentric

factors.¹⁴ That our model which is based on molecular structures like the ones that occur in coal liquids should perform better than these two methods, is therefore not surprising. Nevertheless, further studies are necessary to investigate the nonlinear behavior of the $\ln(\eta)$ versus $(1/T)$ curve for high molecular weight coal liquids.

In summary, the viscosity model for pure coal liquid model compounds has been successfully extended to mixtures of model compounds, and then applied for computation of viscosities of SRC-II coal liquid cuts. Simple mixing rules or even pseudo pure component approaches seem to be adequate to predict the liquid mixture viscosities from pure component values. Application of the model for viscosity computation of SRC-II cuts was in most part successful, other than the unexplained nonlinear behavior of $\ln(\eta)$ with $(1/T)$ for high molecular weight coal liquids.

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Table 1
Evaluation of Mixing Rules Using Experimental Binary
Liquid Viscosity Data

SYSTEM	No. Pts.	Temp range	Pseudo-pure component method	Kendall - Monroe	Quadratic	Literature Sources
Benzene	85	12 to 70	5.14	3.96	5.13	24
Toluene						
Benzene	72	20 to 70	10.68	1.49	10.78	1.49 10.84 24
Ethylbenzene						
Benzene	59	0 to 80	9.29	2.50	9.28	2.56 9.28 18,24
o-Xylene						
Benzene	58	10 to 80	2.49	1.22	2.49	1.22 2.49 16,18,24
p-Xylene						
Benzene	42	10 to 70	10.76	0.70	11.10	0.71 11.28 24
Cumene						
Benzene	153	10 to 120	6.64	11.04	6.71	11.25 6.76 15,19,24,25
Cyclohexane						
Benzene	6	25	5.19	2.72	2.48	4.35 2.65 24
Tetralin						
Benzene	5	25	11.19	8.69	9.19	10.73 8.97 24
Decalin						
Benzene	56	20 to 60	3.74	1.12	2.78	0.60 2.75 24
Naphthalene						
Benzene	9	20 to 60	3.04	0.88	3.32	0.99 3.50 24
Phenanthrene						
Benzene	18	15 to 25	23.57	67.93	45.20	88.73 59.57 24
Phenol						
Benzene	11	20	2.40	0.28	2.39	0.28 2.39 24
Thiophene						
Benzene	4	25	11.39	2.46	7.16	0.90 4.69 24
Biphenyl						
Benzene	14	25 to 30	10.10	4.04	6.08	1.87 4.38 24
Biphenylmethane						
Benzene	11	30	13.52	28.53	26.73	35.83 33.85 24
Guaiacol						
Toluene	84	-20 to 80	12.99	6.56	12.17	6.56 12.25 20,24
Ethylbenzene						
Toluene	66	-20 to 80	8.69	1.22	8.68	1.33 8.68 24
o-Xylene						
Toluene	32	10 to 80	3.60	0.67	3.59	0.67 3.59 24
p-Xylene						
Toluene	55	-20 to 80	16.45	0.54	17.02	0.50 17.31 24
Cumene						
Toluene	34	12 to 50	4.78	6.53	4.89	6.87 4.94 24
Cyclohexane						
Toluene	43	25 to 95	3.64	5.97	6.66	8.38 8.33 17
Tetralin						
Toluene	34	20 to 60	12.29	10.04	10.31	8.85 9.24 24
Naphthalene						
Toluene	9	20 to 60	6.78	1.14	8.30	2.02 9.44 24
Phenanthrene						
Toluene	4	25	4.45	2.19	4.85	6.22 7.85 24
Biphenyl						
Toluene	11	30	19.96	31.78	33.94	39.86 41.47 24
Guaiacol						
Cyclohexane	5	25	48.18	4.59	41.07	5.49 37.25 24
Tetralin						

Table 1 (cont'd)							
SYSTEM	No. Pts.	Temp range C	Pseudo-pure component method	Kendall - Monroe Exp. Pure Model Pure	Quadratic Mixing rule Exp. Pure Model Pure	Literature Sources	
Cyclohexane Decalin	6	25	63.09	0.43 58.95	0.64 56.71	24	
Cyclohexane Biphenylmethane	4	25	46.96	3.89 38.56	5.15 34.08	24	
n-Hexane Cyclohexane	20	25 to 100	5.51	14.01 5.92	14.23 6.39	21	
n-Hexane Methylcyclohexane	5	25	13.62	9.97 15.83	10.79 16.95	18	
n-Hexane O-xylene	5	25	4.58	9.46 4.27	11.04 4.50	18	
n-Hexane p-Xylene	5	25	5.74	6.57 7.48	7.46 8.35	18	
n-Octane Ethylbenzene	24	35 to 40	14.75	3.07 14.51	3.07 14.38	26	
Phenol m-Cresol	13	25	36.29	3.23 36.28	3.45 36.28	23	
Phenol o-Cresol	13	25	21.03	0.99 21.02	0.96 21.02	23	
Phenol p-Cresol	9	25	39.86	2.69 39.85	3.02 39.85	23	
o-Cresol m-Cresol	10	25	32.35	2.08 32.35	2.51 32.35	22	
o-Cresol p-Cresol	10	25	35.39	1.78 35.38	2.37 35.38	22	
m-Cresol p-Cresol	14	25	52.07	0.79 52.06	0.80 52.06	22	
Phenol Pyridine	180	10 to 110	17.38	12.96 14.81	14.28 14.85	23,24	
Phenol Quinoline	112	5 to 175	33.40	29.59 33.13	29.21 33.00	24	
o-Cresol Pyridine	88	0 to 110	24.75	18.78 20.64	20.03 19.93	24	
m-Cresol Pyridine	84	0 to 110	33.58	23.89 28.16	34.12 26.44	24	
p-Cresol Pyridine	84	0 to 110	35.98	27.59 29.82	41.30 27.69	24	
Phenol Aniline	84	20 to 125	20.20	18.23 19.89	17.87 19.73	23,24	
Phenol p-Toluidine	90	30 to 175	17.42	15.79 17.24	15.56 17.16	24	
Phenol α -Naphthylamine	10	30 to 50	29.98	17.86 27.64	15.87 26.61	24	
Phenol Biphenylamine	56	30 to 80	18.11	1.87 19.34	2.26 20.07	24	
Phenol Biphenylmethylaniline	68	10 to 80	66.87	5.88 69.36	6.03 70.61	24	
m-Cresol Aniline	8	25	42.51	17.68 42.01	16.05 41.75	24	
p-Cresol Aniline	13	25	34.51	42.51 34.13	40.94 33.95	24	
m-Cresol m-Toluidine	6	25	44.82	20.97 44.44	19.69 44.25	24	
Pyridine Aniline	4	0 to 110	14.48	14.20 16.48	18.83 17.48	24	

Table 1 (cont'd)							
SYSTEM	No. Pts.	Temp range C	Pseudo-pure component method	Kendall - Monroe Exp. Model Pure Pure	Quadratic Mixing rule Exp. Model Pure Pure	Literature Sources	
Pyridine Ethylaniline	27	0 to 70	14.57	9.73 13.58	9.00 13.08	24	
Quinoline N-ethylaniline	33	0 to 70	19.77	15.74 19.67	15.46 19.68	24	
Biphenyl Biphenylether	48	18 to 350	19.33	6.63 19.33	6.63 19.33	24	
Aniline Biphenylamine	22	60 to 90	85.72	5.77 92.11	6.73 95.37	24	
Quinoline Biphenylamine	22	60 to 90	44.99	15.04 14.51	14.54 43.93	24	
Pyridine Guaiacol	13	30	33.19	61.41 29.15	61.44 27.16	24	
Aniline Guaiacol	14	30	17.94	18.85 17.76	18.69 17.68	24	
Quinoline Guaiacol	16	30	46.86	47.05 46.76	46.97 46.71	24	
Guaiacol o-Toluidine	13	30	16.30	16.79 16.14	16.66 16.06	24	
Total	2213		19.76	11.72 19.31	13.04 19.39		

Table 2

Types and distribution of rings in multi-ring structures

<u>Structure</u>	<u>One-ring</u>	<u>Two-ring</u>	<u>Three-ring</u>	<u>Four-ring</u>	<u>Five-ring</u>
1
2	2	1.6	1.3
0.5	0.4	0.6
0.5	0.4	0.6
0.8	1.5
0.4	0.6
0.2	0.1
0.2	0.1
0.2

Table 3 Composition by Mass of an Average Molecule of SRC-II Coal Liquid Fractions							
SRC-II cut	Mol. wt.	Aromatic	Naphthene	Paraffin	Pyridine	Thiophene	Hydroxyl
1	85	5.94	30.27	45.40	2.63	0.15	0.61
2	95	14.25	31.57	47.37	1.28	0.20	0.33
3	108	22.68	33.26	49.86	1.64	0.28	0.28
4	114	36.37	30.56	45.83	0.70	0.44	0.10
5	124	55.45	23.31	34.97	2.52	1.56	6.19
6	128	90.67	9.21	13.82	5.93	0.22	8.15
7	138	103.63	8.28	12.42	5.60	0.47	7.60
8	158	125.22	6.32	9.48	10.41	1.27	5.30
9	156	130.38	5.62	8.42	7.50	0.85	3.23
10	166	141.70	5.31	7.97	7.13	0.75	3.14
11	222	186.94	6.21	9.33	13.78	1.99	3.75
12	246	209.08	5.90	8.86	15.70	1.55	4.91
13	243	207.81	5.84	8.75	17.55	2.35	0.70
15	213	177.55	5.11	7.67	15.73	2.62	4.32
16	243	199.95	6.80	10.21	19.05	2.31	4.68

Table 4 Group Composition of SRC-II Cuts 1 to 4				
	Cut1	Cut 2	Cut 3	Cut 4
Component 1:				
Mole fraction	0.472	0.577	0.711	0.844
Benzene	0.1616	0.3165	0.4092	0.5523
Cyclohexane	0.7640	0.6512	0.5570	0.4309
Pyridine	0.0706	0.0281	0.0292	0.0105
Thiophene	0.0038	0.0041	0.0047	0.0063
α -CH ₂	0.1658	0.9314	1.9001	2.3833
Component 2:				
Mole fraction	0.528	0.423	0.289	0.156
Paraffin(CH ₂)	5.9896	6.7298	7.6457	8.0988
-OH	0.0674	0.0461	0.0567	0.0395

Table 5										
Group Composition of SRC-II Cuts 5 to 16										
Cut No.	Paraffin (-CH ₂)	Hydroxyl (-OH)	Aromatic No. of Rings & Molar Composition		Cyclohexane No. of Rings & Molar Composition		Pyridine No. of Rings & Molar Composition		Thiophene No. of Rings & Molar Composition	
5	2.4977	0.3643	1-ring 0.6430	2-ring 0.0413	1-ring 0.2509	2-ring 0.0162	1-ring 0.0288	2-ring 0.0019	1-ring 0.0168	2-ring 0.0011
6	0.9871	0.4794	1-ring 0.3913	2-ring 0.4699	1-ring 0.0370	2-ring 0.0442	1-ring 0.0254	2-ring 0.0302	1-ring 0.0010	2-ring 0.0011
7	0.8871	0.4471	1-ring 0.1893	2-ring 0.6943	1-ring 0.0143	2-ring 0.0513	1-ring 0.0102	2-ring 0.0369	1-ring 0.0008	2-ring 0.0029
8	0.6772	0.3120	2-ring 0.6234	3-ring 0.2551	2-ring 0.0295	3-ring 0.0117	2-ring 0.0517	3-ring 0.0204	2-ring 0.0060	3-ring 0.0022
9	0.6017	0.1901	2-ring 0.6205	3-ring 0.2862	2-ring 0.0251	3-ring 0.0112	2-ring 0.0358	3-ring 0.0157	2-ring 0.0040	3-ring 0.0015
10	0.5691	0.1849	2-ring 0.4342	3-ring 0.4838	2-ring 0.0151	3-ring 0.0168	2-ring 0.0221	3-ring 0.0235	2-ring 0.0024	3-ring 0.0021
11	0.6662	0.2209	3-ring 0.2566	4-ring 0.6415	3-ring 0.0080	4-ring 0.0197	3-ring 0.0205	4-ring 0.0449	3-ring 0.0033	4-ring 0.0055
12	0.6325	0.2888	4-ring 0.6895	5-ring 0.2137	4-ring 0.0185	5-ring 0.0052	4-ring 0.0526	5-ring 0.0143	4-ring 0.0054	5-ring 0.0008
13	0.6247	0.0411	4-ring 0.6582	5-ring 0.2347	4-ring 0.0175	5-ring 0.0058	4-ring 0.0570	5-ring 0.0175	4-ring 0.0076	5-ring 0.0017
15	0.5476	0.2541	3-ring 0.4184	4-ring 0.4682	3-ring 0.0114	4-ring 0.0123	3-ring 0.0381	4-ring 0.0394	3-ring 0.0073	4-ring 0.0049
16	0.7293	0.2750	4-ring 0.7500	5-ring 0.1300	4-ring 0.0239	5-ring 0.0039	4-ring 0.0729	5-ring 0.0099	4-ring 0.0088	5-ring 0.0006

Table 6 Comparison of Correlation Results with Experimental Data for SRC-II Coal Liquid Fractions									
SRC-II Cut	No. of Data pts	"Petroleum"-Fraction Correlation		Defined - Compound Correlation		This Work			
		AAD	Bias	AAD	Bias	A _M	B _M	AAD	Bias
1	4	5.30	-4.80	19.30	-19.30	-4.6399	1173.13	20.61	+20.61
2	4	17.60	-17.60	25.10	-25.10	-4.6697	1219.54	10.63	-10.63
3	4	9.10	-6.30	12.70	-12.70	-4.7650	1291.55	7.65	+1.28
4	4	9.30	-3.00	14.00	-14.00	-4.7304	1285.82	16.19	-16.19
5	6	9.60	-9.40	22.00	-22.00	-5.2603	1713.63	8.30	-7.06
6	6	33.20	-2.20	29.30	-29.30	-5.3463	2098.80	53.11	+53.11
7	6	34.90	+3.40	28.90	-28.90	-5.4216	2151.60	37.82	+37.82
8	6	26.50	-8.60	40.30	-40.30	-5.1710	2126.64	12.85	+12.95
9	6	30.40	+14.10	28.30	-28.30	-4.8165	1937.04	11.48	+1.37
10	5	25.90	+23.30	25.30	-25.30	-4.7576	1990.71	8.25	+4.92
11	5	46.50	-46.50	66.20	-66.20	-5.2401	2546.13	25.35	+0.80
12	5	163.60	+163.60	51.10	-51.10	-5.3211	2861.59	55.32	+54.79
13	5	1661.00	+1661.00	49.40	-49.40	-4.5967	2487.38	46.53	+19.84
15	5	140.90	+140.90	38.80	-38.80	-5.1922	2505.37	22.02	+4.13
16	5	9803.00	+9803.00	54.60	-54.60	-5.4139	2820.94	30.27	-2.76
1,2,3,4	16	10.33	-7.93	17.78	-17.78			13.77	-1.23
5 - 10	35	26.77	+2.87	29.12	-29.12			22.36	+17.36
11 - 16	25	2363.00	+2344.40	52.02	-52.02			35.90	+15.36
Total	76	791.80	+770.80	34.30	-34.30			25.01	+12.79

Figure Caption

1. $\ln(\eta)$ is plotted versus $(1/T)$ for a few SRC-II cuts. Symbols represent experimental data and model results are shown as straight lines.

III. LIQUID AND SOLID PHASE THERMODYNAMICS OF COAL MATERIALS

The progress in this area is reported in five sections: a section on data compilation, a literature review section on high pressure density measurements, a section on progress towards development of high pressure equations of state for liquids and solids, and the final two sections include the two manuscripts resulting from the detailed development of predictive methods for vapor pressures and saturated liquid densities of organic liquids. Although, we have set directions for research towards the development of high pressure equations of state for liquids and solids, not much was accomplished in terms of actually formulating such equations. During the initial stages of the project, it was quickly noted that a number of preliminary developments were necessary before formulating a useful high pressure equation of state. These include obtaining predictive methods for density, vapor pressure and heat capacity of liquids and solids at saturation condition. We undertook and completed the development of predictive methods for vapor pressure and density of liquids of coal model compounds. Recommendations for future research in this area are listed below:

1. Investigate literature methods and develop if necessary predictive methods for saturated solid vapor pressures and densities.
2. Investigate literature methods and develop if necessary predictive methods for heat capacities of saturated organic liquids and solids.
3. For organic liquids for which literature high pressure P, V, T data are available, use the Tait equation of state, and regress the coefficients B and C as specific functions of temperature. Investigate the accuracy of the equation so obtained for computation of high pressure liquid heat capacity.
4. Using an appropriate liquid mixture model, such as UNIQUAC equation, at saturation, inves-

tigate the application of the Tait equation to liquid mixtures at high pressure. Further modifications of the Tait equation, such as, mixing rules for B and C, may be necessary for this process.

5. Research the high pressure solid equations of state available in the literature. Choose an appropriate equation of state, and carry out developments similar to steps 3 and 4 for the liquid state.

In what follows we discuss in details all the above developments.

1. Data Compilation

An extensive literature search was carried out, and in all four data sets were compiled: 1. vapor pressures of solid aromatics, vapor pressures of organic liquids, saturated densities of organic liquids, and high pressure thermodynamic properties of organic liquids. A compound by compound listing of these data sets together with literature sources are given in Tables 1 through 4 below.

Table 1
Vapor Pressures of Solid Aromatics

<u>Compound</u>	<u>Temperature Range °K</u>	<u>Pressure Range, Pa</u>	<u>No. of Points</u>	<u>Reference</u>
Naphthalene	264-343	0.23-488.580	22	1
	271-285	0.611-2.80	8	10
	261-343	0.165-500.224	17	27
	274-353	0.87-969.3	67	12
	299-331	10.7-200	11	28
	353-354	1001-	32	5
	273-354	0.80-	63	32
	223-340	281-	13	32
	283-354	2.32-	57	34
	273-354	0.4-	38	35
	280-294	0.163-	11	11
	257-257	0.1-	10	20
	280-305	1.76-	6	1
	264-343	23000-	22	29
	273-313	.8-42.66	7	14
	323-343	109-525.3	3	
1-Methyl- naphthalene	80-304	1303-	63	29
	279-304	1.76-	8	20
Anthracene	354-399	0.55-21.30	12	3
	328-331	.035-.0499	2	7
	339-354	.1147-.524	10	6
	436-478	813-3760	7	33
Hydroquinone	341-400	0.46-92.3	8	3
	428-437	787-1547	3	33
Resorcinol	329-379	0.86-81.3	7	3
	382-383	133-	1	31
Benzoic Acid	293-313	0.060-0.640	18	10
Benz[a]anthracene	330-390	0.001-0.722	7	23
Benzo[a]pyrene	358-428	0.002-1.463	8	23

Benzo[e]pyrene	359-419	0.003-0.789	7	23
Benzo[ghi]- perylene	389-459	0.002-0.965	8	23
Cornene	427-507	0.003-1.294	9	23
Diphenyl	283-339	0.217-67.461	10	26
Diphenyl-Methane	274-299	0.137-1.867	9	26
Diphenyl-Ethane	293-323	0.248-8.373	4	26
O-terphenyl	323-333	0.339-0.684	4	26
Triphenyl-Methane	343-363	0.309-2.786	4	26
Triphenyl-Ethlene	343	0.153-0.156	2	26
Flourene	303-373	0.157-98.925	12	27
	308-348	0.297-13.0	15	28
	286-300	.014-.07	4	7
	306-323	.219-1.11	10	6
Pyrene	353-413	0.300-37.064	9	27
	342-358	.1147-.5066	12	6
Acenaphthene	293-342	0.237-23.5	13	28
	293-368	2.666-	1	17
Phenanthrene	323-348	0.340-4.42	10	28
	293-372	.0076-	1	19
	297-303	.022-.0445	2	7
	310-323	.085-.3213	9	6
Dibenzofuran	299-346	0.506-35.4	14	28
Benzene	261-279	1269-	43	29
	183-196	0.1-	10	11
	273-278	3225-	21	8
1,2,4,5,-Tetra- methylbenzene	347-352	1351-	56	29
	330-352	398.8-	15	15
2,3-Dimethyl- naphthalene	33-378	14.0-	15	24

2,6-Dimethyl-naphthalene	348-383	53.6-	15	24
2,7-Dimethyl-naphthalene	333-369	19.87-	15	24
Cyclohexane	279-280	5350-	22	5
	248-280	720-		36
	228-280	133-	15	31
Cyclohexene	213-280	33-	22	35
	229-248	160-	4	18
Biphenyl	342-344	0.10-	15	5
	288-344	0.416-	75	32
	297	0.118-	15	6
	326-344	16-	4	30
	343-344	109-	16	9
	288-314	.416-6.69	16	6
Thiophene	195-235	2.07-	25	32
	228-235	107-	24	34
	232-235	133-	10	31
3,5-Dimethyl-pyridine	265-267	18-	81	13
7-methyl-quinoline	290-306	1.0-	201	13
2,4Dimethyl-quinoline	295-330	1.0-	203	13
Phenol	273-314	3.73-	33	32
	283-314	10.4-	20	16
	279-314	6.67-	79	34
	313-314	133-	19	31
	273-311	3.7-139	15	4
1,3-Dihydro-cybenzene	382-383	133-	10	31
1,4-Dihydro-cybenzene	432-443	1333-	19	5
	428-443	787-	14	34
	406-443	133-	10	31

Thiophen	195-213	2.1-23.3	4	21
Catechol	377-378	667-	1	31
m-Cresol	273-282	2.133-4.5	3	4
o-Cresol	273-302	2.7-53.3	9	4
p-Cresol	273-307	1.466-38.5	7	4
p-Xylene	264-271	43.99-116	2	17
	273-286	180-539.9	2	25
2,3-Xylenol	283-323	.61-52.9	9	2
2,4-Xylenol	283-293	3.04-8.279	3	2
2,5-Xylenol	283-323	.6-52.8	9	2
2,6-Xylenol	278-313	2.6-100.3	8	2
3,4-Xylenol	283-323	.29-25.46	9	2
3,5-Xylenol	283-323	.44-35.3	9	2
1-Naphthol	367-369	133-	1	31
Carbazole	518	7333-7386	2	22

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Table 2

Summary of Vapor Pressure data of Organic Liquids

<u>No.</u>	<u>Compound</u>	<u>T.R. [K]</u>	<u>P.R. [Bar]</u>	<u>N.P.</u>	<u>Ref</u>
1	ethane	100.00-305.50	0.00007-49.13	23	2
2	propane	189.50-370.00	0.1000-42.650	19	2
3	n-butane	143.15-425.16	0.000025-37.96	31	2
4	isobutane	123.15-408.13	0.0000015-36.47	31	2
5	n-pentane	173.15-469.77	0.000085-33.74	32	2
6	isopentane	173.15-460.95	0.00018-33.33	30	2
7	n-hexane	183.15-507.85	0.000019-30.31	34	2
8	2-2-dimethylbutane	288.53-323.68	0.28955-1.0391	11	5
9	2-3-dimethylbutane	287.41-331.94	0.1992-1.0391	13	5
10	2-methylpentane	285.91-334.22	0.1662-1.0391	14	5
11	3-methylpentane	288.44-337.23	0.1662-1.0391	14	5
12	n-heptane	203.15-540.16	0.000025-27.36	36	2
13	2-2-3-trimethylbutane	285.71-354.92	0.077-1.040	19	5
14	2-2-dimethylpentane	288.48-353.20	0.090-1.0391	18	5
15	2-3-dimethylpentane	290.67-363.83	0.064-1.040	20	5
16	2-4-dimethylpentane	286.86-354.52	0.077-1.040	19	5
17	2-methylhexane	291.68-364.09	0.064-1.040	20	5
18	3-3-dimethylpentane	286.63-360.11	0.064-1.040	19	5
19	3-ethylpentane	294.28-367.52	0.064-1.040	18	5
20	3-methylhexane	293.07-365.89	0.064-1.040	20	5
21	n-octane	243.15-569.35	0.00032-24.96	35	2
22	2-2-4-trimethylpentane	297.51-373.28	0.064-1.039	20	5
23	2-3-4-trimethylpentane	309.72-387.53	0.064-1.039	20	5
24	2-methylheptane	314.86-391.69	0.064-1.039	20	5
25	3-methylheptane	315.82-392.96	0.064-1.039	20	5
26	n-nonane	253.15-595.15	0.00016-22.88	27	2
27	2-2-3-3-tetramethylpentane	330.98-414.46	0.064-1.040	20	5
28	2-2-3-4-tetramethylpentane	325.18-407.17	0.064-1.040	20	5
29	2-2-4-4-tetramethylpentane	316.11-396.42	0.064-1.040	20	5
30	2-2-5-trimethylhexane	319.29-398.20	0.064-1.040	18	5
31	2-3-3-4-tetramethylpentane	332.16-415.72	0.064-1.040	18	5
32	3-3-diethylpentane	336.03-420.34	0.064-1.040	19	5
33	n-decane	263.15-619.15	0.000087-21.07	28	2
34	n-undecane	273.15-640.15	0.00005-19.45	25	2
35	n-dodecane	273.15-659.15	0.000012-18.13	27	2
36	n-tridecane	343.15-677.15	0.0017-17.2	19	2
37	n-tetradecane	393.15-695.15	0.0124-16.20	16	2

38	n-pentadecane	413.15-710.15	0.0164-15.20	16	2
39	n-hexadecane	463.15-553.15	0.0692-0.873	10	5
40	n-heptadecane	433.15-735.15	0.0125-13.16	17	2
41	n-octadecane	453.15-750.15	0.017-13.169	16	2
42	n-nonadecane	463.15-760.15	0.0163-12.156	17	2
43	n-eichosane	473.15-775.15	0.015-11.14	17	2
44	1-butanol	362.36-398.84	0.330-1.333	16	5
45	1-decanol	400.41-528.32	0.0266-1.7795	26	5
46	1-heptanol	336.75-449.55	0.0063-1.014	13	5
47	1-hexanol	325.35-430.45	0.0076-1.010	13	5
48	1-octanol	386.42-479.28	0.051-1.354	18	5
49	1-pentanol	347.91-429.13	0.072-1.772	19	5
50	1-propanol	333.32-377.73	0.204-1.3326	19	5
51	2-butanol	345.54-380.30	0.3303-1.3347	16	5
52	ethanol	292.77-366.63	0.057-1.79	25	5
53	methanol	288.05-356.83	0.09815-2.0565	20	5
54	benzene	278.68-560.00	0.048-47.717	115	10,13,30
55	toluene	252.15-593.75	0.002146-42.254	112	4,11
56	ethylbenzene	243.15-493.15	0.000204-6.229	26	9,11,33
57	<i>o</i> -xylene	253.15-631.59	0.000324-38.08	43	11,34
58	<i>m</i> -xylene	243.15-619.15	0.000169-36.5	47	11,34
59	<i>p</i> -xylene	293.15-618.15	0.008666-36.17	36	11,34
60	<i>n</i> -propylbenzene	348.97-433.39	0.064021-1.04	19	34
61	<i>iso</i> -propylbenzene	253.15-631.05	0.000192-32.09	51	11,22,34
62	1,2,3-trimethylbenzene	363.48-450.28	0.064168-1.04	20	34
63	1,2,4-trimethylbenzene	357.95-443.53	0.064168-1.04	20	34
64	1,3,5-trimethylbenzene	354.64-438.88	0.064155-1.04	19	34
65	1-methyl,2-ethylbenzene	354.30-439.32	0.064168-1.04	20	34
66	1-methyl,3-ethylbenzene	351.26-435.47	0.064168-1.04	20	34
67	1-methyl,4-ethylbenzene	351.46-436.16	0.064168-1.04	19	34
68	<i>n</i> -butylbenzene	273.15-523.15	0.000187-4.094	26	11,33
69	<i>iso</i> -butylbenzene	359.79-446.96	0.064155-1.04	20	34
70	<i>sec</i> -butylbenzene	360.27-447.51	0.064155-1.04	20	34
71	<i>tert</i> -butylbenzene	357.03-443.32	0.065461-1.04	20	34
72	1,4,-diethylbenzene	369.97-457.97	0.064221-1.04	20	34
73	<i>o</i> -cymene	298.15-473.15	0.00221-1.703	15	22,33
74	<i>m</i> -cymene	298.15-473.15	0.00233-1.846	15	22,33
75	<i>p</i> -cymene	263.15-653.15	0.00012-28.0	28	22,33
76	phenol	350.85-440.78	0.018-0.676611	64	34
77	<i>o</i> -cresol	313.15-697.65	0.001235-50.1	25	14
78	<i>m</i> -cresol	323.15-705.85	0.001204-45.6	25	14

79	<i>p</i> -cresol	313.15-704.65	0.000503-51.5	26	14
80	2,4-xyenol	303.15-707.65	0.0002-44.0	26	12,34
81	2,5-xyenol	353.15-707.05	0.006628-49.0	21	12,34
82	3,5-xyenol	353.15-715.65	0.003436-36.0	21	12,34
83	aniline	267.13-699.15	0.000055-53.1	32	11,26
84	2-methyl-aniline	298.15-694.15	0.00034-37.5	33	31
85	3-methyl-aniline	298.15-709.15	0.00025-41.5	33	31
86	dimethylaniline	334.75-467.65	0.006666-1.01725	15	34
87	pyridine	253.15-619.95	0.0014-56.3	47	25,20
88	2-methyl-pyridine	352.94-441.51	0.20-2.7	15	34
89	4-methyl-pyridine	350.06-418.61	0.1035-1.016	21	34
90	chlorobenzene	238.05-404.88	0.000235-1.0136	49	34
91	bromobenzene	394.74-479.20	0.385435-3.1296	12	34
92	benzoic-acid	448.65-521.85	0.094792-0.97325	7	34
93	anisole	346.49-412.52	0.062875-0.6766	6	34
94	phenetole	365.04-428.31	0.076047-0.67661	6	34
95	styrene	303.07-417.92	0.010932-1.0051	16	34
96	furan	275.70-334.58	0.311601-2.7011	13	34
97	thiophene	234.94-579.35	0.00189-56.9	29	28,34
98	cyclohexane	283.15-543.15	0.063315-35.61	27	6,33
99	cyclohexene	213.15-423.15	0.000328-5.287	22	33
100	1,1-dimethylcyclohexane	313.65-393.67	0.064128-1.04	20	34
101	1,2-dimethylcyclohexane	322.33-450.28	0.063528-1.04	20	34
102	<i>n</i> -propylcyclohexane	345.84-430.91	0.064008-1.04	20	34
103	<i>iso</i> -propylcyclohexane	343.67-428.75	0.064115-1.04	20	34
104	<i>n</i> -butylcyclohexane	366.52-455.17	0.063995-1.04	19	34
105	<i>iso</i> -butylcyclohexane	357.90-445.54	0.064115-1.04	20	34
106	<i>tert</i> -butylcyclohexane	357.18-445.82	0.063995-1.04	20	34
107	naphthalene	353.43-471.68	0.009934-0.643	28	3,10,11
108	1-methylnaphthalene	313.15-772.15	0.000276-39.0	36	1,7,23,34
109	2-methylnaphthalene	307.73-761.15	0.0002-35.0	37	7,23,34
110	<i>cis</i> -decalin	233.15-702.25	0.000002-32.0	23	19,34
111	<i>trans</i> -decalin	273.15-687.05	0.00025-28.	20	19,34
112	tetralin	273.15-720.15	0.000062-33.0	31	27
113	quinoline	303.15-773.15	0.000119-42.6	29	25,34
114	isoquinoline	333.15-753.15	0.001088-31.9	27	17,34
115	benzofuran	313.15-473.15	0.006-1.97	14	30
116	indan	273.15-684.95	0.000324-39.5	29	8,16
117	indene	273.15-695.15	0.000192-38.0	21	16
118	indole	373.15-789.15	0.0053-43.0	24	18
119	4-indanol	353.15-553.15	0.0019-2.35	12	21

120	biphenyl	373.15-653.15	0.005733-8.8	13	11,34
121	diphenylmethane	490.69-555.39	0.323293-1.47	9	34
122	anthracene	488.93-673.15	0.049-2.61	32	15,34
123	phenanthrene	372.39-633.15	0.000293-1.429	40	15,34
124	dibenzofuran	423.15-633.15	0.0342-3.86	21	30
125	fluorene	387.94-613.15	0.002718-2.3	26	34,35
126	carbazole	513.15-673.15	0.0676-2.2	11	29
127	acridine	383.15-633.15	0.000483-1.32	15	29
128	pyrene	423.81-673.15	0.00058-1.1	8	24
129	triphenylene	533.15-773.15	0.019-2.1	15	24

Note, T.R. : temperature range ; P.R. : pressure range ; N.P. : No. of Points

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Plots of Vapor Pressure for Different Compounds

Fig. A1. Vapor Pressure of Alkanes (1)

Fig. A2 . Vapor Pressure of Alkanes (2)

Fig . A3 Vapor Pressure of Alcohols

Fig. A4. Vapor Pressure of Phenols

Fig. A5 Vapor Pressure of Aromatics

Fig. A6 Vapor Pressure of Pyridines

Fig. A7 Vapor Pressure of Two-ring Aromatics

Fig. A8 Vapor Pressure of other aromatics

Fig. A9 Vapor Pressure of Alkylbenzenes

Fig. A10 Comparison of Vapor Pressure of Aniline

Table 3

Summary of Saturated Liquid Densities of Coal Model Compounds

<u>Compound</u>	<u>Temperature Range(° C)</u>	<u>NP</u>	<u>State</u>	<u>Ref.</u>
1-methylnaphthalene	0 --- 499	42	L	[23]
2-methylnaphthalene	0 --- 488	44	S,L	[23]
anthracene	20 --- 320	15	S,L	[15]
aniline	0 --- 180	19	L	[11]
	-6.02 --- 426	32	L	[26]
benzene	0 --- 300		L	[10]
	0 --- 280	21	L	[13]
benzofuran	40 --- 200	14	L	[30]
biphenyl	80 --- 400	17	L	[11]
<i>n</i> -butylbenzene	10 --- 40	5	L	[11]
carbazole	246.1--- 320	5	L	[29]
<i>o</i> -cresol	0 --- 424.5	29	S,L	[14]
<i>m</i> -cresol	0 --- 432.7	29	S,L	[14]
<i>p</i> -cresol	0 --- 431.5	29	S,L	[14]
<i>cis</i> -decalin	-40 --- 429.1	24	L	[19]
<i>trans</i> -decalin	-30 --- 413.9	23	L	[19]
Dibenzofuran	150 --- 360	21	L	[30]
ethylbenzene	-90 ---140	24	L	[11]
indan	0 --- 411.8	29	L	[16]
1-indanol	40 --- 240	14	L	[21]
2-indanol	80 --- 240	10	L	[21]
indene	0 --- 422	30	L	[16]
indane	81.91 --- 209.287	25	L	[5]
indole	60 --- 516	28	L	[18]
isopropylbenzene	0 --- 90	11	L	[11]
	-96.008 ---357.	31	L	[22]
isoquinoline	30 --- 260	21	L	[17]
naphthalene	60 --- 475.2	34	S,L	[3]
	80 --- 470		S,L	[10]
	220 --- 340	11	L	[11]
nitrobenzene	0 ---50	11	S, L	[11]
perylene	25 --- 245	23	S	[23]
phenanthrene	30 --- 320	21,	S,L	[15]
phenyl ether	220 ---360	13	L	[11]
pyridine	-40 --- 346.8	29	L	[20]
quinoline	10 --- 240	18	L	[25]
tetralin	0 --- 447	31	L	[27]
thiophene	0 --- 120	15	L	[28]

toluene	-100 ---110	23	L	[11]
<i>o</i> -xylene	-30 --- 140	18	L	[11]
<i>m</i> -xylene	-50 ---20	8	L	[11]
2-4-xyleneol	10 --- 70	7	S,L	[12]
2-5-xyleneol	20 ---200	13	S,L	[12]
3-4-xyleneol	20 --- 240	12	S,L	[12]
3-5-xyleneol	20 --- 200	12	S,L	[12]

Note: S, solid ; L, liquid; NP , Number of Point

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Table 4

**Summary of High Pressure Thermodynamic Properties
of Coal Model Compounds**

<u>Compound</u>	<u>Properties</u>	<u>Temperature Range</u>	<u>Pressure Range</u>	<u>Ref.</u>
Argon	D	91K--143 K	15.2 - 282 Bar	(85)
Methane	D	94 K -- 181 K	14.76--266.27 Bar	(85)
Ethane	D	168K--290K	8.11--725.39 Bar	(85)
propane	D	100K--350K	0.1 -- 600 Bar	(85)
n-butane	D	311K-378K	6.89--689.48 Bar	(85)
n-hexane	D	311K--478K	6.64--672.58 Bar	(85)
n-heptane	D	278K -- 511K	1.51 -- 691.41 Bar	(85)
n-nonane	D	311K -- 511K	2.36 -- 691.54 Bar	(85)
n-dodecane	D	298 K -- 358 K	17.43 -- 942.32 Bar	(85)
n-pentadecane	D	311 K -- 408 K	344.6 -- 689.1 Bar	(85)
n-hexadecane	D	298 K -- 358 K	3.85 -- 972.72 Bar	(85)
n-octadecane	D	333K--408K	344.6 --- 689.1 Bar	(85)
propene	D	273 K -- 344K	6.89 --- 988.5 Bar	(85)
trans-2-butene	D	278 K -- 378 K	13.79 -- 344.74 Bar	(85)
cyclohexane	D	311 K --- 511K	20.9-- 685.04 Bar	(85)
nitrogene	D	64 K -- 119K	0.34 -- 689.48 Bar	(85)
oxygen-	D	56 K -- 144 K	0.07 -- 344.74 Bar	(85)
hydrogen				
sulfide	D	278 K -- 344 K	13.79 -- 689.48 Bar	(85)
Acetonitrils	D	29.8 C -- 450 C	24.0 --- 2000 Bar	(25)
Aniline	D	298.15K -- 323.15K	250 Bar - 1000 Bar	(22)
Athracene	D	299K , 297K	0--2.4GPa	(73)
	D	298.15K	5KBar - 45KBar	(86)
	D	298.15K	19KBar - 547KBar	(97)
	Cp	299K, 297K	0--2.4GPa	(73)
Benzene	D,Cp,H	279K--- 900K	0-1000Bar	(29)*
	D	293.15K , 298.15K	0.1-10MPa	(13)
	D,Cp	296K , 300K	0--2.4GPa	(73)
	Cp	553.2K---598.2K	0.1-10MPa	(13)
	D	298.15K --- 318.15K	1 - 52 Bar	(19)
	D	425K -- 720K	30Bar - 350 Bar	(77)
	Cp	298.15K	1Bar - 681 Bar	(54)
	D	323K---683K	5 - 300MPa	(28)

Butylbenzene	D	318.15K , 333.15K	1Bar - 50 Bar	(19)
Bromobenzene	D	278K , 323K	1Bar - 2800 Bar	(22)
Chlorobenzene	D	298 K -- 358 K	up to 1000 Bar	(107)
Nitrobenzene	D	298K --- 358 K	up to 1000 Bar	(107)
Cumene	D	303.15K	1Bar - 4840Bar	(75)
	D	298.15K	1Bar - 39227Bar	(99)
	D,H	360K---1000K	1Bar - 2000Bar	(99)*
Cyclohexane	D	298.15K -- 313.15K	1 Bar - 437 Bar	(63)
Dibenzofuran	D	391.55K -- 563.15K	5 Bar - 253.31Bar	(21)
<i>p</i> -cumene	D,H	380K---1000K	1Bar - 2000Bar	(99)*
<i>m</i> -cresol	H	291K---655K	207KPa - 690KPa	(24)
	H	314K---669K	0 - 10.3Mpa	(62)
<i>trans</i> -Decalin	H	75F---620F	0 - 1400Psia	(57)
	Comp.	293.15K--373.15K	1Bar - 3600Bar	(12)
<i>cis</i> -decalin	Comp.	293.15K--373.15K	1Bar - 3600Bar	(12)
Diphenyl	D	298.15K	5KBar - 45KBar	(86)
9,10,-Diphenyl				
-anthracene	D	298.15K	5KBar - 45KBar	(86)
ethylbenzene	D	318.15K--373.15K	0.1MPa - 10MPa	(105)
	D	318.15K, 333.15K	1 Bar - 50 Bar	(19)
	Cp	318.15K--343.15K	0.1MPa - 10MPa	(105)
	H	349.00K-- 551.0K	19.94 - 200.13 Bar	(37)
hexamethyl-				
benzene	D	298.15K	5KBar - 45KBar	(86)
	H	349.00K-- 551.0K	19.94 - 200.13 Bar	(37)
hexamethyl-				
benzene	D	298.15K	5KBar - 45KBar	(86)
isoquinoline	D,H	298.15K--1000K	1Bar - 5000 Bar	(89)*
Isopropyl-				
benzene	D	318.15K - 333.15K	1 Bar - 50 Bar	(19)
1-methyl-				
naphthalene	H	291K---669K	0 - 3240KPa	(105)
2-methyl-				
naphthalene	D	298.15K	0 - 39227Bar	(11),(100)
naphthalene	D	298.15K	5KBar - 45KBar	(86)
	D,Cp	299K , 297K	0 - 2.4GPa	(73)
	D,H,Cp	353.43K-1000K	1Bar - 5000Bar	(19)*

phenanthrene	D	298.15K	18KBar - 533KBar	(97)
propylbenzene	D	318.15K, 333.15K	1Bar - 50 Bar	(19)
Pyrene	D	298.15K	18Kbar - 548KBar	(97)
	D	298.15K	5KBar - 45KBar	(86)
	D	298.15K	0 - 500Bar	(47)
quinoline	D,H	298.15K--1000K	1Bar - 5000Bar	(90)*
	H	291K--655K	--103.42Bar	(97)
toluene	D,H,Cp	178K--800K	0 - 1000Bar	(30)*
	Cp	180K--480K	0 - 4000Bar	(61)
	D	348K-- 673K	0 - 35MPa	(77)
	D	318.15K , 333.15K	1Bar - 50 Bar	(19)
	D	273K -- 373K	1Bar - 2500 Bar	(38)
	D	303.15K	1Bar - 4920Bar	(75)
	Cp	255K -- 400K	1Bar - 1000 Bar	(74)
	D	278.15K - 323.15K	2530 Bar - 3690 Bar	(22)
	Cp	305.80K - 345.0K	1 Bar - 675 Bar	(81)
Thiophene	D,H,Cp	340K---1000K	1Bar - 5000Bar	(50)*
Tetralin	D	298.15K	0 - 40000Bar	(49)
	D,H,Cp	298.15K--1000K	1Bar - 5000Bar	(42)*
	H	291K--655K	--- 103.42 Bar	(23)
<i>o</i> -xylene	D	318.15K--373.15K	0.1MPa - 10MPa	(27)
	D	303.15K	1Bar - 2310Bar	(75)
	D	298.15K--548.15K	1Bar - 400Bar	(87)
	Cp	318.15K---343.15K	0.1MPa - 10MPa	(27)
<i>m</i> -xylene	D	318.15K---373.15K	0.1 - 10MPa	(27)
	D	293.15K---548.15K	1Bar - 400Bar	(87)
	D	298.15K , 283.15K	1Bar - 400 Bar	(106)
	Cp	318.15K-- 343.15K	0.1 - 10MPa	(27)
	Cp	305.55K -- 357.85K	34 Bar - 396 Bar	(81)
<i>p</i> -xylene	D	318.15K-- 373.15K	0.1 - 10MPa	(27)
	D	303.15K	1Bar - 680Bar	(97)
	D	298.15K , 283.15K	1Bar - 2000 Bar	(106)
	D	283.15K--548.15K	1Bar - 400Bar	(87)
	Cp	305.55K-- 358.25K	44 Bar - 400 Bar	(81)
	Cp	318.15K--343.15K	0.1MPa - 10Mpa	(27)

Water	D	273.15K--1273.15K	0 --- 100Kbar	(39)
methanol	D	up to 350 C	0 --- 8 KBar	(78)
Carbon dioxide	D	273.2 K -- 300 K	40 -- 600 Bar	(13)
Ammonia	D	310 K --- 390 K	20 --- 1000 Bar	(13)
F-12	D	253.2 K --- 313.2 K	287 --- 1608 Bar	(13)
Methyl acetate	D	253.2 K --- 313.2K	197 --- 1567 Bar	(13)
Ethylene	D	273.1K	50 -- 700 Bar	(13)
Cyclohexanone	D	303.2K--- 323.2K	2.0 --- 104 Bar	(13)
F-22	D	253.2K---313.2K	287 --- 1596 Bar	(13)
1-Chlorobutane	D	303 K	up to 5000 Bar	(107)
1,2- Dichloro-ethane	D	298 K -- 398 K	up to 1010 Bar	(107)
Tetrachloro-ethane	D	298 K	up to 1000 Bar	(107)
Acetone	D	298 K	up to 1000 Bar	(107)
Diethyl ether	D	273 K -- 353 K	up to 1000 Bar	(107)
ethyl acetate	D	253 K -- 313 K	up to 1500 Bar	(107)
Glycerol	D	223 K -- 353 K	up to 2800 Bar	(107)
Pentan -1,5,-diol	D	253 K -- 308 K	up to 2800 Bar	(107)
Polyisobutylene	D	326 K -- 383 K	up to 1000 Bar	(107)
Poly(vinyl acetate)	D	337 K -- 393 K	up to 1000 Bar	(107)

Note : D-Density ; C_p-Heat Capacity at constant pressure ; H-Enthalpy ; Comp-Compressibility; *-- Calculated Data

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2. Data Measurement Techniques - Review of Literature

Experimental Measurement of High Pressure Density:

With the advancement of industrial coal technologies and the requirement of accurate calculation of other thermodynamic properties based on density, more accurate data on various liquid density for coal compounds are required over wide range of temperature and pressure. Consequently, a literature survey for experimental techniques to measure high pressure liquid densities was carried out. A few promising techniques are listed below.

1. Hollow cylinder with sapphire window [1,2,3]

A method is described below which permits the determination of P, V, T data and phase transitions at high temperature and pressure. The measurements are much quicker to make and require less material than is used in sampling method. The entire cell content is observable, which allows the critical phenomena and the behavior in the barotropic region to be investigated.

Fig. 1 (a) High pressure apparatus. (b) Seal of the sapphire window at high temperature (c) O-ring seal of the window AC-Additional cell to determine the position of the piston, Ag-silver packing, CS- steel ring with low thermal expansion, L-leather, M-mirror, MP-moving piston, N-nipple, OR-O-ring, P-pressure, Pt-platinum mirror, R-ruler, S-sapphire window, SR-supporting ring, TC-thermocouple, UA-unsupported area.

The high-pressure vessel was a cylinder (o.d. 50 mm, i.d. 15 mm) horizontally positioned , built of a high-alloyed austenitic steel (ATS 340 ,Deutsche Edelstahlwerke , Witten , Germany).The contents of the cell can be observed through a sapphire window at the end . The system to be studied is separated from the pressure transmitting liquid by an O-ring-sealed moving piston which allows the volume to vary. A platinum mirror is attached at one end of the piston to reflect the incoming light . A thin steel ruler is attached to the other end of the piston and extended through a four-way connector. The position of the piston, and hence the volume , can be accurately determined by reading the ruler through a sapphire window in one arm of this cross . Another arm is connected to the pressure generating . The sapphire windows are sealed on the cylinder surface which makes the handling of such apparatus much safer. In the case of window fracture,the pressure drops gradually preventing further damage to the system. For moderate temperatures, an O-ring seal was used [Fig.1(c)] for the window. At high temperature, a modified area is a ring [Fig.1(b)]. The seal is provided by silver or copper rings . The high thermal expansion coefficient of these metals is compensated by special low thermal expansion steel rings (Invar steel with 42% nickel).

For temperatures higher than the maximum working range of Viton or Teflon O-rings, it is necessary to cool the sealed end of the piston . This is accomplished by a small cooling jacket[Fig. 1(a)] especially designed to permit direct contact of the coolant with the cylinder. The jacket can be moved along the cylinder to correspond to the position of the piston. The piston has to be sufficiently long to take care of the temperature gradient.

High temperature is obtained by using resistance heaters and is measured by a thermocouple (calibrated chromel-to-alumel thermocouple) inside the cylinder. The substances to be studied are introduced into the cylinder through a tube connected to the cell near the window [Fig. 1 (a)] . The substances can be stirred by a small permanent magnet inside the cell which can be moved by larger one on the outside . Pressure in the system is measured by means of calibrated precision Bourdon gauges (Heise, Newhaven, Conn .,U.S.A.).The high pressure parts are commercial units useful for pressures up to 4000 bars.

In working at high temperatures , where cooling of the piston is necessary, it is convenient to increase the temperature and let the pressure increase at a constant volume. The P, T diagram is drawn conveniently by an X-Y recorder, using the outputs of the thermocouple and a pressure gauge which has potentiometric readout. Phase transitions generally cause discontinuities in the P, T diagrams. These transitions also can be observed optically , especially in the critical region. Hence, using this method , there are two independent means of determining the surface of the two phase region.

Accuracy

For the specific or molar volume at room temperature, the maximum uncertainty is less than 0.06 per cent and at high temperature, is less than 0.14 per cent. Similarly the maximum uncertainty in temperature at 373 K is 0.5 K and increases to 2 K at 673 K, and includes the effect of small temperature inhomogeneities. At 100 MPa and higher the uncertainty in pressure is less than 0.3 percent; however, for pressure less than 10 MPa the uncertainty increases to 1 per cent.

The volume of the high-pressure vessel can be calibrated as a function of temperature and pressure with Ar^[12,13] and CO₂^[14,15,16] taking data from the literature. The calibration with different gases shows that the uncertainty of an experimental point is about 0.4 per cent in volume. At high temperatures and pressure below 15 MPa the results are accurate to better than 1 per cent.

2. Density measurement with high-pressure burette ^[11]

Fig. 2 Schematic diagram of the high-pressure burette apparatus: A. oil pump; B. Bourdon gauges; C. Hg cylinder; D. sample vessel; E. thermostats; F. differential transformer; G. burette (made of SS316); H. micro-ammeter; J. magnetic float; V. valves.

The density of liquids has been measured using a high-pressure burette apparatus^[4, 5], whose schematic diagram is shown in Fig. 2. The volume change with temperature and pressure of a sample liquid of known mass, which is introduced into a vessel D and the

upper part of burette G, is measured by the displacement of mercury level in the burette. The position of a magnetic float J on the surface of the mercury column is detected outside the burette by a differential linear transformer F. The pressure is transmitted through mercury filled in C and G by an oil pump A. The sample vessel D consists of coaxial double cylinders. The inner cylinder is a thin-walled sample cell (about 95 cm³), to the outside wall of which a somewhat lower pressure is applied separately from the oil pump in order to minimize the deformation of the cell. The burette is made of a SS316 thick-walled tube, whose inner and outer diameters are 4.742 and 14.0 mm, respectively. The inner volumes of every 10 mm length were carefully calibrated using the weight of mercury. The density is calculated by

$$\rho = \frac{W}{\left[\left(\frac{W}{\rho_0} \right) - (\Delta V + \delta) \right]}$$

Where W is the mass of the sample liquid filled in the system, ρ_0 is the density of the sample at atmospheric pressure, ΔV is the volume change measured in the burette, and δ is a small correction for the volume change of the burette tube with temperature and pressure. The maximum uncertainty in the measured density does not exceed 0.1% over the entire experimental range.

3. Measurement of Compressibilities and Calculation of Density ^[6]

— by Analytical Ultracentrifugation

A Modification ^[7,8] of the procedure described by Dayantis ^[9] for determining isothermal compressibility by analytical ultracentrifugation can be used. Ultracentrifugation of the compounds was performed with a Beckman Instruments Spinco Model E analytical ultracentrifuge. During operation the rotor temperature was automatically controlled to within 0.1 K of the set temperature. Photographs of the schlieren patterns were taken on 5cm×25cm Kodak Metallographic plates, and the height of the schlieren line above the reference pattern was measured with a Nikon two-dimensional microcomparator.

A modified schlieren optical system ^[7,8] can be used for this work. All measurements were made at the green line of mercury, 546.1nm and at a schlieren bar angle of 70°. Isothermal compressibility $k_T(p)$ can be calculated from the following modified equation of Dayantis ^[9]

$$k_T(1 + pk_T) = \frac{6n_p h_p \tan \theta}{\left\{ (L a m_1 m_2) \left(\frac{n_p^2}{p} + 2 \right) \left(\frac{n_p^2}{p} - 1 \right) \rho_0 \omega^2 r_p \right\}}$$

Where n_p is the refractive index of the liquid at pressure P; L, the optical level of the ultracentrifuge schlieren optics; a, the cell thickness; m_1, m_2 , the vertical magnification

of the optical system ; θ the schieren bar angle ; ρ the density of the liquid at 0.1MPa at a given temperature ; ω , the angular velocity; r_p , the distance from the center of rotation for a given pressure ; and h_p , the height of the scholieren pattern at some rotor velocity above the bass line pattern taken at 50 Hz. Pressure was approximated from the relation :

$$P = \omega^2 \rho_0 \frac{r_p^2 - r_0^2}{2}$$

and the refractive index was obtained at each pressure from :

$$n_p = n_0 + \left(1/Lam_1 m_2\right) \int_0^p \left(\frac{dn}{dp}\right) dp$$

with the integral being evaluated by the area under the curve of a plot of dn/dp against p , as shown by Richard et al [7]. Compressibility was fitted to a polynomial in pressure by the method of least squares.

$$k_T = k_T(p_0) - ap + bp^2 - cp^3$$

$k_T(p_0)$ is the isothermal compressibility at 0.1MPa , T , keep constant .

The specific volume of each compound as a function of pressure was calculated from the equation

$$\int_0^p k_T dp = - \int_{v_0}^v \frac{dv}{v} = \ln \frac{v_0}{v}$$

4. Density Measurement with high pressure bellow volumeter system [10]

The high pressure bellow volumeter system at the Nat. Eng. Lab. (UK) has been in use for a number of years and produced a considerable amount of data. Densities are measured by observing the change in length with pressure of a sealed metal bellows containing the sample. All the instrumentation is linked to a microprocessor , the system is capable of outputting density directly as a function of temperature and pressure while measurements are in progress.

Temperature range : 298 K to 373 K

Pressure range : 0.1 MPa to 600 MPa

Conclusion:

The first two methods listed in this review seem promising for measurement of high pressure density. However, considering the limited project budget and a number of other developments necessary in this area, the measurements were deferred until a later date. It is recognized that considering the limited high pressure density data available in the literature, measurements for a number of pure components and mixtures would be necessary if extensive equations of state are to be developed for the liquid and solid phases.

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3. Procedures for Development of Liquid and Solid Phase Equations of State

1. Equation of State

One of the objectives of this project is to develop a liquid state equation of state to represent coal model compounds at high pressures. Several equations were tested and the most satisfactory found to be the Tait equation ^[4]. Thomson et al. ^[1] have extended the Hankinson-Brost-Thomson (HBT) ^[2] method to allow high pressure prediction using Tait equation. Tait equation is given by,

$$V = V_s \left(1 - C \ln \frac{B + P}{B + P_s} \right)$$

P_s , the saturated pressure. V_s , the saturated volume, which be calculated from (HBT) equation. B and C are obtained from,

$$B = P_c \left[-1 + a(1 - Tr)^{\frac{1}{3}} + b(1 - Tr)^{\frac{2}{3}} + d(1 - Tr) + e(1 - Tr)^{\frac{4}{3}} \right]$$

where

$$e = \exp \left(f + g\omega_{srk} + h\omega_{srk}^2 \right)$$

and

$$c = j + k\omega_{srk}$$

The constants a through k are,

Table 1. Constants for Thomson Equation			
a=-9.070217	b=62.45326	c=-135.1102	f=4.79594
g=0.250047	h=1.14188	j=0.0861488	k=0.0344483

2. Hankinson-Brost-Thomson (HBT) Technique :

Hankinson and Thomson^[2] present the following correlation for saturated densities of liquids:

$$V_R^{(0)} = 1 + a(1 - Tr)^{\frac{1}{3}} + b(1 - Tr)^{\frac{2}{3}} + c(1 - Tr) + d(1 - Tr)^{\frac{4}{3}}$$

$$\frac{V_s}{V^*} = V_R^{(0)} \left[1 - \omega_{srk} V_R^{(\delta)} \right]$$

$$0.25 < Tr < 0.95$$

$$V_R^{(\delta)} = \frac{(e + fTr + gTr^2 + hTr^3)}{Tr - 1.00001}$$

$$0.25 < Tr < 1.0$$

Table 2. Constants for HBT Equation			
a=-1.52816	b=1.43907	c=-0.81446	d=0.190454
e=-0.296123	f=0.386914	g=-0.042726	h=-0.048065

V^* is a pure component characteristic volume generally within 1 to 4 percent of critical volume, ω_{srk} is the acentric factor which forces the Soave equation to give a best fit of existing vapor pressure data. If a value of V^* is not available, it may be estimated by :

$$V^* = \frac{RT_c}{P_c} \left(a + b\omega_{srk} + c\omega_{srk} \right)$$

Table 3. Parameters to calculate v^*			
Constants	Cycloparaffin	Aromatics	Hydrocarbon
a	0.6564296	0.2717636	0.2851686
b	-3.391715	-0.05759377	-0.0637911
c	7.442388	0.05527757	0.01379173

3. Vapor Pressure Calculation :

Several investigators have proposed three-parameter forms. The Pitzer expansion is one of the more-successful :

$$\ln P_{sr} = f^{(0)}(Tr) + \omega f^{(1)}(Tr)$$

The functions $f^{(0)}$ and $f^{(1)}$ have been expressed by Lee and Kesler^[3]

$$f^{(0)} = 5.92714 - \frac{6.09648}{Tr} - 1.28862 \ln Tr + 0.169347 Tr^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{Tr} - 13.4721 \ln Tr + 0.43577 Tr^6$$

Lee-kesler equation is generally known to work well for vapor pressure of hydrocarbons.

4. Liquid enthalpy at high-pressure

The effect of pressure on the saturated enthalpy can be written as :

$$\begin{aligned}
 H(T, P) - H(T, P^s) &= \int_{P_s}^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right] dP \\
 &= \int_{P_s}^P \left\{ \left[V_s - T \left(\frac{\partial V_s}{\partial T} \right)_p \right] \left(1 - C \ln \frac{B+P}{B+P_s} \right) - CV_s T \left[\frac{\left(\frac{\partial B}{\partial T} \right)_p + \left(\frac{\partial P_s}{\partial T} \right)_p}{B+P_s} - \frac{\left(\frac{\partial B}{\partial T} \right)_p}{B+P} \right] \right\} dP \\
 &= \left[V_s - T \left(\frac{\partial V_s}{\partial T} \right)_p - CV_s T \frac{\left(\frac{\partial B}{\partial T} \right)_p + \left(\frac{\partial P_s}{\partial T} \right)_p}{B+P_s} \right] (P - P_s) + CV_s T \left(\frac{\partial B}{\partial T} \right)_p \ln \frac{B+P}{B+P_s} \\
 &\quad + C \left[T \left(\frac{\partial V_s}{\partial T} \right)_p - V_s \right] \left[(B+P) \ln(B+P) - (B+P_s) \ln(B+P_s) + P_s - P - (P - P_s) \ln(B+P_s) \right]
 \end{aligned}$$

5. Liquid heat capacity at high-pressure

The effect of pressure on the saturated heat capacity can be written as

$$C_p(P, T) = C_p(P_s, T) - \int_{P_s}^P T \left(\frac{\partial^2 V}{\partial T^2} \right)_p dp$$

Where $C_p(P_s, T)$ is the saturated heat capacity at that temperature T and saturated pressure P_s .

$$V(P, T) = V_s \left(1 - C \ln \frac{B+P}{B+P_s} \right)$$

The first order derivative V :

$$\left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial V_s}{\partial T} \right)_p \left(1 - C \ln \frac{B+P}{B+P_s} \right) + V_s C \left[\frac{\left(\frac{\partial B}{\partial T} \right)_p + \left(\frac{\partial P_s}{\partial T} \right)_p}{B+P_s} - \frac{\left(\frac{\partial B}{\partial T} \right)_p}{B+P} \right]$$

The second order derivative V ,

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_p = \left(\frac{\partial^2 V_s}{\partial T^2}\right)_p \left(1 - C \ln \frac{B+P}{B+P_s}\right) + 2C \left(\frac{\partial V_s}{\partial T}\right)_p \left[\frac{\left(\frac{\partial B}{\partial T}\right)_p + \left(\frac{\partial P_s}{\partial T}\right)_p}{B+P_s} - \frac{\left(\frac{\partial B}{\partial T}\right)_p}{B+P} \right]$$

$$+ CV_s \left\{ \frac{\left[\left(\frac{\partial^2 B}{\partial T^2}\right)_p + \left(\frac{\partial^2 P_s}{\partial T^2}\right)_p \right] (B+P_s) - \left[\left(\frac{\partial B}{\partial T}\right)_p + \left(\frac{\partial P_s}{\partial T}\right)_p \right]^2}{(B+P_s)^2} - \frac{\left(\frac{\partial^2 B}{\partial T^2}\right) (B+P) - \left(\frac{\partial B}{\partial T}\right)^2}{(B+P)^2} \right\}$$

The parameter B in the Tait equation ,

$$B = P_c \left[-1 + a(1-Tr)^{\frac{1}{3}} + b(1-Tr)^{\frac{2}{3}} + d(1-Tr) + e(1-Tr)^{\frac{4}{3}} \right]$$

The first order derivative B ,

$$\left(\frac{\partial B}{\partial T}\right)_p = \frac{-P_c}{3T_c} \left[a(1-Tr)^{-\frac{2}{3}} + 2b(1-Tr)^{-\frac{1}{3}} + 3d + 4e(1-Tr)^{\frac{1}{3}} \right]$$

The second order derivative B ,

$$\left(\frac{\partial^2 B}{\partial T^2}\right)_p = \frac{-P_c}{9T_c^2} \left[2a(1-Tr)^{-\frac{5}{3}} + 2b(1-Tr)^{-\frac{4}{3}} - 4e(1-Tr)^{-\frac{2}{3}} \right]$$

parameter C,

$$C = j + k\omega_{srk}$$

The saturated vapor pressure P_s ,

$$\ln P_{sr} = f^{(0)}(Tr) + \omega f^{(1)}(Tr)$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{Tr} - 1.28862 \ln Tr + 0.169347 Tr^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{Tr} - 13.4721 \ln Tr + 0.43577 Tr^6$$

The first derivative P_s ,

The second derivative P_s :

$$\left(\frac{\partial^2 P_s}{\partial T^2}\right)_p = \left(\frac{\partial P_s}{\partial T}\right) \left[\left(\frac{\partial f^{(0)}}{\partial T}\right)_p + \omega \left(\frac{\partial f^{(1)}}{\partial T}\right)_p \right] + P_s \left[\left(\frac{\partial^2 f^{(0)}}{\partial T^2}\right)_p + \omega \left(\frac{\partial^2 f^{(1)}}{\partial T^2}\right)_p \right]$$

The first and second order derivatives of $f^{(0)}$, and $f^{(1)}$:

$$\left(\frac{\partial f^{(0)}}{\partial T}\right)_p = \left(\frac{\partial f^{(0)}}{\partial Tr}\right)_p \times \left(\frac{\partial Tr}{\partial T}\right)_p = \frac{1}{Tc} \left(\frac{6.09648}{Tr^2} - \frac{1.28862}{Tr} + 1.016082Tr^5 \right)$$

$$\left(\frac{\partial^2 f^{(0)}}{\partial T^2}\right)_p = \frac{1}{Tc^2} \left(-\frac{12.19296}{Tr^3} + \frac{1.28862}{Tr^2} + 5.08041Tr^4 \right)$$

$$\left(\frac{\partial f^{(1)}}{\partial T}\right)_p = \frac{1}{Tc} \left(\frac{15.6875}{Tr^2} - \frac{13.4721}{Tr} + 2.61462Tr^5 \right)$$

$$\left(\frac{\partial^2 f^{(1)}}{\partial T^2}\right)_p = \frac{1}{Tc^2} \left(-\frac{31.375}{Tr^3} + \frac{13.4721}{Tr^2} + 13.0731Tr^4 \right)$$

The saturated volume and first and second order derivatives :

$$\frac{V_s}{V^*} = V_R^{(0)} \left[1 - \omega_{srk} V_R^{(\delta)} \right]$$

$$V_R^{(0)} = 1 + a(1-Tr)^{\frac{1}{3}} + b(1-Tr)^{\frac{2}{3}} + c(1-Tr) + d(1-Tr)^{\frac{4}{3}}$$

$$V_R^{(\delta)} = \frac{(e + fTr + gTr^2 + hTr^3)}{Tr - 1.00001}$$

$$V^* = \frac{RT}{P} \left(a + b\omega_{srk} + c\omega_{srk} \right)$$

$$\left(\frac{\partial V_s}{\partial T}\right)_p = V^* \left[\left(\frac{\partial V_R^{(0)}}{\partial T}\right)_p \left(1 - \omega_{srk} V_R^{(\delta)} \right) + V_R^{(0)} \left(-\omega_{srk} \right) \left(\frac{\partial V_R^{(0)}}{\partial T}\right)_p \right]$$

$$\left(\frac{\partial^2 V_s}{\partial T^2}\right)_p = V^* \left[\left(\frac{\partial^2 V_R^{(0)}}{\partial T^2}\right)_p \left(1 - \omega_{srk} V_R^{(\delta)} \right) + 2 \left(\frac{\partial V_R^{(0)}}{\partial T}\right)_p \left(-\omega_{srk} \right) \left(\frac{\partial V_R^{(0)}}{\partial T}\right)_p + V_R^{(0)} \left(-\omega_{srk} \right) \left(\frac{\partial^2 V_R^{(0)}}{\partial T^2}\right)_p \right]$$

$$\left(\frac{\partial V_R^{(0)}}{\partial T}\right)_p = -\frac{1}{3Tc} \left[a_s (1-Tr)^{-\frac{2}{3}} + 2b_s (1-Tr)^{-\frac{1}{3}} + 3c_s + 4d_s (1-Tr)^{\frac{1}{3}} \right]$$

$$\left(\frac{\partial^2 V_R^{(0)}}{\partial T^2}\right)_p = \frac{-1}{9Tc^2} \left[2a_s (1-Tr)^{-\frac{5}{3}} + 2b_s (1-Tr)^{-\frac{4}{3}} - 4d_s (1-Tr)^{-\frac{2}{3}} \right]$$

$$\left(\frac{\partial V_R^{(6)}}{\partial T}\right)_p = \frac{-e_s - 1.00001f_s - 2.00002g_s Tr - 3.00003h_s Tr^2 + g_s Tr^2 + 2h_s Tr^3}{Tc(Tr - 1.00001)^2}$$

$$\left(\frac{\partial^2 V_R^{(6)}}{\partial T^2}\right)_p = \frac{2e_s + 2.00002g_s + 2.00002f_s + 6.00006h_s Tr - 6.00006h_s Tr^2 + 2h_s Tr^3}{(Tr - 1.00001)^3}$$

(Note, $a_s, b_s, \dots$ are $a, b, \dots$ in HBT equation.)

Now, we have the value of B , and the first and second order derivative of B . The value of P_s and the first and second order derivative of P_s . The value of V_s and the first and second order derivative of V_s . We can then obtain ΔC_p following expression,

$$C_p(P, T) - C_p(P_s, T) = CT \left(\frac{\partial^2 V_s}{\partial T^2}\right)_p \left[(B + P) \ln(B + P) - P + P_s - (B + P_s) \ln(B + P_s) \right]$$

$$+ \left[2CT \left(\frac{\partial V_s}{\partial T}\right)_p \left(\frac{\partial B}{\partial T}\right) + CT V_s \left(\frac{\partial^2 B}{\partial T^2}\right)_p \right] \left[\ln(B + P) - \ln(B + P_s) \right] - CT V_s \left(\frac{\partial B}{\partial T}\right)_p^2 \left(\frac{1}{B + P_s} - \frac{1}{B + P} \right)$$

$$\left[\left(\frac{\partial^2 V_s}{\partial T^2}\right)_p + C \left(\frac{\partial^2 V_s}{\partial T^2}\right)_p \ln(B + P_s) + 2C \left(\frac{\partial V_s}{\partial T}\right)_p \frac{\left(\frac{\partial B}{\partial T}\right)_p + \left(\frac{\partial P}{\partial T}\right)_p}{B + P_s} + CV_s \frac{\left[\left(\frac{\partial B}{\partial T}\right)_p + \left(\frac{\partial P}{\partial T}\right)_p\right](B + P_s) - \left[\left(\frac{\partial B}{\partial T}\right)_p + \left(\frac{\partial P}{\partial T}\right)_p\right]^2}{(B + P_s)^2} \right] (P - P_s)(-T)$$

With HBT equation, we can calculate V_s . We can get P_s from Lee-Kesler equation. These two quantities are needed to calculate density from Tait equation. In the coming months we intend to test this method by comparison with available experimental data. We do expect that some or many modifications will be necessary before our work on development of high pressure liquid equation of state is completed.

Goodwin^[5,6] has compiled data for benzene and toluene and fitted specific expressions so that smoothed data are generated over a large range of temperatures and pressures. We have used these data to test the Tait or Thomson equation for high pressure density and heat capacity predictions. The isotherms and isobars of density data of benzene are plotted in figures 1 and 2 and isobars of density data of toluene are shown in figure 3.

To test the Thomson equation we computed the densities using this equation and the deviations from experimental data are plotted in figures 4 and 5 for benzene and toluene. What is striking is that the error function has a systematic trend with temperature. Although errors in density are reasonably small ($< 1\%$, for $T_r < 0.9$), the correlation of error with temperature is likely to affect the accuracy of calculation of other thermodynamic properties. In fact enthalpy is a function of first derivative of density with temperature and heat capacity is a function of the second derivative. In figure 4, we observe that the error curves exhibit a point of inflection at approximately 450°K . It would therefore be expected that the heat capacity calculated from Thomson equation will agree with the experimental data at 450°K . This is indeed observed in figure 6 where we have plotted the experimental and calculated heat capacity. Over the entire temperature range, the errors in heat capacities calculated from Thomson equation (in excess of heat capacity at saturation pressure) were found to exceed 100% and hence Thomson equation in the current form was judged not very useful to compute other properties of the liquid aromatics besides density. For this purpose, modification of this equation could be necessary.

In addition to the need for better predictive methods for saturated density and vapor pressure, it was also observed that Thomson's expressions for parameters B and C also need to be revised. In figures 7 to 9, we show comparisons of Thomson's B and C and the same parameters regressed from experimental data on benzene and toluene. It is clear that Thomson's assumption of a constant C and the correlation for B in reduced temperature are not sufficiently accurate. Better expressions for B and C are therefore needed.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

figure 7

figure 8

Figure 9 .

4. A Predictive Vapor Pressure Correlation for Organic Liquids

A Predictive Vapor Pressure Correlation
For Organic Liquids

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Abstract

A new vapor pressure correlation has been developed to represent vapor pressures of organic liquids accurately between the melting and the critical temperatures. The model was originally developed for aromatic liquids, but has been applied to other organic liquids as well. It is based on Pitzer's 3-parameter corresponding states equation with two major features, (i) benzene is used as the reference fluid instead of an atomic fluid or noble gas and (ii) Wagner's equation is used to correlate vapor pressure of reference fluid and the perturbation term. The perturbation term is characterized by a parameter Φ . Regressed compound specific values of Φ are tabulated. Also, a correlation of Φ in terms of shape factor Ψ has been developed. Ψ is defined as the ratio of surface area per unit volume of the compound molecule to surface area per unit volume of benzene, or, $(\Psi - 1)$ represents the deviation in shape of the compound molecule from that of benzene molecule. A group contribution method has been developed to predict Ψ 's from volume (R) and surface area (Q) parameters of individual functional groups. In most cases, same R and Q are used as in UNIFAC. Adjustment of Q necessary for some groups is justified based on the polarity of the groups. It is also shown that Ψ is a good correlating parameter for acentric factor ω . In all, a range of vapor pressure correlations are presented from the compound specific regressed Wagner's equation to the predictive model using the group contribution method for Ψ and a correlation for Φ in terms of Ψ . In general, these correlations provide the best accuracy between melting and critical temperatures of all correlations available in the literature.

1. Introduction

A variety of equations for estimating vapor pressures of organic liquids are available in the literature. Most of the methods involve an extension of the Clausius-Clapeyron equation combined with Pitzer's three parameter corresponding states approach (Pitzer et al, 1955). The Lee-Kesler equation (Lee and Kesler, 1975) is the most commonly used equation for engineering applications and generally predicts vapor pressure to within 1% error between the boiling and the critical temperatures. This error, however, increases rapidly at lower reduced temperatures approaching the melting point. An accurate and generalized vapor pressure correlation for organic liquids valid from the melting to the critical temperature is currently not available. Such a correlation is crucial in the development of accurate liquid state and vapor state equations of state where the knowledge of the coexistence boundary between the two phases is essential.

The three parameter corresponding states methods for vapor pressure involve two significant aspects. The first one is the functional form used to represent vapor pressure of a specific compound, and the second one is the choice of the reference fluid and the third parameter that characterizes the perturbation term. In other words, the general representation has the form

$$\ln P_r = f^{(0)}(T_r) + \Phi f^{(1)}(T_r) \quad (1)$$

In Lee-Kesler equation Φ is the acentric factor. Although Lee-Kesler equation has been extensively used for engineering applications, recent literature indicates that improvement of this correlation in terms of better functional forms for $f^{(0)}$ and $f^{(1)}$ and better formulation of the perturbation term are possible and this is the objective of this work.

Exhaustive studies of functional forms to represent vapor pressure of organic liquids are available in the literature (Reid et al, 1987; Ambrose, 1978; Vetere, 1988; Wagner, 1973). Based on equations proposed by many others, Wagner (1973) started with an equation with an excess of twenty

five temperature dependent terms and using sophisticated regression methods determined the statistically most significant of these terms. The final equation (referred to as Wagner's equation) has the form

$$f(T_r) = \frac{1}{T_r} \left(aX + bX^{1.5} + cX^3 + dX^6 \right) \quad (2)$$

where $X = (1 - T_r)$

It has been generally concluded by a number of researchers that this is one of the most accurate forms to represent vapor pressure data (Ambrose, 1986; Reid et al, 1987; Vetere, 1988), and may provide the best method for vapor pressure computation with tabulated values of specific constants a, b, c, and d for various compounds.

For generalization of the correlation, the reference fluid (corresponding to term $f^{(0)}$ in equation (1) and the parameter Φ need to be defined. In Lee-Kesler equation, $f^{(0)}$ is obtained from noble gas vapor pressure and Φ is the acentric factor. In other variations available in the literature is the method of Teja et al (1981) that uses two nonspherical reference fluids while still keeping acentric factor as the third parameter. More recently Twu et al (1994) have developed a vapor pressure equation for heavy hydrocarbons using the Wagner equation and defining the third parameter as the modified acentric factor at $T_r = 0.5$ instead of $T_r = 0.7$. They report this method to work very well at low reduced temperatures.

In all the above methods, parameter Φ either as the acentric factor or the modified acentric factor needs a vapor pressure data point, and no accurate method for estimating these parameters from molecular properties have been successfully developed. In this work, our objective is to develop a vapor pressure correlation similar to that of Twu et al (1994) that is applicable to most organic liquids and make attempts to generalize the regressed parameters Φ in terms of molecular parameters. We

have used benzene as the reference fluid and Van der Waals volumes and surface areas are the molecular parameters explored. In all, four methods are presented ranging from specific to most general. The generalized method allows computation of Φ by a group contribution method that defines molecules in terms of functional groups similar to the UNIFAC groups (Fredensleud et al, 1975) and uses UNIFAC R and UNIFAC Q (modified for some groups) as the group parameters. These four methods provide the most versatile expressions for vapor pressure computation and allow computations from melting point to critical temperature with fair accuracy. The vapor pressure methods and results are discussed in the following sections.

2. Development of Vapor Pressure Methods

A vapor pressure databank of 124 organic compounds with a total of 2971 data points was compiled for the development. The compounds may be classified as alkanes (43 compounds, 906), alcohols (10 compounds, 185 points), alkylbenzenes (22 compounds, 706 points), phenols (7 compounds, 218 points), hydroaromatics (9 compounds, 174 points), two-ring aromatics (13 compounds, 298 points), three and four ring aromatics (8 compounds, 173 points), and other ring compounds (15 compounds, 311 points). Other ring compounds include some pyridines, anilines, thiophenes and furans. The databank is somewhat biased towards aromatic compounds, as initially the method was intended for application to coal liquid model compounds; other compounds were included later when it became clear that the approach was applicable to all organic liquids. Alkenes and acetylenes were, however, not included in the databank, but extension to these compounds is easily possible.

Using the databank, Wagner constants a , b , c , and d for the 127 compounds were regressed using "UNLSF" nonlinear regression subroutine of the IMSL library (IMSL, 1994). Excellent regression fits were obtained. The constants are listed in Table 1 and we denote the method using Wagner's equation with these specific constants as Method 1.

Benzene was chosen as the reference fluid. Thus $f^{(o)}$ in equation 1 was obtained from Wagner's equation with a, b, c, and d of benzene from Table 1. $f^{(1)}$ was also expressed as Wagner's equation and constants a, b, c, and d for $f^{(1)}$ together with 123 Φ 's corresponding to various compounds were regressed simultaneously from the vapor pressure data. Regressed values of a, b, c, and d for $f^{(1)}$ are $a = -1.273103$, $b = -0.219368$, $c = -0.263757$, and $d = -4.487833$. Regressed values of Φ are denoted as Φ_1 and tabulated in Table 1. The method using benzene as the reference fluid, with $f^{(1)}$ represented as above and with Φ_1 from Table 1 is denoted as Method 2.

Analogous to the definition of acentric factor, a third method was devised that uses same $f^{(o)}$ and $f^{(1)}$ as in Method 2, but Φ 's are re-defined to obtain an exact fit with experimental data at $T_r = 0.6$. Choice of $T_r = 0.6$ was considered optimum for maximum accuracy from melting to critical temperature for most compounds. Thus,

$$\Phi_2 = \left[\frac{\ln(P_r) - f^{(o)}(T_r)}{f^{(1)}(T_r)} \right]_{T_r=0.6} \quad (3)$$

These values of Φ denoted as Φ_2 are also given in Table 1 and this method we call Method 3.

The three methods developed so far are compound specific, in that, either a vapor pressure data point, or compound specific parameters are necessary and none of these methods can be applied to compounds for which no data are available. We, therefore, undertook the development of a fourth and generalized method which involves a group contribution method for Φ using basic and known molecular properties as parameters. This method is discussed below.

3. Group Contribution Method for Φ

Some methods are available in the literature for estimation of acentric factors (Reid et al, 1987). However, they use boiling points or other properties that need to be estimated separately. Even so, accuracy of these methods is limited. The approach followed here uses a group contribution method with Van der Waals volumes and surface areas as (Bondi, 1968) group parameters. In particular, we define the shape factor Ψ for a molecule that characterizes the difference in shape of the molecule from that of the reference fluid benzene and is expressed as

$$\Psi = \frac{S/V^{2/3}}{S_b/V_b^{2/3}} \quad (4)$$

where S and V are molecular surface area and volume of the compound and S_b and V_b are the same for benzene. Furthermore, the molecular surface area and volume parameters are obtained as summations over surface areas and volumes of groups constituting the molecule. UNIFAC R and Q (Fredenslund et al, 1975) are used as the group volume and area parameters, so that

$$V = \sum_{g=1}^N n_g R_g \quad (5)$$

$$S = \sum_{g=1}^N n_g Q_g \quad (6)$$

where n_g is the number of groups of type g and N is the number of group types in the molecule.

For all groups same R values are used as in UNIFAC. For non-polar groups the UNIFAC Q 's were used unchanged and rendered excellent results. However for polar groups such as alcohol, amine, halides, carboxylic acid, ether, sulfide etc., instead of defining more parameters the UNIFAC Q was adjusted for better accuracy as is discussed below. Some additional modifications of Q were

also necessary to account for some composite molecular structures.

First, Ψ 's for all compounds were calculated from equations 4, 5 and 6 using UNIFAC R's and Q's. A plot was prepared of Φ versus Ψ . A curve was fitted through the n-alkane data points which followed an excellent trend. Compounds that showed significant deviations from this curve were identified and it was quickly recognized that these compounds either contained polar groups or certain composite molecular structures. Q's for polar groups were next regressed for best fit of Ψ 's of these compounds with the n-alkane curve. Differences between these regressed Q's and original UNIFAC Q's may be seen from Table 2. A simply additive function such as equation 6 does not characterize the shape of the molecule completely. Consequently, some additional contributions to surface area were defined to represent multiple ring structures, alkyl branches and isomeric compounds resulting from ortho, meta or para attachments to rings. It was observed that hydroaromatic and aromatic compounds showed systematic deviations from the n-alkane curve which could be minimized by assigning contributions to S because of composite ring structures, which are listed in Table 3. Modifications were also devised to account for other molecular structures, and as a result equation 6 was reformulated as follows

$$S = \sum_{g=1}^N n_g Q_g + \sum_{r=1}^M n_r Q_r + \sum_{s=1}^L n_s Q_s + \sum_{p=1}^K \left(\sum_{g=1}^N n_{gp} Q_g \right) \Theta_p \quad (7)$$

The first summation in equation 7 is over all the groups in the molecule and is identical to the UNIFAC group contribution method except that a few Q's have been modified to account for polarity. The second summation gives the additional contribution to surface area because of composite ring structures. n_r represents number of ring structures of type r and Q_r the corresponding contribution from Table 3. The third summation is over other selected molecular structures. From the vapor

pressure data, two such structures were identified that affect the model results; they are (1) alkyl branches and (2) alkyl groups in the longest straight chain attached to a ring. n_s is a characteristic integer and Q_s represents contributions listed in Table 4. $s=1$ and 2 correspond to methyl and ethyl branches. For these n_s is defined in the following manner

$$n_s = \sum_{j=1}^{B_s} (n_j^*) \quad (8)$$

For alkyl branches ($s=1$ or 2), n_s is calculated in the following manner. B_s represents total number of branches of type s . For each of these a characteristic integer n_j^* is defined. n_j^* is unity for all branches, with two exceptions; when there are two alkyl branches attached to the same carbon atom, $n_j^*=2$ for each branch, and for an alkyl branch attached to a carbon atom in β position corresponding to an aromatic ring $n_j^*=0.5$. For $s=3$, n_s represents number of carbon atoms in the longest straight chain attached to a ring.

The last summation in equation 7 corrects for some group contributions because of their position in the molecule. These groups were already included in the summation given by the first term. Hence Θ_p represents a small factor that corrects for contributions of groups found in position characterized by p . Only two positional parameters are defined, $p=1$ corresponds to the attachments to aromatic rings in ortho positions and $p=2$ corresponds to double attachment to a carbon atom in a hydroaromatic ring. n_{gp} , therefore, represents number of groups of type g in position corresponding to p . Θ_p for $p=1$ and 2 are listed in Table 4. Although only a few structural and positional parameters are defined, these developments can be extended to various other structures if more extensive vapor pressure data on compounds with these structures are included. However, it should be noted that the dominant contribution to S in equation 7 comes from the first two summations, and the other two terms

serve as minor correction terms for better accuracy. In other words, although it is possible to improve the accuracy of the method by including more molecular structures, equation 7 gives Ψ for most molecular types that correlate very well with Φ and provides a very useful development towards a generalized and predictive vapor pressure correlation.

A few of examples of calculation of Ψ using equations 4-8 are included in the Appendix. Also a plot of Φ versus Ψ for the 127 compounds in our databank is shown in Figure 1. An excellent correlation is observed. The following expression was fitted through these points

$$\Phi = -4.25456 (1-\Psi) + 4.53448 (1-\Psi)^2 + 7.28665(1-\Psi)^3 \quad (9)$$

For the 127 compounds in our databank, Φ 's calculated from equation 9 (called Φ_3) are shown in Table 1.

Method 4 thus involves calculation of Ψ by the group contribution method described above, then using equation 9 to calculate Φ for the compound and finally calculating the vapor pressure from equation 1 with benzene as the reference fluid and using the Wagner parameters listed before.

4. Comparison with Experimental Data

Compound by compound errors were obtained for vapor pressures computed from the four methods described in the last section. Errors were also generated for the Lee-Kesler method. The compounds were aggregated into eight different classes and errors for each class are listed in Table 5. All the errors here and elsewhere in this paper are computed as absolute percentage values normalized by the experimental value as

$$Error (\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_i^{exp} - P_i^{calc}}{P_i^{exp}} \right| * 100 \quad (10)$$

Table 5 further confirms that Wagner's equation provides an excellent mathematic expression for vapor pressure as indicated by extremely low errors of Method 1. Methods 2 and 3 are equivalent to the Lee-Kesler method in that all three of these require a single parameter for each compound, Φ_1 , and Φ_2 for methods 2 and 3 and ω for the Lee-Kesler method. Method 3 and Lee-Kesler method are particularly similar in that both ω and Φ_2 use a single vapor pressure data point. Errors for method 2 are understandably lower than the other two as it uses regressed values of Φ . However, method 3 exhibits consistently lower errors than the Lee-Kesler equation. We attribute this primarily to the superior fit obtained from Wagner's equation. Definition of Φ_2 at $T_r = 0.6$ instead of at $T_r = 0.7$ as in ω also is an advantage as our databank contains significant number of data points at lower temperatures approaching the melting point. What is especially striking is that Method 4 which is completely general with no adjustable parameters gives errors very close to the Lee-Kesler method. An average error of 5.73% for a completely general method with a diverse data set such as this is the most significant result of this work, and this method provides by far the best generalized method for vapor pressure calculations.

To further show the accuracy of various vapor pressure methods we computed average errors in two narrow temperature ranges around the melting points and the boiling points of the compounds. These are shown in Table 6. For the second temperature range a single point closest to the boiling point was selected for each compound. Lee-Kesler method performs very well near the boiling point, but gives large errors near the melting point. The generalized vapor pressure method (Method 4) performs quite adequately in both the temperature ranges. Results for Method 1 are not shown in this table as these errors are significantly lower.

5. Conclusions

A series of methods are presented for the calculation of vapor pressures of organic liquids.

These methods use the Wagner's equation as the functional form and benzene as the reference fluid. The most significant of the methods is a generalized correlation (method 4) that allows computation of Φ in terms of a shape factor Ψ which in turn is evaluated by a group contribution method from the detailed information on functional groups that make up the molecule. Comparisons with experimental data show that this correlation represents the most accurate generalized vapor pressure method in the literature and gives similar accuracy as some of the more specific vapor pressure correlations. Furthermore, the correlation is applicable in the entire temperature range from the melting point to the critical temperature. That Ψ provides a good correlating parameter for vapor pressure is further confirmed by plotting acentric factor ω versus Ψ in Figure 2. Again an excellent correlation is observed and least squares fit through these points resulted in the following expression

$$\omega = -0.54388 + 0.44247 \Psi + 0.32051 \Psi^2 \quad (11)$$

ω calculated from the above expression were found to give an average error of 5.82% when compared with experimental values for the 127 compounds in our databank. Equation 11 thus serves as a good estimation procedure for ω if experimental value is not available.

The current work did not consider unsaturated hydrocarbons such as alkenes and acetylenes. Also, group contributions are listed for only a subset of the original UNIFAC groups (Table 2). However, the correlation can be easily extended to these and other compounds by compiling data and generating Φ 's by the same procedure as discussed above. Method 4 may be applied for vapor pressures of compounds containing groups not defined in Table 2, as it allows for calculation of Ψ of these compounds using UNIFAC R and Q values (Fredenslund et al, 1975). For nonpolar groups, this procedure should give better results than for polar groups. In any case it would be interesting to investigate the accuracy of the vapor pressures of these compounds calculated in this manner and this can serve as another test for the shape factor Ψ as the correlating parameter for Φ .

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Appendix

Examples of calculation of Ψ and Φ by the group contribution method:

1. Benzene ($C_6 H_6$)

Group Composition:

$$Id = g6 \quad n_g = 6$$

$$Id = r1 \quad n_r = 1$$

Volume (V):

$$\text{From eq. 5 and Table 2, } V = 6(0.5313) = 3.1878$$

Surface area (S):

$$\text{From eq. 7 and Tables 2 and 3,}$$

$$S = 6(0.4) + 0.45023 = 2.85023$$

Ψ :

$$\text{From eq. 4, } \Psi = 1$$

Φ :

$$\text{From eq. 9, } \Phi = 0$$

2. 2,2,3,3 - tetramethylpentane ($C_9 H_{20}$)

Group composition:

$$Id = g1 \quad n_g = 6, \quad Id = g2 \quad n_g = 1, \quad Id = g4 \quad n_g = 2$$

$$Id = s1 \quad n_s = 8 \text{ (equation 8)}$$

Volume (V):

$$\text{From eq. 5 and Table 2, } V = 6(0.9011) + 1(0.6744) + 2(0.2195) = 6.5200$$

Surface area (S):

$$\text{From eq. 7 and Tables 2 and 4,}$$

$$S = 6(0.848) + 1(0.5400) + 1(0.00) + 8(-0.08289)$$

$$= + 2(0.000)$$

$$= 4.9649$$

Ψ :

$$\begin{aligned} \text{From eq. 4, } \Psi &= [4.9649/6.5200]^{2/3} [2.85023/(3.1878)^{2/3}] \\ &= 1.0811 \end{aligned}$$

Φ :

$$\begin{aligned}\text{From eq. 9, } \Phi &= -4.25456(-0.0811) + 4.53448(-0.0811)^2 + \\ &\quad 7.28665(-0.0811)^3 \\ &= 0.3709\end{aligned}$$

From vapor pressure data, regressed $\Phi = 0.3535$

3. iso-butylbenzene (C₁₀H₁₄)

Group Composition:

$$\begin{aligned}\text{Id} &= \text{g1} \quad n_g = 2, \quad \text{Id} = \text{g2} \quad n_g = 1, \quad \text{Id} = \text{g3} \quad n_g = 1, \quad \text{Id} = \text{g6} \quad n_g = 5, \quad \text{Id} = \text{g7} \quad n_g = 1 \\ \text{Id} &= \text{r1} \quad n_r = 1 \\ \text{Id} &= \text{s1} \quad n_s = 0.5 \text{ (equation 8), } \quad \text{Id} = \text{s3}, \quad n_s = 3\end{aligned}$$

Volume (V) :

From eq. 5 and Table 2,

$$\begin{aligned}V &= 2(0.9011) + 1(0.6744) + 1(0.4469) + 5(0.5313) + 1(0.3652) \\ &= 5.9452\end{aligned}$$

Surface area (S):

From eq. 7 and Tables 2, 3 and 4,

$$\begin{aligned}S &= 2(0.848) + 1(0.540) + 1(0.2280) + 5(0.400) + 1(0.120) + 1(0.45023) \\ &\quad + 0.5(-0.08289) + 3(-0.02157) \\ &= 4.9281\end{aligned}$$

Ψ :

$$\begin{aligned}\text{From eq. 4, } \Psi &= [4.9281/(5.9452)^{2/3}] / [(2.85023/(3.1878)^{2/3})] \\ &= 1.1412\end{aligned}$$

Φ :

$$\begin{aligned}\text{From eq. 9, } \Phi &= -4.25456(-0.1412) + 4.53448(-0.1412)^2 + 7.28665(-0.1412)^3 \\ &= 0.6705\end{aligned}$$

From vapor pressure data, regressed $\Phi = 0.6638$

Table 1
Compound by Compound Listing of Vapor Pressure Model Parameters

Compound	No. Pts.	Regressed Parameters of Wagner's Equation				Φ_1	Φ_2	Φ_3
		a	b	c	d			
ethane	23	-5.59565	-1.09450	2.78646	-9.31640	-0.4866	-0.4385	-0.4596
propane	19	-6.54611	0.92229	-1.70431	-1.81520	-0.2310	-0.2274	-0.2791
n-butane	31	-6.73400	0.75885	-1.47420	-3.44690	-0.1040	-0.0466	-0.0770
isobutane	31	-6.53199	0.36853	-0.48984	-5.23761	-0.1605	-0.1095	-0.1969
n-pentane	32	-7.30208	1.45347	-2.42139	-4.03716	0.1188	0.1443	0.1327
isopentane	30	-6.91052	0.98570	-1.86811	-4.62577	0.0151	0.0255	0.0145
n-hexane	34	-7.28328	0.87839	-1.91476	-6.36663	0.3350	0.3361	0.3421
2-2-di- methylbutane	11	-7.10888	1.32372	-2.55661	-2.82332	0.0797	0.0763	0.0175
2-3-di- methylbutane	13	-7.24076	1.48146	-2.97980	-1.68744	0.1367	0.1351	0.1176
2-methyl- pentane	14	-7.45418	1.67489	-3.66965	0.00269	0.2581	0.2579	0.2279
3-methyl- pentane	14	-7.45965	1.72423	-3.55217	-0.44062	0.2322	0.2312	0.2279
n-heptane	36	-7.64773	1.15691	-2.59755	-6.70798	0.5506	0.5368	0.5468
2-2-3-tri- methylbutane	19	-7.13165	1.20143	-2.58446	-2.73257	0.1432	0.1454	0.1317
2-2-di- methylpentane	18	-7.31069	1.21186	-2.86826	-3.19086	0.2930	0.2938	0.2325
2-3-di- methylpentane	20	-7.44785	1.42192	-3.21231	-2.31023	0.3259	0.3273	0.3309
2-4-di- methylpentane	19	-7.30440	1.01587	-2.69603	-3.82560	0.3572	0.3582	0.3309
2-methyl- hexane	20	-7.82998	1.98653	-4.42607	-0.19460	0.4577	0.4591	0.4377

Table 1 (continued)

Compound	No. Pts.	Regressed Parameters of Wagner's Equation				Φ_1	Φ_2	Φ_3
		a	b	c	d			
3-3-di-methylpentane	19	-7.25164	1.25263	-2.67538	-2.76706	0.2112	0.2138	0.2325
3-ethyl-pentane	18	-7.49901	1.40655	-3.39867	-2.34554	0.3871	0.3881	0.3875
3-methyl-hexane	20	-7.87710	2.15721	-4.55298	-0.06726	0.4301	0.4312	0.4377
n-octane	35	-7.90361	1.34158	-3.48990	-5.96962	0.7385	0.7196	0.7441
2-2-4-tri-methylpentane	20	-7.36222	1.11796	-2.70643	-3.98400	0.3551	0.3559	0.3447
2-3-4-tri-methylpentane	20	-7.53354	1.40208	-3.28570	-2.61410	0.4016	0.4027	0.4380
2-methyl-heptane	20	-8.04601	1.96651	-4.78937	-0.66482	0.6500	0.6535	0.6407
3-methyl-heptane	20	-8.06158	2.08511	-4.92889	-0.15956	0.6223	0.6253	0.6407
n-nonane	27	-7.89929	0.82183	-3.02933	-8.37942	0.9386	0.9032	0.9325
2-2-3-3-tetra-methylpentane	20	-7.68100	1.89836	-3.97106	-1.08065	0.3535	0.3544	0.3709
2-2-3-4-tetra-methylpentane	20	-7.75707	2.00052	-4.35161	-0.01914	0.3941	0.3954	0.4581
2-2-4-4-tetra-methylpentane	20	-7.83728	2.16374	-4.45979	0.03498	0.3902	0.3912	0.3709
2-2-5-tri-methylhexane	18	-7.64442	1.28515	-3.84325	-2.48831	0.5799	0.5846	0.5519
2-3-3-4-tetra-methylpentane	18	-7.82858	2.14703	-4.48897	0.54966	0.3904	0.3921	0.4581

Table 1 (continued)

Compound	No. Pts.	Regressed Parameters of Wagner's Equation				Φ_1	Φ_2	Φ_3
		a	b	c	d			
3-3-di-ethylpentane	19	-7.85395	1.84927	-3.79489	-1.11196	0.4708	0.4719	0.4704
n-decane	28	-7.81158	0.23995	-2.63460	-10.49723	1.1185	1.0625	1.1112
n-undecane	25	-7.77993	-0.28680	-2.22837	-12.84721	1.3132	1.2362	1.2797
n-dodecane	27	-8.11846	-0.00634	-2.83113	-13.73006	1.4876	1.4139	1.4378
n-tridecane	19	-8.62118	0.68739	-4.13904	-11.97139	1.6090	1.5841	1.5855
n-tetradecane	16	-8.45923	0.00050	-3.32940	-16.35672	1.6839	1.7093	1.7229
n-pentadecane	16	-9.15930	1.31754	-6.11528	-9.61501	1.8254	1.8718	1.8502
n-hexadecane	10	-9.12882	0.61091	-4.85544	-21.52794	1.8879	2.0964	1.9676
n-heptadecane	17	-9.97306	2.26434	-7.83738	-11.89699	2.1494	2.2144	2.0752
n-octadecane	16	-10.72341	3.73760	-11.04394	0.17809	2.2738	2.3531	2.1734
n-nonadecane	17	-10.90346	3.79466	-11.71575	0.40109	2.4203	2.5192	2.2624
n-eicosane	17	-8.56640	-1.82602	-1.60768	-41.44102	2.3889	2.5385	2.3424
methanol	20	-8.53079	0.68536	-2.81112	0.22383	1.2365	1.2998	1.4687
ethanol	25	-8.35306	-0.12418	-4.70599	4.60894	1.6788	1.6948	1.3721
1-propanol	19	-8.09833	0.15845	-7.94358	10.03245	1.6093	1.7141	1.3904
1-butanol	16	-7.88499	0.22139	-8.75789	4.82301	1.4887	1.6678	1.4594
2-butanol	16	-7.76006	0.26168	-9.36987	1.85645	1.4358	1.6530	1.4542
1-pentanol	19	-7.98753	0.54258	-8.66317	-3.32416	1.5312	1.6462	1.5520
1-hexanol	13	-8.57561	0.61328	-5.86025	-15.27990	1.8374	1.7911	1.6548
1-heptanol	13	-7.48636	-0.63080	-5.62355	-21.58660	1.6829	1.6073	1.7608
1-octanol	18	-9.65249	4.11604	-12.77675	-4.75792	1.5928	1.6981	1.8658
1-decanol	26	-8.62059	1.38726	-8.23560	-19.25497	1.6903	1.7753	2.0642
benzene	115	-6.95798	1.27757	-2.56466	-3.40352	0.0000	0.0000	0.0000
toluene	112	-7.39804	1.64984	-3.06826	-2.53253	0.1653	0.1842	0.1668
ethylbenzene	26	-7.31540	0.91993	-1.99607	-5.94949	0.3359	0.3458	0.3469
n-propylbenzene	19	-8.07078	2.32368	-4.81737	-0.09030	0.5176	0.5185	0.5248
n-butylbenzene	26	-7.61102	0.61289	-2.16887	-7.71802	0.7105	0.7029	0.6982
iso-butylbenzene	20	-8.66956	2.95178	-4.54902	-2.53335	0.6638	0.6609	0.6705

Table 1 (continued)

Compound	No. Pts.	Regressed Parameters of Wagner's Equation				Φ_1	Φ_2	Φ_3
		a	b	c	d			
sec-butyl-benzene	20	-6.68538	0.35064	-4.01077	0.81494	0.3361	0.3346	0.6217
tert-butyl-benzene	20	-6.51107	0.10548	-3.70495	-0.39350	0.3007	0.2973	0.4516
iso-propyl-benzene	26	-7.45775	1.06834	-2.71781	-5.74456	0.4671	0.4537	0.4441
1-4-diethyl-benzene	20	-8.00395	1.52750	-4.05704	-2.44118	0.7418	0.7446	0.7424
o-xylene	43	-7.56459	1.41311	-2.72987	-4.59685	0.3586	0.3730	0.3344
m-xylene	47	-7.59129	1.30824	-2.56743	-5.05894	0.4037	0.4209	0.3670
p-xylene	36	-7.75577	1.77479	-3.37221	-2.91407	0.3976	0.4050	0.3670
1-methy-4-ethylbenzene	19	-7.28408	0.97666	-4.12247	0.02666	0.4851	0.4870	0.5443
1-methy-3-ethylbenzene	20	-7.06611	0.62742	-4.39562	2.12164	0.4988	0.5038	0.5443
1-methy-2-ethylbenzene	20	-7.00373	0.87653	-4.85234	3.08004	0.3989	0.3994	0.5049
1-3-5-tri-methylbenzene	19	-7.77784	0.95226	-2.78975	-4.36880	0.7132	0.7143	0.5638
1-2-4-tri-methylbenzene	20	-7.83751	1.40376	-3.53583	-2.18288	0.6268	0.6284	0.5330
1-2-3-tri-methylbenzene	20	-8.09552	2.10620	-4.41847	-0.44484	0.5850	0.5865	0.5177
o-cymene	15	-6.75929	-0.75157	-1.85524	-0.06929	0.5797	0.6247	0.5971
m-cymene	15	-6.56127	-0.78001	-2.51237	-0.04550	0.5651	0.5746	0.5945
p-cymene	28	-7.11186	-0.20253	-1.40842	-7.24285	0.6275	0.6295	0.6408
phenol	74	-9.68802	5.08371	-9.02709	-0.91117	0.9449	0.8875	0.9893

Table 1 (continued)

Regressed Parameters of Wagner's Equation

<u>Compound</u>	<u>No. Pts.</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>Φ_1</u>	<u>Φ_2</u>	<u>Φ_3</u>
o-cresol	25	-7.79020	0.45727	-1.59521	-13.91698	0.9199	0.8691	1.0600
m-cresol	25	-8.03008	1.18752	-4.39333	-9.61539	1.0780	0.9902	1.1026
p-cresol	26	-10.22684	5.17427	-7.86589	-7.98705	1.2237	1.1330	1.1026
2-4-xylene	26	-8.30519	0.90277	-3.31262	-8.22828	1.1924	1.1689	1.1916
2-5-xylene	21	-8.44273	0.13920	-0.00990	-16.83746	1.2903	1.2890	1.1916
3-5-xylene	21	-8.25477	1.55988	-6.24146	-8.12596	1.2298	1.1699	1.2297
cyclohexane	12	-7.18238	1.86726	-3.68252	-0.62253	0.0011	0.0012	0.0013
1-1'-dimethyl- cyclohexane	20	-6.87074	0.90897	-2.93410	-1.88465	0.1275	0.1263	0.1275
1-2-dimethyl- cyclohexane	20	-6.76614	0.77502	-3.31713	-0.80510	0.1497	0.1465	0.1116
n-propyl- cyclohexane	20	-6.62030	0.35418	-3.79283	0.27771	0.2723	0.2701	0.3050
iso-propyl- cyclohexane	20	-6.69060	0.80886	-4.46909	1.74809	0.1930	0.1873	0.2351
n-butyl- cyclohexane	20	-10.19568	6.94164	-10.52176	5.58311	0.5662	0.5577	0.4900
iso-butyl- cyclohexane	20	-7.90431	2.28039	-4.66688	-0.86496	0.4153	0.4150	0.4653
tert-butyl- cyclohexane	20	-6.72956	0.69810	-4.32554	1.44896	0.2485	0.2468	0.2714
cyclohexene	22	-6.60730	0.42158	-1.22426	-5.35363	0.0095	0.0025	0.0402
aniline	32	-6.81477	-0.87110	-0.93187	-7.39148	0.6602	0.6636	0.7430
2-methyl- aniline	33	-9.02981	3.26242	-5.54458	-6.06555	0.9206	0.8804	0.8188
3-methyl- aniline	33	-7.10117	-0.62492	-0.95586	-12.46182	0.8514	0.7879	0.8590
dimethyl- aniline	15	-6.62482	-2.21802	3.24090	-22.52547	0.7751	0.7631	0.7751

Table 1 (continued)

Compound	No. Pts.	Regressed Parameters of Wagner's Equation				Φ_1	Φ_2	Φ_3
		a	b	c	d			
bromobenzene	12	-7.25465	1.51101	-3.14369	-1.34609	0.1488	0.1471	0.1488
chlorobenzene	26	-8.70484	4.86640	-7.75994	5.62787	0.1124	0.1439	0.1128
benzoic acid	7	-7.73299	-0.95846	-4.52363	-6.21157	1.6395	1.6876	1.6395
anisole	6	-8.02577	2.18608	-4.70797	-0.05723	0.5335	0.5346	0.5342
phenetole	6	-8.35803	2.17465	-5.11306	-1.08888	0.8123	0.8112	0.8123
styrene	16	-6.73453	0.84102	-3.90241	-0.10466	0.1773	0.1553	0.1779
pyridine	47	-6.98929	1.07795	-2.78209	-2.54204	0.1187	0.1224	0.1297
2-methyl-pyridine	15	-7.76788	2.15492	-4.36708	0.02985	0.3384	0.3388	0.3125
4-methyl-pyridine	21	-7.19372	1.05260	-3.05789	-2.58571	0.2985	0.2990	0.3125
furan	13	-6.81370	1.09426	-2.72694	-2.33880	-0.0103	-0.0088	-0.0319
thiophene	29	-6.81896	1.08263	-2.02187	-4.49968	-0.0589	-0.0609	-0.0589
naphthalene	10	-7.86714	2.37544	-4.65037	0.58026	0.3321	0.3385	0.3766
1-methyl-naphthalene	42	-8.06523	1.77448	-3.40615	-2.71664	0.5677	0.6137	0.5496
2-methyl-naphthalene	37	-9.34223	4.79077	-7.28657	0.59456	0.5787	0.5846	0.5496
tetralin	31	-5.32759	-3.06718	1.25547	-8.67456	0.3991	0.3735	0.5423
quinoline	29	-7.10013	0.02499	-0.56556	-9.91599	0.4648	0.4541	0.4723
isoquinoline	27	-6.49217	-0.67718	-0.56918	-5.76787	0.2932	0.3170	0.2932
benzofuran	14	-6.73664	-0.91101	1.28075	-13.91238	0.4311	0.4368	0.2910
indan	29	-7.57201	1.52604	-3.12867	-3.13642	0.3394	0.3629	0.3356
indene	21	-6.71210	0.03756	-1.46630	-8.08464	0.3317	0.2737	0.2283
indole	24	-7.75449	1.38708	-4.78508	0.07885	0.6967	0.6979	0.6557
4-indanol	12	-3.24277	-10.05979	8.10013	-11.45164	1.1614	1.2208	1.1768
biphenyl	13	-6.03380	-2.46451	2.47775	-14.43551	0.4938	0.4991	0.6186
diphenyl-methane	9	-8.16299	1.22571	-1.56002	-37.20504	0.8686	0.9488	0.8105
anthracene	32	-13.56760	11.19201	-15.88900	22.81225	1.2200	1.4684	0.8987
pyrene	36	-19.34349	27.21880	-40.83796	53.28185	1.0064	1.0147	0.8768
triphenylene	15	-8.40185	1.69384	-4.40900	12.46838	0.8603	0.8755	0.9967

Table 1 (continued)

<u>Compound</u>	<u>No. Pts.</u>	<u>Regressed Parameters of Wagner's Equation</u>				Φ_1	Φ_2	Φ_3
		<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>			
phenanthrene	17	-12.22745	9.09521	-10.97417	4.85026	1.0264	1.0574	0.8987
dibenzofuran	21	-5.50940	-5.77660	12.38893	-32.23669	0.6187	0.6104	0.8152
fluorene	26	-7.08452	0.00806	-5.27437	7.87133	0.8136	0.8317	0.7464
carbazole	11	-12.43274	11.65961	-23.09508	57.52573	1.0430	1.0464	1.1085
acridine	15	-7.56196	0.07095	-2.13409	-0.27849	0.7480	0.8442	0.9791

Table 2
Volume (R_g) and Surface area (Q_g) Contributions
of various groups (equation 7)

<u>Id</u>	<u>Group Symbol</u>	<u>R_g</u>	<u>Q_g</u>	<u>$Q_{(UNIFAC)}$</u>	<u>Example</u>
g1	CH ₃	0.9011	0.8480	0.8480	2,2,4- trimethylpentane
g2	CH ₂	0.6744	0.5400	0.5400	5 CH ₃ , 1 CH ₂ , 1 CH, 1C
g3	CH	0.4469	0.2280	0.2280	
g4	C	0.2195	0.0000	0.0000	
g5	OH	1.0000	1.7700	1.20000	Ethanol 1 CH ₃ , 1 CH ₂ , 1 OH
g6	ACH*	0.5313	0.4000	0.4000	Iso-butylbenzene
g7	AC	0.3652	0.1200	0.1200	5 ACH, 1 AC, 2 CH ₃ , 1 CH ₂ 1 CH
g8	ACOH	0.8952	1.2562	0.6800	Phenol 5 ACH, 1 ACOH
g9	ACNH ₂	1.0600	1.1975	0.8160	Aniline 5 ACH, 1 ACNH ₂
g10	ACN	0.8978	0.5332	-----	Dimethylaniline 5 ACH, 1 ACN, 2 CH ₃
g11	ACCl	1.1562	0.844	0.844	Chlorobenzene 5 ACH, 1ACCl
g12	ACBr	1.3144	0.9611	0.952	Bromobenzene 5ACH, 1ACBr
g13	ACCOOH	1.6665	2.1967	1.344	Benzoic acid 5 ACH, 1ACCOOH
g14	ACOCH ₃	1.5102	1.3462	1.208	Anisole 5 ACH, 1 ACOCH ₃
g15	ACOCH ₂	1.2835	1.1031	0.900	Phenetole 5 ACH, 1 ACOCH ₂ , 1 CH ₃
g16	ACCH=CH ₂	1.7106	1.2068	1.296	Styrene 5 ACH, 1ACCH=CH ₂
g17	AN	0.3428	0.3675	0.113	Pyridine 5 ACH, 1 AN
g18	ANH	0.5326	0.7742	-----	Carbazole 8 ACH, 4AC, 1 ANH
g19	AO	0.2439	0.2706	-----	Furan 4 ACH, 1 AO
g20	AS	0.9188	0.6747	-----	Thiopene 4 ACH, 1AS

*: All groups starting with "A" are aromatic groups

Table 3
Contributions to Surface Area (Q_r) of Various Ring Structures (Equation 7)

<u>Id.</u>	<u>Structure</u>	<u>Q_r</u>
r1	One aromatic-ring	0.45023
r2	Two aromatic-ring	0.71355
r3	Three aromatic-ring	1.10481
r4	Four aromatic-ring	1.23800
r5	One aromatic -one naphthene (fused)	0.60446
r6	Two aromatic -one naphthene (fused)	1.01571
r7	Cyclohexane (without attachment)	0.102451
r8	Cyclohexane (with attachment)	-0.118173
r9	Isoquinoline	-0.13794

Table 4
Contributions to Surface Area (Q_s) and Positional factors (Θ_p) for Some Molecular Structures (equation 7)

Id.	Structure	Q_s	Θ_p
s_1	CH ₃ branch eg. $\begin{array}{c} \text{---C---} \\ \\ \text{CH}_3 \end{array}$	-0.08289	-----
s_2	CH ₂ -CH ₃ branch eg. $\begin{array}{c} \text{---C---} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$	-0.1233	-----
s_3	An alkyl group in the longest straight chain attached to a ring	-0.02157	-----
p_1	Attachments to an aromatic ring in ortho position	-----	-0.0128
p_2	Two attachments to a carbon in a hydro-aromatic ring	-----	-0.0539

Table 5
Comparison of vapor pressure errors from different methods

Group	No. Pts	Method1	Method2	Method3	Method4	Lee-Kesler
1 alkanes	906	0.260	1.96	2.63	3.07	3.17
2 alcohols	185	0.088	5.75	8.46	16.24	9.62
3 alkylbenzenes	706	0.210	1.12	1.27	3.69	3.34
4 phenols	218	0.884	4.39	7.60	7.47	4.89
5 hydro- aromatics	174	0.141	1.33	1.45	3.78	4.07
6 two-ring aromatics	298	0.612	3.10	4.03	6.98	12.60
7 three and four -ring-aromatics	173	0.724	6.76	9.54	17.23	17.85
8 other ring compounds	311	0.462	1.88	2.11	3.82	3.49
Total	2971	0.360	2.53	3.45	5.73	5.55

Table 6

Comparison between our methods and Lee-Kesler Method in Temperature ranges around melting and boiling points

Temperature Range	No. Pts	Method2	Method3	Method4	Lee-Kesler
$T_m \leq T \leq (T_m + 30^\circ\text{K})$	100	8.06%	15.65%	13.70%	20.29%
T nearest to T_b	127	3.15%	2.92%	5.01%	2.54%

Figure Captions

1. Experimental Φ 's and Φ 's calculated from equation 9 are plotted versus shape factor Ψ .
2. Experimental ω 's and ω 's calculated from equation 11 are plotted versus shape factor Ψ .

5. Generalized Method for Prediction of Saturated Liquid Volumes Using Modified Rackett Equation and Van der Waals Volumes

Generalized Method for Prediction of Saturated Liquid Volumes Using Modified Rackett Equation and Van der Waals Volumes

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Rackett (1970) developed an equation to estimate saturated liquid volumes which was later modified by Spencer and Danner (1972). The modified Rackett equation represents a simple and very widely used method to predict saturated liquid volumes. In addition to being fairly accurate, this equation is mathematically continuous and renders expressions for first and second derivatives of saturated liquid volume needed for computations of thermodynamic properties such as enthalpies and heat capacities from certain liquid state equations of state that use saturated liquid volume like the Tait equation (Thomson et al, 1982). There are other methods available in the literature to calculate saturated liquid volumes. Prominent amongst them is COSTALD (Hankinson and Thomson, 1979). The modified Rackett equation is almost as accurate as COSTALD and somewhat simpler to use. The objective of this work is to further enhance the applicability of the modified Rackett equation by developing a correlation for the parameter Z_{RA} with Van der Waals volume of the molecule and with a volume parameter calculated by summing the UNIFAC volume parameters (R) of individual groups making up the molecule. The modified Rackett equation of Spencer and Danner is written as

$$V_s = RT_c Z_{RA} [1 + (1-T_r)^{2/7}] / P_c \quad (1)$$

Z_{RA} is a parameter which has a unique value for each compound. Z_{RA} 's for a number of

compounds have been tabulated by Spencer and Danner. Yamada and Gunn(1973) proposed a method to estimate Z_{RA}

$$Z_{RA} = 0.29056 - 0.08775 \omega \quad (2)$$

Although, useful, equation 2 results in considerable errors in predicted saturated volumes. It is the objective of this work to develop an accurate predictive correlation for Z_{RA} based on molecular parameters. Van der Waals volume (V_w) of the molecule with the group contributions proposed by Bondi (1968) is used as the correlating parameter. Alternatively, if successful, the UNIFAC group volume parameter R , which is closely related to Bondi's group contributions to Van der Waals volume would provide a good correlating parameter for Z_{RA} . The method so conceived, will be consistent with the recent predictive vapor pressure correlation of Wang and Kabadi (1995) in which the molecular shape parameter is calculated from the UNIFAC volume and surface area parameters R and Q .

Correlation of Z_{RA} with V_w

The data used in this work included 124 compounds classified into various families. The experimentally regressed Z_{RA} 's for most of these compounds (88 compounds) were obtained from Reid et al (1987). Z_{RA} 's of other 36 compounds were regressed using liquid density data obtained from API Monograph Series (1978-1985), and Kudchadker et al (1978a, 1978b). These compounds included high molecular weight aromatics and heterocycles, phenols and some amines. Van der Waals volumes (V_w) were computed using the group contribution tabulations of Bondi (1968). A polynomial fit for Z_{RA} with V_w gave the following expression

$$Z_{RA} = 0.16870 + 0.53719 Z_w + 28.38709 Z_w^2 \quad (3)$$

where

$$Z_w = (P_c V_w) / (RT_c) \quad (4)$$

Equation 3 was obtained using data for all the compounds except alcohols and phenols, and represents an excellent correlation as seen from Figure 1 where Z_{RA} 's calculated from equation 3 and experimental values are plotted. Bondi's Van der Waals volume tabulations include a compound specific correction factor for OH group because of hydrogen bonding. Using the experimental Z_{RA} 's and equation 3, an average contribution for the OH group was regressed as $4.55 \text{ cm}^3/\text{mole}$ which is a correction of $-3.49 \text{ cm}^3/\text{mole}$ to the value of $8.04 \text{ cm}^3/\text{mole}$ tabulated by Bondi. Table 1 shows a comparison between equation 2 and equation 3 for estimation of Z_{RA} . The compounds are divided into various homologous series and average percent errors corresponding to each series are tabulated.. An average absolute error of 1.32 % was obtained when Z_{RA} computed from equation 3 were compared with experimentally regressed Z_{RA} for all 124 compounds. The same comparison using equation 2 gave an error of 2.64 %

Correlation for Z_{RA} Using UNIFAC R

With the success of equation 3, a further attempt was made to replace the group Van der Waals volumes by the UNIFAC group volume parameters R (Fredenslund et al, 1975). Although, the latter were obtained from Bondi's tabulations and an arbitrary normalization factor, the UNIFAC procedure to estimate molecular volumes includes some simplifications of the more rigorous approach of Bondi. Bondi's procedures involve a number of exceptions and corrections that depend on the molecular types; UNIFAC R's, on the other hand, were averaged to a single constant per group and do not include any molecular factors. Some examples of these differences are:

1. Different cycloparaffins i.e. cyclopropane, cyclopentane, cyclohexane, etc. are listed with their own characteristic Van der Waals volumes by Bondi. In the UNIFAC procedure,

methyl groups in cycloparaffins are considered equivalent to paraffinic methyl groups and molecular volume parameter for a cycloparaffin is calculated by simply summing the R's over all the methyl groups.

2. In fused multi-ring aromatic compounds, the condensed carbons between aromatic rings are assigned different contributions from other aromatic carbons in Bondi's tabulations. No such distinction is made in the UNIFAC procedure.
3. Bondi's procedure involves a number of correction factors, such as, correction for OH group in alcohols, correction for cis and trans isomers, correction for amine group in various molecular types, etc. The UNIFAC procedure assigns a single constant value R per group and includes no exceptions and corrections.

UNIFAC group contribution correlation is widely used in vapor-liquid equilibrium calculations. Although, the group parameters R and Q are based on Bondi's tabulations of Van der Waals volumes and surface areas, they are more readily available (Reid et al, 1987) and easier to use. To obtain a correlation for Z_{RA} using UNIFAC R's, first the molecular volume parameter was defined as

$$V_U = \sum R_k \quad (5)$$

where R_k is the UNIFAC R of group k and the summation is over all the groups in the molecule.

The correlation for Z_{RA} was then obtained as

$$Z_{RA} = 0.13041 + 40.4063 Z_U \quad (6)$$

where

$$Z_U = P_c V_U / (R T_c) \quad (7)$$

Equation 6 again represented excellent fit as seen from Figure 2 where experimental and calculated Z_{RA} 's are plotted against Z_U . As with the previous correlation, the R value of OH group was corrected to 0.528 which is a correction of -0.472 from the original UNIFAC value of 1.00. The accuracy of equation 6 to estimate Z_{RA} is compared with equation 2 and equation 3 in Table 1. For the same 124 compounds, equation 6 gave an overall percent error of 1.93 compared to 2.64 for equation 2 and 1.32 for equation 3. Thus, equation 6, although better than Yamada's method is not as good as the method using Van der Waals volumes of Bondi.

Comparison with Experimental Density Data

Saturated liquid density data were compiled for 40 mostly ring compounds with a total of 787 data points. Most of these data were obtained from API Monograph Series (1978 - 1985). Data on benzene were from Chao (1978), toluene from Goodwin (1989), and phenol, cresols and xylenols data were obtained from Kudchadker et al (1977, 1978a, 1978b). Saturated liquid volumes were computed using modified Rackett equation with regressed Z_{RA} , Z_{RA} from equations 3&4, Z_{RA} from equations 6&7, and Z_{RA} from equation 2. Results are shown in Table 2. The compounds are again divided into homologous series and average errors in estimated volumes are listed for each family of compounds. As expected, usage of regressed Z_{RA} 's results in the minimum overall error of 0.87 %. However, of the three estimation methods for Z_{RA} , the two presented here perform appreciably better than the method of Yamada. The method based on Van der Waals volumes (equations 3&4) gave an overall error in density of 3.15 %, Using the UNIFAC R's instead of Bondi's list of contributions (equations 6&7) resulted in an error of 3.66 %, whereas Yamada's correlation performed worst with an average error of 5.81 %. This exercise showed that deviations of estimated Z_{RA} 's from regressed values, also result in proportional deviations in pre-

dicted liquid volumes. Although, the density data set used here is not representative of various families of organic compounds, such an exercise could be carried out with a more extensive density data set, and undoubtedly the results will be quite similar to the results of Table 2.

Yamada's correlation, moreover, has a limitation in that it uses acentric factor as a correlating parameter. For high molecular weight compounds, when accurate vapor pressure data are not available, acentric factors obtained from different sources could easily vary by as much as 10 %. Also, in predicting acentric factors by correlations, average errors of around 10 % are quite common. A pair of correlations are presented here that eliminate this limitation and provide methods that allow estimation of Z_{RA} from simply the group composition of the molecule; and furthermore, these correlations are more accurate for density estimation than currently available predictive correlations.

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Notation

P_c = critical pressure

R = gas constant

R_k = UNIFAC volume parameter of group k

T_c = critical temperature

T_r = reduced temperature

V_s = saturated liquid volume in cm^3/mole

V_U = volume parameter defined by equation 5

V_w = Van der Waals volume in cm^3/mole

Z_{RA} = modified Rackett parameter

Z_U = compressibility factor defined equation 7

Z_w = compressibility factor defined by equation 4

Greek Letter

ω = acentric factor

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Table 1 Comparison of Predicted Z _{RA} 's with the values Regressed from Experimental Data				
Homologous Series	No. Of Points	Percent Errors (Absolute)		
		Eq. 2	Eq. 3,4	Eq. 6, 7
Paraffins	34	1.692	0.756	1.327
Halogenated Paraffins	6	4.815	1.986	2.404
Cycloparaffins	4	0.316	0.167	0.412
Olefins	13	1.549	1.751	2.585
Aromatics	26	2.781	0.899	1.485
Aromatic Derivatives	4	1.474	0.327	2.518
Heterocycles	8	2.021	1.182	1.061
Alcohols	8	4.834	2.546	3.272
Phenols	9	6.954	2.078	3.978
Amines	7	2.673	3.383	2.539
Ethers	3	0.717	1.814	1.027
Sulfides	2	1.259	0.267	1.957
Total	124	2.636	1.322	1.925

* All errors reported in this work are calculated as

$$(|\text{exp}-\text{calc}| / \text{exp}) * 100.$$

exp = experimental value

calc = calculated value

Table 2 Comparison of Predicted Molar Volumes With Experimental Data						
Homologous Series	No. Of Compounds	No. Of Points	Percent Errors (Absolute)			
			Regressed ZRA	ZRA (Eq. 2)	ZRA (Eq. 3, 4)	ZRA (Eq. 6, 7)
Phenols	9	124	.536	10.97	3.079	5.906
Amines	4	120	1.393	6.085	7.413	6.412
Heterocycles	5	96	3.210	2.904	3.875	2.926
Alkylbenzenes	6	141	0.196	1.698	1.055	1.111
Two-ring compounds	11	243	0.383	5.458	2.172	3.101
Three-ring compounds	5	63	0.323	10.14	2.504	3.027
Total	40	787	0.867	5.811	3.148	3.664

Figure Captions

1. For 124 organic liquids, Z_{RA} 's regressed from experimental data and those obtained from correlation given by equation 3 are plotted against the compressibility factor Z_w defined by equation 4.
2. For the same 124 compounds, Z_{RA} 's regressed from experimental data and those obtained from correlation given by equation 6 are plotted against the compressibility factor Z_U defined by equation 7.