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CHEMICAL CHARACTERIZATION OF THE SURFACE SITES OF COAL
Final Report

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I. INTRODUCTION

The attractive forces between interacting pairs of molecules in either the gas or liquid phase results from three kinds of van der Waals interactions: London dispersion forces, which are present for all molecules that are to some degree polarizable, and Keesom and Debye dipole interactions for molecules having dipole moments. In liquids the dipole interactions with nearest and next-nearest neighbors are diminished by the limited ability of mutual orientation of the interacting dipoles. For systems in which Lewis acid-base interactions are absent, only the van der Waals interactions are present and are often loosely termed (London) dispersion forces, as this is usually the dominant contributor. When acid-base interactions are present they add to the dispersion forces and result in a larger overall attractive force. The assignment of these two contributions to the physical properties of binary systems has been successfully used in the literature; such as in the heats of mixing (where $\Delta H_M = \Delta H_M^d + \Delta H_M^{ab}$), in the surface tension of liquids (where $\gamma = \gamma^d + \gamma^{ab}$), and in infrared spectral shifts (where $\Delta\nu = \Delta\nu^d + \Delta\nu^{ab}$). Here the superscript (d) refers to the van der Waals (largely dispersion force) contribution, and (ab) refers to the Lewis acid-base contribution.

In the study of intermolecular interactions between two components such as an acid and a base, it is important to recognize whether or not the interaction takes place in a solvent, since if a neutral solvent is present the van der Waals interactions tend to cancel out, as Drago pointed out many years ago¹. Section III.B. is devoted to the interactions in two-component systems, base and candidate acid, the system Mayer and Gutmann² used for estimating the Acceptor Number for organic liquids. Similar spectral shift studies in three-component systems (such that van der Waals interactions should be minimized) are presented in Section III.C.

Mayer and Gutmann introduced the concept of using the ^{31}P NMR chemical shift of triethylphosphine oxide (Et_3PO), a Lewis base, for characterizing the electrophilic (or acidic) nature of solvents. It was proposed that an empirical parameter, the Acceptor Number (AN), be used to indicate the relative Lewis acidity of solvents. The Acceptor Number was based on the measured ^{31}P chemical shift of Et_3PO in the solvent being evaluated (a two-component system). The acid-base interaction of Et_3PO with an electrophilic site occurs by electron-donation by the oxygen atom of the $\text{P}=\text{O}$ group. This causes a decrease in the electron density at the phosphorus atom and a corresponding down-field ^{31}P shift. Based on the magnitude of this shift, the Acceptor Number (AN) was assigned to the solvent using equation [1], where $\Delta\delta_\infty$ is the NMR chemical shift corrected for volume susceptibility and extrapolated to infinite dilution.

$$\text{AN} = 100 \frac{\Delta\delta_\infty(\text{Solvent}:\text{Et}_3\text{PO})}{\Delta\delta_\infty(\text{SbCl}_5:\text{Et}_3\text{PO})} \quad [1]$$

It was assumed that the Acceptor Number was a measure of the acidity or electrophilicity of the solvent. However as will be shown, the failure to recognize the presence of van der Waals interactions and their concomitant effects on the ^{31}P chemical shift resulted in the erroneous assignment of appreciable AN-values to liquids such as diethyl ether, tetrahydrofuran, dioxane, and pyridine, which are appreciably basic but do not have electrophilic (acidic) sites sufficient even to promote self-association. We will present in this report a method for determining the van der Waals and acid-base contributions to the overall ^{31}P chemical shifts ($\Delta\delta^d$ and $\Delta\delta^{ab}$) and to the Acceptor Numbers (AN^d and AN^{ab}) of the Meyer and Gutmann two-component systems, and to illustrate the method with experimental results for thirty-two liquids.

II. EXPERIMENTAL

II.A. Instrumentation and supplies

Infrared measurements were made using a Mattson FTIR Sirius 100 spectrometer equipped with a liquid cell containing KBr windows. The cell was dried in an oven and loaded in a glove-bag purged with dry nitrogen. IR peak transmissions were generally 20 to 50% with peak centers determined at half-height.

A JEOL FX90Q Multinuclear NMR was used for measuring ^{31}P , ^{29}Si , and ^{199}Hg chemical shifts. Sample tubes were 10 mm in diameter and equipped with a coaxial external reference cell containing diphenyl-phosphinic chloride, trimethyl silane, or a saturated solution of diphenyl mercury in dimethyl sulfoxide. Chemical shifts in two component systems were determined at several different concentrations, corrected for volume susceptibility differences, and extrapolated to infinite dilution. Chemical shifts in three component systems were determined at several concentrations and analyzed by the method given below. All spectra were recorded with proton decoupling in order to maximize accuracy and sensitivity.

Calorimetric measurements were performed on a Setaram C80 calorimeter. This state of the art heat flow calorimeter was equipped with a matching set of membrane mixing cells. All measurements were performed at 30°C.

Triethylphosphine oxide was prepared by the method of Burg and McKee. The material was sublimed several times at room temperature under high vacuum. The anhydrous white crystalline solid had a melting point of 50-51°C. Due to the hygroscopic nature of Et_3PO and some of the solvents, all sample preparations and handling were done in a dry nitrogen purged glove-bag.

Aldrich hexane, benzene, diiodomethane, and spectral grade carbon tetrachloride were dried over freshly activated Linde 4-A molecular sieves for

several weeks prior to use. Pyridine was dried over KOH pellets and distilled from BaO. Squalane was also purchased from Aldrich and stripped of hydrophilic impurities with a basic alumina column. Solvents used for interfacial tension measurements were obtained from Aldrich in high purity and used as received.

II.B. Interfacial Tension

Surface Free Energies of Acidic Liquids. In evaluating liquids having both van der Waals and Lewis acid-base interactions with the test probes, it is necessary to determine the van der Waals contribution to surface free energy (γ^d), from which the van der Waals and acid-base components of the infrared and NMR chemical shifts could be determined. The van der Waals contribution to surface tension (γ^d) was obtained for thirty two acidic test liquids by measuring the interfacial tension between the test liquid and a reference hydrocarbon liquid having only van der Waals interactions, see Table 1. Interfacial tensions were determined using the drop volume/weight method. A micrometer syringe with a dropping tip radius of 0.0435 cm was used for all measurements. The temperature was $23 \pm 0.5^\circ\text{C}$. Squalane, a liquid saturated hydrocarbon, FW 423, for which $\gamma = \gamma^d = 29.2$ dynes/cm, was used as this reference liquid. The extent of solubility in squalane of each immiscible liquid was determined by measuring changes in the refractive index of squalane. Interfacial tensions were measured with the denser liquid in the syringe so that all measurements could be made by dropping downwards into the less dense liquid. All drops were formed in a saturated atmosphere of the liquid. Extreme care was taken to prevent "creep" of the liquid up the outside of the dropping tip. The van der Waals contribution to surface tension (γ^d) for the electrophilic solvents was calculated using the interfacial tension equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} \quad [2]$$

where γ_{12} is the interfacial tension, γ_1 and γ_2 are the surface tensions of liquids 1 and 2, and γ_1^d and γ_2^d are the van der Waals contributions to surface tension for liquids 1 and 2. Test liquids soluble in squalane were assumed to have no acid-base self-association; i.e., for these liquids $\gamma = \gamma^d$.

II.C. Infrared spectral shifts in two component systems

Van der Waals Contributions to Infrared Shifts. Spectral shift studies have previously been reported regarding van der Waals and acid-base contributions to infrared shifts³. The infrared carbonyl shift of ethyl acetate in non-acidic liquids was found to be related to the dispersion force contribution to surface tension (γ^d), and to the cohesive energy density (δ_d^2) by the following expressions:

$$\Delta\nu_{CO}^d = -0.714 \gamma^d \quad [3]$$

$$\Delta\nu_{CO}^d = -0.247 \delta_d^2 \quad [4].$$

A similar approach was taken to study the infrared P=O shift of Et_3PO , P=S shift of tricyclohexylphosphine sulfide (TCHPS), and SiO-H shift of Ph_3SiOH . When these probes interact with solvents, chemical shifts are observed for the infrared peak of the indicated stretch. These shifts are also composed of van der Waals and Lewis acid-base contributions. In order to calculate the van der Waals contribution to infrared shifts, test liquids having only van der Waals intermolecular interactions were interacted with the probes, i.e. $\gamma^d = \gamma$. The liquids selected had a broad range of surface tensions, and none were acidic and none were self-associating; that is, they were squalane-miscible. Typical solvents used were hexane ($\gamma = 18.4 \text{ mJ/m}^2$), CCl_4 ($\gamma = 27.0 \text{ mJ/m}^2$), benzene ($\gamma = 28.9 \text{ mJ/m}^2$), pyridine ($\gamma = 38.0 \text{ mJ/m}^2$), and diiodomethane ($\gamma = 50.8 \text{ mJ/m}^2$). Dilute solutions ($\approx 0.05\text{M}$) of the probes in

these solvents were prepared and the infrared peak position of the indicated stretching frequency absorption determined.

Acid-Base Contributions to Infrared Shifts. Since γ_2^d can be determined by rearranging equation [2], the van der Waals component of the infrared shift can be determined by substitution into appropriate equations having the form of equation [3]. The acid-base contribution is then obtained by using equation [5] which states that the total shift is the sum of the component terms.

$$\Delta\nu = \Delta\nu^d + \Delta\nu^{ab} \quad [5]$$

The $\Delta\nu_{\text{probe}}^{ab}$ contributions were calculated using this method for all two component (probe-solvent) studies. The infrared shifts were then correlated with the heats of acid-base interaction, $-\Delta H^{ab}$ calculated from the Drago E and C equation

$$-\Delta H^{ab} \text{ (kcal/mol)} = C_A C_B + E_A E_B \quad [6]$$

via equations of the form

$$-\Delta H^{ab} = a \Delta\nu^{ab} + b \quad [7]$$

where a and b are constants derived from linearized data for several probes.

II.D. NMR spectral shifts in two component systems

Van der Waals Contributions to NMR Chemical Shifts. In order to calculate the van der Waals contribution to the NMR probe chemical shift correlations were developed between the probe chemical shift and the van der Waals contribution to surface tension. This is expressed mathematically as:

$$\Delta\delta^d = a \gamma^d + b \quad [8].$$

Acid-base contributions to NMR shifts. NMR chemical shifts can be treated in an analogous manner to the infrared shifts. By determining γ^d for the solvent of interest, the van der Waals contribution to the shift, $\Delta\delta^d$, is

obtained from equation [8], and the acid-base contribution, $\Delta\delta^{ab}$, is calculated by difference similarly to equation [5]. Then

$$-\Delta H^{ab} \text{ (kcal/mol)} = a \Delta\delta^{ab} \text{ (ppm)} + b \quad [9].$$

II.E. Infrared spectral shifts in three component systems

The spectral shifts which occur in three component systems are very simple to evaluate. It has been shown by Drago that the shift is directly proportional to the heat of acid-base interaction⁴. The general relationship is given in equation [10]. One need not be concerned about the actual

$$-\Delta H^{ab} \text{ (kcal/mol)} = a \Delta\nu^{ab} \text{ (cm}^{-1}\text{)} + b \quad [10]$$

value of the equilibrium constant since the rate of dissociation of the acid-base complex is slower than the vibrational frequency of the spectral feature under study. Thus two distinct peaks are observed in the infrared spectra, one for the free (uncomplexed) probe and one for the complexed (acid-base adduct) probe. The spectral shift is simply evaluated in cm^{-1} . Care should however be taken to prevent the formation of 1:2 or 2:1 complexes. No corrections due to dispersion force interactions are required as they are equivalent for both the free and complexed probe. In principle the infrared spectral shifts are independent of the solvent. However it is prudent to test this assumption when a new solvent is required as the solvent must not interact with the probe of test molecule by any forces other than dispersion forces.

II.F. NMR spectral shifts in three component systems

In section II.B. and II.C. we describe the method of determining the heat of acid-base interaction in two-component systems (acid and base) from measured infrared and NMR spectral shifts. The basis for this method was that spectral shifts are the sum of shifts owing to two types of molecular

interactions, i.e. van der Waals and Lewis acid-base. Thus if the van der Waals contribution to the spectral shift is determined, the acid-base portion is obtained by difference. However, when two molecules interact in a neutral solvent, a three-component system, the van der Waals interactions tend to cancel out such that spectral shifts are due solely to acid-base interactions.

Infrared spectral shift measurements in three-component systems are in principal more accurate since through the appropriate choice of a neutral solvent, the heat of interaction can be directly obtained. Moreover, since the concentration of reacting species can be controlled, one can prevent undesirable interactions from occurring. For example, the self association of protonic acids can be prevented by using low acid concentrations (≤ 0.02 mole/liter). Low acid and/or base concentrations can also be used to prevent the formation of 2:1 or 1:2 adducts. There is a price to be paid however for being able to remove all but the 1:1 acid-base interactions, namely the mathematical treatment is more involved, the choice of concentrations is restricted, and spectral shift measurements must be performed at several concentration ratios. In this section we will present the theory behind NMR spectral shifts measurements in three component systems. In addition we will show how NMR chemical shifts in three-component systems can be used to characterize the "acidity" of many of the solvents investigated by Gutmann in two-component, base:solvent, systems.

The method of analysis is dependent on the rate of association and dissociation of the complex. The slow exchange and fast exchange conditions represent two extremes for these rates and are the easiest to interpret. Analysis of data in the intermediate exchange condition involves inspection of line shapes and will not be discussed here. A thorough discussion of the intermediate exchange conditions is given by Feeney et al⁵.

Consider first the interaction of a probe molecule P interacting with a ligand molecule L to form a 1:1 complex PL, where P contains an NMR active nucleus in which the electronic environment of that nucleus is perturbed when the complex is formed. Under equilibrium conditions we can write equation [11] where k_a and k_d are the association and dissociation rate constants respectively.

Take the case where the association rate constant is limited by the diffusion rate. If the ligand binds tightly and the dissociation rate constant is small, the slow exchange condition applies and two separate NMR signals will be observed at δ_f and δ_c for the free (P) and complexed (PL) states respectively. Conversely, if k_d is sufficiently large such that the exchange rate is fast compared to the NMR observation time then only one signal is observed. The observed chemical shift δ_o is then dependent on the fractional populations of the free and complexed probe, P_f and P_c respectively, as shown in equation [12].

$$\delta_o = P_c \delta_c + P_f \delta_f \quad [12]$$

The fractional populations are given by equation [13] where $[P^*]$ is the total concentration of the probe molecule.

$$P_c = \frac{[PL]}{[P^*]} = 1 - P_f \quad [13]$$

The chemical shift of the complex could be calculated if the equilibrium concentration $[PL]$ was known; however, in general $[PL]$ is not known before hand nor can it be directly measured by NMR spectroscopy.

Going back to the fact that the complex formation is an equilibrium process, we can express $[PL]$ as a function of the initial concentrations $[P^*]$ and $[L^*]$ and the molar equilibrium K_a as in equation [14].

$$\frac{1}{K_a} = \frac{([P^*] - [PL])([L^*] - [PL])}{[PL]} \quad [14]$$

It must be noted that we should use the thermodynamic equilibrium constant K where $K = K_\gamma K_a$ and $K_\gamma = \gamma_{PL}/(\gamma_P \gamma_L)$ since K_γ and K_a are not constant but depend on the concentrations of P , L , and PL . Since the Raoult activity coefficients, γ_i , for all species is not known, the assumption is necessary. In justification however, the range of concentrations we investigated was small and all concentrations were low such that K_a should be nearly single valued for our measurements.

By combining equations [12] and [13] we obtain

$$\delta_o = \frac{[PL]}{[P^*]} \delta_c + \left[1 - \frac{[PL]}{[P^*]} \right] \delta_f \quad [15]$$

which can be solved for $[PL]$ to give

$$[PL] = \frac{\delta_o - \delta_f}{\delta_c - \delta_f} [P^*] \quad [16]$$

Substitution of equation [16] into equation [14] results in equation [17], where the observed and complexed chemical shifts are now expressed relative to the shift of the free probe, $\Delta\delta_o = \delta_o - \delta_f$ and $\Delta\delta_c = \delta_c - \delta_f$.

$$\frac{1}{K_a} = [P^*] \frac{\Delta\delta_o}{\Delta\delta_c} + [L^*] \frac{\Delta\delta_c}{\Delta\delta_o} - ([P^*] + [L^*]) \quad [17]$$

By measuring $\Delta\delta_o$ for several ratios of $[P^*]:[L^*]$, K_a and $\Delta\delta_c$ can be determined by simultaneous solution of equation [17]. Solving for two unknown parameters requires at least two measurements. We consider four measurements to be the lowest acceptable number in order to minimize the effects of experimental errors.

One complication in using equation [17] which was often handled incorrectly in earlier studies is: What value should be used for the free chemical shift δ_f ? At first glance the answer would be: The shift observed for the probe in the chosen solvent. This reference point removes the probe-

solvent van der Waals contribution to the shift. In general though, the shift is also concentration dependent. This shift is probably the result of probe-probe interactions and can be expressed as a function of probe concentration as in equation [18],

$$\delta_f = \delta_{f,\infty} + \beta_f[P^*] \quad [18]$$

where $\delta_{f,\infty}$ and β_f are the intercept and slope respectively of the linear dependence of δ_f as a function of probe concentration. Since the observation is made at some concentration of P, one might select δ_f to be the value observed for the probe in solvent at concentration $[P^*]$. Conversely one could use δ_f at infinite dilution, however the observed shifts must then also be expressed at infinite dilution.

It may not be immediately obvious but using either $\delta_{f,\infty}$ or $\delta_{f,[P^*]}$ results in the same calculated value for $\Delta\delta_c$. They differ only in how δ_c is defined. By combining equation [15] with three terms equivalent to equation [18] for δ_o , δ_f , and δ_c , we obtain the general expression for the observed shift using the infinite dilution state as the reference point, equation [19], where the subscript ∞ indicates the shift at infinite dilution, and the β_i terms correspond to the change in the shift with probe concentration.

$$\delta_{o,\infty} + \beta_o[P^*] = \frac{[PL]}{[P^*]}[\delta_{c,\infty} + \beta_c[P^*]] + \left[1 - \frac{[PL]}{[P^*]}\right][\delta_{f,\infty} + \beta_f[P^*]] \quad [19]$$

This simplifies to equation [15] when $\beta_o = \beta_c = \beta_f$ and when the chemical shifts are measured at $[P^*]$. (Notice that β_o has no meaning in itself as it is simply the weighted average of β_c and β_f .) It would be expected that β_c and β_f would be nearly equal since they arise from intermolecular interactions of the types, probe-probe, probe-complex, and complex-complex, each of which is to the first approximation probe dependent. The concentration $[P^*]$ is used for all $\beta_i[i]$ terms since all values of β_i are assumed to be equal. However, if

one wishes to remove these constraints, solve equation [19] for [PL] and substitute that expression into equation [14]. The advantage of using $\delta_{f,\infty}$ is that the chemical shift of the complex is calculated at infinite dilution irrespective of the measurement conditions. If δ_c was calculated at some other concentration, then $[P^*]$ must be kept constant in order to obtain a single valued δ_c since it is a function of $[P^*]$.

There are six key assumptions in this model, equation [17], which we are using to determine acid-base interactions through NMR chemical shift measurements.

1. A 1:1 complex PL is formed when dilute solutions of P and L are mixed.
2. The reaction is incomplete such that PL is in equilibrium with P and L.
3. The molar equilibrium constant, K_a , is assumed to be constant throughout the range of concentrations used in this study.
4. The rate of dissociation of PL into reactants is fast in comparison to the NMR observation time. This causes a single NMR peak to be observed at the weighted average of δ_f and δ_c .
5. δ_f , δ_c , and δ_o are all a function of the total concentration of P and this dependence is assumed to be the same for all three chemical shifts.
6. The values for δ_f and δ_o are formally extrapolated to infinite dilution such that δ_c is calculated at infinite dilution, a singular value independent of the measurement conditions.

N.B. In actual practice we solve for $\Delta\delta_o$ by using the value of δ_f measured at $[P^*]$ and then calculate $\Delta\delta_c$. Since we are not determining the actual value of δ_c but rather $\Delta\delta_c$, the magnitude of $\beta[P^*]$ is not required. One must concern oneself with this term only when the absolute value of δ_c is desired, or when it is shown that point five above is invalid.

METHODS OF ANALYSIS

Since the model developed has two unknown quantities, K_a and $\Delta\delta_o$, the observed shift must be measured at several $[P]:[L]$ ratios in order to determine the unknowns simultaneously. The choice of ratios can be arbitrary, however when $[L]$ is kept constant and $[P]$ is varied over a small range, larger changes in δ_o are observed than when $[P]$ is held constant and $[L]$ is varied. This can be seen by inspection of equation [20] which is the solution of equation [17] for $\Delta\delta_o$.

$$\Delta\delta_o = \Delta\delta_c \left[\frac{([P^\circ] + [L^\circ] + K_a^{-1}) - \sqrt{([P^\circ] + [L^\circ] + K_a^{-1})^2 - 4[P^\circ][L^\circ]}}{2[P^\circ]} \right] \quad [20]$$

We have used constant $[L^\circ]$ and varied the $[P^\circ]:[L^\circ]$ ratios between 1 and 10 in this study. For complexes having large K_a values, $[L^\circ]$ was 0.005 mole/liter and for small K_a complexes we used $[L^\circ] = 0.02$ mole/liter. The ligand concentration was limited to ≤ 0.02 mole/liter in order to avoid self-association.

Graphical Analysis The graphical method was first introduced by Drago as a way of determining equilibrium constants from ultraviolet spectroscopic data⁶. The technique is fundamentally the same when NMR data are used. K_a and $\Delta\delta_c$ are determined from a theoretical plot of K_a^{-1} versus $\Delta\delta_c$. For each measurement the appropriate values for $\Delta\delta_o$, $[P^\circ]$, and $[L^\circ]$ are substituted into equation [17]. K_a^{-1} values are then calculated for a range of $\Delta\delta_c$ about the expected value. Some trial and error is necessary as the expected value is unknown. A single line is generated for each measurement and the intersection point from multiple observations gives the simultaneous solution of K_a^{-1} and $\Delta\delta_c$.

Least-Squares Analysis There is no way to write equation [17] in a linear form and consequently linear least-squares analysis is not applicable. Several attempts have been made to linearize this equation, however they

involve approximations which limit their applicability. The most general analysis method would therefore involve the exact solutions of equations [17] or [20]. In the broad sense the problem can be stated as: given a model with m independent variables (x), and n parameters (α), such that $E(y)=f(x,\alpha)$, $E(y)$ being the expected value of the dependent variable (y), determine those estimates of the parameters which minimize the function

$$\Phi = \sum_{i=1}^m [Y_i - \hat{Y}_i]^2 \quad [21]$$

where Y_i is the value of the dependent variable measured experimentally and $\hat{Y}_i$ is the value predicted by the model.

Algorithms for least-squares estimation of nonlinear parameters have been in use for over 30 years. Two approaches are frequently employed. The model can be expanded as a Taylor series and corrections to the parameters calculated at each iteration on the assumption of local linearity. This is sometimes referred to as the Gauss or Gauss-Newton method. Alternatively the steepest-descent or gradient method can be used to explore the error surface. Both methods frequently fail to perform satisfactorily, the Taylor series method because of divergence of the successive iterations when the initial guesses are poor, and the gradient method because of extremely slow convergence after the first few iterations.

The algorithm we have selected was developed by Marquardt⁷ and is a hybrid of these two techniques. It shares with the gradient method the ability to rapidly converge from almost any initial guess, and it shares with the Taylor series method the ability to close in on the convergence values once the vicinity of the convergence values is reached. This combination is referred to as the Marquardt compromise as it retains the best features of both methods while avoiding their most serious limitations. The algorithm seeks to minimize the error function [21] where Y_i is the observed chemical

shift $\Delta\delta_o$, and $\hat{Y}_i$ is the corresponding value calculated using equation [20].

In addition to finding the best fit values, the approximate uncertainty can be calculated. The program calculates the confidence limit for each parameter based on a linear hypothesis, i.e. that the error surface is linear over a small range about the parameter values. This is calculated from the change in Φ with respect to each parameter. This has the effect of making the confidence limit a function of both the error in the measurements and the shape of the model. Thus even for the case when only two measurements are made and an exact solution for K_a and $\Delta\delta_c$ is obtained, an uncertainty in each parameter can be calculated based on the magnitude of the error function's response to changes in each parameter. We have observed that the error function is more sensitive to changes in $\Delta\delta_c$ than in K_a , which results in $\Delta\delta_c$ being more accurately determined than K_a . This is quite fortunate since we are after $\Delta\delta_c$.

II.D. Calorimetry

A Setaram C 80 calorimeter was used for measuring heats of acid-base interaction for test probes with calibrated acids and bases (i.e. acids and bases with known Drago E and C parameters). The acid-base interaction was carried out in three-component systems, acid-base-solvent by placing 2 ml of the probe solution in the top compartment of a membrane mixing cell. In the bottom compartment was placed 2 ml of the calibrated acid or base solution. The molar concentration of the probe and reactant were varied over a mole ratio of 0.1 to 10. The reference cell was loaded and handled in a similar manner except no probe was placed in the top compartment, only 2 ml solvent. The top and bottom compartments of both cells were separated by an aluminum

foil until the reaction temperature of 30°C was reached. The foils were then punctured simultaneously, followed by 2 seconds of slow manual agitation to mix the acid and base and the exothermic heat was recorded. In a separate run the heats of dilution were measured and taken into account in the determination of the heat of interaction.

The formation of 1:1 complexes between acids and bases is of course an equilibrium reaction such that the heat of formation is consequently concentration dependent. Bolles and Drago⁸ have derived a method of determining the molar heat of complex formation, ΔH° , and the equilibrium constant, K_{eq} , from calorimetric measurements made at varying acid and/or base concentrations.

$$E_{eq} = \frac{\frac{1000 \Delta H'}{v \Delta H^\circ}}{\left[A_0 - \frac{1000 \Delta H'}{v \Delta H^\circ} \right] \left[B_0 - \frac{1000 \Delta H'}{v \Delta H^\circ} \right]} \quad [22]$$

in equation [22], $\Delta H'$ is the measured heat in calories, v is the total volume of solution in milliliters, ΔH° is the molar heat of complexation in calories/mole, and A_0 and B_0 are the initial concentrations of the acid and bases respectively.

III. RESULTS AND DISCUSSION

III.A. Interfacial tension

Surface and interfacial tensions with squalane were measured for the solvents in Table 1 as were ³¹P NMR shifts for their 1:1 complexation with Et₃PO. Using these data (see Experimental and Analysis sections above) the Acceptor Numbers were divided into their additive, component parts as shown in the last two columns, $AN^d = (\Delta\delta^d/\Delta\delta) * AN$ and $AN^{ab} = (\Delta\delta^{ab}/\Delta\delta) * AN$. These results are much more satisfying than the originally cited AN numbers since acidity is no longer assigned to basic, non-self-associating compounds.

Table 1 Dispersion Force and Acid-Base Contributions to Acceptor Numbers

Solvent	γ_2	γ_{12}	γ_2^d	$\Delta\delta$	$\Delta\delta^d$	$\Delta\delta^{ab}$	AN	AN ^d	AN ^{ab}
dioxane	33.5	-	33.5	9.83	10.18	0.00	10.8	10.8	0.0
pyridine	38.0	-	38.0	11.28	11.55	0.00	14.2	14.2	0.0
benzene	28.9	-	28.9	8.73	8.79	0.00	8.2	8.2	0.0
hexane	18.4	-	18.4	5.24	5.59	0.00	0.0	0.0	0.0
benzonitrile	39.4	-	39.4	11.85	11.98	0.00	15.5	15.5	0.0
nitrobenzene	43.8	5.7	38.7	11.56	11.76	0.00	14.8	14.8	0.0
tetrahydrofuran	27.2	-	27.2	8.63	8.27	0.36	8.0	7.7	0.3
carbon tetrachloride	27.0	-	27.0	8.88	8.21	0.67	8.6	8.0	0.6
diethyl ether	17.0	-	17.0	6.88	5.17	1.71	3.9	2.9	1.0
ethyl acetate	24.0	-	24.0	9.20	7.30	1.90	9.3	7.4	1.9
methyl acetate	25.4	-	25.4	9.80	7.72	2.08	10.7	8.4	2.3
dimethyl acetamide	32.4	4.3	28.2	11.04	8.52	2.52	13.6	10.5	3.1
1,2-dichloroethane	32.6	-	32.6	12.35	9.91	2.44	16.7	13.4	3.3
N,N-dimethyl formamide	36.8	6.5	30.2	12.06	9.18	2.88	16.0	12.2	3.8
acetone	22.7	1.4	21.9	10.57	6.66	3.91	12.5	7.9	4.6
dimethyl sulfoxide	43.5	14.5	29.0	13.46	8.82	4.64	19.3	12.6	6.7
dichloromethane	26.5	-	26.5	13.91	8.06	5.85	20.4	11.8	8.6
nitromethane	32.5	11.7	25.5	13.97	7.75	6.22	20.5	11.4	9.1
acetonitrile	27.0	6.9	20.9	13.28	6.35	6.93	18.9	9.0	9.9
N-methyl formamide	45.5	6.3	40.1	18.90	12.19	6.71	32.1	20.7	11.4
chloroform	27.1	-	27.1	15.07	8.24	6.83	25.1	13.7	11.4
t-butanol	20.0	-	20.0	16.78	6.08	10.70	27.1	9.8	17.3
isopropanol	21.3	-	21.3	19.50	6.48	13.02	33.6	11.2	22.4
n-butanol	25.4	-	25.4	20.91	7.72	13.19	36.8	13.6	23.2
formamide	57.3	29.3	28.0	22.19	8.51	13.68	39.8	15.3	24.5
ethanol	22.2	1.8	21.0	21.04	6.38	14.66	37.9	11.5	26.4
methanol	22.3	5.5	18.2	22.84	5.53	17.31	41.5	10.0	31.5
acetic acid	27.6	5.2	22.8	27.75	6.93	20.82	52.9	13.2	39.7
water	72.8	52.3	21.1	28.59	6.41	22.18	54.8	12.3	42.5
trifluoroethanol	21.5	10.4	13.5	27.94	4.10	23.84	53.3	7.8	45.5
hexafluoroisopropanol	17.6	10.4	11.8	31.48	3.59	27.89	65.5	7.5	58.0
trifluoroacetic acid	13.5	8.7	9.9	50.07	3.01	47.06	105.3	6.3	99.0

III.B. Spectral Shifts In Two Component Systems

III.B.1. Infrared spectral shifts

Figure 1 is an example of the influence of solvents on the infrared frequency (P=O stretch in this case) where there is only dispersion force interactions, section II.C. above. When equation [5] is used to subtract this

contribution, we get $\Delta\nu^{ab}$ which is plotted in Figure 2 against known $-\Delta H^{ab}$ values. This allows one to determine heats of complexation for Et_3PO with other acids.

Figure 1. Dependence of the infrared P=O stretching frequency of triethylphosphine oxide on the surface tension of the solvent when intermolecular interactions arise solely from London dispersion forces, $\gamma = \gamma^d$. The solid line represent the linear least squares line, equation [6], $\nu_{\text{PO}}^d = -1.06\gamma^d + 1209$.

Figure 2. The linear relationship between the P=O infrared stretching frequency shift of triethylphosphine oxide due to acid-base interactions with the solvent and the heat of that interaction. The solid line represents the linear least squares line, equation [10], $-\Delta H^{ab} = 0.37 \Delta\nu_{PO}^{ab} - 0.07$. The $-\Delta H^{ab}$ values were calculated from the Drago E and C equation.

III.B.2. NMR spectral shifts

NMR spectral shifts are influenced by van der Waals attractive forces in a manner analogous to infrared shifts (section III.B.1). Using equations [8,9] as illustrated in Figures 3 and 4 for Et_3PO , we can determine $-\Delta H^{ab}$, for its acid-base complexes with other acids. Figure 5, for the hard acid, trimethyl aluminum, is analogous to Figure 4.

Figure 3. Dependence of the ^{31}P NMR chemical shift of triethylphosphine oxide on the surface tension of the solvent when intermolecular interactions arise solely from London dispersion forces, $\gamma = \gamma^d$. The solid line represent the linear least squares line, equation [8], $\Delta\delta^d = 0.30\gamma^d - 6.9$.

Figure 4. The linear relationship between the relative ^{31}P chemical shift of triethylphosphine oxide due to acid-base interactions with the solvent and the heat of that interaction. The solid line represent the linear least squares line, equation [9], $-\Delta H^{ab} = 0.39 \Delta\delta_{\text{PO}}^{ab} - 0.43$. The $-\Delta H^{ab}$ values were calculated from the Drago E and C equation.

Figure 5. The linear relationship between the ^{27}Al chemical shift of trimethyl aluminum due to acid-base interactions with the basic solvents and the heat of that interaction. The solid line represent the linear least squares line. The $-\Delta H^{ab}$ values were calculated from the Drago E and C equation. Shifts are measured relative to the free acid in hexane. Ethyl acetate was not included in the fit.

III.C. Spectral Shifts In Three Component Systems

III.C.1. Infrared spectral shifts

Using the procedure of section II.E., the $-\Delta H^{ab}$ for the complexation of Et_3PO with the five acids given in the next section were determined. These results concur with the NMR results of Table 3 very well (average deviation $\approx 1.4\%$).

III.C.2. NMR spectral shifts

In order to use equations [17] or [20] we must first determine the chemical shift of the free Et_3PO probe. The ^{31}P shift was recorded for eight solutions having concentrations bracketing those which were to be used to form

the acid-base adducts. These results are presented in Figure 6. As can be seen from this plot, δ_z is a smooth linear function of the Et_3PO concentration. The data was fit to equation [18] by linear least-squares analysis from which the following constants were obtained, $\delta_{z,\infty}=2.64$ ppm and $\beta_z=1.94$ liter/mole. This equation for the best fit line was used to interpolate δ_z at the initial concentration of Et_3PO when evaluating $\Delta\delta_o$ for Et_3PO -acid adducts.

Figure 6 Concentration dependence of the ^{31}P NMR chemical shift of triethylphosphine oxide in CCl_4 as a function of concentration. The solid line represents the linear least-squares line having the form: $\delta_o = 2.64 + 1.94[\text{Et}_3\text{PO}]$

Five test acids were used to confirm the validity of the fast exchange model and to establish the correlation between $\Delta\delta_c$ and the heat of acid-base interaction. These acids were t-butanol, pyrrole, trifluoroethanol (TFE), phenol, and hexafluoroisopropanol (HFIP). Four solutions having concentration ratios, $[\text{Et}_3\text{PO}]:[\text{acid}]$, from 1:1 to 10:1 were prepared for each acid and the observed chemical shifts, δ_o , were recorded. The observed shifts were then referenced to the free probe, δ_f , obtained from Figure 6, yielding $\Delta\delta_o$ ($\Delta\delta_o = \delta_o - \delta_f$). This data is given in the first five columns of Table 2.

Table 2

Concentration dependence of the observed chemical shifts for triethylphosphine oxide - acid adduct formation, and the adduct chemical shifts and equilibrium constants calculated from the rapid exchange model.

Acid	[Et ₃ PO] (mmole/l)	[acid] (mmole/l)	δ _o (ppm)	δ _F [†] (ppm)	Δδ _o [‡] (ppm)	Δδ _o ^{††} (ppm)
t-butanol	4.8	20.0	3.796	2.649	1.147	1.150
	19.9	20.0	3.634	2.678	0.956	0.952
	35.0	20.0	3.506	2.708	0.798	0.794
	50.1	20.0	3.405	2.737	0.668	0.673
Δδ _c =2.88±0.13 (ppm)			K _a =37±3 (l/mole)		chi-squared=0.003	
pyrrole	19.9	20.2	4.415	2.678	1.737	1.730
	45.3	20.2	3.903	2.728	1.175	1.192
	67.0	20.2	3.655	2.776	0.879	0.885
	94.7	20.2	3.540	2.823	0.717	0.698
Δδ _c =3.9±0.2 (ppm)			K _a =72±13 (l/mole)		chi-squared=0.009	
trifluoro-ethanol	4.8	5.0	6.310	2.649	3.661	3.660
	19.9	5.0	3.930	2.678	1.252	1.263
	35.0	5.0	3.459	2.708	0.751	0.736
	50.1	5.0	3.257	2.737	0.520	0.518
Δδ _c =5.30±0.12 (ppm)			K _a =1350±200 (l/mole)		chi-squared=0.007	
	4.9	5.0	5.815	2.649	3.166	3.166
	9.8	5.0	4.806	2.659	2.147	2.147
Δδ _c =5.06±0.12 (ppm)			K _a =900±200 (l/mole)		chi-squared=0.000	

continued next page

TABLE 2. Continued

Acid	[Et ₃ PO] (mmole/l)	[acid] (mmole/l)	δ_o (ppm)	$\delta_f^\dagger$ (ppm)	$\Delta\delta_o^\ddagger$ (ppm)	$\Delta\delta_o^{\dagger\dagger}$ (ppm)
phenol	4.9	5.0	7.202	2.649	4.553	4.532
	9.8	5.0	5.263	2.659	2.604	2.722
	14.6	5.0	4.523	2.668	1.855	1.855
	19.5	5.0	4.240	2.677	1.563	1.402
$\Delta\delta_c = 5.6 \pm 0.7$ (ppm)			$K_a = 4200$ (l/mole)		chi-squared=0.07	
	4.9	5.0	7.484	2.649	4.835	4.818
	9.9	5.0	5.653	2.659	2.994	3.053
	24.7	5.0	4.051	2.688	1.363	1.311
	49.4	5.0	3.446	2.736	0.710	0.665
$\Delta\delta_c = 6.7 \pm 0.5$ (ppm)			$K_a = 1800 \pm 900$ (l/mole)		chi-squared=0.03	
	4.8	5.1	7.941	2.649	5.292	5.291
	19.9	5.1	4.375	2.678	1.697	1.731
	35.0	5.1	3.755	2.708	1.047	0.999
	50.1	5.1	3.445	2.737	0.708	0.702
$\Delta\delta_c = 7.0 \pm 0.3$ (ppm)			$K_a = 2100 \pm 700$ (l/mole)		chi-squared=0.02	
hexafluoro- isopropanol	4.8	5.1	9.867	2.649	7.218	7.166
	19.9	5.1	4.509	2.678	1.831	1.834
	35.0	5.1	3.755	2.708	1.047	1.043
	50.1	5.1	3.466	2.737	0.729	0.728
$\Delta\delta_c = 7.2 \pm 0.2$ (ppm)			$K_a = 700000$ (l/mole)		chi-squared=0.02	
	4.9	5.0	9.544	2.649	6.895	6.894
	19.8	5.0	4.576	2.678	1.898	1.935
	35.3	5.0	3.803	2.708	1.095	1.086
	50.1	5.0	3.580	2.737	0.743	0.776
$\Delta\delta_c = 7.7 \pm 0.4$ (ppm)			$K_a = 16000$ (l/mole)		chi-squared=0.03	

$\dagger$ Calculated from $\delta_f = \delta_{f,\infty} + \beta_f[\text{Et}_3\text{PO}]$, where $\delta_{f,\infty} = 2.64$, $\beta_f = 1.94$, see Figure 1.

$\ddagger$ Calculated from the measured shift $\Delta\delta_o = \delta_o - \delta_f$.

$\dagger\dagger$ Predicted by the fast exchange model using least-squares $\Delta\delta_c$ and K_a values.

The chemical shifts of the acid-base adducts, $\Delta\delta_c$, were determined by the two methods described above. The graphical method was used in order to inspect visually the accuracy of the measurements and to obtain initial estimates for $\Delta\delta_c$ and K_a . A sample plot is given in Figure 7 for t-butanol. Each solid line represents the solution of equation [17] over a range of $\Delta\delta_c$ values for each measured δ_o . The narrow range of intersections clearly indicates the validity of the fast exchange model.

Figure 7. Graphical solution of K_a and $\Delta\delta_c$ based on the fast exchange model for the interaction of triethylphosphine oxide with t-butanol in CCl_4 . The open circle represents the nonlinear least-squares best fit values: $K_a = 37 \pm 3$ liter/mole, $\Delta\delta_c = 2.88 \pm 0.13$ ppm. The concentrations were $[\text{t-butanol}] = 20.0$ mmole/liter and $[\text{Et}_3\text{PO}] =$ a) 4.8, b) 19.9 c) 35.0, d) 50.1 mmole/liter.

observed shift predicted by the model using the best fit values for $\Delta\delta_c$ and K_a which are reported on the line below each set of measurements, and shown as open circle in Figure 6 as an example. Comparison of the experimentally observed shift with that predicted by equation [20], the last two columns respectively, shows that the model generally reproduces δ_o within 0.02 ppm which is approximately the resolution of the NMR spectrometer under our operating conditions. It should be noted that all intersections between lines do not have the same uncertainty. Those for low Et_3PO :probe ratios have the lowest degree of uncertainty and should be weighted more heavily in the graphical analysis method.

We are now able to test the theory that NMR chemical shifts can be used to predict the heat of acid-base interaction. The values for $-\Delta H^{ab}$ were calculated from equation [7] where the terms E_A and E_B correspond to the electrostatic contribution for the acid and base respectively, and C_A and C_B represent the covalent contributions. The E_A and C_A values for the five acids were taken from the work of Drago and E_B and C_B values for Et_3PO are from our own studies. This information is summarized in Table 3 and shown graphically in Figure 8. The data clearly indicate that chemical shifts can be used to predict $-\Delta H^{ab}$. The linear least-squares line was determined using all of the data points except the two highest $\Delta\delta_c$ values for phenol.

Table 3

Heats of acid-base interaction for triethylphosphine oxide with test acids calculated from equation (12), and the NMR chemical shifts for the adducts.

Acid	E_A	C_A	$-\Delta H^{ab}$ (kcal/mole)	$\Delta\delta_c$ (ppm)
t-butanol	2.04	0.300	4.17	2.9
pyrrole	2.54	0.295	4.98	3.9
trifluoro- ethanol	3.88 "	0.451 "	7.61 "	5.3 5.1
phenol	4.33 " "	0.442 " "	8.32 " "	5.6 6.7 7.0
hexafluoro- isopropanol	5.93 "	0.623 "	11.45 "	7.2 7.7

$E_B = 1.65$, $C_B = 2.67$ for triethylphosphine oxide

Figure 8. Heat of acid-base interaction verses the ^{31}P NMR chemical shift of triethylphosphine oxide adducts with five acids. $\Delta\delta_c$ is the best fit values for the fast exchange model and $-\Delta H$ was calculated from the E and C parameters for Et_3PO and the acids, confidence limits are indicated by the horizontal bars. The solid line corresponds to $-\Delta H^{ab}$ (kcal/mole) = $1.65\Delta\delta_c$ (ppm) - 0.92.

In Section II.D. we presented a method for determining $\Delta\delta^{ab}$, the chemical shift of Et_3PO -acid adducts, in two-component systems. The term $\Delta\delta^{ab}$ in two-component systems should be equivalent to $\Delta\delta_c$ in the three-component work presented here. In both studies a linear relationship was established between the chemical shifts and the heat of acid-base interactions. However, the chemical shifts were approximately four times larger in the two-component study. This could be the result of forming 2:1 adducts, $\text{Acid}:\text{Et}_3\text{PO}$, in the two-component studies since the ligand (test solvent) was in large excess. Multi-ligand adducts are not formed in this three-component study. Another possibility is that solvation effects were present in the two-component work and were solvent dependent. This effect would also be present in this work but would tend to cancel out since the shifts are relative to the free probe (Et_3PO) chemical shift in only the solvent (CCl_4).

Acidity of Solvents. As an additional test of the theory that acidity can be determined from NMR chemical shifts, seventeen of the solvents used in the two-component study were reinvestigated. Two concentration ratios, $[\text{Et}_3\text{PO}]:[\text{test solvent}]$, (1:1 and 2.5:1), in CCl_4 , were used in order to calculate $\Delta\delta_c$ and K_a . These results are given in Table 4.

The model did not hold for five of the solvents; benzene, n-hexane, ethylacetate, tetrahydrofuran, and chloroform. This was apparent from the graphical analysis in that the two lines for each solvent did not intersect for any positive value of K_a . The $\Delta\delta_c$ values reported in the table for these five solvents is an average of the two observed shifts. Because the values

TABLE 4

Concentration dependence of the observed chemical shifts for triethylphosphine oxide - acid adduct formation, and the adduct chemical shifts and equilibrium constants calculated from the rapid exchange model.

Acid	[Et ₃ PO] (mmole/l)	[acid] (mmole/l)	δ_o (ppm)	$\Delta\delta_o^\dagger$ (ppm)	$\Delta\delta_c^\ddagger$ (ppm)	$K_a^\ddagger$ (l/mole)
benzene	19.9 50.1	19.8 19.8	2.692 2.773	0.014 0.036	0.02††	-
n-hexane	19.9 50.1	19.9 19.9	2.719 2.786	0.041 0.049	0.04††	-
ethylacetate	19.9 50.1	20.1 20.1	2.733 2.800	0.054 0.063	0.06††	-
tetrahydro- furan	19.9 50.1	19.7 19.7	2.733 2.807	0.054 0.070	0.06††	-
dichloro- methane	20.2 50.2	19.8 19.8	2.732 2.773	0.053 0.036	0.14±0.07	51±30
nitromethane	20.2 50.2	19.8 19.8	2.766 2.787	0.087 0.050	0.32±0.2	23±10
pyridine	19.9 50.1	20.2 20.2	2.719 2.773	0.041 0.036	0.45±0.2	5±3
acetonitrile	19.9 50.1	20.2 20.2	2.800 2.833	0.122 0.096	0.59±0.3	16±8
dimethyl sulfoxide	19.9 50.1	19.7 19.7	2.840 2.867	0.162 0.130	0.9±0.4	14±7
dimethyl formamide	19.8 50.1	19.8 19.8	2.800 2.840	0.122 0.104	1.0±0.5	8±4
dioxane	19.9 50.1	20.0 20.0	2.813 2.853	0.135 0.116	1.1±0.6	8±4
chloroform	19.9 50.1	19.9 19.9	2.948 2.995	0.270 0.258	0.26††	-
2-propanol	20.2 50.2	19.9 19.9	3.944 3.607	1.265 0.870	3.5±2	46±20
1-butanol	20.2 50.2	20.0 20.0	4.260 3.755	1.581 1.018	3.5±2	76±40
ethanol	20.2 50.2	20.0 20.0	4.200 3.742	1.521 1.005	3.6±2	62±30
methanol	20.2 50.2	19.8 19.8	4.267 3.782	1.588 1.045	3.8±2	63±30
1-propanol	20.2 50.9	20.0 20.0	4.442 3.897	1.763 1.159	4.3±2	61±30

† Calculated from the measured shift $\Delta\delta_o = \delta_o - \delta_f$, where $\delta_f = 2.64 + 1.94[\text{Et}_3\text{PO}]$.

‡ Calculated from the fast exchange model.

†† Average value of $\Delta\delta_o$.

for the first four solvents are only slightly larger than the experimental error, we feel the data indicates no significant adduct formation. That is, these four solvents are not acidic.

Chloroform is known to be acidic, as the average δ_o value of 0.26 ppm would suggest, however the data did not fit the model. Additional measurements are needed to determine whether chloroform does indeed interact with Et_3PO differently than other acidic molecules.

The data for the remaining solvents was found to obey the model. Pyridine and dioxane have small $\Delta\delta_o$ values from which low acidities would be inferred. This is in contrast to chemical intuition, and to our NMR results in two-component systems, Section II.D., where pyridine and dioxane were found to be non-acidic. The acidity of these two compounds as indicated in Table 4 is questionable but confirmation of these predictions would require many more measurements.

All of the other solvents are known to be at least slightly acidic and are also predicted to be acidic based on their $\Delta\delta_o$ values. The overall ranking of acidity is predicted correctly with the alcoholic solvents being the most acidic. The ranking of acidity from three-component NMR chemical shifts is almost the same as was determined from the two-component work. The only major discrepancy is the acidity of 1-propanol which intuitively should be less than that for methanol or ethanol, and almost equivalent to that for 1-butanol. Error analysis of the data for 1-propanol indicates that this inconsistency is larger than that resulting from our estimated error in δ_o of ± 0.01 ppm. As only two concentration ratios were used for each solvent, the values of $\Delta\delta_o$ are somewhat uncertain. Additional measurements would be needed to increase their accuracy. The power of this method for predicting acidity however is clearly evident.

Triethylphosphine oxide - acid adducts in iso-octane. The observed ^{31}P chemical shifts for free (uncomplexed) Et_3PO in iso-octane, measured relative to phosphoric acid, were plotted versus concentration (as in Figure 6 for CCl_4 solutions). The shift at infinite dilution, the intercept, was found to be 41.37 ppm and the slope was 8.97 ppm/mole/liter. These values were used to determine the free shifts, $\delta_f^\dagger$, (the uncomplexed shift at concentration $[\text{P}^*]$) reported in Table 5.

Acid-base adducts were formed between Et_3PO and eight acids at three or four $[\text{acid}]:[\text{Et}_3\text{PO}]$ concentration ratios. The initial concentrations of the acid and Et_3PO solutions are presented in Table 5 along with the measured chemical shift δ_o , the interpolated value for the free shift $\delta_f^\dagger$, and the observed shift relative to the free probe shift $\Delta\delta_o^\dagger$. As can be seen from this table, $\Delta\delta_o$ decreases with increasing Et_3PO concentration as is expected since a greater proportion of the probe is in the free state at the higher concentrations. K_a and $\Delta\delta_o$ were calculated for each acid based on the fast exchange, equilibrium model using a non-linear least-squares algorithm. These best fit values were used to calculate the observed shift predicted by the model which are given in the last column, headed $\Delta\delta_o^{\dagger\dagger}$. The experimentally measured observed shift is reproduced quite well by the model, the difference being on the order of the resolution of the NMR spectrometer which was 0.013 ppm under our experimental conditions. The good agreement is also borne out by the low chi-squared values.

TABLE 5

Concentration dependence of the observed ^{31}P NMR chemical shifts for triethylphosphine oxide - acid adduct formation in iso-octane, and the adduct chemical shifts and equilibrium constants calculated from the rapid exchange model.

Acid	[Et ₃ PO] (mmole/l)	[acid] (mmole/l)	δ_o (ppm)	$\delta_f^\dagger$ (ppm)	$\Delta\delta_o^\ddagger$ (ppm)	$\Delta\delta_o^{\dagger\dagger}$ (ppm)
dichloro- methane	20.3 40.7 61.0 81.3	19.8 19.8 19.8 19.8	41.852 42.007 42.195 42.350	41.549 41.731 41.913 42.096	0.304 0.276 0.281 0.255	0.301 0.285 0.271 0.258
$\Delta\delta_c = 5 \pm 3$ (ppm)		$K_a = 3 \pm 2$ (l/mole)		chi-squared=0.005		
nitromethane	20.3 40.7 61.0 81.3	19.8 19.8 19.8 19.8	42.027 42.196 42.317 42.472	41.549 41.731 41.913 42.096	0.479 0.465 0.403 0.376	0.488 0.446 0.410 0.379
$\Delta\delta_c = 5 \pm 2$ (ppm)		$K_a = 6 \pm 4$ (l/mole)		chi-squared=0.007		
chloroform	20.3 40.7 61.0 81.3	20.0 20.0 20.0 20.0	42.552 42.559 42.653 42.748	41.549 41.731 41.913 42.096	1.003 0.828 0.740 0.652	0.994 0.848 0.735 0.646
$\Delta\delta_c = 5.0 \pm 0.7$ (ppm)		$K_a = 15 \pm 4$ (l/mole)		chi-squared=0.008		
t-butanol	20.3 40.7 61.0 81.3	19.8 19.8 19.8 19.8	44.100 43.645 43.360 43.292	41.549 41.731 41.913 42.096	2.552 1.914 1.447 1.196	2.556 1.897 1.469 1.187
$\Delta\delta_c = 6.0 \pm 0.3$ (ppm)		$K_a = 67 \pm 10$ (l/mole)		chi-squared=0.010		
pyrrole	20.3 40.7 61.0 81.3	19.7 19.7 19.7 19.7	45.520 44.322 43.797 43.582	41.549 41.731 41.913 42.096	3.972 2.591 1.884 1.486	3.961 2.627 1.882 1.454
$\Delta\delta_c = 6.4 \pm 0.3$ (ppm)		$K_a = 220 \pm 50$ (l/mole)		chi-squared=0.02		
trifluoro- ethanol	4.9 20.3 49.8	5.0 5.0 5.0	47.163 43.172 42.505	41.410 41.549 41.813	5.753 1.623 0.692	5.753 1.633 0.670
$\Delta\delta_c = 6.6 \pm 0.2$ (ppm)		$K_a = 8000 \pm 3000$ (l/mole)		chi-squared=0.012		

continued next page

TABLE 5 Continued

Acid	[Et ₃ PO] (mmole/l)	[acid] (mmole/l)	δ_o (ppm)	$\delta_f^\dagger$ (ppm)	$\Delta\delta_o^\ddagger$ (ppm)	$\Delta\delta_o^{\dagger\dagger}$ (ppm)
phenol	4.9	4.8	48.637	41.410	7.226	7.226
	35.1	4.8	42.983	41.681	1.302	1.312
	49.8	4.8	42.754	41.813	0.942	0.928
$\Delta\delta_c = 9.7 \pm 0.2$ (ppm)			$K_a = 2600 \pm 400$ (l/mole)		chi-squared=0.008	
hexafluoro- isopropanol	4.9	4.8	49.420	41.410	8.010	8.010
	35.1	4.8	43.000	41.681	1.319	1.316
	49.8	4.8	42.737	41.813	0.925	0.929
$\Delta\delta_c = 9.77 \pm 0.06$ (ppm)			$K_a = 6300 \pm 500$ (l/mole)		chi-squared=0.003	

$\dagger$ Calculated from $\delta_f = \delta_{f,\infty} + \beta_f^*[\text{Et}_3\text{PO}]$, where $\delta_{f,\infty} = 41.37$, $\beta_f = 8.97$, see Figure 1.

$\ddagger$ Calculated from the measured shift $\Delta\delta_o = \delta_o - \delta_f$.

$\dagger\dagger$ Predicted by the fast exchange model using least-squares $\Delta\delta_c$ and K_a values.

The enthalpies of acid-base adduct formation, $-\Delta H^{ab}$, were calculated from the E and C equation [6]. The E_A and C_A values for the eight acids were taken from the work of Drago⁹ and the E_B and C_B values are from our own studies. These data are given in Table 6. The linear relationship between $-\Delta H^{ab}$ and $\Delta\delta_c$ is shown in Figure 9. Although there is considerable scatter, the data indicate the linear relationship of $\Delta\delta_c$ on the enthalpy of interaction. It is interesting to note that chloroform appeared to fit with the other acids. This is the only system which we have investigated by NMR spectroscopy for which chloroform behaved according to the fast exchange, equilibrium model.

Table 6

Heats of acid-base interaction calculated from equation (5) for triethylphosphine oxide with test acids in iso-octane, and the ^{31}P NMR chemical shifts for the adducts.

Acid	C_A	E_A	$-\Delta H^{ab}$ (kcal/mole)	$\Delta\delta_c$ (ppm)
chloroform	0.159	3.02	5.41	5.0
t-butanol	0.300	2.04	4.17	6.0
pyrrole	0.295	2.54	4.98	6.4
trifluoro- ethanol	0.451	3.88	7.61	6.6
phenol	0.442	4.33	8.32	9.7
hexafluoro- isopropanol	0.623	5.93	11.45	9.8

$C_B = 2.67$, $E_B = 1.65$, for triethylphosphine oxide

Figure 9. Heat of acid-base interaction versus the ^{31}P NMR chemical shift in iso-octane of triethylphosphine oxide adducts with six acids. $\Delta\delta_c$ is the best fit value from the fast exchange model and $-\Delta H$ was calculated from the E and C parameters for Et_3PO and the acids, confidence limits are indicated by the horizontal bars. The solid line corresponds to the best fit linear line:- $\text{DH}^{ab} \text{ (kcal/mole)} = 1.16 \cdot \Delta\delta_c \text{ (ppm)} - 1.41$.

Tricyclohexylphosphine sulfide (TCHPS) - acid adducts in CCl₄. TCHPS is a soft base in contrast to the hard base Et₃PO discussed above. Data was gathered via ³¹P NMR for TCHPS as for Et₃PO and yielded the following relationships.

$$\delta_o = 17.44 + 1.39*[\text{TCHPS}] \quad [23]$$

$$-\Delta H^{ab} \text{ (kcal/mol)} = 4.48\Delta\delta_c \text{ (ppm)} + 3.81 \quad [24]$$

The most striking feature is the magnitude of the chemical shifts of the acid-base complexes. These are an order of magnitude less than those observed for Et₃PO. The association constants are also ≈ 10 times smaller for TCHPS than for Et₃PO. The low values for $\Delta\delta_c$ and K_a result in observed shifts which are marginally greater than experimental error for all but the strongest acids. This may prove to be unfortunate when TCHPS is used to study coal surfaces which may have surface sites of low acidic strength.

Tricyclohexylphosphine sulfide - acid adducts in carbon disulfide.

Adduct formation between TCHPS and six acids were also investigated in carbon disulfide solutions, since TCHPS is only sparingly soluble in iso-octane. The concentration dependence of δ_o was found to obey the following:

$$\delta_o = 16.97 + 0.87*[\text{TCHPS}] \quad [25].$$

The ³¹P NMR data showed shifts for the complexes which were only half as large as those in CCl₄ above, but K_a was ≈ 10 times larger such that the observed shifts in CS₂ were only slightly smaller than those in CCl₄. NMR shifts were correlated with heat of adduct formation with four acids. The best fit of this data was:

$$-\Delta H^{ab} \text{ (kcal/mol)} = 10.53*\Delta\delta_c \text{ (ppm)} + 3.90 \quad [26].$$

Diphenyl mercury - base adducts in CCl₄. The ¹⁹⁹Hg chemical shift of Ph₂Hg in CCl₄ is concentration dependent giving a best fit linear line:

$$\delta_o = 76.59 - 4.81 * [\text{Ph}_2\text{Hg}] \quad [27].$$

The chemical shift decreases with increasing Ph_2Hg concentration indicating that probe-probe interactions cause a delocalization of the electron cloud away from the mercury nucleus, i.e. the mercury nucleus is deshielded.

Acid-base interactions were investigated for seven bases via the ^{199}Hg NMR chemical shift. The fast exchange, equilibrium model was successfully applied to the Ph_2Hg - base adduct formation. The small values for the association constant forced us to use high concentrations of the bases, 0.2 to 0.9 mole/liter, which is ≈ 10 times larger than that used in our ^{31}P studies. Fortunately the chemical shifts for the complexes are fairly large such that reliable chemical shift measurements were possible. In general the fast exchange model predicted the observed shift to ≈ 0.05 ppm which is slightly greater than the spectral resolution of 0.03 ppm under our operating conditions.

In order to determine the ability of using ^{199}Hg chemical shift measurements to predict heats of acid-base interactions, we must either know (or measure) the heat for several of the interactions or determine the E_A and C_A values for Ph_2Hg from which the heat of interaction can be calculated using equation [5]. Our initial attempt was to use the ^{31}P chemical shifts from Et_3PO and TCHPS in order to determine the heat of interaction with Ph_2Hg . This is possible since we have already calibrated the ^{31}P shifts with heats of acid-base interactions. Moreover, because Et_3PO is a hard base and TCHPS is a soft base, we hoped to be able to determine the E and C parameters for Ph_2Hg . We could then calculate the expected heat of interactions for any Ph_2Hg - base adduct. At this time we have had only limited success in this endeavor. Although fairly accurate ^{199}Hg chemical shift measurements have been obtained

for the interaction of Ph_2Hg with Et_3PO , the ^{31}P shifts for Et_3PO and TCHPS with Ph_2Hg are highly suspect. We present these results only to give a rough idea of the accuracy of the ^{199}Hg shifts and to show the method by which E_A and C_A will be determined once more accurate data is collected.

Since the ^{199}Hg shifts upon interaction with Et_3PO gave more accurate results than the ^{31}P shifts, we used the association constant $K_A=4.2$ obtained from ^{199}Hg measurements in the following calculations. Using this value of K_A we calculated $\Delta\delta_c$ for each observed shift using equation [20]. These results were used to develop the following equation:

$$-\Delta H^{ab} \text{ (kcal/mole)} = 1.65 \Delta\delta_c \text{ (ppm)} - 0.92 \quad [28].$$

Triphenylsilanol - base adducts in CCl_4 . Triphenylsilanol is a hard acid chosen to complement the soft acid, diphenyl mercury. The molar heat of complexation, $-\Delta H^{ab}$, was established for three bases of known Drago constants; using calorimetric results for two acids and infrared shifts for the third. This yielded the linear equation:

$$-\Delta H^{ab} \text{ (kcal/mol)} = 0.82 \Delta\delta_c + 0.88 \quad [29].$$

when combined with ^{29}Si NMR shifts treated as per equation [20]. This equation is considered tentative since the correlation coefficient was only 0.82. NMR ^{29}Si shifts for five more Drago bases were used in the above equation to determine $-\Delta H^{ab}$ values for their complexed with Ph_3SiOH . This allowed the graphical determination of $C_A = 0.20 \pm 0.10$ and $E_A = 2.9 \pm 0.2$ for triphenylsilanol.

V. CONCLUSIONS

The infrared P=O stretching frequency and ^{31}P chemical shift of triethylphosphine oxide in solution is dependent on van der Waals and acid-base interactions with the solvent. When non-acidic, non-self-associating

solvents are used, only van der Waals interactions are present and the spectral shifts are directly proportional to the surface tension of the solvent. When acidic or self-associating basic solvents are used, both types of interactions occur and the spectral shifts are separable into the two additive terms. The acidic or basic nature of solvents can be determined from spectral shifts in two-component systems, probe:solvent, only after correcting for shifts due to van der Waals interactions. Using this correction, infrared and NMR spectral shifts are directly proportional to the heat of acid-base interaction.

In addition, the Acceptor Number as defined by Mayer and Gutmann, can be separated into two component parts, AN^d and AN^{ab} , the latter of which is characteristic of the electrophilic nature of the solvent. These AN^{ab} values are more reasonable intuitively, and should be much more useful to the chemist when the choice of reaction solvent is made based on solvent acidity.

Trimethyl aluminum can be used as a hard acid NMR probe when the molecular structure of the base is known. The utility of using trimethyl aluminum for measuring the surface basicity of coal, however, is questionable due to the large natural line width of ^{27}Al and appreciable contact contributions to the chemical shift. Contact shifts are dependent on the magnetic dipole of the basic site and the acid-base adduct geometry, neither of which would be known for surface adducts of coal. Our selection of a hard acid NMR probe is therefore still in progress.

Two methods for evaluating the chemical shift of the adduct, $\Delta\delta_c$, were employed. Both have distinct advantages. The graphical method is convenient for quickly determining the overall integrity of the data and for calculating rough guesses for $\Delta\delta_c$ and K_a . The least-squares method, on the other hand, is much more useful for calculating the best values for these parameters since it

takes into consideration the varying significance of δ_o under different experimental conditions.

The interactions of five acidic molecules with triethylphosphine oxide were found to obey the fast exchange model at low concentration. These acids were used to develop the quantitative relationship between $\Delta\delta_o$ and the heat of acid-base interaction, $-\Delta H^{ab}$. A well behaved linear dependence was observed which could be expressed as: $-\Delta H^{ab}$ (kcal/mole) = $1.65\Delta\delta_o$ (ppm) - 0.92. This relationship is similar to that obtained from two-component studies; however, the chemical shifts in this work were approximately four times smaller. This is possibly the result of solvation effects or the formation of multi-ligand adducts in the two-component systems.

Seventeen of the solvents Gutmann characterized in two-component NMR studies were investigated. Benzene, n-hexane, ethylacetate, and tetrahydrofuran did not obey the fast exchange model. We take this to indicate that these solvents are not acidic since the observed shifts were on the order of the experimental error. Chloroform also violated the model, however, this is probably due to experimental error. All of the other solvents obeyed the model. Those that are known to have significant acidity, e.g. alcohols, had large $\Delta\delta_o$ values, while weakly acidic solvents had significantly smaller values. These results clearly demonstrate that Lewis acidity can be quickly and easily quantified by this method.

The chemical shifts of triethylphosphine oxide adducts with eight acids in iso-octane solutions have been determined. Dichloromethane and nitromethane have chemical shifts which are much too large considering the low acidic strengths of these molecules. The remaining six acids have reasonable shifts and were used to derive a linear relationship between the chemical shift of the complexes and the heat of acid-base interaction. This

relationship is very similar to that obtained for the same adducts formed in CCl_4 solutions.

Similar measurements were performed using tricyclohexylphosphine sulfide using CCl_4 and iso-octane as the solvents. The chemical shifts were ≈ 2 times larger in CCl_4 , however the association constants were generally an order of magnitude smaller such that the observed shifts were nearly equivalent. Linear relationships were observed between the chemical shifts and the heats of interactions in both solvents. In both cases a value of ± 4 kcal/mole was predicted at zero shift. This suggests that the calculated shifts are not solely due to acid-base interactions. One possible source of this extra shift is due to different van der Waals shift contributions by the solvent in the free and complexed states. Non-zero intercepts are often obtained in IR and NMR spectral shift studies.

Diphenyl mercury adducts with seven basic molecules were investigated. Large excesses of base were required in order to perform these measurements because of the small association constants. Crude approximations for C_A and E_A values for diphenyl mercury were calculated. These values were used to test the linear dependence of the chemical shifts of acid-base adducts with the heat of interaction. The overall features of this relationship appears to be valid. Hard bases gave low shifts and small heats, whereas softer bases gave larger shifts and heat of interactions. Pyridine appeared to be anomalous, as is frequently observed, perhaps due to steric hindrance. More accurate ^{31}P NMR measurements for the interactions of triethylphosphine oxide and tricyclohexylphosphine sulfide with diphenyl mercury are needed in order to calculate accurate E_A and C_A values for this acid.

The NMR chemical shifts due to acid-base interactions between triphenylsilanol and seven bases have been obtained and the enthalpy of these

interactions determined by calorimetry and infrared shifts. This allowed the relationship between $-\Delta H^{ab}$ and the NMR shift to be established and C_A and E_A for triphenylsilanol to be calculated.

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