NMR Measurements of Chemical Theory Equilibrium Constants for Hydrogen-Bonded Solutions

Although various chemical theories have often been used to characterize hydrogen-bonded systems with some success, they have been limited by the fact that the equilibrium constants were adjustable parameters. This paper reports a method to measure directly these constants by proton nuclear magnetic resonance spectroscopy. Results are reported for several systems and are used with a chemical-physical theory to predict vapor-liquid equilibria.

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SCOPE

Solution thermodynamicists represent liquid mixture behavior by either physical or chemical theories. The former treatment emphasizes various electrostatic interactions ranging from van der Waals forces to dipole interactions, and may include entropic effects. Typical physical treatments are regular solution theory or the van Laar, Wilson, or Flory-Huggins equations. In some solutions actual dimerization (or oligomerization) occurs, such as in mixtures including organic acids, alcohols, or even liquid metals, and a chemical approach, using a mass action law, is superior. A combination of the two into a chemical-physical approach is attractive for many situations. The greatest limitation of the chemical approach has been that each equilibrium constant was an adjustable parameter and heretofore not subject to any experimental verification. In fact, thermodynamic data always give activities, not concentrations, so any evaluation from such results was subject to the limitations of the solution theory used. However, chemical-shift nuclear magnetic resonance (NMR) measures concentrations directly and permits the first independent evaluation of the true number of dimers or complexes in solution; the equilibrium constant is no longer an adjustable parameter but a relatively easily measured physical property. With such data one may investigate the applicability of a "pure" or ideal chemical theory to a variety of solvated and associated systems, and compare the results with experimental vapor-liquid equilibrium (VLE) data. Further, these data permit the extension to a more realistic chemical-physical theory without using an unreasonable number of adjustable parameters.

CONCLUSIONS AND SIGNIFICANCE

Hydrogen-bonded mixtures can be well characterized by chemical-physical models of solution behavior. These models are no longer limited by the fact that the equilibrium constants are adjustable parameters and are not subject to experimental verification. Equilibrium constants can be measured directly from NMR spectroscopy and used in a chemical-physical model to predict vapor-liquid equilibria successfully without adjustable parameters if one activity coefficient at infinite dilution is available from independent measurements or correlation. This procedure can be easily applied to solvated systems and is shown to be superior to an ideal chemical theory approach.

Introduction

Several models based on the chemical theory of solutions have been used successfully to represent excess thermodynamic properties. They have been used to describe the thermodynamics of liquid metal solutions where intermetallic complexes are formed (Eckert, et al., 1982; Alger and Eckert, 1983) and have frequently been applied to hydrogen-bonded liquid mixtures, to correlate binary vapor-liquid equilibrium and enthalpy data, and to estimate multicomponent vapor-liquid equilibrium. Some examples are the linear associated solution model of Kretschemer and Wiebe (1954) and the associated solution model of Wiehe and Bagley (1967). Renon and Prausnitz (1967) have successfully applied the Kretschemer-Wiebe model to alcohol-saturated hydrocarbon systems. In most of these models, no physical significance was attributed to the equilibrium parameters because the assumptions in the linear association models are an oversimplification for alcohol-hydrocarbon systems. The models were treated as empirical equations. For correlating infinite-dilution activity coefficients, Null and Palmer (1969) have combined chemical and physical theories by including several terms for hydrogen-bonding components. The MOSCED model (Thomas and Eckert, 1984) also includes both chemical and physical contributions to the activity coefficient at infinite dilution.

One of the problems encountered when using a model based on the chemical theory of solutions is the number of equilibrium parameters that must be obtained, especially when physical effects are included or when the molecules in the system have a high degree of self-association. Physical forces should be included in the representation of the interactions between most organic molecules since the magnitude of these forces is large and is dependent on the composition of the mixture. Assumptions may be made to reduce the number of parameters, but this often restricts the use of the model to certain systems and/or limits its accuracy.

The number of parameters in our model is reduced by measuring an equilibrium constant using nuclear magnetic resonance (NMR) spectroscopy. In this work, we deal primarily with solvated solutions, which are computationally simpler, although extensions to associated solutions are in progress.

Measuring Equilibrium Constants

The value of NMR spectroscopy in thermodynamic studies of hydrogen-bonding equilibria was recognized by Gutowsky and Saike (1954), who showed that the observed chemical shift of a hydrogen-bonded proton was the weighted average of the chemical shifts of free and complexed protons. The weighting factors were simply the fraction of the total number of hydrogen-bonded protons that were present in a given state at equilibrium. Two adjustable parameters, an equilibrium constant and a chemical shift characteristic of the complex, were generated for each equilibrium in the model, and their values were determined by reducing the observed chemical shift as a function of composition data.

NMR spectroscopy offers several advantages over other techniques used to study hydrogen bonding, especially if an accurate value of the equilibrium constant is the desired result. The chemical shift can be measured easily to an accuracy of 1.0 ppb with most analytical NMR spectrometers equipped to regulate the probe temperature. The chemical shifts depend on true concentrations, rather than the activities of the various species in solution. Since there is no overlap of peaks, the data obtained are easier to interpret and more useful than infrared spectroscopy data. Also, present Fourier-transform NMR techniques allow very dilute samples to be analyzed. Studying dilute mixtures yields useful information concerning hydrogen bonds between unlike molecules since self-association is avoided. A variety of hydrogen-bonding systems, and hence models of equilibria, have been studied with NMR spectroscopy.

The method by Lussan et al. (1962) has alleviated many difficulties previously encountered, and will be used in this work to obtain equilibrium constants from NMR measurements. This technique is used to study equilibria of the form:

$$AH + B \rightleftharpoons AH\cdot\cdot\cdot B \tag{1}$$

where AH, B, and $AH\cdot\cdot\cdot B$ are the proton donor, proton acceptor, and hydrogen-bonded or AB complex, respectively. In a hydrogen-bonded solution of this type, x_A and x_B will be designated the observed mole fractions, while γ_A and γ_B are the observed activity coefficients. The equilibrium constant for the reaction in Eq. 1 is given by

$$K_{AB} = \frac{z_{AB}}{z_A z_B}\frac{\alpha_{AB}}{\alpha_A \alpha_B} = \frac{z_{AB}}{z_A z_B} K_{\alpha AB} \tag{2}$$

where the z's are the true mole fractions and the α's are the true activity coefficients.

Since self-association of the proton donor must be avoided, the chemical shifts are obtained with the proton donor dilute in proton acceptor and an inert solvent, and are extrapolated to infinite dilution. This simplifies the expression for the observed chemical shifts at infinite dilution, ν_o^∞, to

$$\nu_o^\infty = \left(\frac{N_A^\infty}{N_{AT}}\right)\nu_A + \left(\frac{N_{AB}^\infty}{N_{AT}}\right)\nu_{AB} \tag{3}$$

where

$$N_{AT} = N_A^\infty + N_{AB}^\infty \tag{4}$$

ν_A and ν_{AB} are the characteristic chemical shifts of free proton donor and hydrogen-bonded complex, respectively, and N_A^∞/N_{AT} and N_{AB}^∞/N_{AT} are weighting factors for free and complexed species. The results in Eqs. 2 and 3 are used with the stoichiometric relationships of a ternary mixture to derive the expression

$$\Delta_o^\infty = \frac{K_{AB}(1 - x_S)\,\Delta_{AB}}{[K_{\alpha AB} + K_{AB}(1 - x_S)]} \tag{5}$$

where

$$\Delta_o^\infty = (\nu_o^\infty - \nu_A) \tag{6}$$

$$\Delta_{AB} = (\nu_{AB} - \nu_A)$$

and x_S is the mole fraction of inert solvent.

Ternary mixtures of proton donor, proton acceptor, and an inert solvent, chosen to be structurally similar to the base, are prepared such that the apparent mole fraction x_S is constant and the ratio (x_A/x_B) is varied. The measured chemical shifts with the same value of x_S are extrapolated to infinite dilution of AH in a mixture of B and S. In this manner, the observed infinite dilution chemical shifts, ν_o^∞ and Δ_o^∞, are obtained as a function of x_S. Plots of $(K_{\alpha AB}\,\Delta_o^\infty/(1 - x_S))$ vs. Δ_o^∞ should be linear with a slope equal to $-K_{AB}$. $K_{\alpha AB}$ can be determined from a solution theory based on physical intermolecular interactions. Once K_{AB} and $K_{\alpha AB}$ are determined, the vapor-liquid equilibrium of a binary mixture of proton donor and proton acceptor can be predicted for solvated systems.

Calculation of $K_{\alpha AB}$

Since physical as well as chemical interactions should be used to describe accurately the behavior of hydrogen-bonded systems, a solution theory must be chosen to calculate the activity coefficients of the various species in solution. The molecules and complexes considered in this work are either nonpolar or slightly polar so that regular solution theory provides a reasonable estimate of $K_{\alpha AB}$. The expression for $K_{\alpha AB}$ using regular solution theory is

$$K_{\alpha AB} = \frac{\alpha_{AB}}{\alpha_A\,\alpha_B} = \exp\left[\frac{v_{AB}}{RT}(\delta_{AB} - \bar{\delta})^2 - \frac{v_A}{RT}(\delta_A - \bar{\delta})^2 - \frac{v_B}{RT}(\delta_B - \bar{\delta})^2\right] \quad (7)$$

$\bar{\delta}$ is evaluated for a ternary mixture where the proton donor is infinitely dilute as given by

$$\bar{\delta} = \frac{[x_S v_S \delta_S + (1 - x_S) v_B \delta_B]}{[x_S v_S + (1 - x_S) v_B]} \quad (8)$$

The pure-component values of v_i and δ_i at 25°C are tabulated in the literature.

The only unknown parameters in Eqs. 7 and 8 are v_{AB} and δ_{AB}. Harris and Prausnitz (1969) have shown that reasonably large errors in v_{AB} result in an insignificant error in the value of $K_{\alpha AB}$ calculated from Eq. 7. Therefore, a volume shrinkage at 6.0 mL/mol for the formation of the hydrogen-bonded complex is assumed, and the value of v_{AB} is simply

$$v_{AB} = (v_A + v_B - 6.0)\ \text{mL/mol} \quad (9)$$

However, it has been shown that the value of $K_{\alpha AB}$ is quite sensitive to small variations in the value of δ_{AB}. Since the techniques available to estimate solubility parameters are accurate to only $\pm 1(\text{cal/mL})^{1/2}$, $[\pm 4.19(\text{J/mL})^{1/2}]$, another technique must be used to determine δ_{AB}, $K_{\alpha AB}$, and K_{AB}. Of course one could use δ_{AB} as a single adjustable parameter and fit VLE data, but in this work we choose to measure independently γ_A^∞, the activity coefficient of proton donor infinitely dilute in proton acceptor, to determine δ_{AB}.

An expression relating K_{AB}, δ_{AB}, and γ_A^∞ was derived and is shown in Eq. 10.

$$K_{AB} = \exp\left[\frac{v_{AB}}{RT}(\delta_{AB} - \delta_B)^2\right] \cdot \left\{\frac{1}{\gamma_A^\infty} - \exp\left[\frac{-v_A}{RT}(\delta_A - \delta_B)^2\right]\right\} \quad (10)$$

The value of δ_{AB} is determined by an iterative procedure subject to the constraints that the value of K_{AB} obtained from the NMR chemical shift data with a given value of δ_{AB} is identical to the value of K_{AB} calculated from Eq. 10 using the same value of δ_{AB} and γ_A^∞ data.

Experimental

Materials and purification

Chloroform was washed twice with cold distilled water to remove the ethanol stabilizer. The chloroform was then dried over P_2O_5 for 24 h and fractionally distilled before use.

Dioxane was dried over a sodium wire and fractionally distilled.

Cyclohexanone was dried over anhydrous sodium sulfate and molecular sieves and fractionally distilled.

Acetone and tetrahydrofuran (THF) were fractionally distilled before use.

Piperidine was dried over NaOH pellets for 24 h and then fractionally distilled over chips of sodium.

Reagent grade cyclohexane was washed with a 50/50 mixture of nitric and sulfuric acids and then washed with cold distilled water until the cyclohexane phase was clear. The cyclohexane was dried with a sodium wire and fractionally distilled. The product was again dried with a sodium wire and redistilled.

Hexane was fractionally distilled from anhydrous calcium sulfate.

Methylcyclohexane was dried over a sodium wire and fractionally distilled.

Spectrophotometric grade cyclopentane, cyclohexane, heptane and di-*n*-propylether were used without further purification. These solvents contained less than 0.02% water.

99.9+% NMR grade tetramethylsilane (TMS) was used without further purification.

Preparation of NMR samples

The treatment of NMR chemical shift data developed by Lussan et al. (1962) required infinite dilution chemical shifts as a function of the composition of inert solvent, x_S. These chemical shifts cannot be determined directly from NMR spectra. Therefore, sets of samples must be prepared such that the mole fraction of inert solvent remains constant while the mole fractions of proton donor and proton acceptor are varied. Thus, a plot of the observed chemical shift of the hydrogen-bonded proton, ν_o, vs. its mole fraction in solution, x_A, is a curve of constant solvent mole fraction, x_S. It can be extrapolated to obtain a value of ν_o at $x_A = 0$. Also, the chemical shift of the free proton donor, ν_A, can be obtained from the $x_A = 0$ intercept of a plot of ν_o vs. x_A in which the samples contain only inert solvent and proton donor.

All samples were prepared gravimetrically inside a glove box flushed with pure, dry nitrogen. The samples were weighed on a Mettler H72 analytical balance that was accurate to ±0.1 mg. Liquids were added to NMR tubes directly or to vials and then transferred to NMR tubes. The proton acceptor and proton donor were added using syringes equipped with 26 ga. hypodermic needles.

The closed NMR tubes were removed from the glove box and placed in a Dewar flask of liquid nitrogen. After the liquid was frozen, the NMR tubes were removed from the Dewar flask and flame-sealed. In all cases, the NMR tubes were sealed before any solid in the tube had melted.

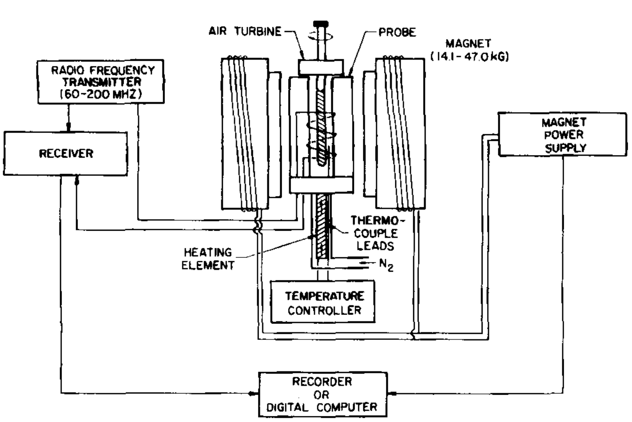

Figure 1. Typical experimental apparatus for NMR measurements.

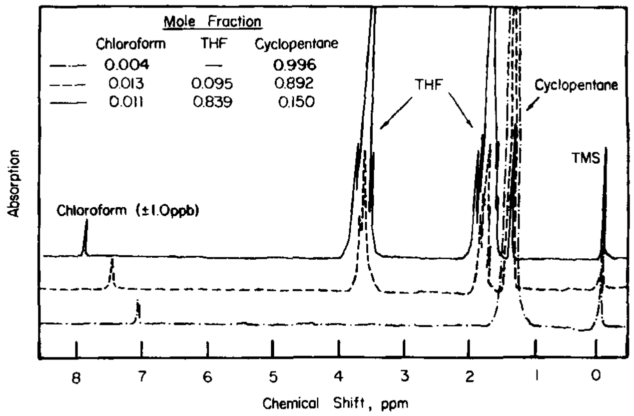

Figure 2. Sample NMR spectra in chloroform-tetrahydrofuran-cyclopentane system at −6°C.

Each sample contained about 1.0 mol % TMS as the internal reference. The values of x_A varied from about 0.003 to 0.05 within each set of samples, while the values of x_S for the different samples varied from 0.15 to 0.95. The variation in x_S from sample to sample within each set was always less than 0.0002, and the arithmetic mean, $\bar{x}_S$, is used in place of x_S in expressions such as Eq. 4.

Measurement of the chemical shift

Available NMR spectroscopy instrumentation has improved over the past several years. Consequently, a Varian A60-A, 60 MHz spectrometer, a Varian, EM-390, 90 MHz spectrometer, and a Varian XL-200, 200 MHz pulse Fourier-transform spectrometer were each used at various times to measure the chemical shifts. The spectrometers were operated in the lock mode with either TMS as the internal lock signal or a deuterated solvent as the external lock signal. A schematic diagram of a typical apparatus is shown in Figure 1, where the sample in the center is rotated for homogeneity in a flowing-gas thermostat within the gap of a magnet. The coils are used to transmit and pick up radio-frequency signals. For the Fourier-transform instrument we are now using, the NMR runs at 200 MHz, the magnet is a 47 kG supercon, and the sample of about 1.0 mL may have a proton donor concentration as low as $x_A = 0.0001$. For more details concerning measurement techniques, the work of Scott (1976), Halas (1977) and McNiel (1985) should be consulted.

For each of the three spectrometers used, the maximum uncertainty in the chemical shift data was ±1.0 ppb. A variable temperature controller provided automatic and accurate control of probe and sample temperatures. The temperature control was periodically checked using a methanol or ethylene glycol sample. The accuracy of the temperature control was ±2.0°C.

Three typical spectra are shown as examples in Figure 2. The bottom (dash-dot) line represents dilute chloroform in pure inert cyclopentane. Reading from right to left, the first peak is the TMS reference, the second at about 1.3 ppm is the cyclopentane protons, and the third small peak near 7.1 ppm is the unbonded chloroform protons. The middle curve (dashed line) represents dilute donor and base (THF) in solvent. The protons in THF are not equivalent and yield two peaks. The chloroform proton shift, for some bonding occurring, is shifted to about 7.5 ppm. The solid-line curve depicts a measurement on a sample with a very high concentration of the base, and the higher chloroform proton shift, about 7.9 ppm, represents a much higher degree of hydrogen bonding.

Results and Discussion

The observed chemical shift data as a function of temperature and mole fraction, x_A and x_S, were measured for each system. Plots of ν_o as a function of x_A at constant $\bar{x}_S$ were constructed using these data, and the curves were extrapolated to $x_A = 0$ in order to determine ν_o^∞. An example of these plots is shown in Figure 3 for the chloroform-THF-cyclopentane system at −6°C. The Δ_o^∞ and υ_A data are presented in Table 1.

Regular solution theory solubility parameters and molar volumes at 25°C were used in an iterative technique to calculate δ_{AB} and K_{AB}. A value of δ_{AB} was chosen and $K_{\alpha AB}$ is calculated from Eq. 7. K_{AB} was calculated from a least-squares fit of $K_{\alpha AB}\,\Delta_o^\infty/(1 - x_S)$ vs. Δ_o^∞ data (see Eq. 5). A value of K_{AB} was also calculated using Eq. 10 and γ_A^∞ data that were obtained by ebullio-

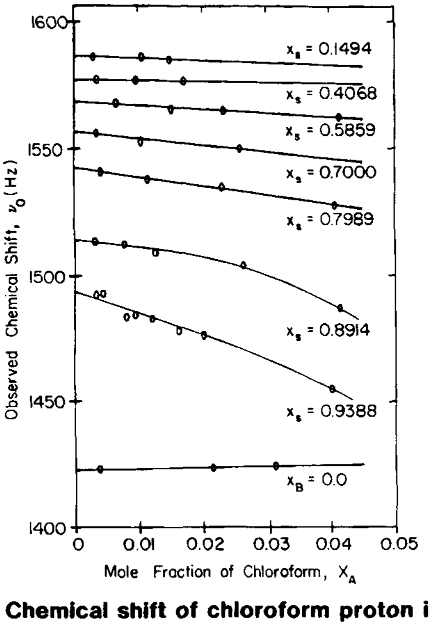

Figure 3. Chemical shift of chloroform proton in chloroform-tetrahydrofuran-cyclopentane system at −6°C.

metric or gas chromatographic techniques or were extrapolated from finite-concentration vapor-liquid equilibrium data. The value of δ_{AB} was adjusted until these two K_{AB} values were approximately equal. A graphical illustration of this procedure is shown in Figure 4 for the chloroform-cyclopentane system, which shows the greatest temperature variation of δ_{AB} of all systems investigated.

Except for the chloroform-THF-cyclopentane system, the variation in δ_{AB} with temperature is small and random. This is consistent with the assumptions of regular solution theory that δ_{AB} must be temperature-independent in order for $v_{AB}(\delta_{AB} - \bar{\delta})^2$ to be independent of temperature. The average value of δ_{AB} was chosen as δ_{AB} at 25°C and was used to generate the K_{AB} values as functions of temperature that are reported for each system in Table 2. The values of K_{AB} listed in Table 2 for the chloroform-piperidine-cyclohexane system were calculated with $K_{\alpha AB} = 1$ (ideal chemical theory) since γ_A^∞ data are not presently available for this system.

The temperature dependence of K_{AB} provides a measurement of the heat of formation, ΔH^f_{AB}, the entropy change, ΔS^f_{AB}, and the change in the Gibbs free energy, ΔG^f_{AB}, upon forming a hydrogen-bonded complex. For this study we have assumed that ΔH^f_{AB} and ΔS^f_{AB} are not a function of temperature.

Table 1. Infinite Dilution Chemical Shifts, Δ_o^∞(Hz)

Chloroform-Tetrahydrofuran-Cyclopentane System

x_s	−28°C	−6°C	19°C	50°C
0.1494	173.6	163.5	151.8	137.1
0.4068	167.1	154.2	140.4	123.1
0.5859	160.2	145.5	129.3	110.4
0.7000	150.4	133.6	115.7	94.9
0.7989	139.8	119.7	99.4	77.5
0.8914	112.3	90.3	70.6	51.4
0.9388	92.6	70.8	53.8	36.6
ν_A	1,422.8	1,422.8	1,422.7	1,422.4

Chloroform-Dipropylether-Heptane System

x_s	10°C	44°C	87°C
0.1498	124.6	97.7	70.3
0.4092	107.8	79.9	54.9
0.6001	91.0	63.7	41.8
0.6996	77.9	53.0	33.2
0.7900	64.1	41.1	24.5
0.8799	42.9	26.4	15.2
0.9298	29.4	18.1	9.9
ν_A	1,420.9	1,421.1	1,421.3

Chloroform-Acetone-Hexane System

x_s	−35°C	0°C	44°C
0.1990	61.6	55.7	49.0
0.3991	59.3	52.9	45.0
0.5983	56.2	48.3	39.0
0.7938	48.3	39.1	28.4
0.8858	39.6	29.3	19.2
0.9497	25.6	16.5	10.2
ν_A	425.7	425.9	425.9

Chloroform-Dioxane-Cyclohexane System

x_s	10°C	44°C	82°C
0.1494	36.1	33.1	29.4
0.4083	33.3	29.7	25.6
0.5868	30.8	26.1	21.6
0.6937	27.6	23.2	18.3
0.7875	23.7	19.3	14.5
0.8871	16.8	12.7	9.1
0.9388	11.1	8.1	5.4
ν_A	425.5	425.6	425.7

Table 1. Cont.

Chloroform-Cyclohexanone-Methylcyclohexane System

x_s	0°C	44°C
0.1995	59.6	52.5
0.3922	57.1	49.1
0.6044	53.0	43.6
0.6948	50.3	39.5
0.8071	43.9	32.9
0.8848	36.0	24.7
0.9488	—	14.1
ν_A	423.7	424.2

Chloroform-Piperidine-Cyclohexane System

x_s	10°C	34°C	76°C
0.1498	357.4	318.3	247.5
0.4092	333.2	291.9	219.3
0.6001	306.6	260.4	184.1
0.7000	285.0	235.2	158.0
0.7901	260.3	207.8	132.0
0.9002	188.2	139.1	78.3
ν_A	1,419.3	1,419.4	1,420.3

Dichloromethane-Cyclohexanone-Methylcyclohexane System

x_s	3°C	29°C
0.1997	43.4	38.7
0.3989	38.4	34.0
0.5989	32.7	28.0
0.7985	23.3	19.6
0.8981	16.4	12.3
0.9493	8.8	6.8
ν_A	461.0	460.4

$$\Delta G^f_{AB} = -RT\ln K_{AB} = \Delta H^f_{AB} - T\,\Delta S^f_{AB} \qquad (11)$$

These values are presented in Table 3.

The change in entropy with the formation of a hydrogen bond is negative, since there is more ordering in the system with the formation of a hydrogen bond. The values of ΔG^f_{AB} at 25°C are small and negative since the reaction to form a hydrogen bond is exothermic and the entropy decreases. The value of ΔG^f_{AB} for the amine with chloroform is much larger than that of any other system.

McGlashan and Rastogi (1958) reported a value of ΔH^f_{AB} for the chloroform-dioxane hydrogen-bonded complex that was obtained from correlating vapor-liquid equilibrium data and assuming that the two hydrogen bonds possible for the base were equivalent. They used the ideal chemical theory approximation that $K_{\alpha AB}$ is equal to unity to obtain a value of $\Delta H^f_{AB} = -2.0$ kcal/mol (−8.38 kJ/mol). The value is about one-third smaller than the value of ΔH^f_{AB} obtained in this work when the composition dependence of $K_{\alpha AB}$ was evaluated using regular solution theory. For every system studied, the assumption of ideal chemical theory results in a different value of K_{AB} and ΔH^f_{AB}.

Prediction of vapor-liquid equilibria

Equilibrium constants and heats of formation of the hydrogen-bonded complex have been obtained for several systems. It is possible to predict the composition of the vapor in equilibrium with a solution of proton donor and proton acceptor using chem-

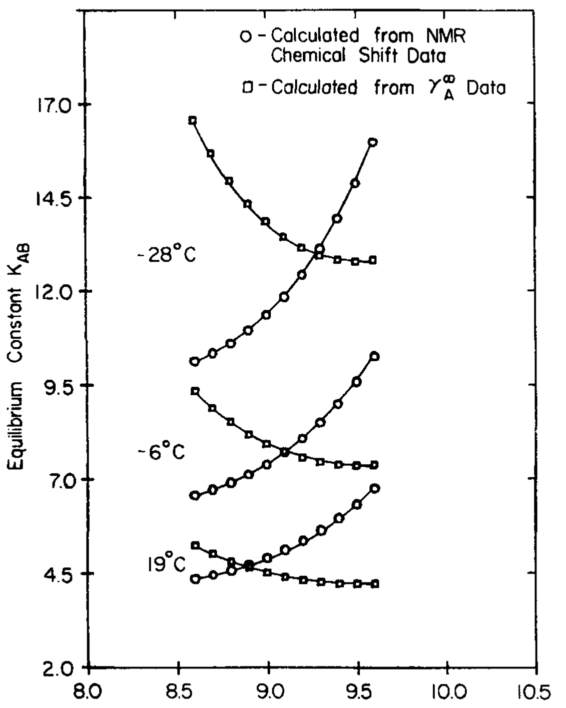

Figure 4. Equilibrium constant as a function of solubility parameter of the complex for chloroform-tetrahydrofuran-cyclopentane system.

Table 2. Values of Equilibrium Constants Calculated from NMR Chemical Shift Data

Chloroform-Tetrahydrofuran				
	−28°C	−6°C	19°C	50°C
K_{AB}	12.99	7.73	4.69	2.68
Chloroform-Dipropylether				
	10°C	44°C	87°C	
K_{AB}	2.21	1.27	0.69	
Chloroform-Acetone				
	−35°C	0°C	44°C	
K_{AB}	3.63	2.05	1.12	
Chloroform-Dioxane				
	10°C	44°C	82°C	
K_{AB}	3.26	2.13	1.14	
Chloroform-Cyclohexanone				
	0°C	44°C		
K_{AB}	3.83	2.24		
Chloroform-Piperidine				
	10°C	34°C	76°C	
K_{AB}	8.87*	5.76*	2.92*	
Dichloromethane-Cyclohexanone				
	3°C	29°C		
K_{AB}	1.84	1.38		

*Calculated using $K_{\alpha AB} = 1$

Table 3. Values of ΔG^f_{AB}, ΔH^f_{AB}, and ΔS^f_{AB} Calculated from NMR Chemical Shift Data

System	$-\Delta G^f_{AB}$ 25°C, kcal/mol)	$-\Delta H^f_{AB}$ kcal/mol	$-\Delta S^f_{AB}$ cal/mol K
Chloroform-Cyclohexanone	0.60	2.09	5.01
Chloroform-Acetone	0.21	2.28	6.94
Chloroform-Dioxane	0.57	2.98	7.82
Chloroform-Dipropylether	0.31	3.07	9.23
Chloroform-Tetrahydrofuran	0.84	3.14	7.74
Chloroform-Piperidine	1.12	3.32	7.37
Dichloromethane-Cyclohexanone	0.22	1.83	5.41

SI conversion: kJ = kcal × 4.19; J = cal × 4.19.

ical theory and the equilibrium constants determined from NMR chemical shift data. Several assumptions are made to simplify the calculations. It is assumed that the proton donor and acceptor form only an AB complex in solution. The complex is assumed to be nonvolatile. Regular solution theory is assumed to provide an accurate description of the thermodynamic behavior of the ternary liquid mixture of proton donor, proton acceptor, and complex, and the previously determined value of δ_{AB} is used. The true mole fractions z are found from the degree of association, such that K_{zAB} is given by,

$$K_{zAB} = \frac{z_{AB}}{z_A z_B} \tag{12}$$

The true activity coefficients of each species in solution and $K_{\alpha AB}$ can be calculated from regular solution theory. Finally, since $K_{AB} = K_{\alpha AB} K_{zAB}$, a value for the equilibrium constant can be determined. This value of K_{AB} is compared to a value obtained from NMR chemical shift data at temperature T. Adjustments are made to the value of the reaction coordinate until both values of K_{AB} are equal. For ideal chemical theory, K_{AB} is equal to K_{zAB}, and a value for the equilibrium constant can also be calculated.

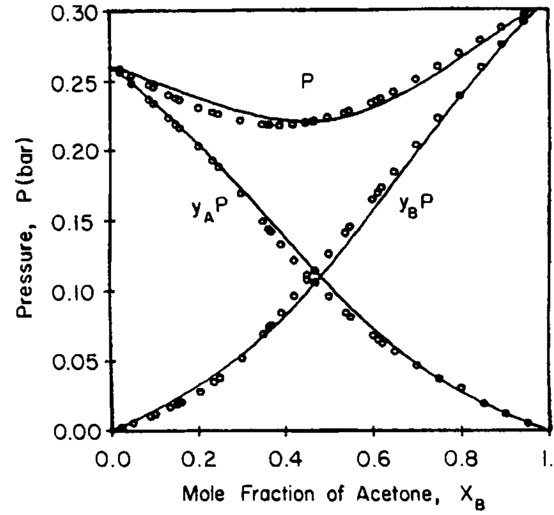

Figure 5. Partial pressures and total pressure for chloroform-acetone system at 25°C (Rabinovich and Nikolaev, 1960).

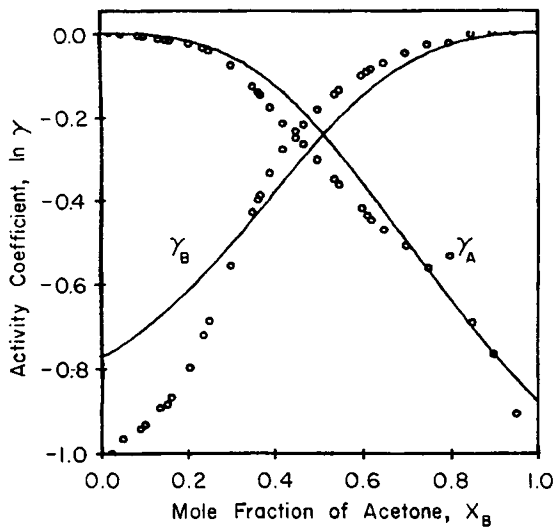

Figure 6. Activity coefficients in chloroform-acetone system at 25°C (Rabinovich and Nikolaev, 1960).

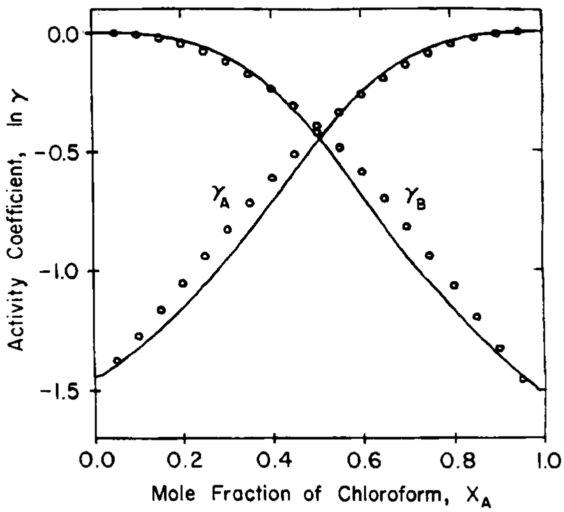

Figure 8. Activity coefficients in chloroform-tetrahydrofuran system at 30°C (Van Ness and Abbott, 1976).

From the actual molar concentrations that are determined, the total pressure is found in the usual manner.

$$P = P_A + P_B \tag{13}$$

where

$$P_i = \frac{x_i \gamma_i P_i^s \phi_i^s \exp\left[\dfrac{v_i(P - P_i^s)}{RT}\right]}{\phi_i} \tag{14}$$

An iterative procedure is used to calculate both the total pressure and vapor phase mole fraction. Fugacity coefficients are determined using the generalized method of Hayden and O'Connell (1975) for nonassociating or weakly associating fluids at moderate densities. If a fluid associates strongly and extensive complexing in the vapor phase is known to occur, such as in the case of carboxylic acids or to a lesser extent aldehydes, a chemical theory treatment such as that of Nothnagel et al. (1973) could be used.

The procedure described above, with $K_{\alpha AB}$ calculated from regular solution theory, was used to predict the vapor-liquid equilibrium and activity coefficients of chloroform-acetone, chloroform-THF, and chloroform-dipropylether. The results of these calculations are shown in Figures 5 through 10 along with data from the literature. The agreement between observed and predicted vapor-liquid equilibria is good with some deviation between observed and predicted activity coefficients, particularly when the proton acceptor is dilute in proton donor. This

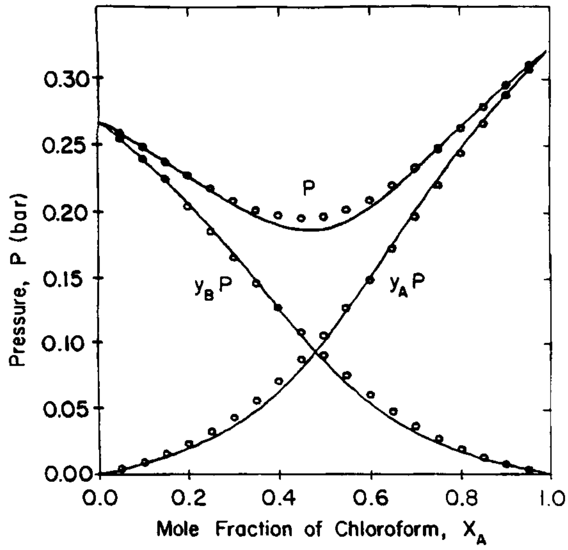

Figure 7. Partial pressures and total pressure for chloroform-tetrahydrofuran system at 30°C (Van Ness and Abbott, 1976).

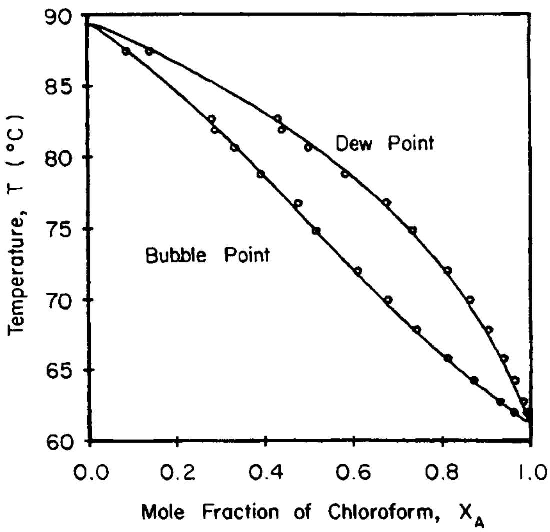

Figure 9. Isobaric dew point and bubble point curves in chloroform-dipropylether system at 760 mm Hg (101 kPa) (Ghemling and Onken, 1977).

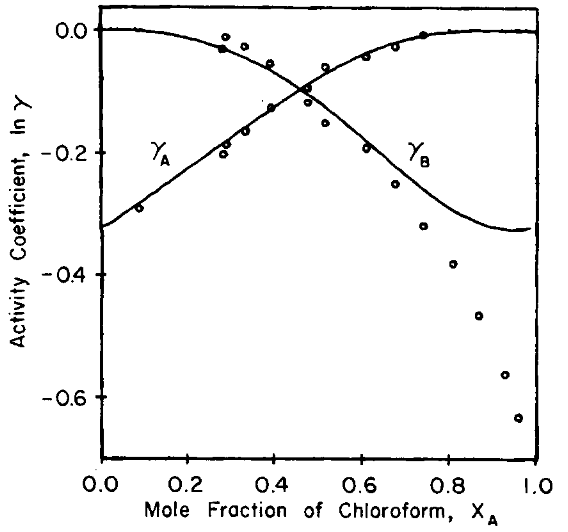

Figure 10. Activity coefficients in chloroform-dipropylether system at 760 mm Hg (101 kPa) (Ghemling and Onken, 1977).

may be due to the formation of other complexes, including possible association, or to the limitations of the physical theory correction.

Ideal chemical theory was also used to predict vapor-liquid equilibria for each system. Table 4 shows the comparison of predicted and observed mole fractions, pressures, and temperatures when ideal chemical theory is used and when chemical theory is combined with regular solution theory. In all cases the assumption of ideal chemical theory resulted in the largest deviation between predicted and experimental vapor-liquid equilibria. Therefore, it is preferable to use chemical-physical theory to represent the behavior of these solvated systems. NMR chemical-shift measurements permit the extension to chemical-physical theory without using an unreasonable number of adjustable parameters.

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Table 4. Comparison of Ideal Chemical Theory with a Chemical-Physical Theory

	Ideal Chemical Theory		Chemical-Regular Solution Theory	
System	Δy*	ΔP*	Δy*	ΔP*
Chloroform-THF	3.1	6.4	1.7	2.3
Chloroform-Acetone	5.5	15.7	1.5	1.2
	Δy*	ΔT*	Δy*	ΔT*
Chloroform-Dipropylether	1.6	2.5	0.6	0.4

*Percent normalized standard deviation.

Notation

AB = 1:1 proton donor-proton acceptor hydrogen-bonded complex
AH = proton donor monomer
$AH^{\cdots}B$ = 1:1 proton donor-proton acceptor hydrogen-bonded complex
B = proton acceptor
ΔG^f_{AB} = molar Gibbs free energy change upon complex formation
ΔH^f_{AB} = molar heat of formation of complex
K_{AB} = equilibrium constant in activities
$K_{\alpha AB}$ = ratio of activity coefficients in activity equilibrium constant expression
K_{zAB} = ratio of $K_{AB}/K_{\alpha AB}$
N_i = number of moles of component i
P = equilibrium pressure
P_i = partial pressure of component i
R = gas constant
S = solvent
ΔS^f_{AB} = molar entropy change upon complex formation
T = absolute temperature
v_i = molar volume of pure component i
$\bar{v}_i$ = partial molar volume of component i in the mixture
x_i = bulk liquid phase mole fraction of component i
y_i = vapor phase mole fraction of component i
z_i = true liquid phase mole fraction of component i

Greek Letters

α_i = true activity coefficient of component i
γ_i = bulk activity coefficient of component i
γ^∞_A = bulk infinite dilution activity coefficient of the proton donor in the proton acceptor
δ_i = solubility parameter of component i
ν_o = observed chemical shift of proton
ν^∞_o = observed chemical shift of proton at infinite dilution
ν_i = chemical shift of proton on component i
ϕ_i = fugacity coefficient of component i in vapor phase mixture
ϕ^s_i = saturation fugacity coefficient of pure component i

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