An FTIR Spectroscopic Study of Hydrogen-Bonding Competition in Entrainer–Cosolvent Mixtures[1]

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In chemical separation processes such as supercritical extraction the use of an entrainer cosolvent can dramatically improve selectivity and yield. Ideally, in an extraction process, an entrainer cosolvent should complex with only the desired solute, pulling it from the feed. But not all cosolvents are entrainers, and a cosolvent that is effective in one application may not be effective in others. Often, competing hydrogen bonding interactions limit the effectiveness of an entrainer cosolvent. In this paper FTIR spectroscopy is used to study hydrogen bonding competition in solute/solvent/entrainer cosolvent mixtures. The extent of hydrogen bonding is determined from analysis of hydrogen-bonded and non-hydrogen-bonded infrared absorption peaks. Since these peaks overlap, curve-fitting and Fourier self-deconvolution techniques are used to resolve them. Concentrations of monomeric and hydrogen-bonded species are modeled using the associated perturbed anisotropic chain theory (APACT). Using APACT it is shown that the equilibrium constant, derived from activities, can be written as the product of a temperature-dependent term and the ratio of concentrations: $K = (RT)^v \Pi C_i^{v_i}$. This gives a statistical mechanical basis for the empirical observation that for hydrogen-bonding equilibria, the ratio of concentrations is approximately equal to the ratio of activities.

KEY WORDS: entrainer; FTIR; hydrogen bonding; supercritical.

1. INTRODUCTION

The solvent strength of a supercritical fluid is a strong function of temperature and pressure near the critical point. By the addition of a small amount of cosolvent not only can the critical point be manipulated, but also the polar/nonpolar/hydrogen bonding character of the solvent can be

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modified. In 1984, Joshi and Prausnitz [1] described the entrainer effect as the enhancement in solubility resulting from preferential intermolecular forces, such as hydrogen bonding, that occur when a relatively small amount of a properly chosen cosolvent is added.

To choose a cosolvent on the basis of hydrogen bonding properties, various empirical correlations of electron donor and electron acceptor strength are available, such as expanded solubility parameters, solvato-chromic parameters, and equilibrium constants. In general, if the desired solute is an electron donor, the entrainer cosolvent should be an electron acceptor, and vice versa. For the entrainer to be most effective it should not hydrogen bond to itself or to the solvent [2]. Either interaction ties up hydrogen-bonding sites that might otherwise be available for solvation between solute and cosolvent.

But self-association of the cosolvent is common. Most hydrogen-bonding compounds either are electron donors or are both electron donors and acceptors which self-associate. Although there are some electron acceptors that do not self-associate (methylene chloride, chloroform), they are too weak for many applications. This means that if the solute is η an electron donor, the best choice for a cosolvent might involve a compromise between electron acceptor strength and self-association tendency. In this case, the cosolvent should be a stronger electron acceptor than it is an electron donor.

Competition from the solvent is also a factor in the choice of a cosol-vent. This is particularly true when CO_2 is the solvent. Hyatt's study [3] of the solvent properties of liquid and supercritical CO_2 suggest that it is a weak electron donor. If the solute is also an electron donor, then it must compete with CO_2 to form hydrogen bonds with the cosolvent. Even if the solute is a strong electron donor, it will be deprived of cosolvent hydrogen-bonding sites by the overwhelming concentration of CO_2 as the solvent. Competition from the solvent, though, unlike competition from cosolvent self-association, can be avoided since there are many supercritical solvents from which to choose.

In order to improve he understanding and the application of entrainer cosolvents, we have cassified the hydrogen bonding interactions that are most likely to occur.

Type I: Solute —— cosolvent

Type II: $\dfrac{\text{Solute}}{\text{Cosolvent}} \!\!>$ cosolvent

Type III: $\begin{matrix} \text{Solute} \\ \text{Cosolvent} \\ \text{Solvent} \end{matrix} \!\!\Rightarrow$ cosolvent

In all three, it is presumed that there is solvation between the solute and the cosolvent. In type I mixtures, solvation occurs without competition. This is the only hydrogen-bonding interaction—the cosolvent does not self-associate and the solvent has no hydrogen-bonding tendency. In type II mixtures, there are two hydrogen-bonding interactions. The solute must compete with cosolvent self-association. In type III mixtures, there three hydrogen-bonding interactions. The solute must compete not only with cosolvent self-association but also with the hydrogen-bonding interaction between the solvent and the cosolvent.

1.1. Scope of the Present Study

In this study, we present experiment and theory for hydrogen-bonding competition in types I, II, and III mixtures. By using FTIR spectroscopy the concentrations of monomeric and hydrogen-bonded species are quantified. For all three types of mixtures the concentration of solute is held constant and the concentration of cosolvent is varied. As the cosolvent concentration increases, the extent of hydrogen bonding increases. These spectroscopic results are modeled using a chemical equilibrium theory that is based on the associated perturbed anisotropic chain theory (APACT). The parameters in this model are equilibrium constants which are determined by least-squares regression of the spectroscopic data.

The solute, solvent, and cosolvent are defined in terms of their relative concentrations. In fact, in one part of the study acetone at low concentration is the solute, while in another part, acetone at moderate concentrations is the cocolvent. In supercritical extraction the solute concentration is of the order of 1 mol % or less; the cocolvent ranges from a few percent to 10 or 20; and the solvent, making up the difference, is typically 80 to 90 %. All of the compounds used in this study have a single hydrogen-bonding functionality and are common organic liquids (acetone, methyl ethyl ketone, methyl isobutyl ketone, methanol, carbon tetrachloride, and diethyl ether). They were chosen on the basis of their chemical functional groups and hydrogen-bonding tendency, which was estimated using solvatochromic parameters as determined by Kamlet et al. [4] from UV measurements for over 250 liquid compounds. Two of the compounds in this study are used only as solvents (CCl_4 and diethyl ether). One of the solvents, CCl_4, has a negligible hydrogen-bonding tendency and is analogous to an inert supercritical fluid such as methane, ethane, nitrogen, or argon. The other solvent, diethyl ether, was chosen for its electron donor properties and is analogous to CO_2, as discussed by Hyatt [3]. Methanol is used as both a solute and a cosolvent, depending on the concentration, and is the only self-associating compound in this study.

In the following sections, typical spectra are presented, the data analysis technique is described, then the associated perturbed anisotropic chain theory (APACT) is presented, and finally, the results of APACT calculations are compared with the results of spectral analyses.

2. EXPERIMENTAL

Infrared spectra were recorded on a Mattson Polaris FTIR spectrophotometer using demountable cells with variable path length. Spectrophotometric-grade chemicals were used, and stored under nitrogen. Purity was checked by gas chromatography and by infrared absorption. All spectra were measured at 298 K.

2.1. Type I Spectra: Noncompetitive Solvation

In type I mixtures, solvation occurs without competition. Solvation between the solute (methanol) and the cosolvent (ketone) is studied directly by using an inert solvent (CCl_4) and by using a low concentration of methanol ($C_{A0} = 0.025 \text{ mol} \cdot \text{L}^{-1}$) such that self-association is minimized. In these mixtures (dilute methanol/CCl_4/ketone), hydrogen bonding occurs between the methanol hydroxyl group and the ketone carbonyl group. For both groups, the infrared spectrum shows peaks due to monomeric and bydrogen-bonded species. The concentrations of these species are determined from the area of the respective peaks. In principle both the solute and the cosolvent peaks could be analyzed for monomeric and hydrogen-bonded concentrations. In practice, though, only the solute peak is analyzed. Since the concentration of the cosolvent is much greater than that of the solute, the hydrogen-bonded portion of the cosolvent peak is too small to analyze accurately.

2.2. Type II Spectra: Solvation with Competition from Cosolvent Self-Association

For type II mixtures, various ketones are used as solutes andmethanol at higher concentration is used as the cosolvent. In these mixtures, self-association of the cosolvent competes with solvation between the solute and the cosolvent. Again, CCl_4 is used as an inert solvent. At these higher concentrations of methanol, the ν_{OH} absorption cannot be used to analyze ketone-methanol solvation because self-association of methanol dominates the ν_{OH} absorption. Instead, the ν_{CO} absorption of the ketone is analyzed.

Figure 1 shows some of the spectra used to study type II interactions. To obtain these spectra, mixtures of methyl ethyl ketone/CCl_4/methanol

solute: MEK
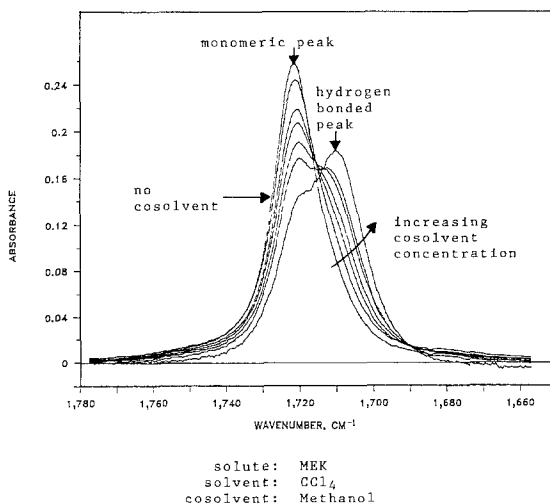solvent: CCl$_4$
cosolvent: Methanol

Fig. 1. Spectra for the system MEK/CCl$_4$/methanol. Six spectra are shown with varying concentrations of methanol and a constant concentration of MEK. These spectra are representative of spectra used to study type II interactions. The spectra show that as the concentration of methanol increases, the height of the hydrogen-bonded MEK peak (low-wavenumber peak) increases[t] and the height of monomeric MEK peak (high-wavenumber peak) decreases. The concentration of MEK is 0.05 mol $\cdot$ L^{-1}; the concentrations of methanol are (in order of increasing cosolvent concentration which is indicated in the figure) 0.0, 0.10, 0.30, 0.49, 0.99, 1.48, and 3.95 mol $\cdot$ L^{-1}.

were used in which the concentration of solute (methyl ethyl ketone; MEK) was held constant ($C_{B0} = 0.05$ mol $\cdot$ L^{-1}), while that of the cosolvent (methanol) was increased. One of the peaks in Fig. 1 corrresponds to a mixture of MEK/CCl$_4$ without methanol, and only one peak corresponding to monomeric ketone is observed for this mixture. As methanol is added, an absorption band appears at lower frequency and increases as the concentration of methanol increases. This lower-frequency peak is not present in either pure MEK or methanol and is due to solvation between MEK and methanol. Notice also that as methanol is added, the height of the monomeric ν_{CO} peak decreases. Notice the decrease in the height (and area) of the band at higher frequency. Since the overall concentration of MEK is constant, the hydrogen-bonded peak grows at the expense of the monomeric peak. From the appearance of these curves it is apparent that as methanol is added, the concentration of monomeric ketone decreases, while the concentration of hydrogen bonded ketone increases.

2.3. Type III Spectra: Solute Solvation with Competition from Cosolvent and Solvent

Type III mixtures are similar to type II mixtures except that an electron donor solvent (diethyl ether) is used instead of an inert solvent (CCl_4). Again, solvation between cosolvent and solute occurs and cosolvent self-association occurs as in type II mixtures, but in type III mixtures the solvent competes with the solute. Representative spectra for type III mixtures are not shown since they appear similar to those of type II which are shown in Fig. 1. The difference between type II and type III spectra is quantitative and is discussed in the following sections.

3. DATA ANALYSIS

Concentrations of hydrogen-bonded and monomeric species are determined from the area of absorption peaks in the inrared spectrum. Beer's law relates the area to the concentration and pathlength:

$$a_i = k_i C_i l \tag{1}$$

in which a_i is the area under the absorption peak, k_i is the absorptivity, C_i is the concentration, and l is the pathlength inside the sample cell. For the methanol hydroxy group used to study type I mixtures, it is straight-forward to determine peak areas since the monomeric and hydrogen-bonded peaks have significantly different shapes and are well separated. For these mixtures we use the method developed by Becker [5]. For the ketone carbonyl group used to study type II and type III mixtures, determination of monomeric and hydrogen-bonded peak areas is complicated by their similarity in shape and by their intrinsic overlap. If the overlap were not intrinsic, the peaks could be separated by increasing the instrument resolution. For these mixtures we developed a spectral analysis technique to determine the areas. The height, width, position, and area of each peak are determined by curve-fitting both the raw spectral data and the Fourier self-deconvolution of the spectral data. Curve-fitting the deconvoluted data was most sensitive to the position and height parameters, whereas curve-fitting the raw data was most sensitive to the width and height parameters. The curve used to fit the spectra was the Lorentzian:

$$\tilde{y} = \frac{1}{1 - \tilde{v}^2} \tag{2}$$

in which, $\tilde{v} = (v - c_2)/c_3$, $\tilde{y} = y/c_1$, c_1 is the height of the peak, c_2 is the wavenumber of the peak maximum, c_3 is the width parameter, and the width at half-height is $2c_3$. The three parameters, c_1, c_2, and c_3, are

referred to as the height, position, and width, respectively. The area under a Lorentzian curve is found by analytic integration:

$$a = \int_{-\infty}^{\infty} y(v)\, dv = \pi c_1 c_3 \tag{3}$$

4. THEORY

The associated perturbed anisotropic chain theory (APACT) is an extension of the perturbed hard chain theory (PHCT), an equation of state developed by Donohue and Prausnitz [6]. Originally developed in the mid-1970s, PHCT is a combination of perturbed hard sphere theory (valid for fluids of simple spherical molecules) and the polymer theories of Flory [7] and Prigogine [8]. Further developments of PHCT have resulted in the group-interaction perturbed anisotropic chain theory (GPACT), which explicitly accounts for nonpolar, polar, and induction interactions between polyatomic molecules, and the associated perturbed anisotropic chain theory (APACT) [9], which explicitly accounts for hydrogen-bonding interactions through the use of a chemical equilibrium model. Although APACT was originally developed to predict fluid phase equilibrium properties, it is extended in this paper to modeling the results of infrared measurements of hydrogen bonding.

In the extension of PHCT to APACT two assumptions are made. The first assumption is that when a hydrogen bond forms between two molecules (A and B), the molecules "react" to form a new species (AB):

$$A + B \rightleftharpoons AB \tag{4}$$

APACT is particularly suited to modeling infrared data because, as described in previous sections, these monomeric (A, B) and hydrogen-bonded species (AB) are quantified using infrared spectroscopy. Having taken the approach that hydrogen bonding is a form of chemical equilibria, the equilibrium constant is written as the product of activities raised to their stoichiometric coefficients. Classical thermodynamics is used to relate the equilibrium constant to the activity of a species and, further, to temperature, concentration, and residual chemical potential:

$$a_i = \gamma_i C_i = RT \exp\{\tilde{\mu}_i / RT\}\, C_i \tag{5}$$

in which $\tilde{\mu}$ is the residual chemical potential ($\tilde{\mu} = \mu - \mu^{ig}$); and C_i is the concentration (mol · L^{-1}) of monomeric ($i = 1$) or hydrogen-bonded species (having i monomeric units). Taking the product of activities raised to their stoichiometric coefficients gives the equilibrium constant:

$$K = \Pi a_i^{v_i} = (RT)^v \exp\left\{\sum v_i \tilde{\mu}_i / RT\right\} [\Pi C_i^{v_i}] \tag{6}$$

This is an exact expression derived from classical thermodynamics. The next step is to use APACT to derive an expression for the sum of residual chemical potentials $(\sum v_i \tilde{\mu}_i)$ in terms of molecular parameters.

The second assumption in APACT is that the parameters for hydrogen-bonded species are linear combinations of the parameters for monomeric species. For example, the characteristic volume of a dimer (v_2^*) is twice the characteristic volume of a monomer $(2v_1^*)$. The same is assumed for the dispersion energy (E^*) and degrees of freedom (c^*) (calculated as the sum of the translational and density-dependent rotational and vibrational degrees of freedom):

	Self association	Solvation
Characteristic volume	$v_j^* = jv_1^*$	$v_{AB}^* = v_A^* + v_B^*$
Dispersion energy	$E_j^* = jE_1^*$	$E_{AB}^* = E_A^* + E_B^*$
Degrees of freedom	$c_j^* = jc_1^*$	$c_{AB}^* = c_A^* + c_B^*$

An important feature of APACT is that using the assumption that the parameters scale linearly gives the result that the residual chemical potential also scales linearly:

$$\tilde{\mu}_j = j\tilde{\mu}_1 \qquad (7)$$

As a result of this scaling behavior, the contribution of the residual chemical potentials drops out of the equilibrium constant:

$$\sum v_i \tilde{\mu}_i = 0 \qquad (8)$$

To understand this result consider that the residual chemical potential is the residual reversible work required to put a molecule into (or take a molecule out of) the fluid. It is intuitively satisfying that the model treats the residual work for a dimer as twice that for a monomer. The actual chemical potential, which is the sum of the residual and ideal gas chemical potentials, does not scale linearly since a dimer has the same ideal gas chemical potential as a monomer (and not double). According to the APACT model, what is most important in a hydrogen-bonding fluid is the number of monomers, dimers, trimers, etc., and this counting-up of species is given by the ratio of concentrations in the expression for the equilibrium constant.

Thus, the equilibrium constant is to within a temperature-dependent factor equal to the ideal solution equilibrium constant:

$$K^A = (RT)^v K^C \qquad (9)$$

in which $K^C = \Pi C_i^{\nu_i}$. This gives a statistical mechanical basis for the observation that the equilibrium constant can be calculated as the ratio of concentrations of monomeric and hydrogen-bonded species. In the following analysis, the equilibrium constant K^C is used exclusively; for simplicitly it is denoted as K.

To model spectroscopic results equilibrium expressions and material balances are solved simultaneously. For type I mixtures there is only solute/cosolvent interaction:

$$A_1 + B_1 \rightleftharpoons AB; \qquad K_{AB} = C_{AB}/C_{A1} C_{B1} \qquad (10)$$

in which K_{AB} is the equilibrium constant for solvation, C_{A1} is the concentration in $mol \cdot L^{-1}$ of cosolvent monomers, C_{B1} is the concentration of solute monomers, and C_{AB} is the concentration of the hydrogen bonded species. By material balance, superficial concentrations are related to concentrations of monomeric and hydrogen bonded species:

$$C_{A0} = C_{A1} + C_{AB}; \qquad C_{B0} = C_{B1} + C_{AB} \qquad (11)$$

in which superficial concentrations (C_{A0} and C_{B0}) are the concentrations that would exist without hydrogen bonding ($mol \cdot L^{-1}$ of compound put into the solution), and the monomer concentrations (C_{A1}, and C_{B1}) are determined spectroscopically as discussed previously.

The equilibrium expression (10) is substituted into the material balance equations (11) to give relations between superficial concentrations and monomer concentrations:

$$C_{A1} \times C_{A0}/(1 + K_{AB} C_{B1}); \qquad C_{B1} = C_{B0}/(1 + K_{AB} C_{A1}) \qquad (12)$$

These equations relate the monomeric and superficial concentrations to the equilibrium constants which are determined by regression of spectroscopic data.

The fraction of the solute that is hydrogen bonded (ξ_B) is an important quantity in evaluating the effectiveness of a prospective entrainer. It ranges between zero (no hydrogen bonding) and one (complete hydrogen bonding) and is defined as

$$\xi_B = \frac{C_{B0} - C_{B1}}{C_{B0}} \qquad (13)$$

Substitution of Eqs. (12) into Eq. (13) gives

$$\xi_B = \frac{K_{AB} C_{A1}}{1 + K_{AB} C_{A1}} \qquad (14)$$

in which the monomeric concentration of the cosolvent C_{A1} is determined by solving Eqs. (12). It is instructive to investigate the behavior of Eq. (14) for the case $C_{A0} \gg C_{B0}$, which is generally true since the solute concentration is low relative to that of the cosolvent. For this case, $C_{A1} \cong C_{A0}$ and the expression for ξ_B becomes

$$\xi_B = \frac{K_{AB}C_{A0}}{1 + K_{AB}C_{A0}} \tag{15}$$

This equation shows the hyperbolic nature of solvation without competition. Also, Eq. (15) predicts that the fraction solvated (ξ_B) is independent of the solute concentration.

The model for type II and type III mixtures is derived next. The significant feature of type II and type III mixtures is that they involve a self-associating fluid. Actually, only the model for type III mixtures is derived. The model for type II mixtures can be obtained as a special case of the more general type III model. For type III mixtures, there are three hydrogen-bonding interactions and three equilibria are assumed:

$$A_1 + A_j \rightleftharpoons A_{j+1}; \qquad A_j + B_1 \rightleftharpoons A_j B; \qquad A_j + S_1 \rightleftharpoons A_j S \tag{16}$$
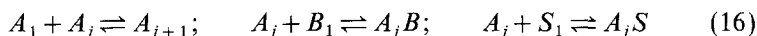
in which the subscripts $(j, j+1)$ refer to the number of cosolvent monomers that occur in an associated species; the monomer is designated A_1. The first equilibrium is for the self-association of the cosolvent (A), the second is for the solvation of the cosolvent with the solute (B), and the third equilibrium is for the solvation of cosolvent with the solvent (S). The equilibrium expressions are manipulated to show explicitly the relations between monomeric and hydrogen-bonded species:

$$C_{Aj} = (K_A)^{j-1}(C_{A1})^j; \qquad C_{AjB} = (K_{AB})^j C_{Aj}^j C_{B1}; \qquad C_{AjS} = (K_{AS})^j C_{Aj}^j C_{S1} \tag{17}$$

By material balance, superficial concentrations are introduced:

$$C_{A0} = \sum_{j=1}^{\infty} jC_{Aj} + \sum_{j=1}^{\infty} jC_{AjB} + \sum_{j=1}^{\infty} jC_{AjS};$$

$$C_{B0} = C_{B1} + \sum_{j=1}^{\infty} C_{AjB}; \qquad C_{S0} = C_{S1} + \sum_{j=1}^{\infty} C_{AjS} \tag{18}$$

in which (C_{B0}, C_{S0}, and C_{A0}) are the superficial concentrations of the solute, solvent, and cosolvent, respectively. The equilibrium expressions

(17) are substituted into the material balance equations (18) to give relations between superficial concentrations and monomer concentrations:

$$C_{A1} = \frac{C_{A0}}{1/(1 - K_A C_{A1})^2 + K_{AB} C_{B1}/(1 - K_{AB} C_{B1})^2 + K_{AS} C_{S1}/(1 - K_{AS} C_{S1})^2}$$

$$C_{B1} = \frac{C_{B0}}{(1 - K_{AB} C_{B0})}; \qquad C_{S1} = \frac{C_{S0}}{(1 - K_{AS} C_{S0})} \tag{19}$$

The fraction of the solute that is hydrogen bonded (ξ_B) is defined as in Eq. (13). Sustitution of Eqs. (19) into Eq. (13) gives

$$\xi_B = K_{AB} C_{A1} \tag{20}$$

For types II and III mixtures, C_{A1} depends on the extent of hydrogen-bonding competition, which is calculated by solving Eqs. (19) numerically. In the next section the model is compared to infrared determinations of hydrogen bonding.


5. RESULTS

In this section results of infrared measurements and APACT calculations are presented. Each of the three parts of the study is presented in turn. The APACT model, presented in the previous section in general form, is simplified depending on the type of hydrogen-bonding interactions present for each case.

5.1. Type I: Noncompetitive Solvation

Results for the direct solvation between cosolvent (ketone) and solute (methanol) are shown in Fig. 2a. There is no hydrogen-bonding competition in these mixtures since CCl_4 is used as the solvent, and self-association of methanol is minimized by using a low concentration typical of that of a solute in supercritical extraction. The modeling results shown in Fig. 2a were calculated using Eq. (12) with the solvation equilibrium constants shown in the figure. The good agreement between the modeling results and the spectroscopic data indicate that it is safe to neglect methanol self-association at low methanol concentrations. At higher methanol concentrations, however, the effect of self-association is dramatic and must be accounted for.

5.2. Type II: Solvation with Competition from Cosolvent Self-Association

Spectroscopic and modeling results for the solvation of a solute in a mixture of an inert solvent and a self-associating cosolvent are shown in Fig. 2b. There is good agreement between the model and the spectroscopic results. The concentrations used in these mixtures are typical of supercritical extraction mixtures in that the solute mole fraction is of the order of 1 % ($C_{B0} = 0.05$ mol $\cdot$ L^{-1}). In practice, cosolvent concentrations range from a few to 10 or 20 % of the solvent. In this study, the cosolvent concentration ranges from 0 to 40 % of the solvent. We extend the cosolvent concentration to higher than is normally found in practice to show the asymptotic nature of type II interactions and to demonstrate that the model is accurate over a wide range of concentrations.
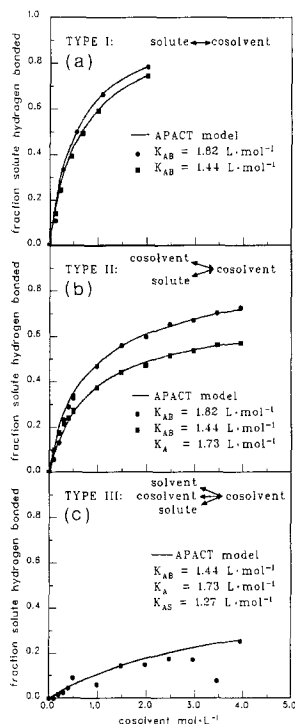
Fig. 2. The extent of solvation is shown as the fraction of the solute that is hydrogen bonded to the cosolvent (ζ) as a function of the cosolvent concentration for types I, II, and III mixtures. The data obtained experimentally are shown as symbols. The results of the APACT model are plotted as solid lines and the equilibrium constants used to obtain the APACT results are given. The text describes the chemicals used and gives those concentrations that are not shown.

As shown in Fig. 2b, as the cosolvent concentration increases, the fraction of ketone hydrogen bonded increases rapidly at first, then levels off. At the higher concentrations of cosolvent, self-association occurs which deprives the solute of hydrogen-bonding sites. The equilibrium constant used in the model for methanol self-association is $K_A = 1.73$ L $\cdot$ mol^{-1}. The solvation equilibrium constants for methanol/acetone and methanol/methyl ethyl ketone are the same as were used in Fig. 2a ($K_{AB} = 1.82$ and $K_{AB} = 1.44$, respectively). A comparison of Fig. 2a (type I) with Fig. 2b (type II) shows that the two sets of data are more widely separated in Fig. 2b. This suggests that a self-associating cosolvent is more selective in hydrogen bonding to a solute than a cosolvent that does not self-associate. Although type I mixtures have greater hydrogen bonding, type II mixtures have greater selectivity.

5.3. Type III: Solute Solvation with Competition from Cosolvent and Solvent

Spectroscopic and modeling results for the solvation of a solute in a mixture of a competing solvent and a self-associating cosolvent are shown in Fig. 2c. The mixture shown here is for MEK/diethyl ether/methanol. As discussed previously, diethyl ether was chosen as a liquid solvent analogue to supercritical CO_2. The equilibrium constant used in the model for the diethyl ether/methanol interaction was determined in a type I mixture to be $K_A = 1.27$ L $\cdot$ mol^{-1}. For this case there are no adjustable parameters in the model; all of the equilibrium constants are determined in either type I or type II mixtures. As the concentration of the cosolvent increases, the extent of hydrogen bonding to the solute increases very gradually. The combined effects of cosolvent self-association and competition from the solvent make the cosolvent useless as an entrainer.

6. CONCLUSIONS

In this paper we present a classification system, experiments, and theory for hydrogen-bonding competition in entrainer cosolvent systems. The main emphasis of this study is to demonstrate the different types of hydrogen-bonding interactions that can occur in entrainer–cosolvent systems and to show spectroscopic and modeling techniques that can be used to understand them.

In choosing an entrainer–cosolvent one must consider not only its hydrogen-bonding characteristics but also its effect on the mixture critical points and their proximity to the desired operating conditions. In the

future we hope to incorporate the knowledge gained in this study in a more comprehensive model for the phase behavior of entrainer–cosolvent mixtures.

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