J. Phys. Chem. A **2003,** *107,* 1891−1895

Thermodynamic Investigation on Self-Association of Alcohols in Carbon Tetrachloride by FT-NMR Spectroscopy

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Received: December 31, 2001; In Final Form: November 12, 2002

The equilibrium constant of the molecular association arises from hydrogen bonding of alcohols in carbon tetrachloride have been calculated by using FT-NMR spectroscopy data and mathematical models. To treat the thermodynamic behavior of the mixtures, association models such as dimer, continuous linear association model (CLAM), trimer, linear association with cyclic trimer association model (LACT), dependent equilibrium constant model (DECM), and dependent equilibrium constant and frequency model (DEFM) have been used to find the most proper model for alcohol + carbon tetrachloride mixtures. The activity coefficients for the mixtures have been calculated by various models and the results have been compared.

Introduction

Phase equilibrium data are often needed for design purposes in the chemical, petrochemical, and pharmaceutical industries. However, most systems are highly nonideal. For investigation of such systems, usually thermodynamic property measurements are performed for the entire concentration range. However, simple prediction methods rather than direct approaches are needed in order to estimate the required data. Many solution theories applied in the investigation of nonideal systems have either physical or chemical aspects, which are used in special ranges of concentrations and do not have general features.[1−4] If these theories are combined together, then better results are obtained.

There are abundant reasons that alcohol molecules associate because of hydrogen bonding.[5−10] Various spectroscopic techniques, such as IR[9−11] and NMR[11−13] spectroscopy, have been used for hydrogen bonding studies.

In this paper, Fourier transform nuclear magnetic resonance (FT-NMR) spectroscopy is used to determine the extent of self-association of alcohols in inert solvents. The main disadvantage of NMR spectroscopy for self-association study is its inability to distinguish the type of association models, which are selected. On the other hand, to fit the chemical shift data in a model, one has to work with only one chemical shift signal for all associating species present in solution.[14]

The chemical shift data derived from NMR spectroscopy have been interpreted with a variety of association models. There are models based on postulating the presence of only one type of associated species[15] or postulating several types of associated species in the mixture.[16]

In this paper, the ability of various associating models for treating the chemical shift data obtained by FT-NMR spectroscopy for self-association of alcohols has been investigated. These models are dimer, continuous linear association model (CLAM), trimer, linear association with cyclic trimer (LACT), dependent equilibrium constant model (DECM), and dependent equilibrium constant and frequency model (DEFM).[17−19]

Experimental Section

Aldrich HPLC grade 1-butanol, 1-propanol, ethanol, methanol, and CCl_4 were dried over Aldrich 3 Å molecular sieves to remove the trace amounts of water. Alcohols and solvent purity were 99.9% with less than 0.01% water. TMS 99.5% of purity from Merck Co. was used without further purification.

Each sample contained less than 0.5 mol % TMS and was used as internal reference for chemical shift measurement. The samples were prepared in 5 mm o.d. NMR tubes and weighed on an analytical balance with accuracy of ±0.1 mg. Measurement was performed by the external locking with D_2O in order to eliminate the undesirable deutrated solvent.

The chemical shift of the OH bond in alcohols was measured by the JEOL-JXNM-90 MHz FT-NMR that performed automatic variable-temperature operations also FT-NMR was calibrated as before with either methanol sample for low-temperature experiments and glycol sample for high-temperature experiments. The chemical shift measurements were done as a function of varying alcohol concentration in inert solvents at fixed temperatures with 20 scans. The maximum uncertainty in the measured chemical shifts was 0.1 ppm resulting from broadening and splitting of the proton peak by spin−spin coupling with adjacent protons.

Theory

In associating mixtures, we assume there is a successive series of equilibrium reactions, which can be represented as follows:

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10.1021/jp014729l CCC: $25.00

$$\begin{gathered} A + A \Leftrightarrow A_2 \\ A_2 + A \Leftrightarrow A_3 \\ \cdots \\ A_i + A \Leftrightarrow A_{i+1} \end{gathered} \tag{1}$$

The equilibrium constant K_{n+1} for each reaction based on volume fractions is given according to the Flory's lattice theory of polymer solutions[20]

$$K_{\mathrm{n+1}} = \left(\frac{\phi_{n+1}}{\phi_n \phi_l}\right)\frac{n}{n+1} = \frac{\mathrm{C}_{n+1}}{\mathrm{C}_n \mathrm{C}_1}\frac{1}{\nu_{\mathrm{a}}} \tag{2}$$

where ϕ, C, and ν_a are respectively volume fraction, molar concentration, and alcohol molar volume.

Gutowsky and Saike[21] primarily have shown that δ_{o} the observed chemical shift of OH bond for formation of an associated species is a weighted average of the chemical shifts of free δ_{f} and associated OH bonds. δ_{f} was evaluated by extrapolation of δ_{o} to alcohol concentration at infinite dilution. The chemical shifts of associated bonds are represented by $\delta_{n\mathrm{l}}$ in case of linear n-mer on and $\delta_{n\mathrm{c}}$ in the case of cyclic n-mer formation. The weighting factors are the fraction of the total number of hydrogen bonded OH in a given state at equilibrium, the final equation is[18]

$$\Delta_{\mathrm{o}} = \sum_{n=2}^{\infty}\left[\left(\frac{n-1}{n}\right)\left(\frac{\phi_{n\mathrm{l}}}{\phi_{\mathrm{a}}}\right)\Delta_{n\mathrm{l}} + \left(\frac{\phi_{n\mathrm{c}}}{\phi_{\mathrm{a}}}\right)\Delta_{n\mathrm{c}}\right] \tag{3a}$$

where

$$\Delta_{\mathrm{o}} = \delta_{\mathrm{o}} - \delta_{\mathrm{f}}; \quad \Delta_{n\mathrm{l}} = \delta_{n\mathrm{l}} - \delta_{\mathrm{f}}; \quad \Delta_{n\mathrm{c}} = \delta_{n\mathrm{c}} - \delta_{\mathrm{f}} \tag{3b}$$

In eqs 3a and 3b, ϕ is the volume fraction and δ is the chemical shift where the subscripts a, 1, nl, and nc represent alcohol, monomer, linear n-mer, and cyclic n-mer, respectively. Also assuming zero excess volume, the volume fractions in eq 3a are related through the mass balance equation as

$$\phi_{\mathrm{a}} = \phi_1 + \sum_{n=2}^{\infty}(\phi_{n\mathrm{l}} + \phi_{n\mathrm{c}}) \tag{4}$$

Modeling

Using eqs 2, 3a, and (4), one can test an infinite number of models for a given associating solution. To reduce the number of models, simplifying assumptions are made.

Association models are sometimes limited by the fact that certain assumptions must be made regarding the equilibrium constant in order to limit the number of adjustable parameter and retain as much as possible physical significance in them.

In the present paper, to obtain the equilibrium constants for self-association of alcohol in inert solvent, the chemical shift data for alcohol−inert solvent systems were fitted to six different models namely: dimer model, CLAM, trimer model, LACT model, DECM, and DEFM. A brief description of these association models is as follows.

Dimer Model.[6] The simplest assumption is that only dimers are formed in solution. This assumption is if the results are compatible with experimental data. By using this assumption and primarily logical combining eqs 2 and 3a, it will be reduced to the following form:

$$\Delta_{\mathrm{o}} = \frac{K_{2\mathrm{l}}{\phi_1}^2}{\phi_{\mathrm{a}}}\Delta_{2\mathrm{l}} \tag{5}$$

In this model $K_{2\mathrm{l}}$ and Δ_n are adjustable parameters.

CLAM.[22] If the species present in the associating mixture are in the linear form, continuous linear association model (CLAM) is a good assumption. In this model, it is assumed that all OH bonds have equal probabilities of reacting irrespective of the size of the hydrogen-bonded species on which they reside. This is equivalent to assuming that: $K_2 = K_3 = ... = K$. Then, on combining eqs 2 and 3b, it will be reduced to the following form:

$$\Delta_{\mathrm{o}} = \left[\frac{2K\,\phi_{\mathrm{a}} + 1 - (4K\,\phi_{\mathrm{a}} + 1)^{1/2}}{2K\,\phi_{\mathrm{a}}}\right]\Delta_n \tag{6}$$

In this model, K and Δ_n are adjustable parameters.

Trimer Model.[23] Spectroscopic evidence indicates that in certain cases cyclic trimer appears to be the dominant hydrogen-bonded species. Then, on combining eqs 2 and 3a, it will be reduced to the following form:[16]

$$\Delta_{\mathrm{o}} = \left(\frac{3K_3\,{\phi_1}^3}{\phi_{\mathrm{a}}}\right)\Delta_n \tag{7}$$

where K_3 is the trimerization constant and refers to the processes of forming cyclic trimer ($3A \rightleftarrows A_3$) and Δ_n are adjustable parameters.

LACT Model.[24] Another model is linear association with cyclic trimer association model (LACT) which assumes that the dominant hydrogen-bonded species is cyclic trimer, and then combining eqs 2 and 3a will be reduced to the following form:

$$\Delta_{\mathrm{o}} = \left[\frac{K_3(K\,\phi_1)^3(3 - 3K\,\phi_1 + (K\,\phi_1)^2)}{K^3\,\phi_{\mathrm{a}}(1 - K\,\phi_1)^2}\right]\Delta_n \tag{8}$$

In this model K, K_3, and Δ_n are adjustable parameters.

DECM[18] and DEFM. DECM and DEFM are different from the previous models in describing the behavior of associating fluids. The DECM model is based on the assumption that as the associative species concentration increases the extent of association increases and as the temperature of the solution increases the n-mers break down to form the more stable trimer. The unique feature of these models is that the probability of forming the various species is no longer equal but depends on the size of n-mers. The simplest function, which can express this model, is in logarithmic form and relates equilibrium constant to a single parameter, D:

$$\ln K_n = \frac{D}{n-2}; \quad n \geq 3 \tag{9}$$

In DECM, the n-mer chemical shifts are equal, and it is assumed that free OH bonds in linear n-mers can be neglected and there is no distinction between linear and cyclic species. Then, eqs 3a and 4 are simplified to

$$\Delta_o = \Delta_n \sum_{n=3}^{\infty}\left(\frac{\phi_n}{\phi_a}\right), \quad \phi_a = \phi_1 + \sum_{n=3}^{\infty}\phi_n \tag{10}$$

Referring to high alcohol concentration, the chemical shift of the OH proton relative to the chemical shift of TMS is large. This large shift is due to the lowered electron density around the nucleus of the proton upon hydrogen bonding. At low concentrations, the chemical shift is smaller because of lower amounts of hydrogen bonding. This shows that *n*-mer chemical shifts depend on association number. Therefore, in this work, the chemical shift of the OH bond is assumed to be proportional to association number *n* in the following equation:

$$\delta_n = F \ln(n) \tag{11}$$

where F is an adjustable parameter.

Using eq 11 in eqs 3a and 3b, the final results for DEFM will be

$$\Delta_\mathrm{o} = \sum_{n=3}^{\infty} \left(\frac{n-1}{n}\right) \frac{\phi_n}{\phi_\mathrm{a}} \Delta_n \tag{12}$$

The experimental results will be used in eqs 9 and 10 to evaluate D for DECM and in eqs 11 and 12 to evaluate F for DEFM.

Mixture Properties

The equilibrium constants derived from NMR data can be used for calculation of mixture properties. The important property for nonideal mixtutres is the activity coefficients. For the associated fluids such as alcohols, the activity coefficients can be expressed by Flory−Huggins theory[25] as

$$\ln \gamma_\mathrm{s} = \ln \frac{\phi_\mathrm{s}}{X_\mathrm{s}} - \phi_\mathrm{a} - \frac{\phi_\mathrm{a}}{\bar{X}_n} \cdot \frac{\nu_\mathrm{a}}{\nu_\mathrm{s}} + \frac{\beta}{RT} \nu_\mathrm{s} \phi_\mathrm{a}^{\,2} \tag{13}$$

$$\ln \gamma_a = \ln\left(\frac{\phi_{\mathrm{a}1}}{X_\mathrm{a} \phi_{\mathrm{a}1*}}\right) - \phi_\mathrm{s} - \frac{\nu_\mathrm{a}}{\nu_\mathrm{s}} + \frac{1}{\bar{\mathrm{X}}_n^*} - \frac{\phi_\mathrm{a}}{\bar{\mathrm{X}}_n} + \frac{\beta}{RT} \nu_\mathrm{a} \phi_\mathrm{s}^{\,2} \tag{14}$$

where ϕ, X, and ν are respectively the volume fractions, mole fractions, and molar volumes of alcohol (a) and solvent (s), respectively. In the above equations, $\phi_{\mathrm{a}1}^*$ is the monomer volume fraction in pure alcohol and β is defined as

$$\beta = (\delta_\mathrm{s} - \delta_\mathrm{a})^2 \tag{15}$$

where δ is the solubility parameter.[26−27]

The average number of segments in eqs 13 and 14 is defined as

$$\bar{\mathrm{X}}_n = \frac{\phi_\mathrm{a}}{\displaystyle\sum_{n=1}^{\infty} \frac{\phi_n}{n}} \tag{16}$$

where for a pure alcohol ($\phi_\mathrm{a} = 1$) the average number of segments is represented as $\bar{\mathrm{X}}_n^*$.

Results and Discussion

Table 1 reports the root-mean-square deviation (RMSD) of various association models used for fitting of the measured chemical shifts of the OH bond of alcohols in inert solvents at different temperatures. According to this table, DEFM has the best fitting for measured chemical shifts. This is due to the fact that, although in this model the trimer is considered as the dominant species, the possibility of the presence of another species in the mixtures has not been ignored, and the association constants for all species have been taken into account. In Table 2, the association constants and association parameters D and F calculated based on various models are reported. As it is seen from the results in this table, the trimerization constant for the trimer is high. This indicates that the trimer is the dominant species in these mixtures. The results in Table 2 show that, as expected, on incresasing temperature the association constant, association parameters, and trimerization constant decrease for all the models. On decreasing polarity from ethanol to 1-butabol, the association constants and the parameter constant D also show a decrease, which is the usual trend for their variations.[28]

TABLE 1: RMSD of Various Associations Models on Fitting the Measured Chemical Shift (Hz) Data

system	T (°C)	dimer	trimer	CLAM	LACT	DECM	DEFM
EtOH + CCl_4	45	13.61	4.16	13.61	6.06	7.27	4.23
	55	12.99	4.97	12.99	7.92	8.19	4.40
	65	12.50	5.19	12.50	7.68	8.64	4.10
1-PrOH + CCl_4	35	11.22	7.16	11.62	11.04	10.52	4.41
	45	10.49	7.94	10.49	10.57	11.8	5.07
	55	9.90	8.06	9.90	8.97	12.09	4.99
1-BuOH + CCl_4	40	11.16	7.93	11.16	10.61	11.05	4.27
	50	11.05	7.14	11.05	9.91	11.12	4.70
	60	10.32	7.96	10.32	10.14	11.79	5.35

TABLE 2: Equilibrium Constants and Adjustable Parameters (*D* and *F* in eqs 9 and 11) Calculated Based on Various Association Models for Alcohol−CCl_4 Systems at Different Temperatures

		dimer	trimer	CLAM	LACT		DECM	DEFM	
alcohol	T (°C)	K	K_3	K	K	K_3	D	D	F
EtOH	45	31.20	1010.99	31.20	26.72	583.00	6.45	7.17	439.5
	55	23.12	643.76	23.12	16.62	437.80	6.01	6.70	435.5
	65	17.29	416.65	17.29	2.88	351.20	5.58	6.24	429.1
1-PrOH	35	30.16	986.67	30.31	28.35	587.80	6.38	7.10	436.9
	45	21.14	580.77	21.14	16.36	400.61	5.84	6.53	429.9
	55	15.23	358.51	15.23	2.95	298.72	5.36	6.03	423.5
1-BuOH	30	29.03	1041.31	29.02	48.20	674.70	6.30	7.02	439.6
	40	19.63	510.73	19.69	16.62	328.90	5.74	6.42	433.5
	50	14.11	315.35	14.11	2.42	275.70	5.24	5.90	428.3

It is worth nothing that the values of D, in Table 2, for the DEFM model are a fixed multiple of D for the DECM model. The reason for this can be explained by considering eq 9 where for the same association number n the ratio of association constants for the two model can be expressed in terms of ratio D parameters for the two models.

As it is seen from Table 2, the values of K in columns 2 and 4 are the same. The reason for this can be explained by considering the similarity of eqs 5 and 6 that are used for calculating the association constant K in dimer and CLAM models. Therefore, it is not surprising that the same results are obtained from their application. However the values of the second parameter in these equations which are, respectively, for the chemical shifts of dimer and *n*-mer are quite different.

Figures 1 and 2, as examples, show the fitting of chemical shift data with different models for 1-propanol + CCl_4 system at 35 °C at low and high concentrations, respectively. Figure 3 shows the distribution function defined as

$$F(\mathrm{n}) = \frac{\phi_n}{\phi_\mathrm{a}} = \frac{n\left(\prod_{n=3}^{n} K_i\right) \phi_1^n}{\left[\phi_1 + \sum_{n=3}^{n} \phi_n\right]} \tag{17}$$

for 1-propanol + CCl_4 at 35 °C system. The distribution function $F(n)$ indicates that for DEFM in low concentrations the trimer population is dominant over other associated species, whereas at high cocentrations, tetramers are dominant. This same trend is observed for all of the three alcohols studied.

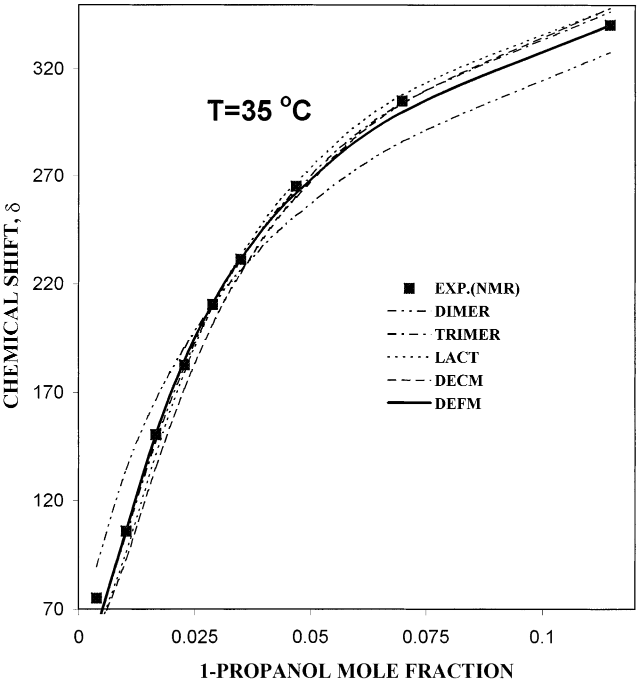

Figure 1. Fitting of various models for the observed chemical shifts of the OH proton for 1-propanol + CCl_4 at low concentration (35 °C).

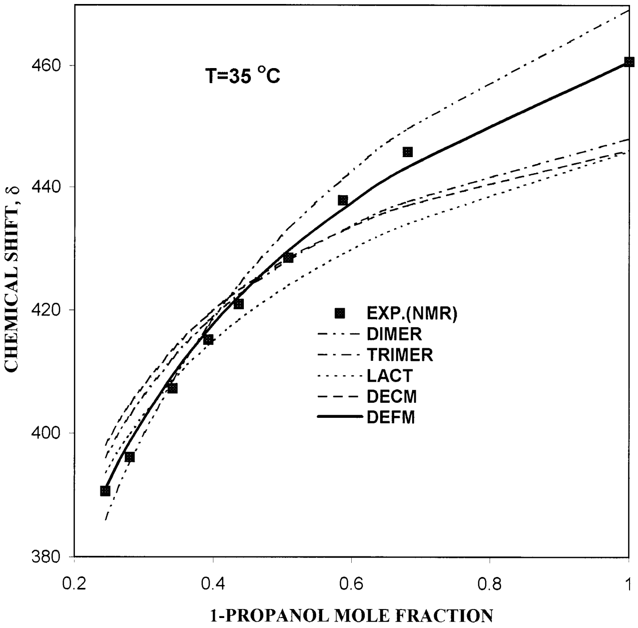

Figure 2. Fitting of various models for the observed chemical shifts of the OH proton for 1-propanol + CCl_4 at high concentration (35 °C).

In Figures 4–6, activity coefficients for the mixture of alcohol + inert solvent calculated based on NMR results and DEFM model have been compared with those obtained from vapor pressure measurements.[29] The good fit shows the ability of DEFM in treating the results.

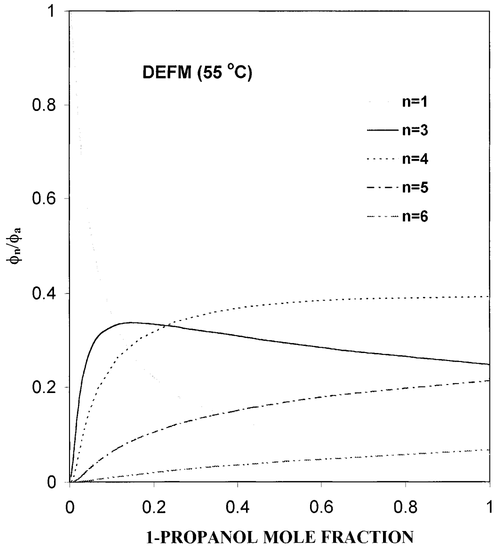

Figure 3. Hydrogen-bonded species distribution based on DEFM model at for 1-propanol + CCl_4 at 55 °C.

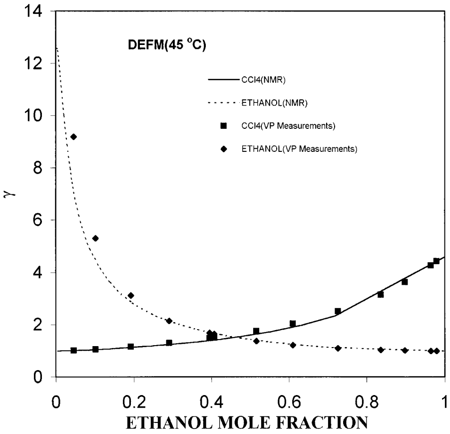

Figure 4. Activity coefficients prediction DEFM model for ethanol + CCl_4 at 45 °C.

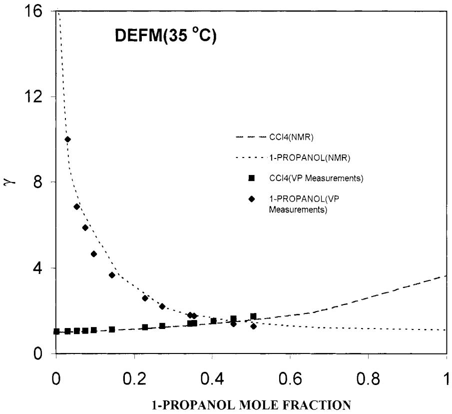

Figure 5. Activity coefficients prediction DEFM model for 1-propanol + CCl_4 at 35 °C.

Conclusion

NMR spectroscopy is used to produce chemical shift data for a number of associating alcohols mixed with inert solvent. A number of existing association models has been used. It is demonstrated that DEFM is a more realistic model and can correlate the chemical shift data quite accurately. The distinguishing feature of DEFM over other models as it is expected in the real cases is its ability to show that the species in solution do not have equal probabilities of formation.

DEFM is used to obtain information about the distribution of various species in the associating fluids as well as their thermodynamic properties.

It is concluded that for the alcohol systems studied the trimer is the predominant species at low alcohol concentrations, whereas the tetramer is predominant at high concentrations.

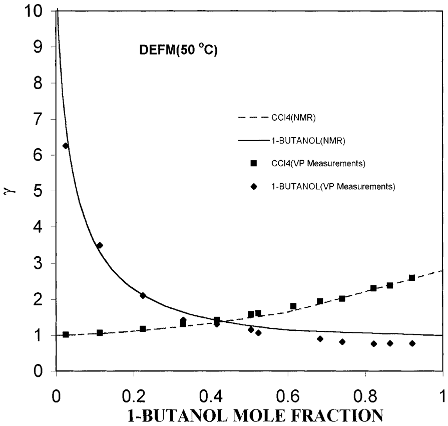

Figure 6. Activity coefficients prediction DEFM model for 1-butanol + CCl_4 at 50 °C.

Acknowledgment. The authors acknowledge NMR laboratory support in Tarbiat Modarress University and computer center of Department of Chemical Engineering of Amir-Kabir Unversity of Technology.

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