Development of the AVEC Model for Associating Mixtures Using NMR Spectroscopy

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Common models for excess Gibbs energy account primarily for physical forces and do not represent strong specific interactions. However, purely chemical models neglect strong nonspecific forces and combined chemical-physical treatments involve an unreasonable number of adjustable parameters. One way to ameliorate this limitation is to make independent measurements of the parameters by a nonthermodynamic technique. We report an investigation of hydrogen bonding, a localized and very directional specific interaction, conducted in various alcohol mixtures using Fourier transform nuclear magnetic resonance to measure the number of complexed species in solution. A chemical-physical association model with variable equilibrium constants has been developed. The distinguishing feature of this model is that the species in solution do not have equal probability of forming yet require only a single chemical interaction parameter determined from fitting NMR data and a physical interaction parameter determined from infinite dilution activity coefficients. The AVEC model successfully predicts vapor-liquid equilibrium and excess enthalpy as well as liquid-liquid equilibrium, an especially stringent test.

Introduction

Prediction of solution behavior for mixtures with specific chemical interactions (hydrogen bonding) is a challenge. Chemical-physical models describe solution behavior more realistically than purely physical models but require a large number of model parameters. In this study, Fourier transform nuclear magnetic resonance (FT-NMR) spectroscopy, a nonthermodynamic probe, was used to determine the extent of complex formation and to reduce the number of necessary model parameters. In the chemical-physical association model with variable equilibrium constants (AVEC model), which will be presented, the chemical model parameters (equilibrium constants) are further reduced by linearization. The NMR data are used to determine the chemical interaction parameters (the equilibrium constants for complex formation) in the model, which can then be used to predict various thermodynamic properties such as activity coefficients, excess enthalpy, and liquid-liquid equilibrium (LLE) when applicable. Adequate representation of the NMR data, as well as prediction of the thermodynamic properties, is sensitive to model formulation.

There are many experimental data supporting the concept of complex formation, or oligomerization. Neutron scattering (Boutin et al., 1963; Boutin and Safford, 1965; Ring and Egelstaff, 1969), X-ray diffraction (Janzen and Bartell, 1969), and infrared (Maybury et al., 1955; Smith, 1958) studies on hydrogen fluoride all indicate that intermolecular bonds are responsible for hydrogen-bonded polymer chains. The hydrogen bonds in the HF polymer configurations are among the strongest type of hydrogen bond known, with the energy of bond formation approximately 24–28 kJ/mol (Pimentel and McClellan, 1960). The results of X-ray diffraction studies (Warren, 1933; Pierce and MacMillan, 1938; Harvey, 1938, 1939; Wertz and Kruh, 1967; Narten et al., 1978; Narten and Sandler, 1979; Narten, 1979) on *t*-butyl alcohol and ethanol, infrared studies by the matrix isolation technique on methanol (Fox

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and Martin, 1940; Van Thiel et al., 1957; Bourderon et al., 1972; Luck, 1976), and the determination of average degree of association from viscosity measurements for the primary alcohols—methanol, ethanol, 1-propanol, and 1-butanol (Ratkovics et al., 1974)—can also be explained in terms of chain formation. The bond strength of the alcohol complexes is slightly weaker than the HF bond strength and is approximately 12-16 kJ/mol.

There is also theoretical support for oligomerization. Jorgensen used transferable intermolecular potential functions (TIPS) derived from *ab initio* molecular orbital calculations for methanol (Jorgensen, 1980b, 1981b), water (Jorgensen, 1979a, 1980a, 1981a), and HF (Jorgensen, 1978, 1979a). The results indicate that winding chains are the dominant multimers in solution. He estimates that the average chain length is about five or six monomers with no one particular species dominating. Instead, there is a spectrum of hydrogen bond strengths and geometries. The results of Jorgenson's studies give little indication of the existence of dimers, although various higher order oligomers are evident. This conclusion is also supported by experimental studies (Saunders and Hyne, 1958a,b; Tucker and Becker, 1973). Smith and Nezbeda (1984) have also performed Monte Carlo simulations using a simple site-site interaction model and obtained the basic qualitative properties of associating fluids:

1. The distribution functions do not exhibit pronounced damped oscillations beyond the first sharp narrow peak
2. Low coordination number (Pings, 1968; Ben-Naim, 1974)

The purpose of this paper is to present a chemical-physical association model based upon a new formulation. The model's concept was developed after an examination of excess enthalpy data. Excess enthalpy for alcohol-hydrocarbon binary mixtures exhibits unusual behavior: it increases with increasing temperature. One would initially expect excess enthalpy to decrease with increasing temperature. Examining the other excess properties for such alcohol-hydrocarbon mixtures, the excess Gibbs energy decreases with increasing temperature. Given the relationship between excess Gibbs free energy, excess enthalpy, and excess entropy,

$$G^E = H^E - TS^E \tag{1}$$

if the enthalpy increases and the Gibbs energy decreases with increasing temperature, the excess entropy must therefore increase with increasing temperature. This is an indication that the solution is getting more ordered with increasing temperature, while at the same time the species in solution require ever increasing amounts of energy to break them up into their constituent monomers. The increasing order in the solution can be viewed as an increase in the population of hydrogen-bonded species in solution. Essentially, one can view the low-temperature solution as a mixture of monomers, high-order unstable hydrogen-bonded complexes, and low-order stable hydrogen-bonded complexes. As the temperature is increased the high-order unstable complexes decompose into low-order stable complexes such that the total population of hydrogen-bonded species increases relative to the low-temperature solution. This results in an increase in the excess entropy with an increase in temperature as well as an increase in the excess enthalpy. This redistribution of hydrogen-bonded species with variations in temperature is the underlying feature of the model developed in this paper and one that distinguishes it from previous association models.

Development of Association Model and Solution Property Equations

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

$$A + A = A_2 \tag{2}$$

$$A_2 + A = A_3$$

$$\bullet \quad \bullet \quad \bullet$$

$$A_n + A = A_{n+1}$$

Associated with each equilibrium reaction is an equilibrium constant. The equilibrium constant, K_n, can be defined in terms of mole fractions, concentrations, or volume fractions. In our study, the equilibrium constants are based on volume fractions and are defined according to Flory's lattice model for polymer solutions (Flory 1944, 1953):

$$K_{n+1} = \left(\frac{\Phi_{n+1}}{\Phi_n \Phi_1}\right)\left(\frac{n}{n+1}\right) = \left(\frac{C_{n+1}}{C_n C_1}\right)\frac{1}{V_a} \tag{3}$$

where, Φ is volume fraction, C is concentration, and $n \geq 3$.

These equilibrium constants can be used to calculate solution properties. The Gibbs energy in a binary solution of alcohol a in solvent s is related to the activity coefficients:

$$g^E = RT\,(x_a \ln\gamma_a + x_s \ln\gamma_s) \tag{4}$$

and

$$\ln\gamma_s = \ln\left(\frac{\Phi_s}{x_s}\right) + \Phi_a - \frac{\Phi_a V_s}{\bar{x}_n V_a} + \frac{\beta}{RT} V_s \Phi_a^2 \tag{5}$$

where,

$$\ln\gamma_a = \ln\left(\frac{\Phi_1}{x_a \Phi_1^*}\right) - \frac{\Phi_s V_a}{V_s} + \frac{1}{\bar{x}_n^*} - \frac{\Phi_a}{\bar{x}_n} + \frac{\beta}{RT} V_a \Phi_s^2$$

$$\bar{x}_n = \frac{\Phi_a}{\sum_{n=1}^{\infty} \frac{\Phi_n}{n}} \tag{6}$$

x_n is the average number of segments per n-mer in the alcohol, x_n^* is the average number of segments per n-mer in the pure alcohol, Φ_1 is the alcohol monomer volume fraction, and Φ_1^* is the alcohol monomer volume fraction in the pure alcohol. More detailed information on the solution property equations and their derivation is given by McNiel (1987), Karachewski (1988), and Karachewski et al. (1989).

In the chemical-physical association model presented in this paper, the chemical interaction parameter is determined from fitting NMR chemical shift data to a specific association model and the physical interaction parameter is determined from infinite dilution activity coefficients determined experimentally

by ebulliometry (Trampe and Eckert, 1990a). The physical model we chose to use is a Scatchard-Hildebrand type equation for which the physical interaction parameter, β, is defined as the interaction energy density between solute-solvent pairs (Flory, 1944; Kretschmer and Wiebe, 1954). Evaluating the activity coefficient expressions in the dilute region results in two equations for alcohol-hydrocarbon mixtures, which are used to evaluate the physical interaction parameter, β.

$$\ln\gamma_s^\infty = \ln\left(\frac{V_s}{V_a}\right) + 1 - \frac{V_s}{\bar{x}_n^* V_a} + \frac{\beta}{RT} V_s \tag{7}$$

$$\ln\gamma_a^\infty = \ln\left(\frac{V_a}{V_s \Phi_1^*}\right) + \frac{1}{\bar{x}_n^*} - \frac{V_a}{V_s} + \frac{\beta}{RT} V_a \tag{8}$$

Development of the NMR Association Model

Various techniques can be used to study hydrogen bonding (Coggeshall and Saier, 1951; Liddel and Becker, 1957; Bolles and Drago, 1965; Lamberts, 1971; Mullens et al., 1985). Spectroscopic techniques allow one to probe solution behavior from a molecular perspective and have become increasingly common in recent years. Nuclear magnetic resonance in particular (Gutowsky and Saike, 1953; Foster and Fyfe, 1965; Bruno et al., 1983; Eckert et al., 1986; Karachewski et al., 1989) has been used quite successfully to probe the solution structure. In the NMR spectra, as the extent of hydrogen bonding changes so does the chemical shift of complex formation. It is this change in chemical shift that allows for the study of hydrogen bonding. The complexes formed in solution can be linear, having an open structure, or cyclic, having a closed structure. Gutowsky and Saike (1953) have shown that the observed chemical shift for complex formation, ν_o, is a weighed average of the chemical shifts of the free and complexed protons, where the weighting factors are the fraction of the total number of hydrogen-bonded protons present in a given state at equilibrium, namely:

$$\nu_0 = \left(\frac{C_1}{C_a}\right)\nu_1 + \sum_{n=3}^{\infty}\left[\left(\frac{n C_{nc}}{C_a}\right)\nu_{nc} + \left(\frac{(n-1)C_{nl}}{C_a}\right)\nu_{nl} + \left(\frac{C_{nl}}{C_a}\right)\nu_1'\right] \tag{9}$$

Therefore, NMR provides direct evidence for the number of complexed species. In Eq. 9, C_{nc} is the concentration of cyclic n-mers, C_{nl} is the concentration of linear n-mers, C_a is the total concentration of hydrogen-bonding species, ν_1 is the chemical shift of the proton on a monomer, ν_1' is the chemical shift of the free proton on an n-mer, ν_{nc} is the chemical shift of the bonded protons on a cyclic n-mer, and ν_{nl} is the chemical shift of the bonded proton on a linear n-mer. In the NMR model formulation it is assumed that $\nu_{nl} = \nu_{nc} = \nu_n = \text{constant}$.

Assuming that the formation of a hydrogen bond causes no volume change and the proton on the end of a linear chain has the same chemical shift as that on a monomer, the above equation can be rewritten as follows:

$$\Delta_o = \sum_{n=3}^{\infty}\left[\left(\frac{n-1}{n}\right)\left(\frac{\Phi_{nl}}{\Phi_a}\right)\Delta_{nl} + \left(\frac{\Phi_{nc}}{\Phi_a}\right)\Delta_{nc}\right] \tag{10}$$

where $\Delta_{nl} = \nu_{nl} - \nu_1$, $\Delta_{nc} = \nu_{nc} - \nu_1$, and $\Delta_o = \nu_o - \nu_1$.

This is the equation used to relate spectroscopic information to thermodynamic information. Also, one may calculate the alcohol monomer volume fraction, Φ_1,

$$\Phi_a = \Phi_1 + \sum_{n=3}^{\infty}(\Phi_{nc} + \Phi_{nl}) \tag{11}$$

Chemical-physical models are sometimes limited by the fact that certain assumptions must be made regarding the equilibrium constants in order to limit the number of adjustable parameters and retain some physical significance. For example, the continuous linear association model (CLAM), used by Kretschmer and Wiebe (1954) and Renon and Prausnitz (1967) for alcohol-hydrocarbon mixtures, restricted complex formation to linear species only, all with equal probability of forming. The CLAM model, with only one chemical model parameter, is able to represent NMR solution behavior well in the concentrated alcohol region but in the more difficult dilute alcohol region, it is poorer (Karachewski et al., 1989). The CLAM model predicts activity coefficients well over the entire composition range, but it is not able to predict well the temperature dependence of the excess enthalpy (Karachewski et al., 1989).

Another example is the linear association with cyclic trimer (LACT) model (Karachewski et al., 1989), which was developed because of experimental spectroscopic evidence suggesting that the cyclic trimer is the first important complex to be formed in solution (Saunders and Hyne, 1958a,b; Tucker and Becker, 1973). The formation of the cyclic trimer is treated specially and has a unique equilibrium constant for complex formation assigned to it. All higher order complexes in solution are linear. This model, like the CLAM, assumes that the formation of all linear species is equally probable and gives a good representation of NMR chemical shift data in both the concentrated and the dilute alcohol regions. The LACT model is able to predict activity coefficients quite well and is able to predict the correct composition and temperature dependence of the excess enthalpy. However, the LACT model fails to predict the liquid-liquid coexistence curve for methanol systems. In the LACT model there are two chemical model parameters, one representing cyclic trimer formation and another representing linear complex formation.

There are also a number of other one-complex models that could be used to predict solution behavior, such as trimer-only or tetramer-only models, but they have limited application. Often, prediction of activity coefficients is poor and prediction of more sensitive solution properties such as excess enthalpy or liquid-liquid equilibrium may be very poor (Karachewski et al., 1989).

In this work, a new association model (AVEC) has been developed; it is different from previous attempts at describing solution behavior in alcohol-hydrocarbon mixtures. The AVEC model is based on the assumption that as the temperature of the solution increases, the oligomers break down to form the more stable complex, the trimer (Saunders and Hyne, 1958a,b; Tucker and Becker, 1973). This is indicated by the heat of formation of the oligomers being greater than the heat of formation for the trimer. The hydrogen bond strength decreases as the complex becomes larger yet the heat of formation for the complex still increases as the size of the oligomer grows.

The unique feature of this model is that the probability of forming the various species is no longer equal but depends on the size of the complex. For linear species,

$$\ln K_{nl} = \left(\frac{L_g}{n-1}\right) \tag{12}$$

where there are $(n-1)$ hydrogen bonds in a complex containing n monomers, with an end proton that is free. L_g is an adjustable chemical model parameter. For the formation of cyclic complexes, where there are n hydrogen bonds in a complex containing n monomers,

$$\ln K_{nc} = \left(\frac{C_g}{n}\right) \tag{13}$$

and C_g is an adjustable chemical model parameter.

The AVEC model, which includes both linear and cyclic species but assumes negligible dimer formation, was tested and initially required two chemical model parameters. From fitting of NMR chemical shift data for a number of systems, it was observed that the two chemical parameters were not independent but instead were interrelated:

$$C_g = \left(\frac{4}{3}\right) L_g \tag{14}$$

The AVEC model was thus used to fit the experimental NMR data and subsequently to predict solution behavior with a single chemical interaction parameter. The results of the various predictions with this model are illustrated in the Results and Discussion section. Other versions of the AVEC model were tested and rejected (see Appendix).

Table 1. NMR ^{1}H Chemical Shifts for Methanol in Hydrocarbons as a Function of Temperature

System	x_a	ν_o at 51°C Hz	ν_o at 58°C Hz	ν_o at 64°C Hz
Methanol-cyclohexane	0.0799	665.62	604.04	547.54
	0.1814	811.79	776.71	736.72
	0.2280	822.90	—	757.03
	0.2362	825.76	802.11	769.41
	0.3025	857.81	824.64	800.36
	0.3710	870.67	842.10	826.39
	0.5867	926.06	909.71	893.36
	0.7723	929.87	912.89	897.49
		ν_o at 55°C Hz	ν_o at 60°C Hz	ν_o at 64°C Hz
Methanol-heptane	0.2410	721.48	685.14	665.62
	0.2939	751.48	719.42	699.90
	0.3374	775.60	743.23	701.65
	0.6580	918.12	906.06	896.70
	0.6844	918.28	906.38	897.17
	0.8024	919.55	907.81	898.60
	0.8203	919.87	908.28	899.40
	0.8698	919.71	907.97	899.08
	0.9152	919.23	907.49	898.13
	0.9700	922.57	911.30	901.78

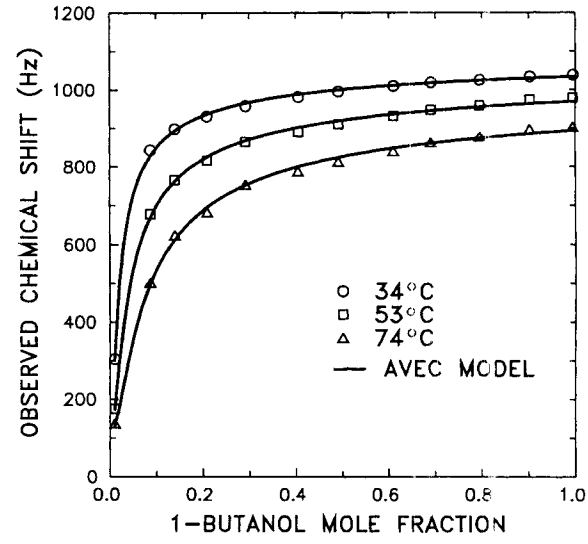

Figure 1. Fit of observed chemical shift of OH proton for 1-butanol and cyclohexane.

Experimental Technique

The experimental technique used to obtain NMR chemical shift data was similar to that described previously by Karachewski et al. (1989). A Varian XL-200 FT-NMR spectrometer and a Nicolet 360 FT-NMR spectrometer were used. Stringently water-free samples were measured over a range of concentration and temperature. The NMR was calibrated as before with either a methanol sample for low-temperature experiments or with a glycol sample for high-temperature experiments.

Results and Discussion

Table 1 includes the NMR ^{1}H chemical shifts for methanol in both cyclohexane and heptane as a function of composition and temperature. The experimental data for 2-propanol mix-

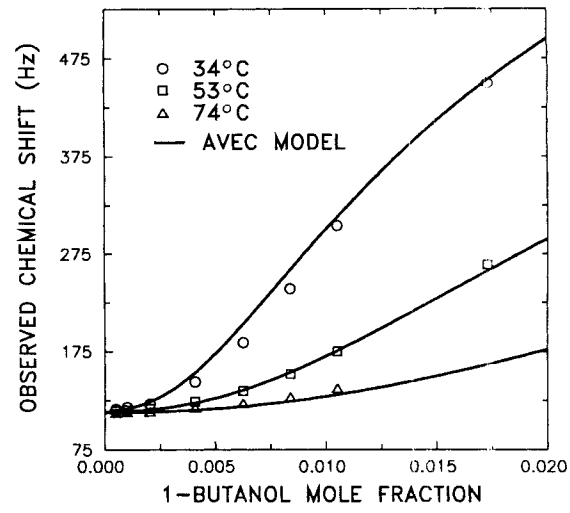

Figure 2. Fit of the observed chemical shift of OH proton in dilute alcohol region of 1-butanol and cyclohexane.

tures and 1-butanol mixtures can be found in a previous publication (Karachewski et al., 1989). The monomer chemical shift for methanol was measured to ±0.2 ppm and was independent of temperature.

Figures 1 and 2 show typical model fits of concentrated and dilute NMR data for the system 1-butanol-cyclohexane, to yield the equilibrium constants. Table 2 lists the chemical model parameter values of L_g and C_g. In order to truly test the model's predictive ability, various types of solution behavior such as activity coefficients, excess enthalpy, and the liquid-liquid equilibrium were predicted.

If a model is to portray realistically what transpires in solution, it must account for both chemical and physical interactions. In this study, NMR spectroscopy is used to obtain information on the chemical interactions. The physical interaction contribution is then calculated by using experimentally determined, limiting-activity coefficients. To calculate the single physical contribution constant, one must choose whether to use γ_s^∞, where the solute is the hydrocarbon solvent, or γ_a^∞, where the solute is the alcohol. We recommend that γ_s^∞ be used to evaluate the physical interaction parameter, because it represents the region where the alcohol is completely hydrogen bonded. Since the hydrocarbon does not hydrogen bond, the important interactions that the hydrocarbon undergoes in this region are physical. Table 3 lists the γ_s^∞ expressions as a function of temperature for the various alcohol-hydrocarbon mixtures studied. These expressions were obtained using ebulliometric measurements (Trampe and Eckert, 1990a). Table 4 lists the physical interaction parameter, β, for the systems investigated.

Table 2. Model Parameters for Methanol, 2-Propanol, and 1-Butanol in Various Hydrocarbons

Alcohol Mixture	T °C	L_g	C_g	Δ_n Hz $(\nu_n - \nu_1)$
Methanol-cyclohexane	51	14.8	19.7	1,079
	58	13.7	18.3	1,070
	64	12.8	17.1	1,063
Methanol-heptane	55	12.1	16.1	1,088
	60	11.3	15.1	1,086
	64	10.8	14.4	1,083
2-propanol-cyclohexane	34	13.3	17.7	1,064
	61	9.8	13.1	981
	74	8.4	11.1	933
2-propanol-heptane	34	13.7	18.3	1,060
	48	11.5	15.4	1,018
	61	9.9	13.2	973
2-propanol-hexane	34	13.5	18.0	1,061
	48	11.4	15.1	1,020
	61	9.6	12.8	977
2-propanol-methylcyclohexane	34	13.3	17.7	1,063
	48	11.4	15.2	1,019
	61	9.6	12.8	977
1-butanol-cyclohexane	34	13.1	17.4	1,100
	53	10.4	13.8	1,045
	75	8.0	10.6	989

Table 3. Limiting Activity Coefficient Expressions Determined from Ebulliometric Measurements

2-propanol-cyclohexane

$$0.58 + \frac{332.1}{T} = \ln\gamma_s^\infty$$

2-propanol-heptane

$$0.25 + \frac{527.8}{T} = \ln\gamma_s^\infty$$

2-propanol-hexane

$$0.49 + \frac{404.4}{T} = \ln\gamma_s^\infty$$

2-propanol-methylcyclohexane

$$0.00 + \frac{582.3}{T} = \ln\gamma_s^\infty$$

Methanol-cyclohexane

$$0.29 + \frac{843.0}{T} = \ln\gamma_s^\infty$$

Methanol-heptane

$$-0.79 + \frac{1348.1}{T} = \ln\gamma_s^\infty$$

1-butanol-cyclohexane

$$0.62 + \frac{215.7}{T} = \ln\gamma_s^\infty$$

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Table 4. Values for the Physical Interaction Parameter, β

Alcohol Mixture	β J/cm^3
Methanol-cyclohexane	38.7
Methanol-heptane	36.0
2-propanol-cyclohexane	15.5
2-propanol-heptane	13.2
2-propanol-hexane	13.0
2-propanol-methylcyclohexane	16.8
1-butanol-cyclohexane	10.5

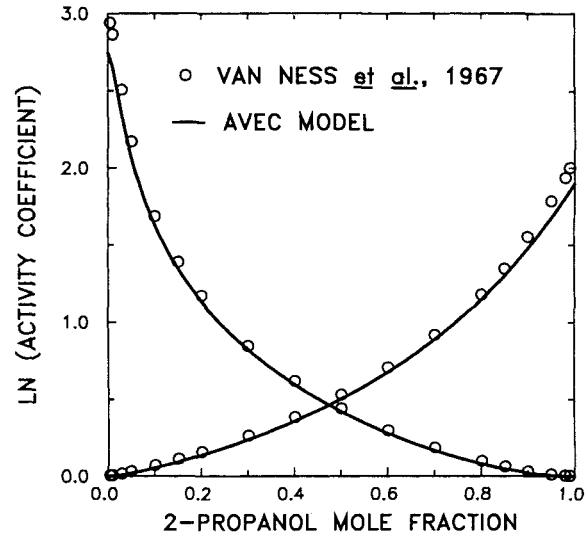

Figure 3. Prediction of activity coefficients for 2-propanol and heptane at 30°C.

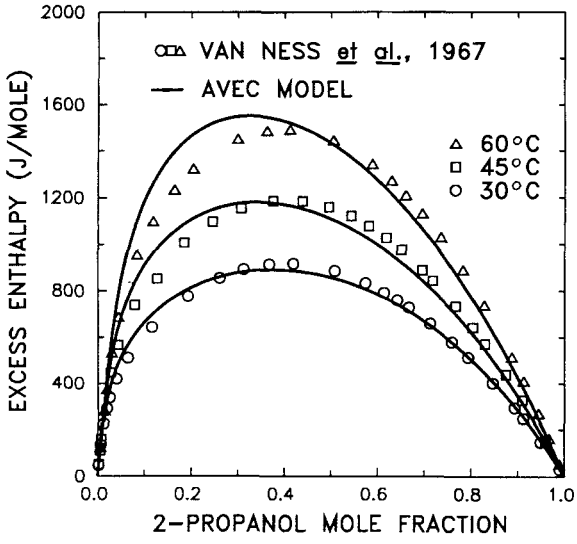

Figure 4. Prediction of excess enthalpy for 2-propanol and heptane.

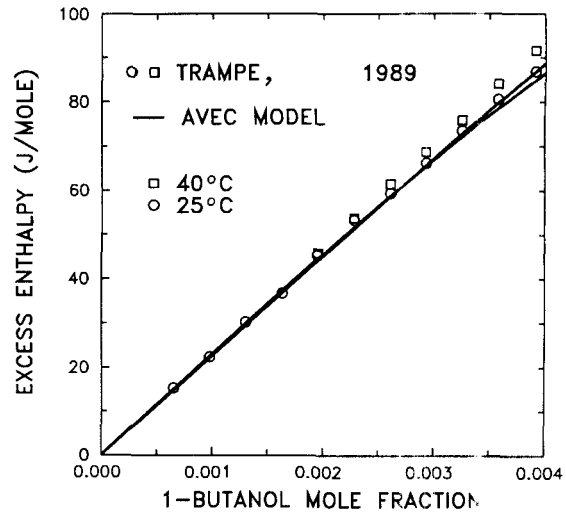

Figure 6. Prediction of dilute excess enthalpy for 1-butanol and cyclohexane.

Figure 3 shows a typical prediction of activity coefficients for alcohol-hydrocarbon mixtures with the AVEC model; and good agreement is obtained between the predictions and experimental vapor-liquid equilibrium data. Activity coefficients are a good test of a solution model; however, a more stringent test of a solution model is prediction of derivative properties such as excess enthalpy, Figures 4 and 5. Differences between the association models are not apparent in the prediction of activity coefficients but are in the prediction of excess enthalpy. The AVEC model, which includes both linear and cyclic species with one chemical interaction parameter, has a slightly better composition dependence in the excess enthalpy curve and thus better agreement with experimental data, than a model that accounts for either linear or cyclic complex formation only.

The AVEC model is able to compare both the composition dependence and the temperature dependence of the experimental data quite well.

The dilute alcohol region is particularly interesting for these types of mixtures, because it is in this region that the first complexes are beginning to form. Some dilute excess enthalpy data have been measured recently (Trampe and Eckert, 1990b) and thus the AVEC model was also used to predict such data, Figure 6.

Figure 7 illustrates the average segment length of the complexes as a function of alcohol mole fraction at three temperatures using the AVEC model. Other experimental investigations (Van Thiel et al., 1957; Smith, 1958; Ratkovics et al., 1974; Jorgensen, 1981b) indicate that the average segment length of complexes over the whole composition region

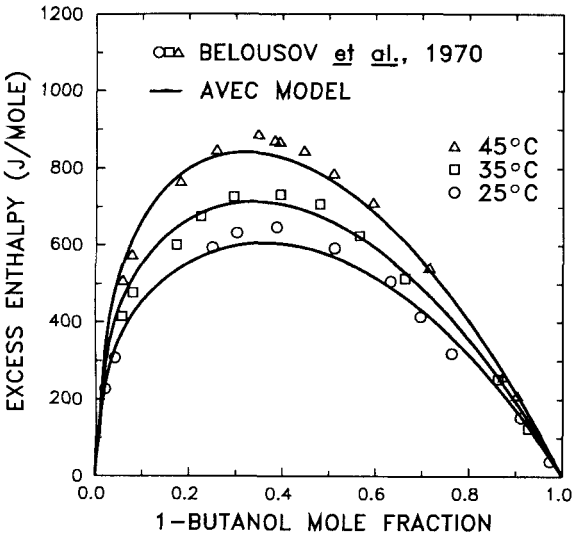

Figure 5. Prediction of excess enthalpy for 1-butanol and cyclohexane.

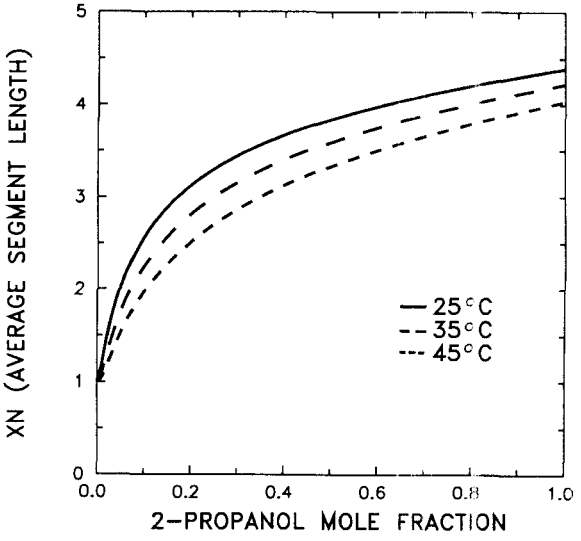

Figure 7. Temperature variation of average segment length of complexes for 2-propanol and heptane (AVEC model).

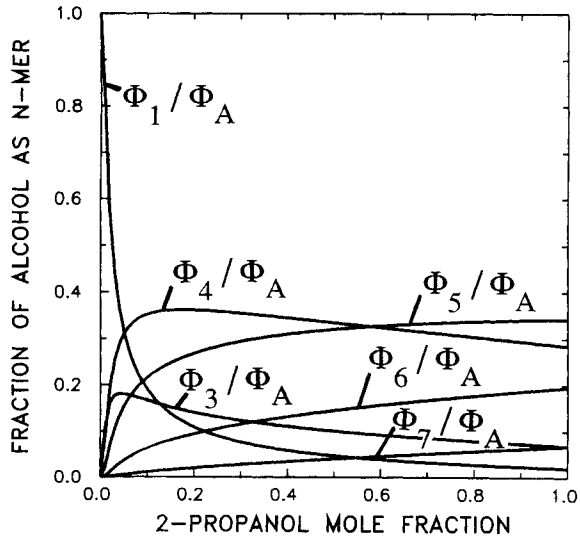

Figure 8. Distribution of hydrogen-bonded species for 2-propanol and heptane at 25°C (AVEC model).

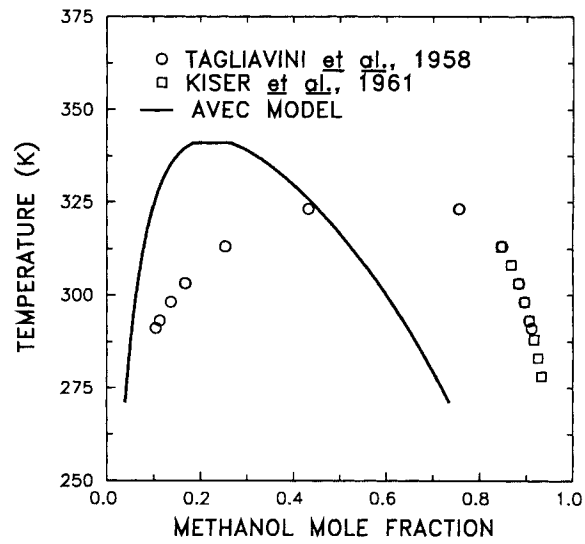

Figure 10. Coexistence curve prediction for methanol and heptane.

is on the order of 5. The results from this study agree with these other investigations. This figure illustrates the fact that lower order complexes dominate, and a model that prefers the formation of the lower order species is able to predict solution behavior more accurately. Figure 8 shows that for 2-propanol-heptane at 25°C, the dominant species in solution throughout most of the composition region are the tetramer, pentamer, and hexamer.

To push the model's predictive ability further two methanol systems which exhibit partial miscibility were investigated. Only the lower alcohols exhibit particularly strong chemical interactions that can lead to phase splitting. As a second derivative property, LLE is an especially stringent test of a solution model. Unlike previous chemical physical models, which were unable to obtain reasonable predictions of the LLE curve, the AVEC model is able to capture the essential features of the coexistence curve, Figures 9 and 10. The reasons for this are:

1. The model favors the formation of lower orders, higher strength species
2. The probability of forming the species depends on the size of the complex.

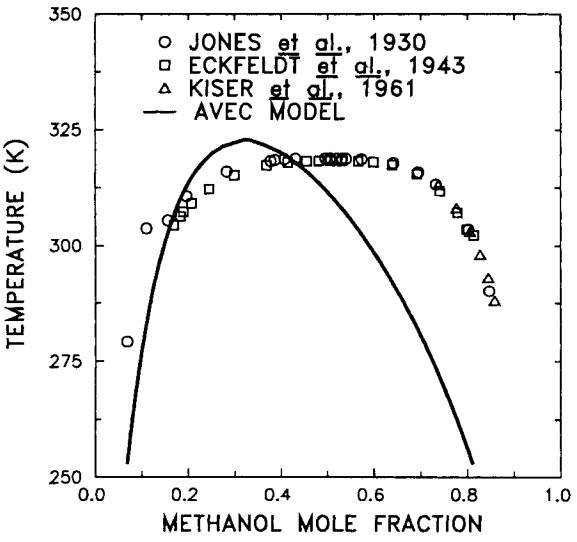

Figure 9. Coexistence curve prediction for methanol and cyclohexane.

Conclusions

The AVEC association model, which accounts for linear and cyclic complex formation with negligible dimer formation, has been presented. The distinguishing feature of this model is that the species in solution do not have equal probability of forming, yet require only a single chemical interaction parameter. In this study, the chemical interaction parameter (equilibrium constant) is obtained from nonthermodynamic measurements, Fourier transform nuclear magnetic resonance ^1H chemical shifts, and the physical interaction parameter is obtained from limiting activity coefficients. The chemical and physical model parameters were used to accurately predict various types of solution behavior: vapor-liquid equilibrium, excess enthalpy, and liquid-liquid equilibrium.

Acknowledgment

We gratefully acknowledge very useful interaction with Leon Scott of E. I. DuPont de Nemours Co. as well as financial support from DuPont. Additional financial support came from the U.S. Environmental Protection Agency, through the Advanced Environmental Control Technology Research Center at the University of Illinois, supported under cooperative agreement CR-806819.

Notation

C = concentration, mol/L
g = Gibbs energy, kcal/mol
h = enthalpy, kcal/mol

K = equilibrium constant
n = n-mer
R = ideal gas constant
T = temperature, K
V = volume, cm^3/gmol
x = apparent mole fraction

Greek letters

β = physical interaction parameter, cal/cm^3
γ = activity coefficient
Δ = change
ν = chemical shift, Hz
Φ = volume fraction

Subscripts

a = alcohol
nc = cyclic n-mer
nl = linear n-mer
o = observed
s = solvent
1 = alcohol monomer

Superscripts

E = excess
∞ = infinite dilution

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Appendix

Various permutations of the AVEC model were tested. When dimer formation was included in a model, a large majority of the complexes formed were dimers. In fitting NMR chemical shift data to a model that included dimers, both the concentrated and dilute chemical shift data were fitted poorly. In predicting solution behavior for various alcohol-hydrocarbon mixtures with this type of model, poor predictions of solution behavior were obtained for both activity coefficients and excess enthalpy. Since the formation of dimers is already questionable and spectroscopic investigations suggest that dimer formation is minimal, dimer formation was removed from the AVEC model.

Manuscript received July 3, 1990, and revision received Oct. 30, 1990.