Molecular Interactions in Chloroform-Diluent Mixtures

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Plausible stoichiometries for solvation and association complexes in binary mixtures of chloroform and one of six organic diluents (n-hexane, p-dioxane, acetone, diethyl ether, tri-n-butyl phosphate, or triethylamine) are examined parametrically. A range of stoichiometric assumptions based on hydrogen bonding are examined, but only a few such combinations yield statistically significant fits to the experimental vapor–liquid equilibria and NMR chemical shift data. Hydrogen bonding considerations and the "true" chemical species are much more important than nonspecific physical factors such as molecular sizes, shape differences, and regular solution terms. Thermodynamic equilibrium constants are presented for the most significant chloroform solvation complexes. Nonspecific dilution shift is important and more helpful in fitting NMR data than the assumption of a chloroform dimer. Physical effects and an orientation factor are used to predict excess enthalpy in chloroform/n-hexane mixtures where no solvation or association reactions occur. Model parameters are used to predict excess molar volumes and enthalpies. Commonly reported stability constants are concentration dependent.

Introduction

In liquid mixtures, specific chemical interactions can occur between molecules through hydrogen bonding and other reactions leading to solvates of dissimilar molecules or self-association. Chemical theory can be applied to explain such nonideal behavior (Acree, 1984; Prausnitz et al., 1986). Dolezalek (1908) was one of the first to do so. Since then, chemical theory has been applied to a wide range of thermodynamic problems (Economou and Donohue, 1991; Abbott and Van Ness, 1992; Campbell, 1994; Rabie and Vera, 1995).

Lattice theories (Prausnitz et al., 1986) enable one to consider nonspecific physical forces (e.g., molecular dipole moments, induction effects, and London dispersion forces). Guggenheim (1952) was the first to develop a quasi-chemical theory using lattice models. Wilson (1964), Renon and Prausnitz (1968), Abrams and Prausnitz (1975), and Vera et al. (1977) modified it for nonrandom mixtures. Panayiotou and Vera (1980, 1982) developed expressions for estimating local surfaces and compositions based on quasi-chemical theory. Kumar et al. (1987) revised the equations for multicomponent mixtures. Martinez (1994) applied lattice theory to clustering and dissociation. Sayegh and Vera (1980) provide a review.

Vapor–liquid equilibrium (VLE) data are frequently used as a basis for measuring nonideality in mixtures. More recently, Karachewski et al. (1989) and Eckert et al. (1986) used ^{1}H-NMR (nuclear magnetic resonance) chemical-shift data to develop chemical models for alcohol mixtures. More commonly, chloroform solvation constants have been estimated by evaluating NMR-shift data alone, rather than simultaneously with VLE measurements.

Table 1 summarizes published results. Huggins et al. (1955) explained ^{1}H-shift behavior in chloroform/acetone and chloroform/triethylamine (TEA) using AB (chloroform is designated as species "A," the diluent is always species "B.") solvation complexes. Al'per et al. (1991) concluded that 1:1 and 2:1 chloroform:acetone complexes were formed. McGlashan and Rastogi (1958) found both AB and A_2B complexes were formed in chloroform/dioxane mixtures; Appelblat et al.

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Table 1. Published Stability Constants for Chloroform Solvation Reactions

2nd Species	Temp. (°C)	K_{z_j}		$-\Delta h_j$ (kJ/mol)		Δ_j^{a*} (ppm)		Method	Reference
		AB	A_2B	AB	A_2B	AB	A_2B		
p-Dioxane	50	1.11	1.24					VLE	McGlashan and Rastogi (1958)
	50			8.4	15.1			HE**	McGlashan and Rastogi (1958)
	28	1.39	1.87					VH†	Kaiser (1963)
	28					1.20	0.85	NMR	Kaiser (1963)
Acetone	25	0.77	—					VLE	Sarolea-Mathot‡ (1953)
	25			11.3				HE**	Sarolea-Mathot‡ (1953)
	28	1.8						NMR	Huggins et al. (1955)
	28			10.5				NMR	Huggins et al. (1955)
	25			11.3				NMR	Campbell and Kartzmauk (1960)
	28					1.29		NMR	Kaiser (1963)
	25	0.97	1.12					VLE	Kearns (1961)
	25			10.1	13.8			HE**	Kearns (1961)
	25			10.3	13.0			HE**	Morcom and Travers (1965)
	25			10.2	14.0			NMR	Al'per et al. (1991)
	25					1.29	0.90	NMR	Al'per et al. (1991)
Diethyl ether	20	0.5						VLE	Earp and Glasstone (1935)
	20			29.9				HE**	Earp and Glasstone (1935)
	25			25.4				HE**	McLeod (1935)
	28	0.36						VH†	Kaiser (1963)
	28					2.68		NMR	Kaiser (1963)
Triethylamine	28	3.0						NMR	Huggins et al. (1955)
	28			16.7				NMR	Huggins et al. (1955)
	25	3.3						CM††	Matsui et al. (1955)
	25			15.8				CM††	Matsui et al. (1955)
	28					1.88		NMR	Kaiser (1963)

*Chemical shift of complex *j* relative to chloroform monomer shift.
**From heat of mixing data.
†van't Hoff's equation.
††Calorimetry.
‡Published in 1953.

(1980) correlated excess thermodynamic functions for chloroform/acetone mixtures by assuming ideal mixtures of true species: A, B, AB, and A_2B.

Other investigators have hypothesized the existence of a chloroform dimer and used self-association to explain observed behavior, especially in mixtures of chloroform and normal paraffins (Reeves and Schneider, 1957; Korinek and Schneider, 1957). Kaiser (1963) assumed the existence of the chloroform dimer, but also corrected for nonspecific dilution shift.

Molecular simulation (e.g., using Monte Carlo or molecular dynamic models) can be used to identify the stoichiometries of molecular complexes and predict excess properties. Number pressure temperature (NPT) calculations, for example, assume a constant number of molecules and constant pressure and temperature. Such calculations usually require many assumptions (e.g., the characteristics of the chemical potentials, molecular interactions, and combining rules, etc.), but they also allow the simulation to identify the nature and stoichiometry of molecular complexes rather than requiring the investigator to assume complex stoichiometry. Thus, they can provide additional insight into factors leading to complexation.

Prausnitz (1995) identifies molecular simulation using supercomputers as an important area of investigation that can shed new light on fundamental behavior and it is clearly a growing area of investigation. Satoh and Nakanishi (1995), for example, simulated aqueous solutions of acetonitrile and water and obtained semiquantitative agreement with experimental data, but also found that mixing is not uniform for the whole composition range. According to their results, acetonitrile head-to-head dimer formation occurs in dilute aqueous solutions. In other cases, agreement between theory and experiment is excellent [e.g., Shukla (1994a) for pure fluids and Shukla (1994b) for binary mixtures].

Hydrogen bonding is widely accepted as a reasonable explanation for abnormal behavior in some fluids (e.g., the relatively high boiling points of water, HF, and NH_3). It is commonly associated with the alcohol (OH) group. Morrison and Boyd (1966), for example, describe its characteristics as "'a hydrogen atom serves as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely electrostatic forces. This electrostatic bond has a strength of about 5 kcal/mol (21 kJ/mol) (compared with 50–100 kcal/mol (210–418 kJ/mol)) for most covalent bonds."

When hydrogen bonding occurs, the hydrogen atom bridges atoms X and Y so that $Y \cdots HX$ where X and Y are usually electronegative atoms (e.g., O, N, F, Cl, and S). March (1968) and Kaplan (1986) point out that weak hydrogen bonding (0.5–4 kJ/mol) involving a hydrogen bonded directly to carbon (e.g., $CHCl_3$) can only hydrogen bond with a Y atom in cases where the carbon atom is also bonded to strong electronegative groups (e.g., $HCCl_3$ and HCN). In the case of chloroform, we only expect hydrogen bonding to occur if a diluent has atoms capable of sharing electrons (e.g., diluents *p*-dioxane, acetone, diethyl ether, tri-*n*-butyl phosphate, and triethylamine) that have either O or N with lone pairs of electrons that can be shared. We do not expect hydrogen bonding between chloroform and *n*-hexane since the latter species has no electron releasing atom.

Here we use three chemical parameters to describe each assumed equilibrium: (1) its thermodynamic equilibrium constant; (2) a volume adjustment factor to estimate the molar volumes of specific aggregates; and (3) a heat of reaction to estimate the chemical contribution to excess enthalpy H^E_{chem}. All three parameters have physical meaning. The first two are assumed to contribute to the excess Gibbs energy g^E model that we use to fit the VLE and NMR data. Additional parameters are used to describe NMR chemical shift.

Maximum likelihood parameter estimates for the equilibrium constants and volume-adjustment factors are obtained by simultaneously fitting ^{1}H-NMR chemical shift and VLE data. These results are then used to fit excess enthalpy data by estimating heats of reaction for assumed complexation equilibria. Excess molar volume data are used to critically review the model, particularly the validity of the volume adjustment factors.

Model Description

Our model considers both chemical (specific) and physical (nonspecific) contributions to excess Gibbs energy. We assume that the physical and chemical contributions are separable so that:

$$g^E = g^E_{\text{chem}} + g^E_{\text{phys}}. \tag{1}$$

The chemical contribution is then computed from the estimated "true" mole fractions and, in ideal mixtures, chemical activities simply equal the true mole fractions of monomeric species. Regardless of the solvation or association reactions (Prigogine and Defay, 1954), in ideal mixtures of true species with $g^E_{\text{phys}} = 0$:

$$\hat{a}_i = \gamma_{i,s} x_{i,s} = z_{i_1}, \tag{2}$$

where $\hat{a}_i$ and $\gamma_{i,s}$ are the activity and activity coefficient based on the stoichiometric composition $x_{i,s}$, and z_{i_1} is the true mole fraction of the ith monomer. The reference states for A and B in this case are the pure, unassociated liquids with chemical potentials, pure-component Gibbs energies, fugacities, and activities related by $(\mu_i - G_i^o)/RT = \ln \hat{a}_i = \ln f_i/f_i^o$.

We do not consider our mixtures to be ideal since the molecules are not uniform in size and other, nonspecific interactions may occur. We therefore use the true mole fractions to estimate physical contributions to g^E via molecular size and shape difference terms and using regular solution theory.

Concentration definitions

The stoichiometric mole fractions of chloroform and diluent (with $i = \{A, B\}$, respectively) are simply the overall mole fractions $x_{i,s}$, molar concentrations $C_{i,s}$, or volume fractions $\phi_{i,s}$ from each experiment.

True mole fractions z_i, molar concentrations C_i, and volume fractions ϕ_i are computed from pure-component properties assuming that the excess molar volume $V^E = 0$. This assumption is made initially in order to satisfy component volume and material balances exactly for each mixture. So using the pure-component molar volumes V_i at 22°C (also see Table 2), $V = \Sigma_{i=1}^2 x_{i,s} V_i$, $C_{i,s} = x_{i,s}/V$, and $\phi_{i,s} = V_i C_{i,s}$.

Table 2. Pure Component Data Used to Model Monomeric Species

Species	V_i (cm^3/mol)	r_i	Solubility Parameters,* δ_i (J/cm^3)$^{0.5}$	(J/mol)$^{0.5}$
p-Dioxane	85.2	2.49	19.88	116.18
Acetone	73.4	2.15	19.90	116.29
Diethyl ether	103.8	3.04	16.00	93.50
Hexane	130.8	3.83	14.91	87.19
Chloroform	80.0	2.34	18.92	110.57
Triethylamine (TEA)	139.0	4.07	15.30	89.41
tri-*n*-Butyl phosphate (TBP)	272.0	7.96	18.14	106.01

*Used in units of (J/mol)$^{0.5}$ in the model.

Chemical interactions

Specific chemical interactions are considered by assuming appropriate combinations of solvation and self-association reactions. The true species are the chloroform and diluent monomers, z_{A_1} and z_{B_1}, the chloroform dimer z_{A_2}, and various combinations of aggregates or complexes (e.g., AB, z_{AB}; A$_2$B, z_{A_2B}; etc.) that are presumed to exist. For the jth solvation or self-association reaction in a binary mixture of chloroform (A) and diluent (B):

$$n_j A_1 + m_j B_1 \rightleftharpoons A_{n_j} B_{m_j}, \tag{3}$$

where n_j molecules of A$_1$, the chloroform monomer, and m_j molecules of B$_1$, the diluent monomer, are assumed to form a complex. At equilibrium, the chemical potentials of the two monomeric species and the complex are equal and the product of their activities equals the thermodynamic equilibrium constant $K_{\hat{a}_j}$:

$$K_{\hat{a}_j} = \frac{\hat{a}_{A_{n_j}B_{m_j}}}{\hat{a}_{A_1}^{n_j}\hat{a}_{B_1}^{m_j}}. \tag{4}$$

We define volume fraction-based activity coefficients for the jth species γ_j', where $\hat{a}_j = \gamma_j' \phi_j$, and:

$$K_{\hat{a}_j} = K_{\phi_j} K_{\gamma_j'} = K_{z_j} K_{\gamma_j}; \tag{5}$$

also $\hat{a}_j = \gamma_j z_j$ for each species and γ_j is the true mole fraction-based activity coefficient for the jth species. The thermodynamic equilibrium constant $K_{\hat{a}_j}$ only depends on temperature, but $K_{\gamma_j'}$, K_{γ_j}, K_{ϕ_j}, and K_{z_j} are simply composition-dependent products of activity coefficients, volume, and mole fractions, respectively.

Rearranging Eq. 5, the chemical contribution to the jth equilibrium can be described on a volume fraction basis as

$$K_{\hat{a}_j}/K_{\gamma_j'} = K_{\phi_j} = \frac{\phi_{A_{n_j}B_{m_j}}}{\phi_{A_1}^{n_j}\phi_{B_1}^{m_j}} \tag{6}$$

$$K_{\hat{a}_j}/K_{\gamma'_j} = K_{C_j}K_{V_j} = \left(\frac{C_{A_{n_j}B_{m_j}}}{C_{A_1}^{n_j}C_{B_1}^{m_j}}\right)\left(\frac{V_{A_{n_j}B_{m_j}}}{V_{A_1}^{n_i}V_{B_1}^{m_i}}\right), \tag{7}$$

where V_{A_1} and V_{B_1} are the pure component molar volumes of the chloroform and diluent, respectively, and $V_{A_{n_j}B_{m_j}}$ is the molar volume of the complex estimated in the chemical part of our model as

$$V_{A n_j B m_j} = n_j V_{A_1} + m_j V_{B_1}. \tag{8}$$

As previously defined, K_{V_j} is treated as a constant, but K_{C_j}, commonly reported as a stability constant in $(\mathrm{L/mol})^{n_j+m_j-1}$, is composition dependent because of $K_{\gamma'_j}$ and, more generally, because of K_{V_j} (i.e., if $V^E \neq 0$). Similarly, K_{z_j} is also composition-dependent due to K_{γ_j}. The true volume fractions ϕ_j are computed by balancing the stoichiometric volume fractions for chloroform and each diluent, assuming $V^E = 0$:

$$\phi_{A,s} = \phi_{A_1} + \sum_{j=1}^{N_r} K_{\phi_j}\phi_{A_1}^{n_j}\phi_{B_1}^{m_j}\left(\frac{n_j V_{A_1}}{n_j V_{A_1} + m_j V_{B_1}}\right). \tag{9}$$

$$\phi_{B,s} = \phi_{B_1} + \sum_{j=1}^{N_r} K_{\phi_j}\phi_{A_1}^{n_j}\phi_{B_1}^{m_j}\left(\frac{m_j V_{B_1}}{n_j V_{A_1} + m_j V_{B_1}}\right). \tag{10}$$

For a given value of $K_{\hat{a}_j}$ and an assumed value for $K_{\gamma'_j}$ (initially, we assume $K_{\gamma'_j} = 1$), the volume fraction product K_{ϕ_j} is computed iteratively and used to solve the two volume balances, Eqs. 9 and 10, for each binary mixture. Linearization and matrix diagonalization are used to give a set of true species volume fractions ϕ_j that satisfy the diluent and chloroform material balance constraints. The resulting set of true species volume fractions are then used to compute true mole fractions, K_{z_j}, K_{γ_j}, and $K_{\gamma'_j}$, which, in turn, are used to update $K_{\phi_j} = K_{\hat{a}_j}/K_{\gamma_j}$ and to recompute the true species volume fractions until $K_{\gamma'_j}$ is constant.

Reference states

Our reference states are the pure liquids at 22°C. The pure diluents are usually considered to be unassociated liquids with $\hat{a}^o_{B_1} = z^o_{B_1} = \gamma^o_{B_1} = 1.0$. In the case of chloroform dimerization, pure chloroform is considered to be a partly ordered, nonideal liquid containing reference concentrations of dimer $z^o_{A_2}$ and monomer $z^o_{A_1}$, with reference state activities of $\hat{a}^o_{A_2} = \gamma^o_{A_2} z^o_{A_2}$ and $\hat{a}^o_{A_1} = \gamma^o_{A_1} z^o_{A_1}$. In the case of self-associating liquids, the exact reference state values that are computed depend upon the assumed set of equilibria.

Physical interactions

The available surface areas q_i of monomeric species are estimated using the empirical correlation developed by Vera et al. (1977):

$$z' q_i = 0.2342 V_i + 2 \tag{11}$$

with an assumed coordination number $z' = 10$ and the pure-component liquid molar volume V_i in cm^3/mol at 22°C (see Table 2). The reduced volumes for monomeric species are computed from $r_i = 0.554 V_i/V^*$, with $V^* = 18.92$ cm^3/mol. As Sayegh and Vera (1980) explain, the coefficient 0.554 results from data regression between van der Waals volumes and molar volumes for 33 species including alkanes, alcohols, esters, ketones, alkyl chlorides, and aromatics.

Nonzero excess molar volumes are allowed by introducing a volume adjustment factor β_j for each aggregate that may assume values other than unity. The values of r_j and q_j for each complex, consisting of two or more molecules, are estimated as

$$r_j = \beta_j (n_j r_{A_1} + m_j r_{B_1}) \tag{12}$$

$$q_j = \beta_j^{2/3} (n_j q_{A_1} + m_j q_{B_1}). \tag{13}$$

Using r_j from Eq. 12, we estimate true mole fractions as

$$z_j = \frac{\phi_j/r_j}{\sum_{j=1}^{N_r+2} \phi_j/r_j}, \qquad V^E \neq 0, \tag{14}$$

and true volume fractions and surface fractions:

$$\phi_j^* = \frac{z_j r_j}{\sum_k^{N_r+2} z_k r_k}, \qquad \theta_j = \frac{z_j q_j}{\sum_k^{N_r+2} z_k q_k}, \qquad V^E \neq 0. \tag{15}$$

So Eqs. 9 and 10 are used to calculate the volume fractions ϕ_i that are used to satisfy material balances on a volume fraction basis with the assumption that $V^E = 0$. However, z_i and ϕ_i^* are calculated from Eqs. 14 and 15, and are used to calculate the nonspecific physical contributions to nonideality with the assumption that $V^E \neq 0$. In our model, monomeric species do not contribute to excess molar volume.

Given a set of true species compositions, differences in molecular sizes, available surface areas, and cohesive energy densities still exist. We assume that the physical effects contributing to nonideality can be divided into three terms:

$$g^E_{\mathrm{phys}} = g^E_{ms} + g^E_{sd} + g^E_{rs}. \tag{16}$$

For convenience, we divide what Sayegh and Vera (1980) refer to as the athermal Guggenheim–Staverman equation into separate molecular size (g^E_{ms}) and shape differences (g^E_{sd}) terms. Using our definitions, combinatorial terms applied to both the mixtures and the reference states:

$$(\ln \gamma_j)_{ms} = \ln \frac{\phi_j^*}{z_j} + 1 - \frac{\phi_j^*}{z_j} \tag{17}$$

$$(\ln \gamma_j)_{sd} = \frac{z' q_j}{2}\left(\ln \frac{\theta_j}{\phi_j^*} - 1 + \frac{\phi_j^*}{\theta_j}\right) \tag{18}$$

$$(\ln \gamma_j)_{\mathrm{com}} = (\ln \gamma_j)_{ms} + (\ln \gamma_j)_{sd}. \tag{19}$$

Regular solution theory is used to describe positive deviations from Raoult's law and to estimate physical contributions to excess enthalpy. We apply it using r_j and ϕ_j:

$$(\ln \gamma_j)_{rs} = \left(\frac{r_j}{RT}\right)\left[\sum_{i \neq j}^{N_r+2} \phi_i(\delta_j - \delta_i)\right]^2, \tag{20}$$

where δ_j are solubility parameters of monomers or complexes (i.e., true species j). The solubility parameters for monomers (see Table 2) are taken as their respective pure components values:

$$\delta_j = \left(\frac{\Delta u_j^v}{r_j}\right)^{1/2}, \tag{21}$$

where Δu_j^v is the internal energy of vaporization and the reduced volume r_j is defined using Eq. 12. Note, however, that our δ_j has units of $(\text{J/mol})^{0.5}$, rather than the usual $(\text{J/cm}^3)^{0.5}$. The solubility parameters of complexes are calculated using values from those monomers that form them:

$$\delta_j^2 = \frac{n_j r_A \delta_A^2 + m_j r_B \delta_B^2}{r_j}. \tag{22}$$

The excess enthalpy is considered to have both physical and chemical contributions. The physical part of H^E is estimated using the changes in activity coefficients and compositions for true species between each mixture and its reference state:

$$\left(\frac{H^E}{RT}\right)_{\text{phys}} = g_{rs}^E = \sum_{j}^{N_r+2} z_j[(\ln \gamma_j)_{rs} - (\ln \gamma_j^o)_{rs}], \tag{23}$$

where $(\ln \gamma_j^o)_{rs}$ is evaluated using Eq. 20 at reference conditions with ϕ_j^o, z_j^o, and r_j. Similarly, for the excess entropy:

$$\left(\frac{S^E}{R}\right)_{\text{phys}} = g_{ms}^E + g_{sd}^E = \sum_{j=1}^{N_r+2} z_j[(\ln \gamma_j)_{\text{com}} - (\ln \gamma_j^o)_{\text{com}}], \tag{24}$$

and we can also write:

$$K_{\hat{a}_j} = K_{\phi_j} K_{\gamma_j'} = K_{\phi_j}(K_j)_{\text{com}}(K_j)_{rs} \tag{25}$$

and

$$K_{\phi_j}(K_j)_{\text{com}}(K_j)_{rs} = \left(\frac{\phi_{A_{n_j}B_{m_j}}}{\phi_{A_1}^{n_j}\phi_{B_1}^{m_j}}\right)\left(\frac{\gamma_{A_{n_j}B_{m_j}}}{\gamma_{A_1}^{n_j}\gamma_{B_1}^{m_j}}\right)_{\text{com}}\left(\frac{\gamma_{A_{n_j}B_{m_j}}}{\gamma_{A_1}^{n_j}\gamma_{B_1}^{m_j}}\right)_{rs}, \tag{26}$$

so the thermodynamic equilibrium constant is expressed as a product of combinatorial and regular solution contributions to nonideality multiplied onto the true species volume fraction product K_{ϕ_j}. The first product K_{ϕ_j} assumes $V^E = 0$. The second product $(K_j)_{\text{com}}$ is a molecular size and shape effect; the third product $(K_j)_{rs}$ is a cohesive energy density effect. Both the second and third terms assume $V^E \neq 0$.

By equating activities for the stoichiometric species with those for the monomer, we obtain an expression for the stoichiometric activity coefficient:

$$\gamma_{i,s} = \frac{\gamma_{i_1} z_{i_1}}{x_{i,s}\gamma_{i_1}^o z_{i_1}^o} \tag{27}$$

in terms of monomeric mole fractions in the true mixture and reference states, the stoichiometric mole fraction, and activity coefficients in the true mixture and reference states.

V^E and H^E calculations

Since we adjust the molar volumes of complexes to improve the data fit using Eq. 12, we can estimate excess molar volumes by

$$V^E = \sum_{j=3}^{N_r+2}\left(\frac{V^* r_j}{0.554} - V_j^L\right)\left(\frac{n_j - n_j^o}{n_T}\right), \tag{28}$$

where the term $(V^* r_j/0.554 - V_j^L)$ is only nonzero for complexes where $\beta_j \neq 1.0$. The moles n_j and n_j^o are the moles of the jth complex in the mixture and reference states, but using the same stoichiometric basis in either case. Note, however, that n_j^o is only nonzero in the case of self-association. Also, n_T are the total stoichiometric moles in the mixture.

The enthalpic contributions from the formation of each complex $A_{n_j}B_{m_j}$ are added together to estimate the chemical contribution to the heat of mixing:

$$H_{\text{chem}}^E = \sum_{j=3}^{N_r+2} \Delta h_j \left(\frac{n_j - n_j^o}{n_T}\right) \tag{29}$$

$$H^E = H_{\text{chem}}^E + H_{\text{phys}}^E, \tag{30}$$

where Δh_j is the estimated heat of reaction for the jth complex and H_{phys}^E is estimated from Eq. 23.

Chemical shift

We use NMR spectroscopic data as additional information sources. Solvation and complexation can change the electron distribution in the chemical bonds of molecules and may cause a proton chemical shift in ^{1}H-NMR. Since monomeric and complex species are in rapid equilibrium, an NMR peak is observed that shifts with composition. The observed shift in this peak is an average resulting from the discrete, stationary peaks of those monomeric and complexed nuclei that are in equilibrium. The weighting factors are simply the number fractions of those spectrometric nuclei that are attending the complex formation in a given state at equilibrium (see Gutowsky and Saike, 1953). Assuming that all other factors (e.g., nonspecific bulk solvent effects) are constant:

$$\nu_c^H = \frac{z_{A_1}}{z_A}\nu_{A_1}^H + \sum_i \frac{n_i z_{A_{n_i}}}{z_A}\nu_{n,i}^H + \sum_i \frac{n_i z_{A_{n_i}B_{m_i}}}{z_A}\nu_{ab,i}^H, \tag{31}$$

where

$$z_A = z_{A1} + \sum_i n_i z_{A_{n_i}} + \sum_i n_i z_{A_{n_i}B_{m_i}} \tag{32}$$

and z_A is the total true mole fraction of ^{1}H. We place Eq. 31 into a more useful form by substracting $\nu_{A_1}^H$ from Eq. 31 to obtain

$$\Delta_c^H = \sum_i \frac{n_i z_{A_{n_i}}}{z_A} \Delta_{n,i}^H + \sum_i \frac{n_i z_{A_{n_i}B_{m_i}}}{z_A} \Delta_{ab,i}^H, \tag{33}$$

where

$$\Delta_c^H = \nu_c{}^H - \nu_{A_1}^H,\ \Delta_{n,i}^H = \nu_{n,i}^H - \nu_{A_1}^H, \text{ and } \Delta_{ab,i}^H = \nu_{ab,i} - \nu_{A_1}^H. \tag{34}$$

Most investigators who have used NMR chemical shift to analyze specific interactions assumed that the $\nu_i{}^H$ are independent of composition, but nonspecific factors (e.g., bulk solvent shift) may also contribute to chemical shift and make them composition-dependent. Kaiser (1963) discusses such factors in detail. The most important factors are potential effects on nuclear screening due to changes in the bulk solvent characteristics with composition (e.g., average susceptibility). We assess the significance of these effects on $\nu_i{}^H$ by expanding each one in a Taylor series:

$$\nu_i{}^H = \nu_{io}^H + \left(\frac{1}{1!}\right) \frac{d\nu_{io}^H}{dx_{B,s}} dx_{B,s} + \cdots. \tag{35}$$

We then substitute $dx_{B,s} = (x_{B,s} - 0)$, retain only the first-order terms, and further assume that the first derivatives are independent of composition and the same value of $\nu_{p,h}^\infty$ for all species. After rearranging, we arrive at

$$\nu_p{}^H = \nu_{p,h}^\infty x_{B,s}. \tag{36}$$

If the observed chemical shift is a result of nonspecific, bulk solvent effects, then Eq. 36 should be combined with Eq. 31:

$$\nu_o{}^H = \nu_c{}^H + \nu_p{}^H \tag{37}$$

and $\nu_{p,h}^\infty \neq 0$. On the other hand, very small values for $\nu_{p,h}^\infty$ computed from data fitting indicate that nonspecific dilution shift is unimportant or, at least, that the variance in the data set for a given mixture can be predicted using other assumptions.

Data Weighting, Analysis and Basis

Parameter estimates resulting from the application of our model depend upon the data sets from which they are derived and the weighting factors that are used to estimate the residual sum-of-the-squares errors. Data sets for six different binary mixtures were analyzed simultaneously; 12 independent data sets were used altogether (see Table 3). In each case, chloroform was one of the species. Parameters for the assumed chloroform dimer A_2, if any, were common to all data sets, but any assumed solvation complex was unique to each binary mixture since each diluent was different.

Table 3. Sources and Number of Data Points Arranged by Type*

Species	Number of Data Points				
	VLE	^{1}H-NMR	H^E	V^E	Totals
Dioxane	18	11	27	18	74**
Acetone	6	11	10		27†
Diethyl ether	15	8	8	17	48††
Hexane	12	6	10		28‡
Triethylamine	9	12	9	9	39‡‡
tri-*n*-Butyl phosphate	6	19	30		55§
Totals	66	67	94	44	271

*All measurements taken at 25 ± 3°C; some data were adjusted to 25°C.

**Kaiser (1963); Winterhalter and Van Ness (1966); Inglese et al. (1989); Byer et al. (1976).

†Reckmann and Faust (1914); Huggins et al. (1995); Chevalier and Bares (1969).

††Becker et al. (1974); Korinek and Schneider (1957); Beath and Williamson (1969).

‡Bissell et al. (1984); Korinek and Schneider (1957); Bissell and Williamson (1979).

‡‡Fenby (1987); Huggins et al. (1955); Bourrelly et al. (1975); Chand et al. (1975).

§Kharchenko et al. (1964); Choi (1995); Tsimering and Kertes (1977); Choi and Tedder (1995).

The VLE data were used to predict the total vapor pressure exerted by each mixture. The objective function for these data was

$$f^V = \sum_k^M \frac{1}{\sigma_V^2} \left[Y_k - P_o^V(x_{i,s}, K_{\hat{a}_j}, \beta_j, \gamma_{i,s})\right]^2, \tag{38}$$

where $P_o^V = \Sigma_{i=1}^2 \gamma_{i,s} x_{i,s} P_i^{\text{sat}}$ are the total pressure predictions and Y_k are the experimental data. Similarly, the objective function based on the proton chemical shift data was

$$f^H = \sum_k^L \frac{1}{\sigma_H^2} \left[Y_k - \nu_o{}^H\left(z_i, \nu_{A_1}^H, \nu_{n,i}^H, \nu_{ab,i}^H, x_{B,s}, \nu_{p,h}^\infty\right)\right]^2, \tag{39}$$

where $z_i = f(x_{i,s}, K_{\hat{a}_j}, \beta_j, \gamma_{i,s})$ and where M and L are the numbers of VLE and H-shift NMR measurements and σ_V and σ_H are the weighting factors based on the experimental uncertainties in VLE and H-NMR measurements, respectively.

All data sets were analyzed simultaneously by adding the respective objective functions (i.e., Eqs. 38 and 39):

$$f^{\text{Total}} = f^V + f^H$$

and f^{Total} was minimized using nonlinear least squares (see Marquardt, 1963) to find the maximum likelihood parameter estimates for an assumed set of equilibria. The computed minimum values for f^{Total} were then used as measures of the validity of each assumed set of complexes. Combinations of equilibria were compared using f^{Total} values. We used σ_V = 1.0 mm Hg for pressure and σ_H = 0.01 ppm for all mixtures. The sources and number of data points arranged by type are summarized in Table 3. A total of 66 VLE and 67 NMR data were used.

After fitting the VLE and NMR data, the resulting $K_{\hat{a}_j}$ and β_j values for each chloroform mixture were used to generate maximum likelihood estimates of Δh_j by first computing H_{chem}^E using Eq. 30. A total of 94 excess enthalpy data were used to fit the Δh_j. Similarly, Eq. 28 was used to estimate V^E, which were compared with 44 experimental measurements on several chloroform and diluent systems.

Results

All other factors being equal, the expected concentrations of a complex decrease as its molecular order increase (i.e., as n_j and m_j in Eq. 4 increase). The larger the values of n_j and m_j, then the lower are the likely concentrations of a complex simply due to its higher-order dependence on monomer activities. While higher-order complexes (e.g., A_3B_2, A_4, B_3,, etc.) may exist, their concentrations are likely smaller than for lower-order complexes (e.g., AB and A_2B). The higher-order complexes are thus less likely to be statistically significant when fitting experimental data.

Considering the effect of molecular order on complex concentrations, we expect one-to-one (i.e., AB) complexation to predominate, particularly in the cases of acetone, diethyl ether, and triethylamine, since each of these donor molecules has only a single atom capable of sharing electrons. In the case of *p*-dioxane, we expect both the AB and A_2B complexes to be important since that molecule has two donor oxygen atoms in the *para* positions and, therefore, allows bonding with little or no steric hindrance.

Tributyl phosphate (TBP) is a more complicated case since each TBP molecule has four oxygen atoms and is itself capable of dimerizing by association (see Choi, 1995) of its phosphoryl–phosphoryl bonds. In principle, up to four $HCCl_3$ molecules may associate with any one TBP, but the three ether linkages are less electronegative than the phosphoryl oxygen and proximate to it. Thus, hydrogen bonding with the phosphoryl oxygen is expected to predominate. In the case where TBP dimerizes, then, additional $HCCl_3$ molecules could associate with the dimer except that steric hindrance may effectively preclude such associations.

Since specific sets of solvation and self-association equilibria must be assumed in order to use our model effectively to search for maximum-likelihood parameter estimates, we have varied our stoichiometric assumptions parametrically for cases A_iB_k, where i, $k = 1, 2, \ldots, 4$ in order to comprehensively consider all plausible complexes based on hydrogen-bonding considerations. The number of complexes assumed to coexist in a mixture were also varied depending upon the results obtained from simpler cases. Choi (1995) presents results for additional stoichiometric cases that have been considered. Here we summarize the most interesting results based on experimental fit.

While reasonable complexation assumptions usually yield plausible parameter estimates, unreasonable assumptions frequently make it impossible to obtain any meaningful parameter estimates at all. This result is largely due to the pronounced effect that the assumed equilibria have on the computed values for z_j and, therefore, on K_{z_j} and $K_{\hat{a}_j}$ through Eq. 5. To a lesser extent, K_{γ_j} values are affected because the computed values of ϕ_j^* and θ_j also depend on the assumed reactions, but g_{phys}^E is usually much less important g_{chem}^E in these systems.

Virtually without exception, we find that it is essential to make reasonable equilibrium assumptions, consistent with the principles of hydrogen bonding, in order to apply our model successfully. Because of its highly nonlinear nature and the complex effects chemical equilibria have on the calculations, our model simply does not accommodate arbitrary assumptions made for convenience.

If fact, the user is forced to address the underlying chemistry realistically in order to use our model successfully to fit experimental data. Contrary to what might be expected, increasing the number of adjustable parameters by arbitrarily assuming a set of reactions does not necessarily lead to a statistically better fit to the data. More likely, the quality of the fit will be reduced by this approach as we demonstrate below.

Five adjustable parameters ($K_{\hat{a}_j}$, β_j, Δh_j, and two ν_j^H (diluent monomer and complex)) are required to model each solvation complex. Separate ν_j^H-values are required for each solvation complex in each chloroform mixture, but $K_{\hat{a}_j}$, β_j, Δh_j are shared between mixtures whenever the chloroform dimer or trimer is assumed since that complex is presumed to exist in all six mixtures. In the case of nonspecific dilution shift without the $CHCl_3$ dimer, $\nu_{A_1}^H$ for the chloroform monomer is the only shared parameter. However, it is a constrained parameter since in pure chloroform $\nu_{A_1}^H = \nu_{\text{pure}}^H$, assuming no dimer or trimer exists. If the dimer is presumed, for pure chloroform:

$$\nu_c^H = \frac{z_{A_1}}{z_A}\nu_{A_1}^H + \frac{2z_{A_2}}{z_A}\nu_{A_2}^H = \nu_{\text{pure}} \tag{41}$$

and the ν_{A_1} and ν_{A_2} are constrained to satisfy conditions in the reference state.

Plausible equilibria

F-statistics were computed by removing an individual equilibrium from the assumed set and then recomputing f^{Total} for the remaining subset, or by comparing relative residual errors for a particular chloroform mixture, if a complex was assumed to exist only in that mixture. The degrees of freedom in the numerator and denominator range from 95 to 117 depending upon the model assumptions.

Qualitative hydrogen-bonding considerations were used to guide the trial-and-error process of selecting sets of equilibria to test as explained earlier. The most interesting cases are summarized in Table 4. While we readily agree that our statistical analysis does not prove the existence of any particular set of equilibria, it does enable us to exclude statistically unreasonable assumptions. As we have already pointed out, unrealistic chemical assumptions usually either made it virtually impossible to obtain numerical convergence or, if convergence was somehow obtained, resulted in implausible parameter estimates (e.g., $K_{\hat{a}_j} \approx 0$ or $K_{\hat{a}_j} \gg 1.0$). On the other hand, plausible chemical assumptions provide reasonable data fits and meaningful parameter estimates.

Case 9 in Table 4 gives the best fit overall, but the A_2B equilibrium constant for chloroform/diethyl ether mixtures is very small and we cannot reject the hypothesis that it is actu-

Table 4. Chemical Species Studied in Chloroform Mixtures (A = chloroform, B = diluents)*

	$CHCl_3$		*p*-Dioxane		Acetone		DEE		TEA	TBP				
Case	A_2	A_3	AB	A_2B	AB	A_2B	AB	A_2B	AB	AB	AB_2	B_2	RMS**	DF†
With nonspecific dilution shift allowed														
1	x		x	x	x		x		x	x	x	x	3.57	101
2	x		x	x	x	x	x		x	x	x	x	3.32	98
3	x		x	x	x	x	x	x	x	x	x	x	3.18	95
4	x		x	x	x		x	x	x	x	x	x	3.56	98
5	x		x	x	x	x		x	x	x	x	x	14.85	98
6	x		x		x		x		x	x	x	x	5.56	104
7			x	x	x		x		x	x	x	x	1.87	104
8			x	x	x	x	x		x	x	x	x	1.52	101
9			x	x	x	x	x	x	x	x	x	x	1.45	98
10			x		x		x		x	x	x	x	2.48	107
11		x	x	x	x		x		x	x	x	x	7.46	101
12		x	x	x	x	x	x		x	x	x	x	10.12	98
13		x	x	x	x	x	x	x	x	x	x	x	7.35	95
14		x	x	x	x		x	x	x	x	x	x	8.18	98
15		x	x	x	x	x		x	x	x	x	x	16.51	98
16		x	x		x		x		x	x	x	x	10.43	104
17	x												58.60	113
Without nonspecific dilution shift														
1b	x		x	x	x		x		x	x		x	8.89	105
2b	x		x	x	x	x	x		x	x		x	11.22	102
3b	x		x	x	x	x	x	x	x	x		x	8.75	99
4b	x		x	x	x		x	x	x	x		x	8.73	102
5b	x		x	x	x	x		x	x	x		x	15.90	105
6b	x		x		x		x		x	x		x	10.22	111
7b			x	x	x		x		x	x	x	x	6.56	108
8b			x	x	x	x	x		x	x	x	x	6.37	105
9b			x	x	x	x	x	x	x	x	x	x	6.01	102
10b			x		x		x		x	x	x	x	7.00	111
17b	x												48.73	117

*Diluents include *n*-hexane, *p*-dioxane, acetone, diethyl ether (DEE), tri-*n*-butyl phosphate (TBP), and triethylamine (TEA). Each "x" designates an assumed complex for that case.

**Root-mean-squared residual errors, $\sqrt{f^{\text{Total}}/DF}$.

†Degrees of freedom.

ally zero. So we favor Case 8 overall as it gives the best fit with reasonable parameters.

The assumed complexes for Case 8 in Table 4 are illustrated in Figures 1 and 2. No self-association is assumed for chloroform, but either one or both oxygens in *p*-dioxane may hydrogen bond with chloroform. Similarly, we find that either one or two chloroform molecules may coordinate with acetone, but only one chloroform molecule associates with diethyl ether. This result is plausible since the carbonyl oxygen in the former species is more polar and less sterically hindered than the ether oxygen in the latter diluent. In the case of triethylamine, it is sufficient to assume that only a single chloroform molecule hydrogen bonds with it. Similarly, our analysis suggests that only a single chloroform molecule hydrogen bonds with the phosphoryl oxygen in TBP or with the TBP dimer.

Table 4 clearly shows that a poorer data fit may result from increasing the number of adjustable parameters. Compare Cases 3 and 8, for example, where Case 3 makes the unrealistic assumption that chloroform dimerizes and the unnecessary assumption that both one and two chloroform molecules hydrogen bond with diethyl ether, rather than just assuming that only a one-to-one complex forms in this mixture. Case 3 requires six more adjustable parameters than Case 8, but the root-mean-squared error in Case 3 is over twice that in Case 8. Similarly, Case 5 has the same number of adjustable parameters as Case 8, but the assumed equilibria are less plausible and the resulting root-mean-squared error is about an order of magnitude greater than in Case 8. As Table 4 shows, the data fit is much more sensitive to the assumed complexation reactions than to the number of adjustable parameters *per se*.

Our chemically based models contradict popular opinion because it is usually not possible to obtain a better data fit simply by increasing the number of adjustable parameters. The primary reason for this is that the parameters themselves become more confounded with each other as the number of assumed complexes is increased. This parameter confounding effect is largely due to increasingly similar stoichiometries among the set of assumed complexes as the size of that set of complexes is increased. On the other hand, a less confounded subset of parameters often yields a better data fit, especially if the assumed complexes make chemical sense.

Thus the use of a chemically based model as presented here constrains the use of arbitrary assumptions regarding complexation reactions. The fact that our thermodynamic calculations are based on true mole fractions z_j, rather than stoichiometric mole fractions x_i, yields a significant statistical

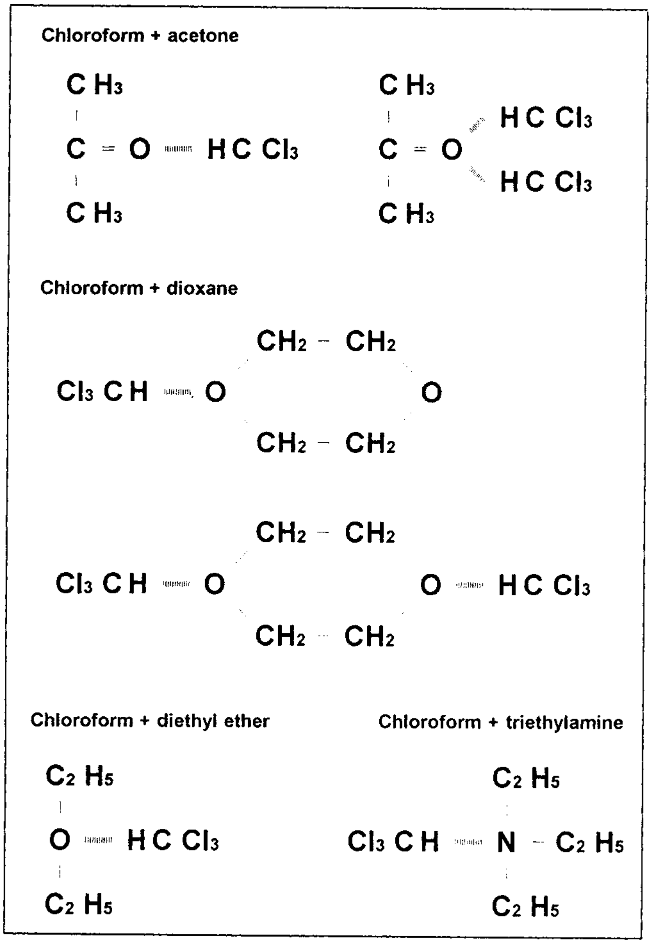

Figure 1. Assumed complexes for Case 8, based on plausible hydrogen-bonding assumptions.

benefit because it makes our calculations more sensitive to the assumed set of complexation equilibria. Also, the user cannot automatically achieve a better fit simply by increasing the number of assumed equilibria, but is forced to realistically consider what are probable complexation mechanisms.

NMR and VLE data fit

Statistically better fits to the NMR and VLE data sets can usually be obtained by fitting them separately, rather than simultaneously as described here. However, the resulting parameter values will not be the same and inconsistencies result whenever a parameter should theoretically be treated as common to several (e.g., $K_{\hat{a}_j}$). More importantly, our ability to discern those equilibria that are essential for a particular system is reduced if the data sets are analyzed separately.

It is very easy, for example, to fit VLE data without considering any chemical reactions at all (e.g., using the Wilson equation). Similarly, some chemical-shift behavior can be explained without resorting to chemical reactions as explained below. However, totally ignoring the effects of chemical equilibria on physical behavior reduces our study to simple data fitting when the actual goal has always been to improve our understanding of molecular interactions by using an integrated approach to data analysis.

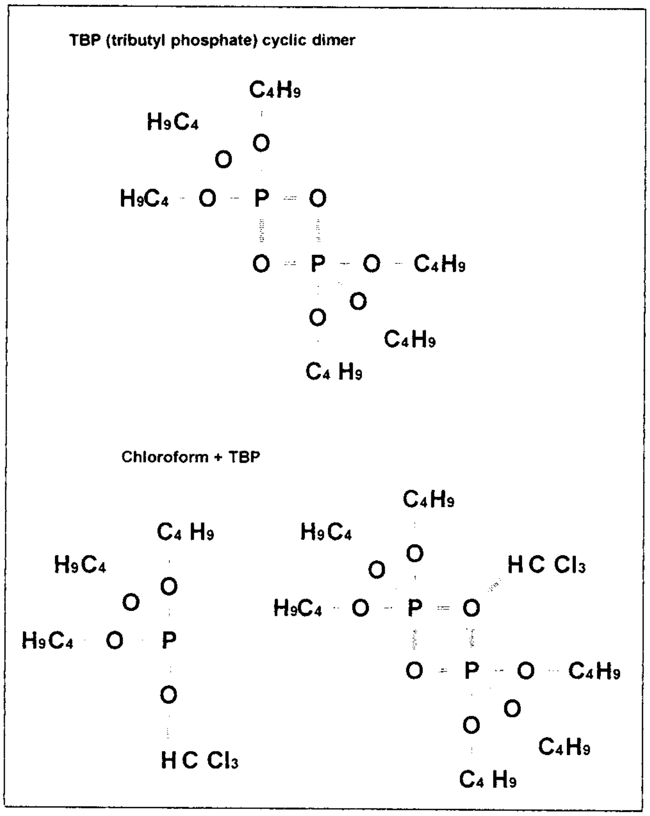

Figure 2. Assumed complexes for Case 8, based on plausible hydrogen-bonding assumptions.

For these reasons, we have focused on the simultaneous fitting of NMR and VLE data. Our parameter estimates from fitting the experimental data sets for Case 8 are summarized in Tables 5 and 7. Figures 3–5 show our results. The fit is least accurate for the ^{1}H-NMR shift data for the chloroform/diethyl ether system as can be seen in Figure 4. Also, in Figure 4, we see that the ^{1}H-shift data for the chloroform/hexane system are essentially linear. Assuming the A_2B solvate has a relatively minor effect on fitting the chloroform/triethylamine data, but assuming that chloroform associates with both the TBP monomer (AB) and the TBP dimer (AB_2) significantly improves the ^{1}H-shift fit in the latter system (see Figure 5).

Table 5 summarizes the parameter estimates for Case 8 together with their 95% nonlinear confidence intervals. Using nonlinear confidence intervals, we are able to reject the null hypothesis for all parameters in this case except for β_{A_2B} in chloroform–dioxane mixtures, and $\nu_{p,h}^{\infty}$ in chloroform–acetone and chloroform–TBP mixtures. The estimated A_2B concentrations are small in chloroform–dioxane mixtures, which contributes to the uncertainties in β_{A_2B} and $K_{\hat{a}_{A_2B}}$ in that system. The nonspecific dilution shift parameters $\nu_{p,h}^{\infty}$ are only marginally significant in chloroform–acetone and chloroform–TEA mixtures.

Nonspecific dilution shift

Comparison of Cases 1–6 and Cases 1b–6b with Cases 7–10 in Table 4 shows that the assumption of a chloroform dimer tends to give less accurate fits than the assumption of non-

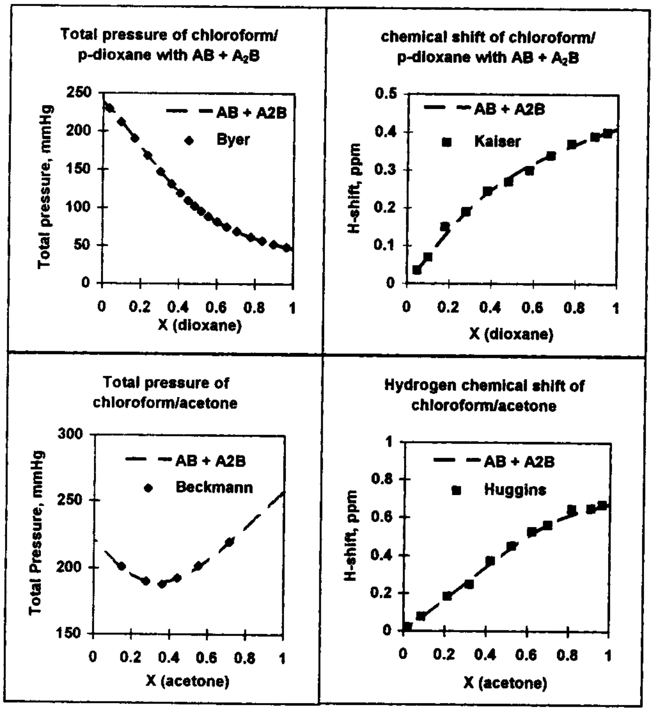

Figure 3. Experimental and predicted total pressures and ^{1}H chemical shift in $CHCl_3$/*p*-dioxane and $CHCl_3$/acetone mixtures.

specific dilution shift without the $CHCl_3$ dimer. We conclude, therefore, that nonspecific dilution shift is a more meaningful assumption than the existence of a chloroform dimer.

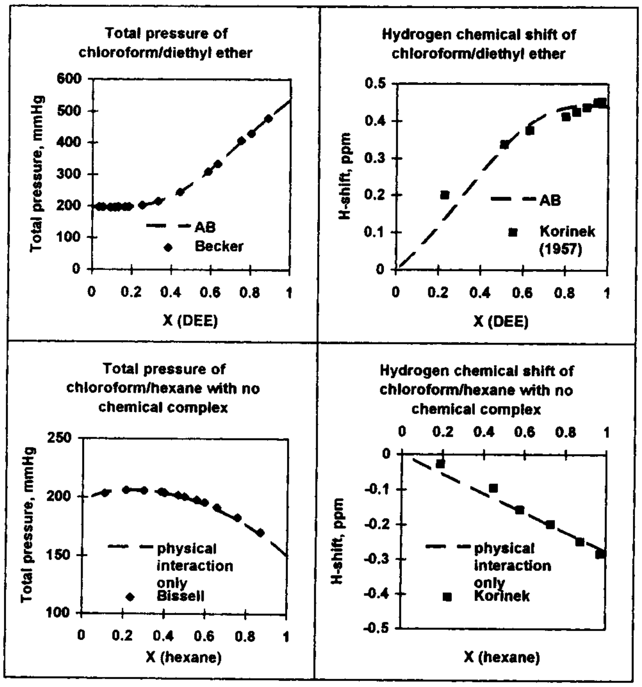

Figure 4. Experimental and predicted total pressures and ^{1}H chemical shift in $CHCl_3$/diethyl ether and $CHCl_3$/*n*-hexane mixtures.

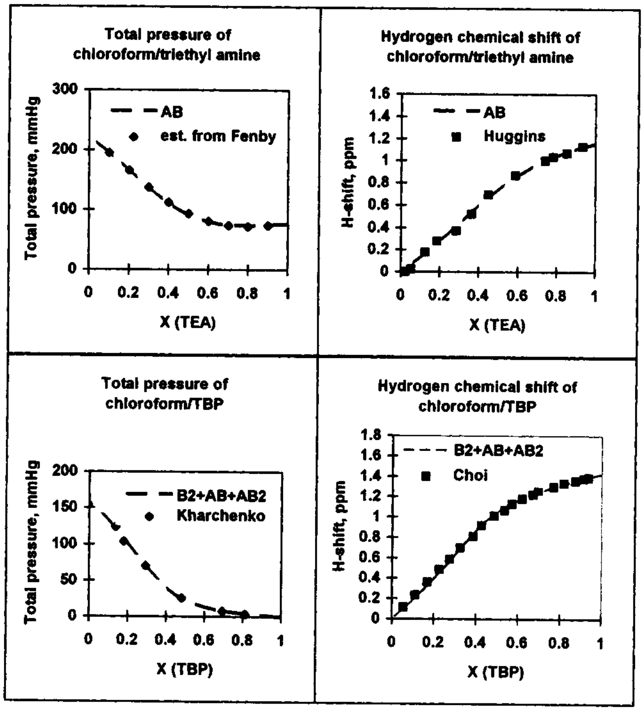

Figure 5. Experimental and predicted total pressures and ^{1}H chemical shift in $CHCl_3$/TEA and $CHCl_3$/TBP.

We also find that nonspecific dilution shift is a more meaningful assumption on theoretical grounds. If we consider the hydrogen-shift data for the $CHCl_3$/*n*-hexane system in Figure 4, we see essentially linear behavior. In Figure 6, we compare theoretical ^{1}H-shift from either a single chloroform dimerization reaction or nonspecific dilution shift. While nonspecific dilution shift correctly predicts linear shift with the chloroform mole fraction, the presumption of the chloroform dimerization reaction to predict this behavior always predicts a curved response. The amount of curvature increases with the assumed value for $K_{\hat{a}_{A_2}}$. Thus, the dimerization model does not predict the correct behavior and only approximates the experimental data if the chloroform dimerization constant is relatively small. Alternatively, Karachewski (1985) has shown that linear behavior is predicted by using a continuous linear association model (CLAM). In this case, however, chloroform is considered to consist of a mixture of dimer, trimer, tetramer, etc., which we find even less plausible than the presumed formation of chloroform dimer alone.

H^E estimates

Equation 30 gives an excellent fit for the excess enthalpy data for mixtures of $CHCl_3$ diluted with *p*-dioxane, acetone, diethyl ether, TEA, or TBP. In all of these cases, the term H^E_{phys} is a minor contributor, and the Δh_j^o provide adequate adjustable parameters to fit the data. Figure 7 shows the typical results for chloroform/*p*-dioxane mixtures. Table 6 summarizes the hydrogen bonding energies, Δh_j, for the complexes assumed from Case 8 equilibria.

The one exception is $CHCl_3$/*n*-hexane, where no reactions are assumed and H^E_{phys}, although relatively larger than for

Table 5. Reaction Parameters and Approximate* 95% Nonlinear Confidence Intervals (Case 8 Equilibria)

Reactions	β_j	$K_{\hat{a}_j}$	Δ_j^{b**} (ppm)	$\nu_{p,h}^{\infty}$ (ppm)
Chloroform–dioxane (AB)	1.00±0.33	1.14±0.51	0.49±0.09	0.114±0.06
Chloroform–dioxane (A_2B)	0.80±0.84	1.93±1.4	0.44±0.17	
Chloroform–acetone (AB)	0.57±0.01	2.42±0.20	1.94±0.14	−0.044±0.04
Chloroform–acetone (A_2B)	1.00±0.16	0.77±0.60	0.51±0.15	
Chloroform–DEE (AB)	1.01±0.08	2.02±0.30	1.18±0.06	−0.432±0.04
Chloroform–TEA (AB)	1.01±0.23	2.82±0.36	1.49±0.06	0.052±0.05

*Confidence intervals are not symmetrical.
**The H-shift of chloroform monomer (ν_{A_1}) was set to zero.

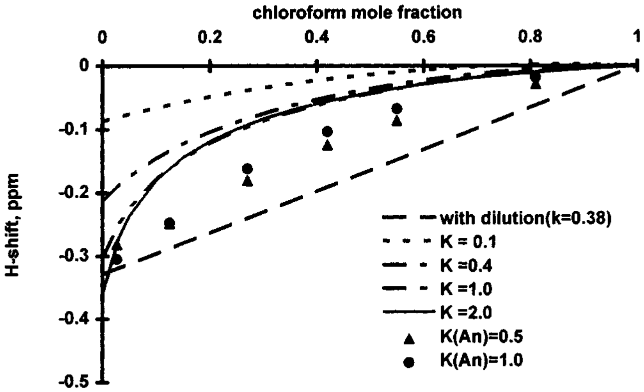

Figure 6. Theoretical comparison of ^{1}H-NMR shift from nonspecific dilution and $CHCl_3$ dimerization; dimerization predicts nonlinear behavior.

the other systems, is not able to predict H^E. In this case, we have fit H^E by adopting a suggestion by Patterson and coworkers (Tancrède et al., 1977; de St. Romain et al., 1979a, 1979b; Fenby et al., 1980). We have assumed that there is also a large positive contribution to the excess enthalpy that arises from the destruction of the orientation order that exists in purely linear molecules when they are diluted with approximately spherical molecules. Since we assume no chemical reactions in this system and $H^E_{\text{chem}} = 0$, we have

$$H^E = H^E_{\text{phys}} + H^E_{\text{ornt}} \tag{42}$$

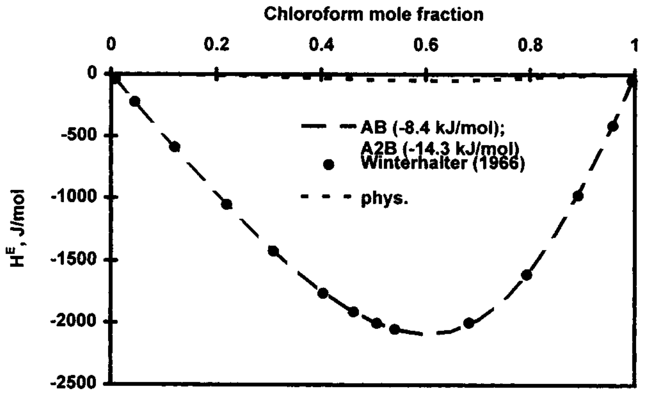

Figure 7. Experimental and predicted heat of mixing in chloroform / *p*-hexane mixtures.

$$H^E_{\text{ornt}} = N_A^o w x_A x_B, \tag{43}$$

where N_A^o is Avogadro's number and w is the interchange energy. In the $CHCl_3$/*n*-hexane system, this additional assumption gives an excellent fit with $N_A^o w = 1{,}500$ J/mol and $w/kT = 0.602$. These results are shown in Figure 8. Alternatively, Karachewski (1985) found the CLAM model to give an excellent fit to these data with $\Delta H = 3{,}700$ J/mol.

The CLAM model and our model for fitting isothermal data are statistically indistinguishable. The main difference is whether it is more plausible to ascribe the observed chemical

Table 6. Reaction Parameters in Binary Chloroform + Diluent Mixtures at 25°C

Reactions	β_j	$K_{\hat{a}_j}$	− ΔG kJ/mol	− Δh* kJ/mol
Case 8				
Chloroform–dioxane (AB)	1.001	1.142	0.33	8.4
Chloroform–dioxane (A_2B)	0.804	1.934	1.63	14.3
Chloroform–acetone (AB)	0.565	2.415	2.18	10.5
Chloroform–acetone (A_2B)	1.002	0.774	−0.63	14.6
Chloroform–DEE (AB)	1.009	2.021	1.74	11.4
Chloroform–TEA (AB)	1.007	2.824	2.57	16.6
TBP dimer (B_2)	0.834	11.16	5.92	11.5**
Chloroform–TBP (AB)	0.870	46.84	9.43	21.7**
Chloroform–TBP (AB_2)	0.661	65.91	10.27	33.2**

*Heat of complex formation was estimated by fitting H^E data.
**The parameters were obtained using the ^{1}H and VLE data; slightly different from those obtained by fitting the ^{1}H, ^{31}P, and VLE data (Choi, 1995).

Table 7. Calculated Chemical Shift Parameters and Nonspecific Dilution Shift Parameters (Assuming Case 8 Equilibria)*

	H-shift, ν^H, in ppm**			
Diluent	ν_{A_1}	Δ_{AB}	Δ_{A_2B}	$\nu_{p,h}^{\infty}$
Chloroform systems (Case 8) with dilution shift				
p-Dioxane	0.0	0.49	0.44	0.114
Acetone	0.0	1.94	0.51	−0.044
Diethyl ether	0.0	1.18	—	−0.432
n-Hexane	0.0	—	—	−0.275
Triethylamine	0.0	1.49	—	0.052
TBP†	0.0	1.17	1.21	0.416††

*Nonspecific dilution shift is important.
**H-NMR data were transformed relative to chemical shift of pure chloroform.
†Using the combined VLE and H-NMR data.
††Slightly different estimate of $\nu_{p,h}^{\infty} = 0.379$ if ^{31}P-NMR are also combined.

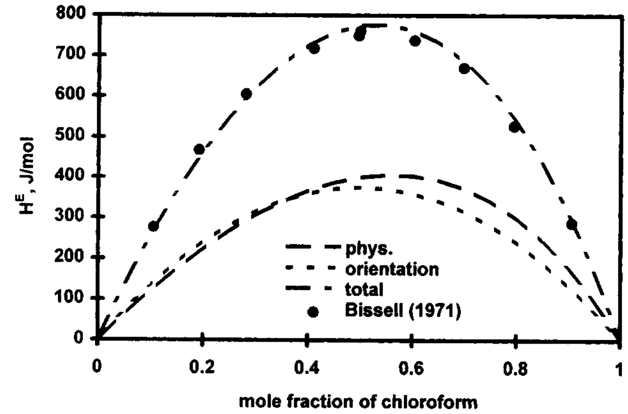

Figure 8. Experimental and predicted heat of mixing in chloroform/*n*-hexane mixtures.

shift to continuous linear associated chloroform or changes in chloroform NMR average susceptibility due to nuclear screening in chloroform/*n*-hexane mixtures. We prefer the latter interpretation since there is no compelling reason to believe that chloroform hydrogen bonds with itself.

V^E *estimates*

Since we introduce a volume adjustment parameter β_j to estimate the relative molar volumes of complexes, we are able to compute the excess molar volume of each mixture as a dependent variable. Figure 9 compares the predicted excess volumes with experimental data. As can be seen, small positive values for V^E are predicted in chloroform/diethyl ether and chloroform/triethylamine, which have larger negative experimental V^E data. There are negative deviations for chloroform with *p*-dioxane, acetone, or TBP. For the chloroform/*p*-dioxane mixture, we find that there are smaller excess volumes than those predicted, and that $V_E < 0$. For chloroform/*n*-hexane mixture, we predict $V^E = 0$ since no chemical reactions are assumed.

There are several possible explanations for the discrepancies between our predictions and experimental V^E. First, our model includes an inconsistency. We assume that $V^E = 0$ whenever we solve the volume balance equations using Eqs. 9 and 10 so that we always have an exact solution to the corresponding material balance equations that apply to each experiment. Later on, we relax this assumption using Eqs. 14 and 15. Thus, our results may be somewhat improved by devising a computational method that avoids this inconsistency.

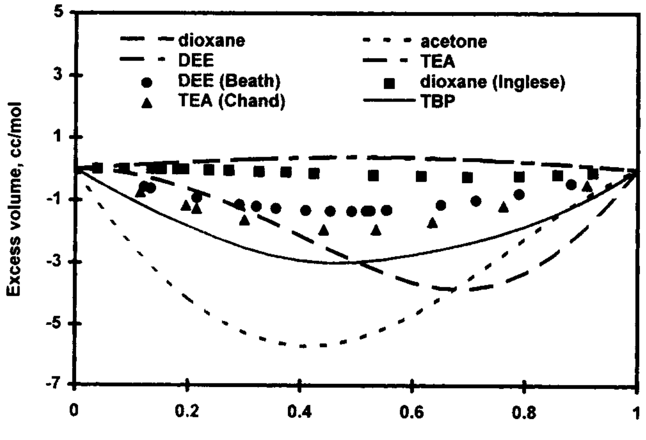

Figure 9. Predicted and experimental excess volumes for chloroform mixtures.

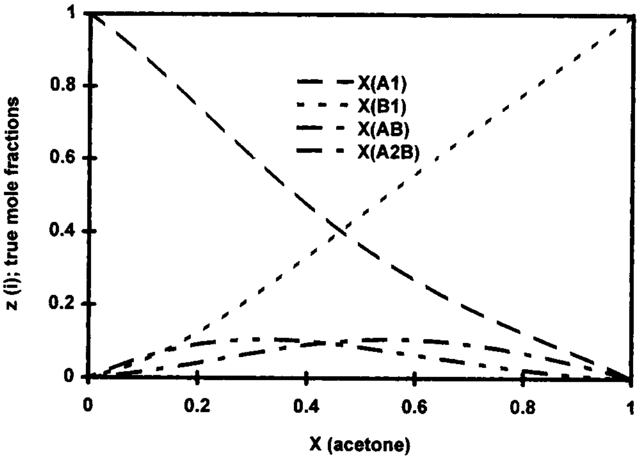

Figure 10. Projected species distribution in chloroform and acetone mixtures, assuming Case 8 equilibria.

Second, our model assumes that all contributions to excess molar volume result from the molar volumes of solvation complexes. No consideration is given to possible changes in the effective molar volumes of monomeric species, or to possible changes in molar volumes of true complex species with composition (i.e., the β_j are assumed to be independent of composition). Figure 9 suggests that these latter assumptions are also an oversimplification to the actual situation. Moreover, it is doubtlessly more realistic to treat effective molar volumes as being composition dependent for all species, especially since molecular volumes are not fixed quantities, but are essentially electromagnetic fields that clearly change with their environment.

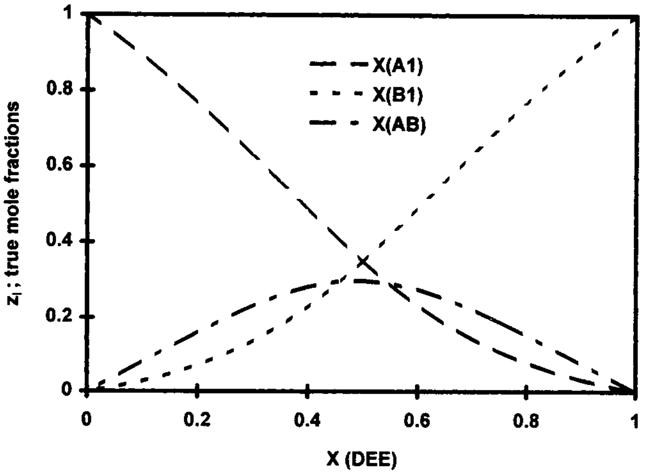

Figure 11. Projected species distribution in chloroform and diethyl ether mixtures, assuming Case 8 equilibria.

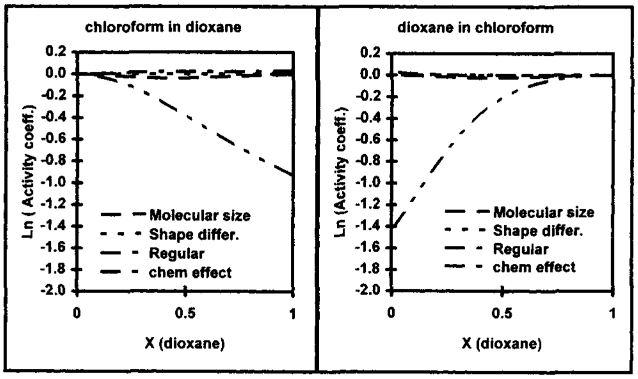

Figure 12. Relative contributions of chemical, molecular size, shape difference, and regular solution terms to species nonideality in chloroform and p-dioxane mixtures (Case 8 equilibria).

Projected species distributions

Figures 10 and 11 show the estimated species distributions for chloroform/*p*-acetone and chloroform/diethyl ether mixtures, respectively, assuming Case 8 equilibria. These results are typical for cases with AB and A_2B complexes and with AB complex only. The solvate concentration is higher in Figure 11 than Figure 10 because of larger estimated values of K_{z_j} in the chloroform/diethyl ether system (see Figures 17 and 18). As shown in Figure 10, the estimated concentrations of the A_2B complex are lower than those of AB complex if the acetone mole fraction exceeds 0.4.

Estimated contributions to activity coefficients

Figures 12 through 16 plot the contributions of the chemical, molecular size, shape difference, and regular solution terms to the activity coefficients for chloroform and five of the diluents we studied, assuming Case 8 equilibria. The chemical contributions were calculated from $\gamma_i = z_{i_1}/(x_{i,s} z^o_{i_1})$. The other three activity coefficient terms are relative to their respective contributions in the reference state (e.g., $\gamma_{ms}/\gamma^o_{ms}$).

In most cases, the chemical contribution to nonideality is far greater than all other terms. The chloroform/*n*-hexane system is an exception since no chemical reaction is assumed and the regular solution contribution predominates. In Figure 13, we see that the A_2B complex yields unusual curvature in the activity coefficient for chloroform that goes through a minimum at an acetone mole fraction of about 0.8. As the chloroform concentration is further reduced, the A_2B concentration decreases rapidly (see Figure 10) and the activity coefficient for chloroform increases slightly by $\gamma_i = z_{i_1}/x_{i,s} z^o_{i_1}$.

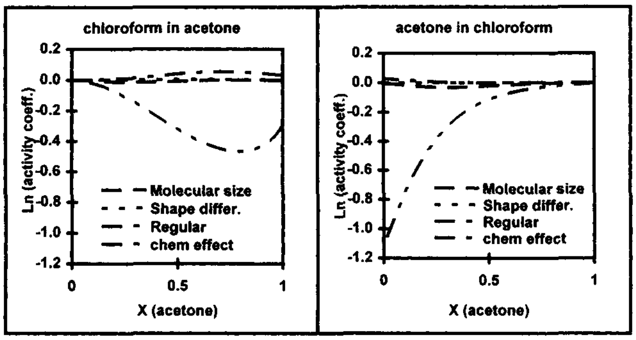

Figure 13. Relative contributions of chemical, molecular size, shape difference, and regular solution terms to species nonideality in chloroform/acetone mixtures (Case 8 equilibria).

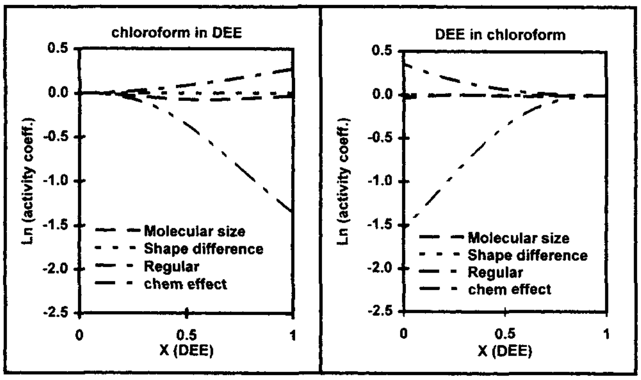

Figure 14. Relative contributions of chemical, molecular size, shape difference, and regular solution terms to species nonideality in chloroform/diethyl ether mixtures (Case 8 equilibria).

Stability constants

Much of the published literature provides estimates of K_{z_j} (see Table 1). From Eqs. 5, it is clear that both K_{γ_j} and K_{z_j} are composition dependent, and that the predicted variation in K_{z_j} depends largely upon relative molecular sizes and β_j.

Figures 17 through 19 show how the K_{z_j}-values change with composition using Case 8 equilibria. All the values are consistent with the published values in Table 1. The curvature in $K_{z_{A_2B}}$ is largely due to mass action that changes the chemical contribution, $z_{A_1}/x_{A,s} z^o_{A_1}$, as can be seen in Figure 13. The changes in $K_{z_{AB}}$ are particularly large for the

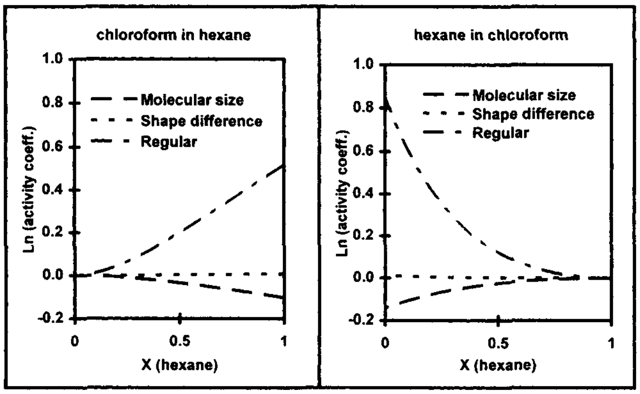

Figure 15. Relative contributions of chemical, molecular size, shape difference, and regular solution terms to species nonideality in chloroform/*n*-hexane mixtures (Case 8 equilibria).

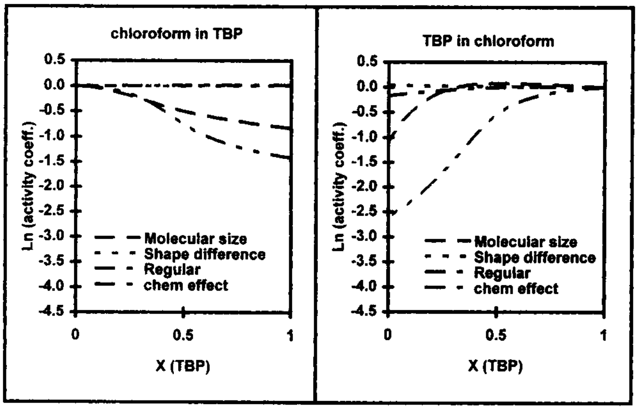

Figure 16. Relative contributions of chemical, molecular size, shape difference, and regular solution terms to species nonideality in chloroform/TBP mixtures (Case 8 equilibria).

chloroform/TBP system since the chemical effect, $z_{A_1}/x_{A,s}z^o_{A_1}$ rapidly changes and the molecular size term, $\gamma_{ms}/\gamma^o_{ms}$ also changes over the concentration range (see Figure 16).

Conclusions

Nonspecific dilution shift apparently contributes to the observed ^{1}H-NMR chemical shift in chloroform mixtures. We find that ^{1}H-NMR susceptibilities are diluent-dependent. The bulk solvent effect on chloroform corresponds to the order: acetone < TEA < *p*-dioxane < *n*-hexane < TBP < DEE.

Our model is able to accurately fit the available VLE and NMR chemical shift data for the chloroform binary mixtures. The H^E data are fit accurately by assuming appropriate values for hydrogen bonding energies in all the system except for chloroform/*n*-hexane, where we find it more plausible to exclude chemical reaction. In this latter system, we interpret the ^{1}H-shift using nonspecific dilution shift. We explain H^E for chloroform/*n*-hexane mixture partly in terms of the destruction of orientation order.

We find that our model overestimates the V^E. This suggests that other factors besides the effective molar volumes of complexes contribute to V^E.

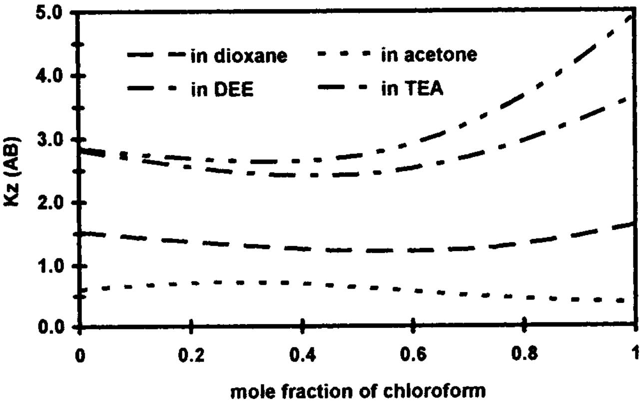

Figure 17. Composition and diluent dependence of K_{z_j} for chloroform + diluent 1:1 solvates (Case 8 assumptions).

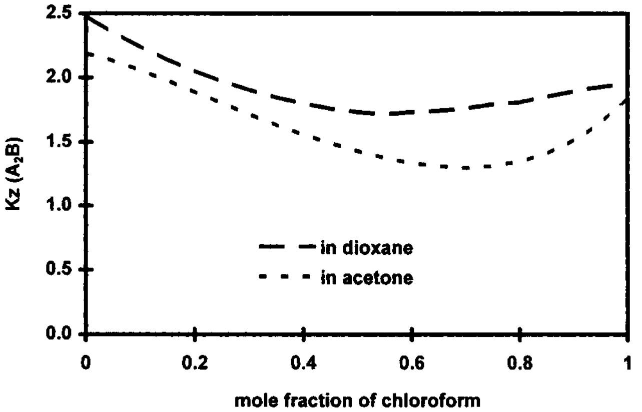

Figure 18. Composition and diluent dependence of K_{z_j} the chloroform + diluent 2:1 solvates (Case 8 assumptions).

Chemical interactions by hydrogen bonding are important in explaining the nonideality in chloroform mixtures. Contributions of molecular size and regular solution terms are smaller than the chemical effects. The contribution of shape difference is also relatively small. The failure to adopt a reasonable set of reactions makes it difficult or impossible to obtain parameter estimates with these models. As a consequence, the nearly linear hydrogen chemical shift with stoichiometric mole fraction that is observed experimentally in some chloroform mixtures is more easily explained in terms of bulk solvent effects than specific chemical reactions.

Stability constants expressed on a mole fraction basis are composition dependent. The published variation in K_{z_j}-values may be partly attributable to the concentration range over which measurements were made.

Acknowledgment

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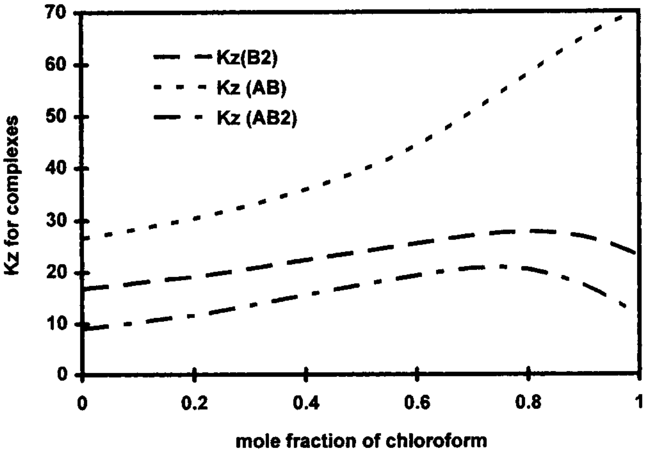

Figure 19. Composition and diluent dependence of K_{z_j} for chloroform + TBP 1:1 and 1:2 solvates (Case 8 assumptions).

Notation

f_i^o = fugacity of pure liquid in reference state
$\hat{f}_i$ = fugacity of ith species in solution
k = Boltzmann constant, J/K
K_{C_j} = product of true molar concentrations for jth complex
m_j = diluent coordination number in jth complex
N_r = number of complexes in a binary mixture
n_j = chloroform coordination number in jth complex
P_i^{sat} = pure component vapor pressure for ith species, mm Hg
R = universal gas constant, J/mol·K
S^E = excess entropy, J/mol·K
T = temperature, K
z' = coordination number $z' = 10$

Greek letters

Δ_o = observed chemical shift relative to its monomer
ν_o^H = observed ^{1}H-chemical shift
σ_H = experimental uncertainty in NMR measurements, ppm
σ_V = experimental uncertainty in VLE measurements, mm Hg
θ_j = available surface fraction for jth complex in mixture

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