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THERMOCHEMICAL INVESTIGATIONS OF ASSOCIATED SOLUTIONS.

9. PREDICTION OF EXCESS ENTHALPIES OF TERNARY ACETONE + CYCLOHEXANE + CHLOROFORM MIXTURES FROM MEASURED BINARY DATA

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ABSTRACT

A conventional non-electrolyte solution model which has led to successful predictive expressions for the thermochemical properties of a solute in simple binary solvent mixtures is extended to ternary systems having AC and AC_2 molecular complexes. The general mixing model used assumes that the Gibbs free energy of mixing and excess enthalpy can be separated into a chemical and a physical term. The chemical-interaction term results from the formation of molecular complexes and the physical contribution describes non-specific interactions between the uncomplexed and associated species in solution. Ten A_{ij} parameters are initially needed to describe all the binary non-specific interactions present. Simplifying approximations and mathematical manipulations reduce the number of binary interaction parameters to only three A_{ij} values. Expressions derived from the general mixing model are used to estimate the excess enthalpies of ternary acetone + cyclohexane + chloroform mixtures.

INTRODUCTION

Molecular complexation occurs in many systems having chemical and biological significance. The calculation of meaningful association constants is an important first step in understanding molecular interactions and solution non-ideality. Spectroscopic and solubility methods have been developed to facilitate equilibrium-constant determination. Spectroscopic methods require differences between the UV-visible absorbances of the molecular complex and the monomeric solute, and are generally limited in application to those systems in which the complexing solvent concentration is considerably greater than the solute molarity. Equilibrium constants are obtained

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through a least-squares analysis of absorbance versus concentration data. Christian and Lane [1] and more recently Zubkov and Ivanova [2] have reviewed the various linearized mathematical forms used to calculate association parameters. The authors recommended the expression(s) most appropriate for a given set of experimental conditions.

Solubility methods attribute the increase in solute solubility at constant fugacity in a complex–inert-solvent mixture, relative to the solubility in pure inert solvent, to the formation of molecular complexes. This primary assumption is common to several experimental methods, such as the partitioning of solutes between two immiscible liquid phases, the measurement of infinite-dilution gas–liquid chromatographic partition coefficients, and the increased solubility of solid solutes. The extraction of a meaningful equilibrium constant from solubility data requires a thermodynamic solution model for assessing what portion of the observed enhancement is due to specific solute–solvent complexation. The model used should provide a smooth transition between complexing and non-complexing systems without pre-assuming the strength of the molecular complex believed to be formed. A major difficulty encountered in using solubility methods has been the lack of thermodynamic models for systems containing very weak association complexes.

Earlier papers in this series [3–8] were primarily devoted to the development of mixing models for describing the thermochemical properties of a solute near infinite dilution in binary solvent mixtures. Expressions were derived for the calculation of solute–solvent association constants from measured solute solubility based on the extended nearly ideal binary solvent (NIBS) model [3–6]

$$\mathrm{A}_1 + \mathrm{C}_1 \rightleftharpoons \mathrm{AC} \qquad K^{\phi}_{\mathrm{AC}} = \hat{\phi}_{\mathrm{AC}}/\left(\hat{\phi}_{\mathrm{A}_1}\hat{\phi}_{\mathrm{C}_1}\right)$$

$$\begin{aligned}\ln \phi_{\mathrm{A}}^{\mathrm{sat}} = {} & \phi_{\mathrm{B}}^{0} \ln\left(\phi_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{B}} + \phi_{\mathrm{C}}^{0} \ln\left(\phi_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{C}} + \ln\left[1 + \bar{V}_{\mathrm{A}} K^{\phi}_{\mathrm{AC}} \phi_{\mathrm{C}}^{0}/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{C}}\right)\right] \\ & - \phi_{\mathrm{C}}^{0} \ln\left[1 + \bar{V}_{\mathrm{A}} K^{\phi}_{\mathrm{AC}}/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{C}}\right)\right] + \frac{\bar{V}_{\mathrm{A}}\, \Delta \bar{G}^{\mathrm{fh}}_{\mathrm{BC}}}{RT\left(X_{\mathrm{B}}^{0} \bar{V}_{\mathrm{B}} + X_{\mathrm{C}}^{0} \bar{V}_{\mathrm{C}}\right)} \end{aligned} \tag{1}$$

and the competitive associated NIBS model [7]

$$\mathrm{A}_1 + \mathrm{C}_1 \rightleftharpoons \mathrm{AC} \qquad K^{\phi}_{\mathrm{AC}} = \hat{\phi}_{\mathrm{AC}}/\left(\hat{\phi}_{\mathrm{A}_1}\hat{\phi}_{\mathrm{C}_1}\right)$$

$$\mathrm{A}_1 + \mathrm{B}_1 \rightleftharpoons \mathrm{AB} \qquad K^{\phi}_{\mathrm{AB}} = \hat{\phi}_{\mathrm{AB}}/\left(\hat{\phi}_{\mathrm{A}_1}\hat{\phi}_{\mathrm{B}_1}\right)$$

$$\begin{aligned}\ln \phi_{\mathrm{A}}^{\mathrm{sat}} = {} & \phi_{\mathrm{B}}^{0} \ln\left(\phi_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{B}} + \phi_{\mathrm{C}}^{0} \ln\left(\phi_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{C}} - \phi_{\mathrm{B}}^{0} \ln\left[1 + \bar{V}_{\mathrm{A}} K^{\phi}_{\mathrm{AB}}/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{B}}\right)\right] \\ & + \ln\left[1 + \bar{V}_{\mathrm{A}} K^{\phi}_{\mathrm{AB}} \phi_{\mathrm{B}}^{0}/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{B}}\right) + \bar{V}_{\mathrm{A}} K^{\phi}_{\mathrm{AC}} \phi_{\mathrm{C}}^{0}/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{C}}\right)\right] \\ & - \phi_{\mathrm{C}}^{0} \ln\left[1 + \bar{V}_{\mathrm{A}} K^{\phi}_{\mathrm{AC}}/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{C}}\right)\right] + \frac{\bar{V}_{\mathrm{A}}\, \Delta \bar{G}^{\mathrm{fh}}_{\mathrm{BC}}}{RT\left(X_{\mathrm{B}}^{0} \bar{V}_{\mathrm{B}} + X_{\mathrm{C}}^{0} \bar{V}_{\mathrm{C}}\right)} \end{aligned} \tag{2}$$

In the absence of solute–solvent complexation, eqn. (1) (with $K^{\phi}_{\mathrm{AC}} = 0$) and eqn. (2) (with $K^{\phi}_{\mathrm{AC}} = K^{\phi}_{\mathrm{AB}} = 0$) reduce to the basic NIBS model which has been shown to provide very reasonable predictions for enthalpies of solution [9], gas–liquid chromatographic partition coefficients [10,11], and solid solute solubilities [12–18] in systems containing only non-specific interactions. The symbols used in eqns. (1) and (2) are defined in the Appendix.

McCargar and Acree [5,6,8,19] compared values of the carbazole–dibutyl ether association constant calculated from experimental carbazole solubilities in 10 binary dibutyl ether + alkane solvent mixtures. A simple stoichiometric complexation model based entirely on specific solute–solvent interactions required two equilibrium constants to describe the solubility data mathematically. Calculated constants in isooctane cosolvent were significantly different from values for cyclooctane. In comparison, the extended NIBS model describes the experimental solubilities to within an average absolute deviation of about $\pm 2\%$ using a single carbazole–dibutyl ether association constant. The variation of the calculated constant with inert co-solvent was slight, numerical values ranging from $K_{AC}^{\phi} = 22$ for n-heptane to $K_{AC}^{\phi} = 30$ for isooctane cosolvent. In follow-up studies [7,20] the competitive associated NIBS model was derived to explain the solubility behavior of carbazole in binary chloroalkane + dibutyl ether solvent mixtures. Assuming the presence of a very weak chloroalkane–carbazole complex, the authors illustrated the surprisingly large effect that a weak secondary AB complex can have on the calculated K_{AC}^{ϕ} constant. Neglect of a presumed weak carbazole–chlorohexane complex with $K_{AB}^{\phi} = 2$ resulted in a more than two-fold decrease in the calculated carbazole–dibutyl ether equilibrium constant. The competitive associated NIBS model suggests a novel experimental solubility method for studying weak association complexes.

The success of the three NIBS models is impressive, particularly if one realizes that the derived expressions do provide a very smooth transition between non-complexing and associated solutions, and that well over 80 systems have been described to date. Readers are reminded that it is fairly easy to describe Gibbs free energies, because enthalpy–entropy compensation often occurs, even in the more non-ideal associated solutions. Comparisons between the experimental and predicted enthalpies of mixing (or entropies of mixing) will provide a better indication of a solution model's applications and limitations. In this paper we extend the generalized NIBS mixing model to the excess enthalpies of ternary systems containing AC and AC_2 molecular complexes. The application of the derived expression is illustrated using previously published data for the acetone + cyclohexane + chloroform system [21].

DEVELOPMENT OF THE THERMODYNAMIC MODEL

Thermodynamic models of associated non-electrolyte solutions generally assume that the Gibbs free energy of mixing can be separated into a chemical and physical contribution. The chemical-interaction term results from the formation of molecular complexes and the physical contribution describes non-specific interactions between the uncomplexed and associated species in solution. Other thermodynamic properties can also be expressed as the sum of a chemical and a physical contribution. However, it is often more convenient to derive the corresponding expressions for the enthalpy and volume of mixing through the appropriate differentiation of the Gibbs free energy.

The simplest thermodynamic mixing model for a multicomponent system would take the form

$$\Delta G^{\text{mix}}_{1,2,\ldots,N} = RT\sum_{i=1}^{N} n_i \ln X_i + \left(\sum_{i=1}^{N} n_i\Gamma_i\right)\left(\sum_{i=1}^{N}\sum_{j>i} f_i f_j A_{ij}\right) \qquad (3)$$

$$f_i = n_i\Gamma_i \Big/ \left(\sum_{j=1}^{N} n_j\Gamma_j\right)$$

where X_i and f_i refer to the mole fraction and weighted mole fraction of component i, respectively, n_i is the number of moles of component i and A_{ij} is a binary interaction parameter which is independent of composition. The weighting factors (Γ_i) represent a rough measure of the skew of the binary excess mixing property from a symmetric curve with an extrenum at the equimolar composition. For simplicity, weighting factors are assumed to be independent of both temperature and pressure. Therefore, molar volumes and other experimentally determined weighting factors must be regarded as approximations of these "true" weighting factors. Replacement of the weighting factors with molar volumes requires that a specified condition, such as 25 °C and 1 atm, be used.

Application of eqn. (3) to a pentanary system

$$A_1 + C_1 \rightleftharpoons AC \qquad K^x_{AC} = \hat{X}_{AC}\big/\left(\hat{X}_{A_1}\hat{X}_{C_1}\right)$$

$$A_1 + 2C_1 \rightleftharpoons AC_2 \qquad K^x_{AC_2} = \hat{X}_{AC_2}\big/\left(\hat{X}_{A_1}\hat{X}^2_{C_1}\right)$$

yields the following expression for the Gibbs free energy of mixing

$$\begin{aligned}
\Delta G^{\text{mix}}
&= RT\left[\hat{n}_{A_1}\ln\hat{X}_{A_1} + \hat{n}_B\ln\hat{X}_B + \hat{n}_{C_1}\ln\hat{X}_{C_1} + \hat{n}_{AC}\ln\hat{X}_{AC} + \hat{n}_{AC_2}\ln\hat{X}_{AC_2}\right] \\
&\quad + \left(\hat{n}_{A_1}\Gamma_A + \hat{n}_B\Gamma_B + \hat{n}_{C_1}\Gamma_{C_1} + \hat{n}_{AC}\Gamma_{AC} + \hat{n}_{AC_2}\Gamma_{AC_2}\right) \\
&\quad \times\Big[\hat{f}_{A_1}\hat{f}_B A_{A_1B} + \hat{f}_{A_1}\hat{f}_{C_1}A_{A_1C_1} + \hat{f}_{A_1}\hat{f}_{AC}A_{A_1AC} + \hat{f}_{A_1}\hat{f}_{AC_2}A_{A_1AC_2} \\
&\quad + \hat{f}_B\hat{f}_{C_1}A_{BC_1} + \hat{f}_B\hat{f}_{AC}A_{BAC} + \hat{f}_B\hat{f}_{AC_2}A_{BAC_2} + \hat{f}_{C_1}\hat{f}_{AC}A_{C_1AC} \\
&\quad + \hat{f}_{C_1}\hat{f}_{AC_2}A_{C_1AC_2} + \hat{f}_{AC}\hat{f}_{AC_2}A_{ACAC_2}\Big]
\end{aligned} \qquad (4)$$

Inspection of eqn. (4) reveals that it contains 10 binary interaction A_{ij} parameters which must somehow be evaluated. Through clever mathematical manipulations and judicious approximations

$$A_{A_1AC} = \Gamma_C^2(\Gamma_A + \Gamma_C)^{-2} A_{A_1C_1}$$

$$A_{C_1AC} = \Gamma_A^2(\Gamma_A + \Gamma_C)^{-2} A_{A_1C_1}$$

$$A_{A_1AC_2} = 4\Gamma_C^2(\Gamma_A + 2\Gamma_C)^{-2} A_{A_1C_1}$$

$$A_{C_1AC_2} = \Gamma_A^2(\Gamma_A + 2\Gamma_C)^{-2} A_{A_1C_1}$$

$$A_{ACAC_2} = \Gamma_C^2\Gamma_A^2(\Gamma_A + \Gamma_C)^{-2}(\Gamma_A + 2\Gamma_C)^{-2} A_{A_1C_1}$$

Acree and Tucker [22] were able to significantly reduce to the number of A_{ij} terms. For the pentanary system, the Gibbs free energy of mixing can be expressed in terms of

$$\Delta G^{\text{mix}} = RT\left[n_A \ln \hat{X}_{A_1} + n_B \ln \hat{X}_B + n_C \ln \hat{X}_{C_1}\right] + (n_A\Gamma_A + n_B\Gamma_B + n_C\Gamma_C)\left(f_A f_B A_{A_1B} + f_A f_C A_{A_1C_1} + f_B f_C A_{BC_1}\right) \quad (5)$$

only three binary interaction parameters, one parameter evaluated from each of the three subbinaries which make up the ternary system. The two interaction parameters involving the inert co-solvent, B, and the molecular complexes, A_{BAC} and A_{BAC_2}, did not have to be approximated as they were eliminated from the mixing model mathematically. Several alternative approximations for $A_{A_1\text{Complex}}$ and $A_{C_1\text{Complex}}$ have been proposed in the past [23,24]. To our knowledge, only the method outlined above permits reduction to the simple three-parameter expression.

In the absence of complexation ($K_{AC} = 0$ and $K_{AC_2} = 0$), eqn. (5) reduces to the general NIBS mixing model as the mole fractions of all uncomplexed species equal those of the stoichiometric components ($\hat{X}_{A_1} = X_A$, $\hat{X}_B = X_B$ and $\hat{X}_{C_1} = X_C$). As mentioned previously, the NIBS equations have been shown to be quite dependable for estimating the enthalpies of solution, the gas–liquid chromatographic partition coefficients and the solid solubilities in binary solvent mixtures which are free of association. In addition, the BAB equation [25,26] for predicting integral thermodynamic excess properties and select physical properties of multicomponent systems from measured binary data was derived from the generalized non-complexing form of eqn. (4). Previous computations have shown that the "best" predictions are obtained when weighting factors are determined from experimental binary data, particularly in systems having highly skewed excess properties. Weighting factors, which give a measure of the skew of the binary excess mixing property, can only be evaluated in a relative sense as the ratio of two weighting factors (Γ_i/Γ_j) rather than absolutely. A ratio of raw weighting factors is calculated from each binary combination of the components of the multicomponent system (which in this case is a ternary system), and then normalized to ensure the mathematical exactness required by

$$(\Gamma_A/\Gamma_B)(\Gamma_B/\Gamma_C) = (\Gamma_A/\Gamma_C)$$

Weighting-factor calculations become meaningless if a ratio of raw weighting factors is a negative value (or an abnormally high or low value) as can happen if the mixing property of the binary shows a point of inflection when plotted versus the mole fraction. The approximation of weighting factors by using molar volumes simplifies the predictive method. For a number of systems studied, this approximation only slightly affects the predictive accuracy.

Application of eqn. (5) depends on the availability of experimental data for systems having well-defined molecular complexes. The chemical literature contains data for a large number of binary systems. Thermodynamic data for ternary mixtures is scarce, and data for simple complexing systems is virtually non-existent. A search of the chemical literature, however, did uncover enthalpic data for the acetone + cyclohexane + chloroform system [21]. The acetone + chloroform subbinary system has been widely studied since Dolezalek [27] noted that the observed deviations from Raoult's law could be explained on the basis of heterogeneous molecular complexation between acetone and chloroform molecules in solution. Apelblat et al. [28] reviewed existing data for the acetone + chloroform system, and showed that the excess Gibbs free energies, excess enthalpies, excess volumes and excess isobaric heat capacities could be satisfactorily described by the ideal associated solution model ($A_{A_1C_1} = 0$) assuming both 1 : 1 and 1 : 2 acetone–chloroform complexes.

An expression for predicting the excess enthalpies of the acetone + cyclohexane + chloroform system can be obtained by differentiating eqn. (5) with respect to temperature (i.e., $\partial(\Delta\bar{G}^{ex}/T)/\partial(1/T) = \Delta\bar{H}^{ex}$)

$$\Delta\bar{H}^{ex} = \frac{\hat{X}_{A_1}\hat{X}_{C_1}\left(K^x_{AC}\,\Delta\bar{H}^0_{AC} + K^x_{AC_2}\,\Delta\bar{H}^0_{AC_2}\hat{X}_{C_1}\right)}{1 + \hat{X}_{A_1}\hat{X}_{C_1}\left(K^x_{AC} + 2\hat{X}_{C_1}K^x_{AC_2}\right)} + (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C)\left[f_Af_BB_{A_1B} + f_Af_CB_{A_1C_1} + f_Bf_CB_{BC_1}\right] \tag{6}$$

As mentioned previously, weighting factors are assumed to be independent of temperature and $B_{ij} = \partial(A_{ij}/T)/\partial(1/T)$. The standard reaction enthalpies for the formation of the AC and AC$_2$ complexes are denoted as $\Delta\bar{H}^0_{AC}$ and $\Delta\bar{H}^0_{AC_2}$, respectively. Careful examination of eqn. (6) reveals that for model systems obeying this equation, the enthalpic properties of the two non-complexing contributive binary systems would obey (per mole of binary solution)

$$(\Delta\bar{H}^{ex}_{AB})^* = X^0_AX^0_B\Gamma_A\Gamma_BB_{A_1B}/(X^0_A\Gamma_A + X^0_B\Gamma_B) \tag{7}$$

and

$$\left(\Delta \overline{H}^{\mathrm{ex}}_{\mathrm{BC}}\right)^* = X^0_{\mathrm{B}} X^0_{\mathrm{C}} \Gamma_{\mathrm{B}} \Gamma_{\mathrm{C}} B_{\mathrm{BC}_1} / \left(X^0_{\mathrm{B}} \Gamma_{\mathrm{B}} + X^0_{\mathrm{C}} \Gamma_{\mathrm{C}} \right) \tag{8}$$

where the "0" superscript indicates binary mole fraction compositions calculated as if the third were not present.

Equation (6) can then be rearranged to the following form

$$\begin{aligned}\Delta \overline{H}^{\mathrm{ex}} = {} & \frac{\hat{X}_{\mathrm{A}_1} \hat{X}_{\mathrm{C}_1} \left(K^x_{\mathrm{AC}}\, \Delta \overline{H}^0_{\mathrm{AC}} + K^x_{\mathrm{AC}_2}\, \Delta \overline{H}^0_{\mathrm{AC}_2} \hat{X}_{\mathrm{C}_1} \right)}{1 + \hat{X}_{\mathrm{A}_1} \hat{X}_{\mathrm{C}_1} \left(K^x_{\mathrm{AC}} + 2 K^x_{\mathrm{AC}_2} \hat{X}_{\mathrm{C}_1} \right)} \\ & + \left(X_{\mathrm{A}} \Gamma_{\mathrm{A}} + X_{\mathrm{B}} \Gamma_{\mathrm{B}} + X_{\mathrm{C}} \Gamma_{\mathrm{C}} \right) f_{\mathrm{A}} f_{\mathrm{C}} B_{\mathrm{A}_1 \mathrm{C}_1} \\ & + (f_{\mathrm{A}} + f_{\mathrm{B}})(X_{\mathrm{A}} + X_{\mathrm{B}}) \left(\Delta \overline{H}^{\mathrm{ex}}_{\mathrm{AB}} \right)^* + (f_{\mathrm{B}} + f_{\mathrm{C}})(X_{\mathrm{B}} + X_{\mathrm{C}}) \left(\Delta \overline{H}^{\mathrm{ex}}_{\mathrm{BC}} \right)^* \end{aligned} \tag{9}$$

for one mole of ternary solution. Most of the specific elements of the model eqn. (3) have been removed, with only the weighting factors required to relate f_i to the composition of the system. The single $B_{\mathrm{A}_1\mathrm{C}_1}$ binary interaction parameter, which must normally be evaluated, will be equal to zero in the case of the acetone + chloroform system. This simplification arises because the numerical values of the two equilibrium constants, K^x_{AC} and $K^x_{\mathrm{AC}_2}$, and standard reaction enthalpies, $\Delta \overline{H}^0_{\mathrm{AC}}$ and $\Delta \overline{H}^0_{\mathrm{AC}_2}$, were calculated assuming that $B_{\mathrm{A}_1\mathrm{C}_1} = 0$. The two $(\Delta \overline{H}^{\mathrm{ex}}_{\mathrm{ij}})^*$ terms in eqn. (9) correspond to actual experimental excess enthalpies of the binary system at X^0_i and X^0_j. The predictive equation is independent of the manner in which the binary data are mathematically represented.

Unfortunately, the mole fractions in the chemical contribution term refer to the "true" concentrations in the associated solution. The stoichiometric compositions (X_{A}, X_{B} and X_{C}) are related to true mole fractions via

$$X_{\mathrm{A}} = \frac{\hat{X}_{\mathrm{A}_1} + \hat{X}_{\mathrm{AC}} + \hat{X}_{\mathrm{AC}_2}}{1 + \hat{X}_{\mathrm{AC}} + 2\hat{X}_{\mathrm{AC}_2}} \tag{10}$$

$$X_{\mathrm{B}} = \frac{\hat{X}_{\mathrm{B}}}{1 + \hat{X}_{\mathrm{AC}} + 2\hat{X}_{\mathrm{AC}_2}} \tag{11}$$

$$X_{\mathrm{C}} = \frac{\hat{X}_{\mathrm{C}_1} + \hat{X}_{\mathrm{AC}} + 2\hat{X}_{\mathrm{AC}_2}}{1 + \hat{X}_{\mathrm{AC}} + 2\hat{X}_{\mathrm{AC}_2}} \tag{12}$$

Since we were unable to express explicitly the true mole fractions $\hat{X}_{\mathrm{A}_1}$ and $\hat{X}_{\mathrm{C}_1}$ in terms of the stoichiometric mole fractions, eqns. (10)–(12) were solved by using a trial-and-error method. Assumed values of $\hat{X}_{\mathrm{A}_1}$ and $\hat{X}_{\mathrm{C}_1}$ for a given ternary mixture were varied until eqns. (10)–(12) gave the experimental composition. This computational procedure is inconvenient, but not too time-consuming. Acetone and chloroform form fairly weak association complexes and the monomeric mole fractions differ slightly from the stoichiometric values.

EXCESS ENTHALPIES OF TERNARY ACETONE + CYCLOHEXANE + CHLOROFORM MIXTURES

Table 1 compares the experimental excess enthalpies with the calculated values based on eqn. (9). Careful examination of Table 1 reveals that there are two sets of predicted values; columns 4 and 5 versus columns 6 and 7. There is little difference between the predicted values calculated with molar-volume weighting factors (columns 4 and 6) and the corresponding values based on weighting factors evaluated from acetone + cyclohexane and cyclohexane + chloroform binary data (columns 5 and 7). The $\Gamma_{\mathrm{Acetone}}/\Gamma_{\mathrm{CHCl_3}}$ weighting-factor ratio could not be calculated from the measured binary properties as the $X_A^0 X_C^0 \Gamma_A \Gamma_C B_{A_1C_1}/(X_A^0 \Gamma_A + X_C^0 \Gamma_C)$ term always equals zero for an ideal associated solution.

The primary difference in the two sets of predicted values results from the different association parameters used. Apelblat et al. [28] reported "best" equilibrium constants, $K_{AC}^x = 1.148$ and $K_{AC_2}^x = 0.890$, and standard reaction enthalpies, $\Delta \bar{H}_{AC}^0 = -10.3$ kJ mol^{-1} and $\Delta \bar{H}_{AC_2}^0 = -20.1$ kJ mol^{-1}, after critically evaluating published enthalpic and free-energy data determined over a broad (10–90 ° C) temperature interval. The authors noted in their discussion that there was excellent agreement between literature $\Delta \bar{H}_{AC}^0$ values and significant scatter in $\Delta \bar{H}_{AC_2}^0$ values. A numerical value of $\Delta \bar{H}_{AC_2}^0 = -20.1$ kJ mol^{-1} was considerably larger than values reported by three other research groups. In comparison, Matsui et al. [29] obtained their two equilibrium constants, $K_{AC}^x = 0.967$ and $K_{AC_2}^x = 1.117$, and standard reaction enthalpies, $\Delta \bar{H}_{AC}^0 = -10.3$ kJ mol^{-1} and $\Delta \bar{H}_{AC_2}^0 = -13.0$ kJ mol^{-1}, from experimental data measured at 25 ° C, which happens to correspond to the temperature of the ternary acetone + cyclohexane + chloroform system. It is not too surprising that this latter set of association parameters provides the better prediction of ternary properties, with the average absolute deviation between calculated and observed values being on the order of ± 39 J mol^{-1} in the case of binary-data evaluated weighting factors. For several of the ternary compositions, the predicted value falls within (or nearly within) the experimental uncertainty of the measured value. In comparing predicted and measured values, it must be remembered that each calculated value does have a propagated uncertainty which is a direct result of the experimental uncertainties associated with the inputted binary data. At present, we are unable to explain the few large deviations. We do believe, however, that re-evaluating the equilibrium constants and standard reaction enthalpies with $B_{A_1C_1} \neq 0$ might give a more realistic set of association parameters. The predicted values do depend on the numerical values of

TABLE 1

Comparisons between experimental and predicted excess enthalpies (J mol^{-1}) for ternary acetone (A) + cyclohexane (B) + chloroform (C) mixtures at 25 ° C

X_A	X_B	$(\Delta\bar{H}^{ex})^{exp}$	Predicted values (J mol^{-1})			
			$\Delta\bar{H}^{ex\ a}$	$\Delta\bar{H}^{ex\ b}$	$\Delta\bar{H}^{ex\ c}$	$\Delta\bar{H}^{ex\ d}$
0.4551	0.0779	−1236.1	−1563.1	−1561.3	−1273.9	−1272.1
0.5715	0.0976	−836.5	−1045.0	−1044.8	−838.3	−838.1
0.3196	0.0547	−1378.3	−1786.0	−1783.9	−1442.9	−1440.8
0.3048	0.0522	−1372.5	−1747.8	−1745.8	−1430.8	−1428.8
0.4052	0.0693	−1334.8	−1693.3	−1691.1	−1387.6	−1385.4
0.3452	0.0590	−1385.3	−1763.7	−1761.4	−1445.9	−1443.6
0.3684	0.0629	−1389.1	−1753.7	−1751.5	−1432.3	−1430.1
0.4204	0.0872	−1188.1	−1537.9	−1538.2	−1248.1	−1248.4
0.5287	0.3487	770.0	790.8	756.1	850.1	815.4
0.3946	0.4479	779.3	815.1	759.5	885.9	830.3
0.6320	0.2722	753.6	739.8	719.9	786.5	766.6
0.7602	0.1774	620.6	603.6	596.8	636.0	629.2
0.5259	0.3507	776.8	788.3	753.3	851.4	816.4
0.4011	0.4431	770.1	814.5	759.9	886.5	831.9
0.4508	0.4063	775.4	810.1	763.2	872.5	825.6
0.4592	0.4001	768.1	806.2	760.6	871.8	826.2
0.6938	0.2264	703.4	685.7	673.1	724.9	712.3
0.4335	0.2105	−372.0	−591.6	−620.4	−372.7	−401.5
0.4155	0.1544	−748.9	−1024.0	−1039.3	−784.5	−799.8
0.3434	0.2440	−313.4	−521.2	−563.1	−325.3	−367.2
0.7005	0.1119	−231.8	−336.9	−338.9	−231.8	−233.8
0.3499	0.2415	−313.2	−530.9	−571.7	−333.5	−374.3
0.6338	0.1358	−317.9	−417.7	−434.8	−284.4	−301.5
0.4653	0.0870	−1155.5	−1520.5	−1519.8	−1190.8	−1190.1
0.6202	0.0617	−1012.8	−1199.7	−1195.4	−997.4	−993.1
0.2970	0.1138	−983.0	−1345.0	−1354.2	−1064.9	−1074.1
0.7122	0.0468	−805.5	−945.3	−941.3	−803.7	−799.7
0.4589	0.0896	−1160.7	−1451.7	−1451.6	−1180.3	−1180.2
0.3291	0.1091	−1058.1	−1401.9	−1408.9	−1123.7	−1130.7
0.7170	0.0458	−792.9	−939.5	−935.6	−793.6	−789.7

[a] Values based on the association parameters of Apelblat et al. [28] ($K^x_{AC} = 1.148$, $K^x_{AC_2} = 0.890$, $\Delta\bar{H}^0_{AC} = -10.3$ kJ mol^{-1} and $\Delta\bar{H}^0_{AC_2} = -20.1$ kJ mol^{-1}) and molar volumes equal to weighting factors. [b] Values based on the association parameters of Apelblat et al. [28] and weighting factors calculated from binary acetone + cyclohexane and cyclohexane + chloroform data. [c] Values based on the association parameters of Matsui et al. [29] ($K^x_{AC} = 0.967$, $K^x_{AC_2} = 1.117$, $\Delta\bar{H}^0_{AC} = -10.3$ kJ mol^{-1} and $\Delta\bar{H}^0_{AC_2} = -13.0$ kJ mol^{-1}) and molar volumes equal to weighting factors. [d] Values based on the association parameters of Matsui et al. [29] and weighting factors calculated from binary acetone + cyclohexane and cyclohexane + chloroform data.

K^x_{AC}, $K^x_{AC_2}$, $\Delta\bar{H}^0_{AC}$ and $\Delta\bar{H}^0_{AC_2}$ inputted into the enthalpy calculations. As shown in our earlier solubility studies involving carbazole in binary alkane + dibutyl ether [5,6,8,19] and chloroalkane + dibutyl ether [7,20] solvent mixtures, the neglect of weak non-specific interactions can have a rather dramatic effect on the calculated association parameters.

Readers are reminded that there is an important difference between eqn. (9) and the many empirical equations developed specifically for predicting multicomponent thermodynamic properties. Equation (9) is based on an associated solution mixing model, and thus provides valuable insight into molecular interactions in solution. In comparison, empirical equations are often much better at predicting desired thermodynamic properties, but they cannot estimate association parameters such as equilibrium constants or standard reaction enthalpies. Solution models for three-component systems, such as the one developed in this work, enable one to examine the effect of inert co-solvents (or inert components) on calculated association parameters, provided that sufficient data are available. Both volumetric and enthalpic data for several ternary acetone + alkane + chloroform systems are needed to test further the limitations and applications of eqn. (9). It is only through testing, of which failures are an important part, that we recognize the deficiencies in our ability to thermodynamically describe a particular non-electrolyte system. Deficiencies, once recognized, will prompt the future development of better thermodynamic solution models.

APPENDIX

A_{ij}	Binary interaction parameters for components i and j used in the Gibbs free energy model.
B_{ij}	Binary interaction parameter for components i and j used in the excess enthalpy model.
f_i	Stoichiometric weighted-mole fraction of component i.
$\hat{f}_i$	Weighted mole fraction of component i, calculated assuming an associated solution.
ΔG^{mix}	Gibbs free energy of mixing.
$\Delta \bar{G}_{ij}^{\text{ex}}$	Excess molar Gibbs free energy of mixing of the ij binary system based on Raoult's law.
$\Delta \bar{G}_{ij}^{\text{fh}}$	Excess molar Gibbs free energy of mixing of the ij binary system based on the Flory–Huggins model for solution ideality.
$\Delta \bar{H}^{\text{ex}}$	Excess molar enthalpy of mixing.
$(\Delta \bar{H}_{ij}^{\text{ex}})^*$	Excess molar enthalpy of mixing of the ij binary system at a mole-fraction composition $X_i^0 = 1 - X_j^0 = X_i/(X_i + X_j)$.
$\Delta \bar{H}_{\text{AC}}^0$	Standard reaction enthalpy for the formation of the AC molecular complex.
$\Delta \bar{H}_{\text{AC}_2}^0$	Standard reaction enthalpy for the formation of the AC_2 molecular complex.
K_{AC}^x	Mole-fraction based equilibrium constant for the formation of the AC complex.

$K^{x}_{\mathrm{AC}_2}$	Mole-fraction based equilibrium constant for the formation of the AC_2 molecular complex.
K^{ϕ}_{AC}	Volume-fraction based equilibrium constant for the formation of the AC complex.
n_i	Stoichiometric number of moles of component *i*.
$\hat{n}_i$	True number of moles of component *i* in the associated solution.
$\bar{V}_i$	Molar volume of component *i*.
X_i	Stoichiometric mole fraction of component *i*.
$\hat{X}_i$	True mole fraction of component *i* in the associated solution.
X_i^0, X_j^0	Mole fraction composition of the *ij* binary mixture, calculated as if the third component were not present.
ϕ_i	Ideal volume fraction of component *i*.
$\hat{\phi}_i$	Ideal volume fraction of component *i*, calculated assuming an associated solution.
$\phi_{\mathrm{A}}^{\mathrm{sat}}$	Ideal volume fraction solubility of solute.
Γ_i	Weighting factor of component *i*.

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