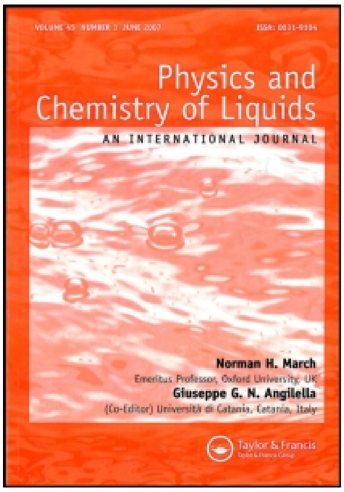

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Thermochemical Investigations of Associated Solutions: 8. Development of Model for Systems Containing AC and AC_2 Molecular Complexes

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THERMOCHEMICAL INVESTIGATIONS OF ASSOCIATED SOLUTIONS:

8. DEVELOPMENT OF MODEL FOR SYSTEMS CONTAINING AC AND AC$_2$ MOLECULAR COMPLEXES

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A conventional nonelectrolyte solution which has led to successful predictive expressions for the thermomechanical 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 volume 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 nonspecific interactions between the uncomplexed and associated species in solution. Ten A_{ij} parameters are initially needed to describe all binary nonspecific interactions present. Simplifying approximations and mathematical manipulations reduce the number of binary interaction parameters to only $3A_{ij}$ values. Expressions derived from the general mixing model are used to estimate excess volumes of ternary acetone + cyclohexane + chloroform mixtures.

KEY WORDS: Thermodynamic properties-associated solutions, associated solutions-excess volumes, ternary excess volumes, molecular complexation.

LIST OF SYMBOLS

A_{ij}	binary interaction parameter for components i and j used in Gibbs free energy model
B_{ij}	binary interaction parameter for components i and j used in excess volume 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
$\Delta \bar{G}_{ij}^{\mathrm{ex}}$	excess molar Gibbs free energy of the ij binary mixture based on Raoult's law
$\Delta \bar{G}_{ij}^{\mathrm{fh}}$	excess molar Gibbs free energy of the ij binary mixture based on the Flory-Huggins model for solution ideality.

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K^x_{AC}	mole fraction based equilibrium constant for the formation of the AC complex
$K^x_{AC_2}$	mole fraction based equilibrium constant for the formation of the AC_2 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
$(\Delta \bar{V}^{ex}_{ij})^*$	excess molar volume of the ij binary mixture at a mole fraction composition $X^0_i = 1 - X^0_j = X_i/(X_i + X_j)$
$\Delta \bar{V}^0_{AC}$	standard reaction volume for the formation of the AC molecular complex
$\Delta \bar{V}^0_{AC_2}$	standard reaction volume for the formation of the AC_2 molecular complex
X_i	stoichiometric mole fraction of component i
$\hat{X}_i$	mole fraction of component i, calculated assuming an associated solution
X^0_i, X^0_j	mole fraction composition of the ij binary mixture, calculated as if the third component were not present
X^{sat}_A	mole fraction solubility of solute
ϕ_i	ideal volume fraction of component i
$\hat{\phi}_i$	ideal volume fraction of component i, calculated assuming an associated solution
ϕ^{sat}_A	ideal volume fraction solubility of solute
Γ_i	weighting factor of component i

INTRODUCTION

For many years the chemical industry has recognized the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow and heat transfer. The development of flow calorimeters, continuous dilution dilatometers and vibrating-tube densimeters has enabled the experimental determination of excess enthalpies, heat capacities and volumes of nonelectrolyte liquid mixtures with convenience and accuracy. The utilization of continuous dilution methods, combined with modern chromatographic head-space sampling techniques, has reduced the experimental time needed for the determination of excess Gibbs energies and activity coefficients through conventional vapor pressure measurements. But even with today's modern instrumentation, experimental measurements of thermodynamic properties become progressively more difficult and time-consuming with each additional component beyond binary mixtures.

In the chemical literature, properties for binary systems are relatively abundant, properties for ternary systems are scarce and properties for higher-order multicomponent systems are virtually nonexistent. To address this problem, researchers have turned to predictive methods as a way to generate desired quantities. Numerous equations have been derived separately in the metallurgical and chemical industries. Hillert[1] reviewed expressions used for metallic systems and suggested new ones which in one case coincided with an equation proposed for organic mixtures. Bertrand, Acree and Burchfield[2,3] examined published methods to estimate excess enthalpies, excess volumes, excess free energies and several physical properties. The authors illustrated the accuracy of select literature methods and proposed a new method based on normalized weighting factors calculated from binary data. Prchal[4,5] reviewed the prediction and correlation of ternary excess enthalpy data. Acree[6] devoted two chapters of his monograph on thermodynamic properties of nonelectrolyte solutions to describe many of the empirical expressions for predicting multicomponent properties from either binary data or group contribution parameters. More recently, Pando *et al.*[7] discussed the limitations of various predictive methods using enthalpy data for 42 ternary systems. For the most part, the predictive methods provide fairly reasonable estimates for noncomplexing systems. There still remains, however, the need to develop better mixing models to describe the more nonideal associated solutions which are encountered in organic[6,7] and liquid metal[8] systems.

Earlier papers in this series[9–15] presented the calculation of volume fraction based and mole fraction based solute–solvent association constants from:

$$A_1 + C_1 \rightleftharpoons AC \qquad K^{\phi}_{AC} = \hat{\phi}_{AC}/\hat{\phi}_{A_1}\hat{\phi}_{C_1}$$

$$K^{x}_{AC} = \hat{X}_{AC}/\hat{X}_{A_1}\hat{X}_{C_1}$$

$$\ln\phi^{\text{sat}}_A = \phi^0_B \ln(\phi^{\text{sat}}_A)_B + \phi^0_C \ln(\phi^{\text{sat}}_A)_C + \ln[1 + \bar{V}_A K^{\phi}_{AC}\phi^0_C/(\bar{V}_A + \bar{V}_C)] - \phi^0_C \ln[1 + \bar{V}_A K^{\phi}_{AC}/(\bar{V}_A + \bar{V}_C)] + \frac{\bar{V}_A\,\Delta\bar{G}^{\text{fh}}_{BC}}{RT(X^0_B\bar{V}_B + X^0_C\bar{V}_C)} \tag{1}$$

$$\ln X^{\text{sat}}_A = \phi^0_B \ln(X^{\text{sat}}_A)_B + \phi^0_C \ln(X^{\text{sat}}_A)_C + \ln[1 + K^x_{AC}X^0_C] - \phi^0_C \ln[1 + K^x_{AC}] + \frac{\bar{V}_A\,\Delta\bar{G}^{\text{ex}}_{BC}}{RT(X^0_B\bar{V}_B + X^0_C\bar{V}_C)} \tag{2}$$

measured solubility as a function of solvent composition and the excess Gibbs free energy of the binary solvent mixture. The superscript (0) denotes initial solvent compositions which are calculated as if the solute were not present. (The nomenclature is defined in the List of Symbols at the start of this paper.)

McCargar and Acree[11,12] compared values of the carbazole–dibutyl ether association constant calculated from experimental carbazole solubilities in ten binary dibutyl ether + alkane solvent mixtures. A simple stoichiometric complexation model based entirely on specific solute–solvent interactions required two equilibrium constants to mathematically describe the solubility data. Calculated equilibrium constants in isooctane cosolvent were significantly different from values for the cyclooctane system. In comparison, Eqs (1) and (2), derived from the nearly ideal binary solvent (NIBS) model, described the experimental carbazole solubilities to within an average deviation of 2% using a single carbazole–dibutyl ether association constant. Variation of the calculated equilibrium constant with inert cosolvent was less in the case of K^{ϕ}_{AC}, the numerical values ranging from $K^{\phi}_{AC} = 22$ for *n*-heptane to $K^{\phi}_{AC} = 30$ for isooctane. The success of Eqs (1) and (2) is even more remarkable if one realizes the carbazole mole fraction solubilities covered a 25-fold range, and the inert cosolvents included both small (cyclohexane, *n*-hexane) and large (*n*-hexadecane, squalane) hydrocarbons.

As a continuation of our studies on thermodynamic properties of associated solutions, we extend the basic NIBS model to excess volumes. Expressions are derived for excess volumes of a ternary system containing AC and AC_2 molecular complexes. The derived expression enables the excess volume of ternary mixtures to be estimated from binary data. Application of the predictive expression is illustrated using previously published data for the acetone + cyclohexane + chloroform system.[16]

DEVELOPMENT OF THERMODYNAMIC MODEL

Thermodynamic models of associated nonelectrolyte 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 nonspecific interactions between the uncomplexed and associated species in solution. Other thermodynamic properties can also be expressed as the sum of a chemical and physical contribution. It is often more convenient, though, 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:

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

$$f_i = n_i\Gamma_i \Bigg/ \left(\sum_{j=1}^{N} n_j\Gamma_j\right) \tag{3}$$

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 extremum 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 weighting factors with molar volumes requires that a specified condition, such as 25°C and 1 atm, or to an extrapolated state such as "close packed" volume.

Application of Eq. (3) to a pentanary system

$$A_1 + C_1 \rightleftharpoons AC \qquad K^{x}_{AC} = \hat{X}_{AC}/\hat{X}_{A_1}\hat{X}_{C_1}$$

$$A_1 + 2C_1 \rightleftharpoons AC_2 \qquad K^{x}_{AC_2} = \hat{X}_{AC_2}/\hat{X}_{A_1}\hat{X}^2_{C_1}$$

yields the following expression for the Gibbs free energy of mixing:

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

Chemical potentials of the individual components relative to the pure liquids ($\mu_i^{\bullet}$) are obtained through the appropriate differentiation:

$$\begin{aligned}\hat{\mu}_{A_1} - \mu_A^{\bullet} = {} & RT\ln\hat{X}_{A_1} + \Gamma_A[\hat{f}_B(1-\hat{f}_{A_1})A_{A_1B} + \hat{f}_{C_1}(1-\hat{f}_{A_1})A_{A_1C_1} \\ & + \hat{f}_{AC}(1-\hat{f}_{A_1})A_{A_1AC} + \hat{f}_{AC_2}(1-\hat{f}_{A_1})A_{A_1AC_2} - \hat{f}_B\hat{f}_{C_1}A_{BC_1} - \hat{f}_B\hat{f}_{AC}A_{BAC} \\ & - \hat{f}_B\hat{f}_{AC_2}A_{BAC_2} - \hat{f}_{C_1}\hat{f}_{AC}A_{C_1AC} - \hat{f}_{C_1}\hat{f}_{AC_2}A_{C_1AC_2} - \hat{f}_{AC}\hat{f}_{AC_2}A_{ACAC_2}]\end{aligned} \tag{5}$$

and

$$\begin{aligned}\hat{\mu}_B - \mu_B^{\bullet} = {} & RT\ln\hat{X}_B + \Gamma_B[\hat{f}_{A_1}(1-\hat{f}_B)A_{A_1B} + \hat{f}_{C_1}(1-\hat{f}_B)A_{BC_1} + \hat{f}_{AC}(1-\hat{f}_B)A_{BAC} \\ & + \hat{f}_{AC_2}(1-\hat{f}_B)A_{BAC_2} - \hat{f}_{A_1}\hat{f}_{C_1}A_{A_1C_1} - \hat{f}_{A_1}\hat{f}_{AC}A_{A_1AC} - \hat{f}_{A_1}\hat{f}_{AC_2}A_{A_1AC_2} \\ & - \hat{f}_{C_1}\hat{f}_{AC}A_{C_1AC} - \hat{f}_{C_1}\hat{f}_{AC_2}A_{C_1AC_2} - \hat{f}_{AC}\hat{f}_{AC_2}A_{ACAC_2}]\end{aligned} \tag{6}$$

and

$$\begin{aligned}\mu_{C_1} - \mu_C^{\bullet} = {} & RT\ln\hat{X}_{C_1} + \Gamma_C[\hat{f}_{A_1}(1-\hat{f}_{C_1})A_{A_1C_1} + \hat{f}_B(1-\hat{f}_{C_1})A_{BC_1} \\ & + \hat{f}_{AC}(1-\hat{f}_{C_1})A_{C_1AC} + \hat{f}_{AC_2}(1-\hat{f}_{C_1})A_{C_1AC_2} - \hat{f}_{A_1}\hat{f}_B A_{A_1B} - \hat{f}_{A_1}\hat{f}_{AC}A_{A_1AC} \\ & - \hat{f}_{A_1}\hat{f}_{AC_2}A_{A_1AC_2} - \hat{f}_B\hat{f}_{AC}A_{BAC} - \hat{f}_B\hat{f}_{AC_2}A_{BAC_2} - \hat{f}_{AC}\hat{f}_{AC_2}A_{ACAC_2}]\end{aligned} \tag{7}$$

As shown in many thermodynamic textbooks [e.g., Acree[6]], the chemical potential of stoichiometric component A (and also C) is equal to the chemical potential of the monomeric (uncomplexed) species in the solution:

$$\mu_C = \hat{\mu}_{C_1} \quad \text{and} \quad \mu_A = \hat{\mu}_{A_1}$$

Combining Eqs (5)–(7), the Gibbs free energy of mixing of the ternary solution (A, B and C) can be written as:

$$\begin{aligned}\Delta G^{\text{mix}} = {} & RT[\hat{n}_A\ln\hat{X}_{A_1} + \hat{n}_B\ln\hat{X}_B + \hat{n}_C\ln X_{C_1}] + n_A\Gamma_A[f_B A_{A_1B} + \hat{f}_{C_1}(1-\hat{f}_{A_1})A_{A_1C_1} \\ & + \hat{f}_{AC}(1-\hat{f}_{A_1})A_{A_1AC} + \hat{f}_{AC_2}(1-\hat{f}_{A_1})A_{A_1AC_2} - \hat{f}_{C_1}\hat{f}_{AC}A_{C_1AC} - \hat{f}_{C_1}\hat{f}_{AC_2}A_{C_1AC_2} \\ & - \hat{f}_{AC}\hat{f}_{AC_2}A_{ACAC_2}] + n_B\Gamma_B[f_C A_{BC_1} - \hat{f}_{A_1}\hat{f}_{C_1}A_{A_1C_1} - \hat{f}_{A_1}\hat{f}_{AC}A_{A_1AC} \\ & - \hat{f}_{A_1}\hat{f}_{AC_2}A_{A_1AC_2} - \hat{f}_{C_1}\hat{f}_{AC}A_{C_1AC} - \hat{f}_{C_1}\hat{f}_{AC_2}A_{C_1AC_2} - \hat{f}_{AC}\hat{f}_{AC_2}A_{ACAC_2}] \\ & + n_C\Gamma_C[\hat{f}_{A_1}(1-\hat{f}_{C_1})A_{A_1C_1} + \hat{f}_{AC}(1-\hat{f}_{C_1})A_{C_1AC} + \hat{f}_{AC_2}(1-\hat{f}_{C_1})A_{C_1AC_2} \\ & - \hat{f}_{A_1}\hat{f}_{AC}A_{A_1AC} - \hat{f}_{A_1}\hat{f}_{AC_2}A_{A_1AC_2} - \hat{f}_{AC}\hat{f}_{AC_2}A_{ACAC_2}]\end{aligned} \tag{8}$$

where $n_A = \hat{n}_{A_1} + \hat{n}_{AC} + \hat{n}_{AC_2}$ and $n_C = \hat{n}_{C_1} + \hat{n}_{AC} + 2\hat{n}_{AC_2}$. Two interaction parameters, A_{BAC} and A_{BAC_2}, are removed from the thermodynamic model as a natural consequence of expressing the Gibbs free energy in terms of the stoichiometric three-component solution. While this simplification does reduce the number of parameters that must be evaluated, Eq. (8) still contains $8A_{ij}$ terms which is far too many for practical applications. Treatment of all interaction parameters involving the AC and AC_2 complexes in a manner similar to that employed by Bertrand[17] for the chloroform-triethylamine complex leads to

$$\begin{aligned}
A_{A_1AC} &= \Gamma_C^2(\Gamma_A + \Gamma_C)^{-2}A_{A_1C_1}\\
A_{C_1AC} &= \Gamma_A^2(\Gamma_A + \Gamma_C)^{-2}A_{A_1C_1}\\
A_{A_1AC_2} &= 4\Gamma_C^2(\Gamma_A + 2\Gamma_C)^{-2}A_{A_1C_1}\\
A_{C_1AC_2} &= \Gamma_A^2(\Gamma_A + 2\Gamma_C)^{-2}A_{A_1C_1}\\
A_{ACAC_2} &= \Gamma_C^2\Gamma_A^2(\Gamma_A + \Gamma_C)^{-2}(\Gamma_A + 2\Gamma_C)^{-2}A_{A_1C_1}
\end{aligned}$$

Substitution of these approximations into Eq. (8), after suitable mathematical manipulations, enables the Gibbs free energy to be expressed

$$\begin{aligned}
\Delta G^{\text{mix}} = RT[n_A \ln \hat{X}_{A_1} + n_B \ln \hat{X}_B + n_C \ln \hat{X}_{C_1}] + (n_A\Gamma_A + n_B\Gamma_B + n_C\Gamma_C)[f_A f_B A_{A_1B}\\
+ f_A f_C A_{A_1C_1} + f_B f_C A_{BC_1}] \qquad (9)
\end{aligned}$$

In terms of only three interaction parameters. Simplification of the general thermodynamic mixing model, Eq. (4), resulted primarily because of the judicious treatment of the binary interaction parameters. Several other methods[18,19] have been proposed for treating $A_{A_1\,\text{Complex}}$ and $A_{C_1\,\text{Complex}}$ parameters. To our knowledge, only the method of Bertrand permits reduction to the simple three-parameter expression.

PREDICTIVE APPLICATION OF THERMODYNAMIC MODEL

In the absence of complexation ($K_{AC} = 0$ and $K_{AC_2} = 0$), Eq (9) 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 $\hat{X}_{C_1} = X_C$). The NIBS equations have been shown to be quite dependable for estimating heats of solution,[20] gas-liquid partition coefficients,[21,22] and solute solubilities[6,23–25] in binary systems that are free of association. In addition, the BAB equation[2,3] for predicting integral thermodynamic excess properties of multi-component systems from measured binary data was derived from the generalized noncomplexing form of Eq. (9). 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 (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), and then normalized to insure 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 system shows a point of inflection when plotted versus mole fraction. Approximation of weighting factors with molar volumes does simplify the predictive method. For a number of systems studied, this approximation only affects the predictive accuracy slightly.

Application of Eq. (9) 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 nonexistent. A search of the literature, however, did uncover volumetric data for the acetone + cyclohexane + chloroform system.[16] The acetone + chloroform subbinary system has been widely studied since Dolezalek[26] noted that observed deviations from Raoult's law could be explained on the basis of molecular complexation between acetone and chloroform molecules in solution. Apelblat *et al.*[27] reviewed existing data for the acetone + chloroform system, and showed that 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 volumes of the acetone + cyclohexane + chloroform system can be obtained by differentiating Eq. (9) with respect to pressure.

$$\Delta\bar{V}^{\mathrm{ex}} = \frac{\hat{X}_{A_1}\hat{X}_{C_1}(K^x_{AC}\Delta\bar{V}^0_{AC} + K^x_{AC_2}\Delta\bar{V}^0_{AC_2}\hat{X}_{C_1})}{1 + \hat{X}_{A_1}\hat{X}_{C_1}(K^x_{AC} + 2\hat{X}_{C_1}K^x_{AC_2})} + (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C) \times [f_A f_B B_{A_1B} + f_A f_C B_{A_1C_1} + f_B f_C B_{BC_1}] \tag{10}$$

Weighting factors are assumed to be independent of pressure and $B_{ij} = (\partial A_{ij}/\partial P)$. The standard reaction volumes for the formation of the AC and AC_2 complexes are denoted as $\Delta\bar{V}^0_{AC}$ and $\Delta\bar{V}^0_{AC_2}$, respectively. Inspection of Eq. (10) reveals that for model systems obeying this equation, the volumetric properties of the two non-complexing contributive binary systems would obey (per mole of binary solution)

$$(\Delta\bar{V}^{\mathrm{ex}}_{AB})^* = X^0_A X^0_B \Gamma_A \Gamma_B B_{A_1B}/(X^0_A\Gamma_A + X^0_B\Gamma_B)$$

and

$$(\Delta\bar{V}^{\mathrm{ex}}_{BC})^* = X^0_B X^0_C \Gamma_B \Gamma_C B_{BC_1}/(X^0_B\Gamma_B + X^0_C\Gamma_C)$$

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

Equation (10) can then be rearranged to the following form:

$$\Delta\bar{V}^{\mathrm{ex}} = \frac{\hat{X}_{A_1}\hat{X}_{C_1}(K^x_{AC}\Delta\bar{V}^0_{AC} + K^x_{AC_2}\Delta\bar{V}^0_{AC_2}\hat{X}_{C_1})}{1 + \hat{X}_{A_1}\hat{X}_{C_1}(K^x_{AC} + 2\hat{X}_{C_1}K^x_{AC_2})} + (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C)f_A f_C B_{A_1C_1} + (f_A + f_B)(X_A + X_B)(\Delta\bar{V}^{\mathrm{ex}}_{AB})^* + (f_B + f_C)(X_B + X_C)(\Delta\bar{V}^{\mathrm{ex}}_{BC})^* \tag{11}$$

for one mole of ternary solution. Most of the specific elements of the model Eq. (4) have been removed, with only the weighting factors required to relate f_i to the composition of the system. The single $B_{A_1C_1}$ binary interaction parameter, which must normally be evaluated, will equal zero in the case of the acetone + chloroform. This simplification arises because the numerical values of the two equilibrium constants, $K^x_{AC} = 1.148$ and $K^x_{AC_2} = 0.890$, and standard reaction volumes, $\Delta \bar{V}^0_{AC} = 0.42\ \text{cm}^3/\text{mol}$ and $\Delta \bar{V}^0_{AC_2} = -4.40\ \text{cm}^3/\text{mol}$, were calculated assuming that $B_{A_1C_1} = 0$. The two $(\Delta \bar{V}^{ex}_{ij})^*$ terms in Eq. (11) correspond to actual experimental excess volumes of the binary systems at X^0_i and X^0_j. The predictive equation is independent of the manner in which the binary data is mathematically represented.

Mole fractions in the chemical contribution term refer to the "true" concentrations in the associated solution. Stoichiometric compositions (X_A, X_B and X_C) are related to the true mole fractions *via*

$$X_A = \frac{\hat{X}_{A_1} + \hat{X}_{AC} + \hat{X}_{AC_2}}{1 + \hat{X}_{AC} + 2\hat{X}_{AC_2}} \tag{12}$$

$$X_B = \frac{\hat{X}_B}{1 + \hat{X}_{AC} + 2\hat{X}_{AC_2}} \tag{13}$$

$$X_C = \frac{\hat{X}_{C_1} + \hat{X}_{AC} + 2\hat{X}_{AC_2}}{1 + \hat{X}_{AC} + 2\hat{X}_{AC_2}} \tag{14}$$

Since we were unable to explicitly express the true mole fractions $\hat{X}_{A_1}$ and $\hat{X}_{C_1}$ in terms of the stoichiometric mole fractions, Eqs (12)-(14) were solved by a trial and error method. Assumed values of $\hat{X}_{A_1}$ and $\hat{X}_{C_1}$ for a given ternary mixture were varied until Eqs (12)-(14) gave the experimental composition. This computational procedure is inconvenient, but not too time-consuming. Acetone and chloroform form fairly weak association complexes as indicated by the magnitude of the two equilibrium constants. Monomeric mole fractions differ slightly from the stoichiometric values.

Table 1 compares experimental excess molar volumes to calculated values based on Eq. (11). Careful examination of the last 3 columns of Table 1 reveals that the predictive expression does provide reasonable estimates of $\Delta \bar{V}^{ex}$ at several ternary compositions. There is little difference between predicted values calculated with molar volume weighting factors and values based on weighting factors evaluated from acetone + cyclohexane and cyclohexane + chloroform binary data. The $\Gamma_{\text{Acetone}}/\Gamma_{\text{CHCl}_3}$ weighting factor ratio could not be calculated from the measured binary properties as the $X^0_A X^0_C \Gamma_A \Gamma_C (X^0_A \Gamma_A + X^0_C \Gamma_C)^{-1} B_{A_1C_1}$ term always equals zero for an ideal associated solution. Significant deviations are noted between experimental and predicted values for a number of ternary compositions. At present, we are unable to explain why the predictive expression fails. We do note, however, that in instances where Eq. (11) fails badly, the estimated $\Delta \bar{V}^{ex}$ is always considerably more positive than the measured value. The two physical interaction terms, $(X_A + X_B)(f_A + f_B)(\Delta \bar{V}^{ex}_{AB})^*$ and $(X_B + X_C)(f_B + f_C)(\Delta \bar{V}^{ex}_{BC})^*$ are always positive and their sum comprises more than 70% of the "positive character" of the predicted value. The contribution in the $\Delta \bar{V}^{ex}$ predictions is both positive and negative, depending upon mixture composition. For several ternary solutions, Eq. (11) appears to mathematically over-estimate the physical interactions relative to the chemical contributions.

Table 1 Comparison between experimental and predicted excess molar volumes for ternary acetone (A) + cyclohexane (B) + chloroform (C) mixtures.

			Eq. (11) *Predictions*[a]	
X_A^0	X_B^0	$\Delta \bar{V}^{ex}$ (*cm*^{3}/*mol*)	$\Delta \bar{V}^{ex}$ (*cm*^{3}/*mol*)	$\Delta \bar{V}^{ex}$ (*cm*^{3}/*mol*)
0.1809	0.7436	0.700	0.742	0.733
0.1230	0.5139	0.565	0.746	0.721
0.1101	0.4524	0.528	0.708	0.685
0.0487	0.1999	0.296	0.356	0.349
0.0125	0.0513	0.086	0.087	0.085
0.2051	0.5070	0.632	0.836	0.809
0.1803	0.4507	0.548	0.777	0.749
0.1610	0.4060	0.503	0.719	0.687
0.0312	0.0333	0.061	0.033	0.033
0.4207	0.5136	0.983	1.055	1.046
0.1884	0.2300	0.290	0.449	0.433
0.0960	0.1172	0.127	0.178	0.173
0.0191	0.0233	0.034	0.025	0.025
0.4305	0.1944	0.447	0.532	0.523
0.4127	0.1863	0.413	0.494	0.486
0.1593	0.0719	0.014	0.050	0.049
0.0886	0.5471	0.558	0.704	0.684
0.0809	0.4993	0.546	0.693	0.674
0.0720	0.4448	0.524	0.665	0.647
0.0675	0.4170	0.505	0.646	0.629
0.0506	0.3127	0.424	0.532	0.520
0.0399	0.2465	0.348	0.467	0.428
0.0281	0.1740	0.277	0.314	0.309
0.5157	0.2329	0.682	0.709	0.697
0.5197	0.2347	0.687	0.715	0.704
0.4009	0.2531	0.564	0.663	0.646
0.3892	0.2877	0.618	0.731	0.712
0.4078	0.3062	0.683	0.786	0.766
0.5718	0.1765	0.578	0.594	0.588
0.5279	0.1793	0.545	0.569	0.563

[a] First column of $\Delta \bar{V}^{ex}$ values calculated assuming that the weighting factors equal molar volumes. Values for the second column are based on weighting factors determined from measured binary data using the method of Bertrand *et al.*[2]

Cyclohexane seems to favor the formation of hydrogen-bonded acetone-chloroform complexes.

Readers are reminded that there is an important difference between Eq. (11) and the many empirical equations developed specifically for predicting multicomponent thermodynamic properties. Equation (11) is based on an associated solution mixing model, and thus provides valuable insight on 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 volumes. Solutions models for three-component systems, such as the one developed in this paper, enable one to examine the effect of inert cosolvents (or inert components) on calculated association parameters, provided that sufficient data is available. Both volumetric and enthalpic data for several ternary acetone + alkane + chloroform systems are needed to further test the limitations and applications of Eq. (11). 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 nonelectrolyte system. Deficiencies once recognized, will prompt the future development of better thermodynamic solution models.

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