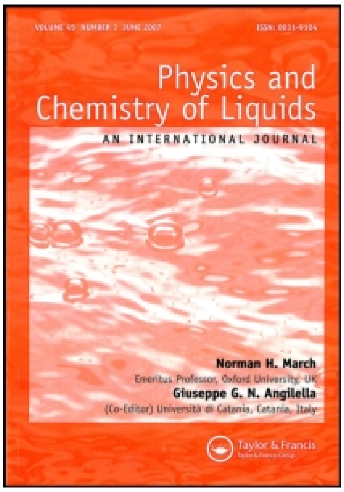

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Comments on "Thermochemical Investigations of Associated Solutions. 8. Development of Model for Systems Containing AC And AC_2 Molecular Complexes"

William E. Acree Jr.[a]; Anita I. Zvaigzne[a]; Sheryl A. Tucker[ab]
[a] Department of Chemistry, University of North Texas, Denton, Texas, USA [b] Kent State University, Kent, Ohio, USA

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COMMENTS ON "THERMOCHEMICAL INVESTIGATIONS OF ASSOCIATED SOLUTIONS. 8. DEVELOPMENT OF MODEL FOR SYSTEMS CONTAINING AC AND AC$_2$ MOLECULAR COMPLEXES"

WILLIAM E. ACREE, JR.,* ANITA I. ZVAIGZNE
and SHERYL A. TUCKER†

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068, USA

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An alternative description of nonspecific interactions is incorporated into our previously proposed mixing model. Expressions are derived for predicting excess volumes of ternary acetone + cyclohexane + chloroform mixtures.

KEY WORDS: Associated solutions, excess molar volumes, nonspecific interactions, ternary systems

In a recent paper[1] appearing in this journal, we proposed a relatively simple mixing model for describing thermodynamic properties of ternary associated solutions

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

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

containing both AC and AC$_2$ molecular complexes. An expression was derived for predicting excess volumes, $\Delta\bar{V}^{ex}$,

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

by assuming that the total solution nonideality could be separated into both chemical and physical contributions. The first term in Eq. (1) represents the chemical contribution which results from the formation of AC and AC$_2$ molecular complexes, and the remaining 3 terms describe the nonspecific physical interactions between the various species in solution. Ten binary B_{ij} interaction parameters were initially introduced into the mixing model to account for nonspecific interactions, but simplifying approximations and mathematical manipulations reduced the number to

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* To whom correspondence should be addressed.

† Currently a student at Kent State University, Kent, Ohio 44242 (USA).

a single $B_{A_1C_1}$ parameter and to 2 $(\Delta\bar{V}_{ij}^{ex})^*$ terms which correspond to actual experimental excess volumes of the AB and BC subbinary systems at mole fractions X_i^0 and X_j^0. The various symbols in Eq. (1) are defined in our earlier paper.

As shown in Table 1, Eq. (1) with $B_{A_1C_1} = 0$ did provide fairly reasonable predictions of the experimental $\Delta\bar{V}^{ex}$ data for acetone + cyclohexane + chloroform mixtures at many of the ternary compositions using published acetone-chloroform mole fraction based equilibrium constants, $K_{AC}^x = 1.148$ and $K_{AC_2}^x = 0.890$, and standard reaction volumes, $\Delta\bar{V}_{AC}^0 = 0.42\ \text{cm}^3/\text{mol}$ and $\Delta\bar{V}_{AC_2}^0 = -4.40\ \text{cm}^3/\text{mol}$.[2] There was very little difference between predicted values calculated with molar volume weighting factors ($\Gamma_i = \bar{V}_i$) and values based on weighting factors evaluated from acetone + cyclohexane and chloroform + cyclohexane binary data. The

Table 1 Comparison between experimental and predicted excess molar volumes for ternary acetone (A) + cyclohexane (B) + chloroform (C) mixtures at 25 °C.

X_A	X_B	$\Delta\bar{V}^{ex}(cm^3/mol)^a$	*Predicted* $\Delta\bar{V}^{ex}$ *values* (cm^3/mol)		
			Eq. (1)[b]	*Eq.* (1)[c]	*Eq.* (5)
0.1809	0.7436	0.700	0.742	0.733	0.620
0.1230	0.5139	0.565	0.746	0.721	0.458
0.1101	0.4524	0.528	0.708	0.685	0.439
0.0487	0.1999	0.296	0.356	0.349	0.299
0.0125	0.0513	0.086	0.087	0.085	0.112
0.2051	0.5070	0.632	0.836	0.809	0.475
0.1803	0.4507	0.548	0.777	0.749	0.412
0.1610	0.4060	0.503	0.719	0.687	0.378
0.0312	0.0333	0.061	0.033	0.033	0.041
0.4207	0.5136	0.983	1.055	1.046	0.914
0.1884	0.2300	0.290	0.449	0.433	0.192
0.0960	0.1172	0.127	0.178	0.173	0.125
0.0191	0.0233	0.034	0.025	0.025	0.036
0.4305	0.1944	0.447	0.532	0.523	0.202
0.4127	0.1863	0.413	0.494	0.486	0.170
0.1593	0.0719	0.014	0.050	0.049	−0.014
0.0886	0.5471	0.558	0.704	0.684	0.483
0.0809	0.4993	0.546	0.693	0.674	0.480
0.0720	0.4448	0.524	0.665	0.647	0.473
0.0675	0.4170	0.505	0.646	0.629	0.474
0.0506	0.3127	0.424	0.532	0.520	0.425
0.0399	0.2465	0.348	0.467	0.428	0.375
0.0281	0.1740	0.277	0.314	0.309	0.301
0.5157	0.2329	0.682	0.709	0.697	0.390
0.5197	0.2347	0.687	0.715	0.704	0.386
0.4009	0.2531	0.564	0.663	0.646	0.284
0.3892	0.2877	0.618	0.731	0.712	0.339
0.4078	0.3062	0.683	0.786	0.766	0.400
0.5718	0.1765	0.578	0.594	0.588	0.295
0.5279	0.1793	0.545	0.569	0.563	0.273

[a] Experimental values are from Lark, Kaur and Singh.[4]

[b] Predicted values calculated assuming that the weighting factors equal molar volumes.

[c] Predicted values are based on weighting factors determined from measured binary data using the method of Bertrand, Acree and Burchfield.[5]

$\Gamma_{\text{Acetone}}/\Gamma_{\text{CHCl}_3}$ weighting factor ratio could not be calculated from the measured binary acetone + chloroform volumetric data as $B_{A_1C_1}$ was set equal to zero in the equilibrium constant calculations.

Significant deviations are noted between experimental and predicted values for a number of the ternary compositions. Failure of Eq. (1) at several compositions could perhaps be a result of the manner in which nonspecific interactions were incorporated into the basic mixing model. Smith and Hepler[3] proposed a slightly different method in their thermodynamic description of the triethylamine + cyclohexane + chloroform system. The authors calculated the heat of complex dissociation by subtracting the heat caused by triethylamine + cyclohexane and cyclohexane + chloroform interactions, $Q_{\text{TEA},\text{C}_6\text{H}_{12}}$ and $Q_{\text{C}_6\text{H}_{12},\text{CHCl}_3}$, from the measured heat of dilution

$$Q^{\text{dis}} = \Delta\hat{n}_{\text{AC}}\Delta\bar{\text{H}}^0_{\text{AC}} = Q^{\text{exp}} - Q_{\text{TEA},\text{C}_6\text{H}_{12}} - Q_{\text{C}_6\text{H}_{12},\text{CHCl}_3} \tag{2}$$

The last two terms in Eq. (2) were evaluated for the two subbinaries from expressions of the form:

$$Q_{\text{TEA},\text{C}_6\text{H}_{12}} = 2\hat{X}_{\text{TEA}}\hat{X}_{\text{C}_6\text{H}_{12}}(\hat{n}_{\text{TEA}} + \hat{n}_{\text{C}_6\text{H}_{12}})h_{\text{TEA},\text{C}_6\text{H}_{12}} \tag{3}$$

$$Q_{\text{C}_6\text{H}_{12},\text{CHCl}_3} = 2\hat{X}_{\text{C}_6\text{H}_{12}}\hat{X}_{\text{CHCl}_3}(\hat{n}_{\text{C}_6\text{H}_{12}} + \hat{n}_{\text{CHCl}_3})h_{\text{C}_6\text{H}_{12},\text{CHCl}_3} \tag{4}$$

where $2\hat{X}_i\hat{X}_j$ represents the probability of an *i-j* interaction in a random mixture of the two components and h_{ij} is an interaction parameter determined by fitting the binary data to this mathematical representation. Surprisingly, the model ignores nonspecific interactions between the inert cosolvent and molecular complex. Significant portions of the complex should resemble the complexing cosolvents. Naturally, one would expect that many of the interactions between inert cosolvent and AC complex (also AC_2 complex in the present study) would be similar in nature to those between the cosolvents and two complexing solvents.

Extension of this latter approach to integral thermodynamic excess properties should give the following predictive expression for excess volumes

$$\Delta\bar{V}^{\text{ex}} = \frac{\hat{X}_{\text{A}_1}\hat{X}_{\text{C}_1}(K^x_{\text{AC}}\Delta\bar{V}^0_{\text{AC}} + K^x_{\text{AC}_2}\hat{X}_{\text{C}_1}\Delta\bar{V}^0_{\text{AC}_2})}{1 + \hat{X}_{\text{A}_1}\hat{X}_{\text{C}_1}(K^x_{\text{AC}} + 2\hat{X}_{\text{C}_1}K^x_{\text{AC}_2})} + \frac{\hat{X}_{\text{A}_1}\hat{X}_{\text{B}}(\hat{n}_{\text{A}_1} + \hat{n}_{\text{B}})v_{\text{A}_1\text{B}}}{n_{\text{A}} + n_{\text{B}} + n_{\text{C}}} + \frac{\hat{X}_{\text{B}}\hat{X}_{\text{C}_1}(\hat{n}_{\text{B}} + \hat{n}_{\text{C}_1})v_{\text{BC}_1}}{n_{\text{A}} + n_{\text{B}} + n_{\text{C}}} \tag{5}$$

of ternary acetone + cyclohexane + chloroform. Stoichiometric compositions (X_{A}, X_{B} and X_{C}) are related to the true mole fractions and mole numbers *via*

$$X_{\text{A}} = \frac{\hat{X}_{\text{A}_1} + \hat{X}_{\text{AC}} + \hat{X}_{\text{AC}_2}}{1 + \hat{X}_{\text{AC}} + 2\hat{X}_{\text{AC}_2}} \tag{6}$$

$$X_{\text{B}} = \frac{\hat{X}_{\text{B}}}{1 + \hat{X}_{\text{AC}} + 2\hat{X}_{\text{AC}_2}} \tag{7}$$

$$X_{\text{C}} = \frac{\hat{X}_{\text{C}_1} + \hat{X}_{\text{AC}} + 2\hat{X}_{\text{AC}_2}}{1 + \hat{X}_{\text{AC}} + 2\hat{X}_{\text{AC}_2}} \tag{8}$$

$$\frac{\hat{n}_{\mathrm{A}_1} + \hat{n}_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}} = X_{\mathrm{A}} + X_{\mathrm{B}} - \frac{\hat{X}_{\mathrm{A}_1}\hat{X}_{\mathrm{C}_1}(K^x_{\mathrm{AC}} + K^x_{\mathrm{AC}_2}\hat{X}_{\mathrm{C}_1})}{1 + \hat{X}_{\mathrm{A}_1}\hat{X}_{\mathrm{C}_1}(K^x_{\mathrm{AC}} + 2K^x_{\mathrm{AC}_2}\hat{X}_{\mathrm{C}_1})} \tag{9}$$

$$\frac{\hat{n}_{\mathrm{B}} + \hat{n}_{\mathrm{C}_1}}{n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}} = X_{\mathrm{B}} + X_{\mathrm{C}} - \frac{\hat{X}_{\mathrm{A}_1}\hat{X}_{\mathrm{C}_1}(K^x_{\mathrm{AC}} + 2K^x_{\mathrm{AC}_2}\hat{X}_{\mathrm{C}_1})}{1 + \hat{X}_{\mathrm{A}_1}\hat{X}_{\mathrm{C}_1}(K^x_{\mathrm{AC}} + 2K^x_{\mathrm{AC}_2}\hat{X}_{\mathrm{C}_1})} \tag{10}$$

Since we were unable to explicitly express the true mole fractions $\hat{X}_{\mathrm{A}_1}$ and $\hat{X}_{\mathrm{C}_1}$ in terms of the stoichiometric mole fractions, Eqs. (6)-(8) were solved by 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 Eqs. (6)-(8) 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. It should be noted that the thermodynamic model and computational method will become much more involved if one tries to describe the Gibbs free energy of mixing as the physical contributions are expressed in terms of true mole fractions, rather than stoichiometric compositions. Remember $\Delta\bar{V}^{\mathrm{ex}}$ and $\Delta\bar{H}^{\mathrm{ex}}$ are obtained by differentiating $\Delta\bar{G}^{\mathrm{mix}}$ with respect to pressure and temperature, respectively, and the true mole fractions are functions of both T and P.

The last column in Table 1 lists the predicted $\Delta\bar{V}^{\mathrm{ex}}$ values based on Eq. (5). Careful examination of Table 1 reveals that the overall predictive abilities of the various equations are fairly comparable. Equation (5) provides the better $\Delta\bar{V}^{\mathrm{ex}}$ estimates for many of the mixtures near the beginning of Table 1, whereas Eq. (1) is by far the best predictive expression for the last seven ternary compositions. Based on this limited $\Delta\bar{V}^{\mathrm{ex}}$ comparison for the ternary acetone + cyclohexane + chloroform system it is impossible for us to conclude which particular equation and treatment of nonspecific interactions will give the best $\Delta\bar{V}^{\mathrm{ex}}$ predictions for ternary associated solutions. As additional experimental thermodynamic data becomes available, the limitations and applications of each method will be re-examined. For now, we note that Eq. (1) can be derived from a fairly realistic thermodynamic mixing model, and at the moment, we have not been able to rigorously derive Eq. (5) from basic thermodynamic considerations. We must therefore regard Eq. (5) as a strictly empirical predictive expression.

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