COMMENTS ON "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

An alternative description of non-specific physical interactions is incorporated into our previously proposed mixing-model and expressions are derived for predicting excess enthalpies in associated solutions containing both AC and AC_2 molecular complexes. Applications and limitations of the newly derived predictive expression are illustrated using experimental data for ternary acetone + cyclohexane + chloroform mixtures.

In a recent paper [1] appearing in this journal, we proposed a relatively simple mixing model for describing thermodynamic properties of ternary associated solutions containing both AC and AC_2 molecular complexes

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

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

An expression was derived for predicting excess enthalpies, $\Delta \overline{H}^{ex}$

$$\Delta \overline{H}^{ex} = \frac{\hat{X}_{A_1}\hat{X}_{C_1}\left(K_{AC}^x \Delta \overline{H}_{AC}^{\ominus} + K_{AC_2}^x \hat{X}_{C_1}\Delta \overline{H}_{AC_2}^{\ominus}\right)}{1 + \hat{X}_{A_1}\hat{X}_{C_1}\left(K_{AC}^x + 2\hat{X}_{C_1}K_{AC_2}^x\right)}$$
$$+ (X_A + X_B)(f_A + f_B)\left(\Delta \overline{H}_{AB}^{ex}\right)^* + (X_B + X_C)(f_B + f_C)\left(\Delta \overline{H}_{BC}^{ex}\right)^*$$
$$+ (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C)f_A f_C B_{A_1C_1} \qquad (1)$$

by assuming that the total solution non-ideality could be separated into both chemical and physical contributions. The first term in eqn. (1) represents the

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chemical contribution which results from the formation of AC and AC_2 molecular complexes, and the remaining 3 terms describe the non-specific physical interactions between the various species in solution. Ten binary B_{ij} interaction parameters were initially introduced into the mixing model to account for non-specific interactions, but simplifying approximations and mathematical manipulations reduced the number to a single $B_{A_1C_1}$ parameter and to two $(\Delta \overline{H}_{ij}^{ex})^\star$ terms which correspond to actual experimental excess enthalpies of the AB and BC sub-binary systems at mole fractions $X_i^\ominus$ and $X_j^\ominus$. The various symbols in eqn. (1) are defined in our earlier paper [1].

As shown in Tables 1 and 2, eqn. (1) with $B_{A_1C_1} = 0$ did provide fairly reasonable predictions of the experimental $\Delta \overline{H}^{ex}$ data for acetone + cyclohexane + chloroform mixtures at many of the ternary compositions, using published acetone–chloroform mole-fraction-based equilibrium constants and standard reaction enthalpies. There was very little difference between predicted values calculated with molar volume weighting factors $(\Gamma_i = \overline{V}_i)$ and values based on weighting factors evaluated from acetone + cyclohexane and cyclohexane + chloroform binary data. The primary difference in the two sets of predicted values results from the different association parameters used. Apelblat et al. [2] reported 'best' equilibrium constants, $K_{AC}^x = 1.148$ and $K_{AC_2}^x = 0.890$, and standard reaction enthalpies, $\Delta \overline{H}_{AC}^\ominus = -10.3$ kJ mol^{-1} and $\Delta \overline{H}_{AC_2}^\ominus = -20.1$ 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 $\Delta \overline{H}_{AC}^\ominus$ values and significant scatter in $\Delta \overline{H}_{AC_2}^\ominus$ values. A numerical value of $\Delta \overline{H}_{AC_2}^\ominus$, -20.1 kJ mol^{-1}, was considerably larger than values reported by three other research groups. In comparison, Matsui et al. [3] obtained their two equilibrium constants, $K_{AC}^x = 0.967$ and $K_{AC_2}^x = 1.117$, and standard reaction enthalpies, $\Delta H_{AC}^\ominus = -10.3$ kJ mol^{-1} and $\Delta \overline{H}_{AC_2}^\ominus = -13.0$ kJ mol^{-1}, from experimental data measured at 25°C, which happens to correspond to the temperature of the acetone + cyclohexane + chloroform system. It is not too surprising that this latter set of association parameters provides the better prediction of ternary properties. For several of the ternary compositions, the predicted value falls within (or nearly within) the experimental uncertainty of the measured value.

Significant deviations are noted between experimental and predicted values for a number of the ternary compositions. Failure of eqn. (1) at several compositions could perhaps be a result of the manner in which non-specific interactions were incorporated into the basic mixing model. Smith and Hepler [4] 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 +

TABLE 1

Comparison between experimental and predicted excess enthalpies (J mol^{-1}) for ternary acetone (A) + cyclohexane (B) + chloroform (C) mixtures at 25°C (association parameters from Apelblat et al. [2])

X_A	X_B	$\Delta \overline{H}^{\text{ex a}}$	Predicted $\Delta \overline{H}^{\text{ex}}$ values		
			Eqn. (1) [b]	Eqn. (1) [c]	Eqn. (5)
0.4551	0.0779	−1236.1	−1563.1	−1561.3	−1777.0
0.5715	0.0976	−836.5	−1045.0	−1044.8	−1280.2
0.3196	0.0547	−1378.3	−1786.0	−1783.9	−1850.3
0.3048	0.0522	−1372.5	−1747.8	−1745.8	−1871.7
0.4052	0.0693	−1334.8	−1693.3	−1691.1	−1881.4
0.3452	0.0590	−1385.3	−1763.7	−1761.4	−1915.4
0.3684	0.0629	−1389.1	−1753.7	−1751.5	−1921.4
0.4204	0.0872	−1188.1	−1537.9	−1538.2	−1768.7
0.5287	0.3487	770.0	790.8	756.1	506.8
0.3946	0.4479	779.3	815.1	759.5	401.7
0.6320	0.2722	753.6	739.8	719.9	541.4
0.7602	0.1774	620.6	603.6	596.8	477.6
0.5259	0.3507	776.8	788.3	753.3	498.7
0.4011	0.4431	770.1	814.5	759.9	407.1
0.4508	0.4063	775.4	810.1	763.2	451.4
0.4592	0.4001	768.1	806.2	760.6	453.7
0.6938	0.2264	703.4	685.7	673.1	529.0
0.4335	0.2105	−372.0	−591.6	−620.4	−1011.7
0.4155	0.1544	−748.9	−1024.0	−1039.3	−1377.9
0.3434	0.2440	−313.4	−521.2	−563.1	−955.5
0.7005	0.1119	−231.8	−336.9	−338.9	−527.8
0.3499	0.2415	−313.2	−530.9	−571.7	−992.3
0.6338	0.1358	−317.9	−417.7	−434.8	−681.8
0.4653	0.0870	−1155.5	−1520.5	−1519.8	−1753.3
0.6202	0.0617	−1012.8	−1199.7	−1195.4	−1356.7
0.2970	0.1138	−983.0	−1345.0	−1354.2	−1578.9
0.7122	0.0468	−805.5	−945.3	−941.3	−1050.0
0.4589	0.0896	−1160.7	−1451.7	−1451.6	−1688.7
0.3291	0.1091	−1058.1	−1401.9	−1408.9	−1654.5
0.7170	0.0458	−792.9	−939.5	−935.6	−1044.1

[a] Experimental data is taken from Lark, Kaur and Singh [5].
[b] Predicted values are calculated with weighting factors equal to molar volumes.
[c] Predicted values are calculated with weighting factors evaluated from binary data.

chloroform interactions, $Q_{\text{TEA},C_6H_{12}}$ and $Q_{C_6H_{12},CHCl_3}$, from the measured heat of dilution

$$Q^{\text{dis}} = \Delta \hat{n}_{AC} \Delta \overline{H}_{AC}^{\ominus} = Q^{\text{exp}} - Q_{\text{TEA},C_6H_{12}} - Q_{C_6H_{12},CHCl_3} \tag{2}$$

The last two terms in eqn. (2) were evaluated for the two sub-binaries from

TABLE 2

Comparison between experimental and predicted excess enthalpies (J mol^{-1}) for ternary acetone (A) + cyclohexane (B) + chloroform (C) mixtures at 25°C (association parameters from Matsui et al. [3])

X_A	X_B	$\Delta \bar{H}^{ex}$ [a]	Predicted $\Delta \bar{H}^{ex}$ values		
			Eqn. (1) [b]	Eqn. (1) [c]	Eqn. (5)
0.4551	0.0779	−1236.1	−1273.9	−1272.1	−1481.7
0.5715	0.0976	−836.5	−838.3	−838.1	−1066.4
0.3196	0.0547	−1378.3	−1442.9	−1440.8	−1577.9
0.3048	0.0522	−1372.5	−1430.8	−1428.8	−1555.7
0.4052	0.0693	−1334.8	−1387.6	−1385.4	−1573.4
0.3452	0.0590	−1385.3	−1445.9	−1443.6	−1597.2
0.3684	0.0629	−1389.1	−1432.3	−1430.1	−1596.9
0.4204	0.0872	−1188.1	−1248.1	−1248.4	−1474.8
0.5287	0.3487	770.0	850.1	815.4	573.9
0.3946	0.4479	779.3	885.9	830.3	486.8
0.6320	0.2722	753.6	786.5	766.6	592.6
0.7602	0.1774	620.6	636.0	629.2	516.6
0.5259	0.3507	776.8	851.4	816.4	573.8
0.4011	0.4431	770.1	886.5	831.9	493.3
0.4508	0.4063	775.4	872.5	825.6	522.4
0.4592	0.4001	768.1	871.8	826.2	530.2
0.6938	0.2264	703.4	724.9	712.3	569.9
0.4335	0.2105	−372.0	−372.7	−401.5	−782.3
0.4155	0.1544	−748.9	−784.5	−799.8	−1131.1
0.3434	0.2440	−313.4	−325.3	−367.2	−779.9
0.7005	0.1119	−231.8	−231.8	−233.8	−418.3
0.3499	0.2415	−313.2	−333.5	−374.3	−778.5
0.6338	0.1358	−317.9	−284.4	−301.5	−540.8
0.4653	0.0870	−1155.5	−1190.8	−1190.1	−1418.5
0.6202	0.0617	−1012.8	−997.4	−993.1	−1149.3
0.2970	0.1138	−983.0	−1064.9	−1074.1	−1312.2
0.7122	0.0468	−805.5	−803.7	−799.7	−908.0
0.4589	0.0896	−1160.7	−1180.3	−1180.2	−1413.2
0.3291	0.1091	−1058.1	−1123.7	−1130.7	−1376.1
0.7170	0.0458	−792.9	−793.6	−789.7	−892.8

[a] Experimental data is taken from Lark, Kaur and Singh [5].
[b] Predicted values are calculated with weighting factors equal to molar volumes.
[c] Predicted values are calculated with weighting factors evaluated from binary data.

expressions of the form

$$Q_{TEA,C_6H_{12}} = 2 \hat{X}_{TEA} \hat{X}_{C_6H_{12}} \left(\hat{n}_{TEA} + \hat{n}_{C_6H_{12}} \right) h_{TEA,C_6H_{12}} \tag{3}$$

$$Q_{C_6H_{12},CHCl_3} = 2 \hat{X}_{C_6H_{12}} \hat{X}_{CHCl_3} \left(\hat{n}_{C_6H_{12}} + \hat{n}_{CHCl_3} \right) h_{C_6H_{12},CHCl_3} \tag{4}$$

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 de-

termined by fitting the binary data to this mathematical representation. Surprisingly, the model ignores non-specific interactions between the inert co-solvent and molecular complex. Significant portions of the complex should resemble the complexing co-solvents. Naturally, one would expect that many of the interactions between inert co-solvent and AC complex (also AC_2 complex, in the present study) would be similar in nature to those between the co-solvents and two complexing solvents.

Extension of this latter approach to integral thermodynamic excess properties should give the following predictive expression for excess enthalpies of ternary acetone + cyclohexane + chloroform

$$\Delta \overline{H}^{ex} = \frac{\hat{X}_{A_1} \hat{X}_{C_1} \left(K^x_{AC} \Delta \overline{H}^{\ominus}_{AC} + K^x_{AC_2} \hat{X}_{C_1} \Delta \overline{H}^{\ominus}_{AC_2} \right)}{1 + \hat{X}_{A_1} \hat{X}_{C_1} \left(K^x_{AC} + 2 \hat{X}_{C_1} K^x_{AC_2} \right)} + \frac{\hat{X}_{A_1} \hat{X}_B \left(\hat{n}_{A_1} + \hat{n}_B \right) h_{A_1 B}}{n_A + n_B + n_C}$$
$$+ \frac{\hat{X}_B \hat{X}_{C_1} \left(\hat{n}_B + \hat{n}_{C_1} \right) h_{BC_1}}{n_A + n_B + n_C} \tag{5}$$

Stoichiometric compositions (X_A, X_B and X_C) are related to the true mole fractions and mole numbers via

$$X_A = \frac{\hat{X}_{A_1} + \hat{X}_{AC} + \hat{X}_{AC_2}}{1 + \hat{X}_{AC} + 2 \hat{X}_{AC_2}} \tag{6}$$

$$X_B = \frac{\hat{X}_B}{1 + \hat{X}_{AC} + 2 \hat{X}_{AC_2}} \tag{7}$$

$$X_C = \frac{\hat{X}_{C_1} + \hat{X}_{AC} + 2 \hat{X}_{AC_2}}{1 + \hat{X}_{AC} + 2 \hat{X}_{AC_2}} \tag{8}$$

$$\frac{\hat{n}_{A_1} + \hat{n}_B}{n_A + n_B + n_C} = X_A + X_B - \frac{\hat{X}_{A_1} \hat{X}_{C_1} \left(K^x_{AC} + K^x_{AC_2} \hat{X}_{C_1} \right)}{1 + \hat{X}_{A_1} \hat{X}_{C_1} \left(K^x_{AC} + 2 K^x_{AC_2} \hat{X}_{C_1} \right)} \tag{9}$$

$$\frac{\hat{n}_B + \hat{n}_{C_1}}{n_A + n_B + n_C} = X_B + X_C - \frac{\hat{X}_{A_1} \hat{X}_{C_1} \left(K^x_{AC} + 2 K^x_{AC_2} \hat{X}_{C_1} \right)}{1 + \hat{X}_{A_1} \hat{X}_{C_1} \left(K^x_{AC} + 2 K^x_{AC_2} \hat{X}_{C_1} \right)} \tag{10}$$

Because we were unable to express explicitly the true mole fractions $\hat{X}_{A_1}$ and $\hat{X}_{C_1}$ in terms of the stoichiometric mole fractions, eqns. (6)–(8) 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 eqns. (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 be-

come 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 $\Delta \overline{V}^{ex}$ and $\Delta \overline{H}^{ex}$ are obtained by differentiating $\Delta \overline{G}^{mix}$ with respect to pressure and temperature, respectively, and the true mole fractions are functions of both T and P.

The last column in Tables 1 and 2 lists predicted $\Delta \overline{H}^{ex}$ values based on eqn. (5). Careful examination of both tables reveals that eqn. (1) is always superior to eqn. (5), irrespective of the set of association parameters used in the calculations. The last 2 terms in eqn. (5) grossly underestimate the non-specific physical interactions, particularly in those ternary mixtures having appreciable complexation as the mole fractions of uncomplexed acetone and chloroform molecules are significantly less than the stoichiometric concentrations. Remember that eqn. (5) completely ignores non-specific interactions between the inert hydrocarbon co-solvent and the various molecular complexes which are formed. Based on our calculations, we feel that the treatment of Smith and Hepler provides an incorrect description of non-specific interactions for the acetone + cyclohexane + chloroform system. As additional experimental thermodynamic data become available, the limitations and applications of both predictive methods will be re-examined. For now, we note that eqn. (1) can be derived from a fairly realistic thermodynamic mixing model, and at the moment, we have not been able to rigorously derive eqn. (5) from basic thermodynamic considerations. We must therefore regard eqn. (5) as a strictly empirical predictive expression.

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