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THERMOCHEMICAL INVESTIGATIONS OF ASSOCIATED SOLUTIONS. 12. MOLE FRACTION VERSUS VOLUME FRACTION BASED ASSOCIATION CONSTANTS FOR PREDICTING EXCESS MOLAR ENTHALPIES OF ACETONE–BROMOFORM–ALKANE MIXTURES

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ABSTRACT

Excess molar enthalpies are reported for ternary acetone–bromoform–cyclohexane, acetone–bromoform–*n*-heptane and acetone–bromoform–*n*-decane mixtures at 308.15 K, as well as enthalpic data for the seven subbinary systems. Results of these measurements are used to test the applications and limitations of two associated solution models containing either a mole fraction based or a volume fraction based equilibrium constant. The effect of the inert hydrocarbon cosolvent on calculated acetone–bromoform association parameters is briefly discussed.

INTRODUCTION

The chemical industry has long recognized the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow and heat transfer. 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 use of continuous dilution methods, combined with modern chromatographic headspace sampling techniques, has reduced the experimental time needed for the determination of excess Gibbs free energies and activity coefficients through conventional vapor pressure measurements. However, even with today's sophisticated instrumentation, experimental measurements

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of thermodynamic properties become progressively more difficult and time-consuming with each additional component beyond binary mixtures. To address this problem, engineers have turned to predictive methods as a means to generate the desired quantities.

In several previous papers in this series, we have derived expressions for predicting excess molar enthalpies ($\bar{H}^{ex}$) and excess molar volumes ($\bar{V}^{ex}$) of systems containing a single AB molecular complex [1]

$$A_1 + B_1 \rightleftharpoons AB \qquad K^x_{AB} = \hat{X}_{AB}/\left(\hat{X}_{A_1}\hat{X}_{B_1}\right)$$

$$\begin{aligned}\bar{H}^{ex} = {} & \frac{\hat{X}_{A_1}\hat{X}_{B_1}K^x_{AB}\,\Delta\bar{H}^0_{AB}}{1 + K^x_{AB}\hat{X}_{A_1}\hat{X}_{B_1}} + (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C) f_A f_B C_{A_1B_1} \\ & + (X_A + X_C)(f_A + f_C)\left(\bar{H}^{ex}_{AC}\right)^\star + (X_B + X_C)(f_B + f_C)\left(\bar{H}^{ex}_{BC}\right)^\star \end{aligned} \tag{1}$$

$$\begin{aligned}\bar{V}^{ex} = {} & \frac{\hat{X}_{A_1}\hat{X}_{B_1}K^x_{AB}\,\Delta\bar{V}^0_{AB}}{1 + K^x_{AB}\hat{X}_{A_1}\hat{X}_{B_1}} + (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C) f_A f_B B_{A_1B_1} \\ & + (X_A + X_C)(f_A + f_C)\left(\bar{V}^{ex}_{AC}\right)^\star + (X_B + X_C)(f_B + f_C)\left(\bar{V}^{ex}_{BC}\right)^\star \end{aligned} \tag{2}$$

and both AB and AB_2 complexes [2,3]

$$A_1 + B_1 \rightleftharpoons AB \qquad K^x_{AB} = \hat{X}_{AB}/\left(\hat{X}_{A_1}\hat{X}_{B_1}\right)$$

$$A_1 + 2B_1 \rightleftharpoons AB_2 \qquad K^x_{AB_2} = \hat{X}_{AB_2}/\left(\hat{X}_{A_1}\hat{X}^2_{B_1}\right)$$

$$\begin{aligned}\bar{H}^{ex} = {} & \frac{\hat{X}_{A_1}\hat{X}_{B_1}\left(K^x_{AB}\,\Delta\bar{H}^0_{AB} + K^x_{AB_2}\,\Delta\bar{H}^0_{AB_2}\hat{X}_{B_1}\right)}{1 + \hat{X}_{A_1}\hat{X}_{B_1}\left(K^x_{AB} + 2\hat{X}_{B_1}K^x_{AB_2}\right)} \\ & + (X_A + X_C)(f_A + f_C)\left(\bar{H}^{ex}_{AC}\right)^\star \\ & + (X_B + X_C)(f_B + f_C)\left(\bar{H}^{ex}_{BC}\right)^\star \\ & + (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C) f_A f_B C_{A_1B_1} \end{aligned} \tag{3}$$

$$\begin{aligned}\bar{V}^{ex} = {} & \frac{\hat{X}_{A_1}\hat{X}_{B_1}\left(K^x_{AB}\,\Delta\bar{V}^0_{AB} + K^x_{AB_2}\,\Delta\bar{V}^0_{AB_2}\hat{X}_{B_1}\right)}{1 + \hat{X}_{A_1}\hat{X}_{B_1}\left(K^x_{AB} + 2\hat{X}_{B_1}K^x_{AB_2}\right)} + (X_A + X_C)(f_A + f_C)\left(\bar{V}^{ex}_{AC}\right)^\star \\ & + (X_B + X_C)(f_B + f_C)\left(\bar{V}^{ex}_{BC}\right)^\star \\ & + (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C) f_A f_B B_{A_1B_1} \end{aligned} \tag{4}$$

from measured binary $(\bar{H}^{ex}_{ij})^\star$ and $(\bar{V}^{ex}_{ij})^\star$ data, which are determined at mole fraction compositions $X_i^0 = 1 - X_j^0 = X_i/(X_i + X_j)$. In eqns. (1)–(4), $\Delta\bar{H}^0_{AB_i}$ and $\Delta\bar{V}^0_{AB_i}$ refer to the standard molar reaction enthalpies and volumes for AB_i complex formation, $B_{A_1B_1}$ and $C_{A_1B_1}$ denote volumetric and enthalpic binary interaction parameters for the AB subbinary system, and f_i is the weighted mole fraction composition of component i, i.e., $f_i = X_i\Gamma_i/(\Sigma X_j\Gamma_j)$. 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 the values be referred to a specified condition, such as 25 °C and 1 atm, or to an extrapolated state such as "close packed" volume.

Past comparisons [1–5] have demonstrated that eqns. (1)–(4) with $B_{A_1B_1} = C_{A_1B_1} = 0$ provide fairly reasonable estimates of $\bar{H}^{ex}$ and $\bar{V}^{ex}$ values for acetone–chloroform–cyclohexane (AB and AB_2 complexes) mixtures, of $\bar{H}^{ex}$ values for the acetone–bromoform–cyclohexane system and of $\bar{V}^{ex}$ values for four ternary acetone–bromoform–alkane mixtures, particularly in light of the many simplifying approximations made in the original derivations. The expressions are by no means perfect, however, and significant deviations between calculated and observed values were noted at several of the ternary compositions studied. Failure of eqns. (1)–(4) could result from an incorrect description of physical interactions (e.g. $B_{A_1B_1} \neq 0$ and/or $C_{A_1B_1} \neq 0$), or from the formation of a higher-order molecular complex as might be the case for acetone and bromoform, since only a single AB complex was assumed, or from the configurational entropic contribution being expressed in terms of mole fraction (Raoult's law) rather than volume fraction (Flory–Huggins model) compositions. Raoult's law gives rise to a mole fraction based equilibrium constant, $K^x_{AB_i}$, whereas in the Flory–Huggins model the association constant ($K^\phi_{AB_i}$) is defined as a volume fraction ratio. Equations (1)–(4) were originally derived by differentiating an expression for the Gibbs free energy of mixing with respect to both pressure ($\bar{V}^{ex}$) and temperature ($\bar{H}^{ex}$). These concerns can be addressed partially by studying how the size and shape of the inert hydrocarbon cosolvent affects the calculated association parameters for complex formation. To examine the entropic configurational term further, we report excess enthalpies of ternary acetone–bromoform–cyclohexane, acetone–bromoform–*n*-heptane and acetone–bromoform–*n*-decane mixtures at 308.15 K, plus enthalpic data for the seven contributing subbinary systems. The three inert hydrocarbon cosolvents were selected so as to cover approximately a two-fold range in molar volumes. Results of these measurements are used to test the limitations of eqn. (1) and its Flory–Huggins based counterpart, which is derived in the present study.

EXPERIMENTAL

Acetone (Glaxo, 99.5 + %), bromoform (E. Merck, 98 + %), cyclohexane (Sisco Research Lab., 99.5 + %), *n*-heptane (Sisco Research Lab., 99.1 + %) and *n*-decane (Fluka, 95 + %) were purchased from commercial sources and

TABLE 1

Comparison between measured pure component densities at 298.15 ± 0.01 K and corresponding literature values

Compound	Density (g cm^{-3})		Ref.
	Experimental	Literature	
Acetone	0.78512	0.78508	27
		0.78516	28
		0.78508	29
Bromoform	2.87576	2.8758	30
Cyclohexane	0.77392	0.77389	31
		0.77392	32
n-Heptane	0.67954	0.67958	33
		0.67955	34
		0.67952	35
n-Decane	0.72611	0.72608	36

purified according to published methods. [6–10] Purities of the final samples were checked by measuring their densities at 298.15 ± 0.01 K; these agreed to within ±0.00005 g cm^{-3} with the corresponding literature values, as shown in Table 1.

Excess molar enthalpies, $\overline{H}^{\mathrm{ex}}$, for the various binary systems at 308.15 K were determined using an LKB-2107 flow microcalorimeter (LKB, Bromma, Sweden) in the manner described by Monk and Wadsö [11]. The precision and stability of the instrument in terms of temperature are 0.1 K and ±0.01 K over 24 h, respectively. Two identical Braun perfusor pumps (B. Braun Melsungen AG, F.R.G.) and gas-tight Hamilton syringes were employed to pump liquids through the calorimeter. Using 10 and 20 cm^3 syringes and the 10-speed gear boxes of the perfusor pumps, different mixing ratios were achieved. Flow rates were determined by pumping distilled water through the calorimeter and weighing the amounts collected in a specific time interval. For each typical $\overline{H}^{\mathrm{ex}}$ measurement, different calibration constants were determined according to the flow rate, the amplification needed and the composition of the mixture. Molar excess enthalpies of ternary mixtures were determined in a similar manner except that one of the syringes contained a binary mixture of known mole fraction composition. Estimated uncertainties in the measured $\overline{H}^{\mathrm{ex}}$ values are believed to be on the order of ±1% or better. The performance of the calorimeter has been previously checked [12] by comparing measured $\overline{H}^{\mathrm{ex}}$ data for the binary benzene–carbon tetrachloride system to published literature data [13].

Experimental excess molar enthalpies of the seven subbinary systems are tabulated in Table 2, along with the coefficients and corresponding standard deviations for

$$\overline{H}^{\mathrm{ex}} = X_i X_j \sum_{n=0}^{2} h_{ij}^{(n)} (X_i - X_j)^n \tag{5}$$

TABLE 2

Experimental $\overline{H}^{\text{ex}}$ data at 308.15 K for the various binary mixtures as a function of mole fraction composition

X_i	$\overline{H}^{\text{ex}}$ (J mol^{-1})	X_i	$\overline{H}^{\text{ex}}$ (J mol^{-1})
Acetone (i) + bromoform (j)			
0.0892	−522	0.5352	−1521
0.1644	−880	0.5357	−1528
0.1672	−890	0.6982	−1230
0.2874	−1309	0.7028	−1224
0.3380	−1425	0.7349	−1127
0.3472	−1437	0.8572	−668
0.5114	−1543	0.8623	−645
0.5165	−1537	0.9314	−338
$h_{ij}^{(0)} = -6183.06$; $h_{ij}^{(1)} = 656.37$; $h_{ij}^{(2)} = 474.97$; $\sigma = 3.1$			
Bromoform (i) + cyclohexane (j)			
0.0975	350	0.5784	1365
0.1896	651	0.5833	1370
0.1962	677	0.7337	1220
0.3458	1080	0.7416	1207
0.3826	1152	0.7842	1092
0.3878	1164	0.8795	733
0.5595	1360	0.8816	717
0.5599	1367	0.9374	422
$h_{ij}^{(0)} = 5309.36$; $h_{ij}^{(1)} = 1864.84$; $h_{ij}^{(2)} = 279.13$; $\sigma = 2.8$			
Cyclohexane (i) + acetone (j)			
0.1138	727	0.4346	1810
0.1182	755	0.6021	1817
0.2249	1258	0.6118	1805
0.2539	1363	0.6661	1725
0.2581	1380	0.8003	1290
0.4109	1776	0.8035	1280
0.4113	1770	0.8914	806
0.4296	1802		
$h_{ij}^{(0)} = 7430.78$; $h_{ij}^{(1)} = 716.38$; $h_{ij}^{(2)} = 590.88$; $\sigma = 4.0$			
Bromoform (i) + n-heptane (j)			
0.1279	458	0.6506	1175
0.2410	765	0.6553	1173
0.2489	785	0.7891	950
0.4178	1100	0.7958	927
0.4569	1139	0.8315	825
0.4623	1145	0.9083	522
0.6329	1183	0.9100	508
0.6334	1190	0.9531	292
$h_{ij}^{(0)} = 4710.70$; $h_{ij}^{(1)} = 1321.34$; $h_{ij}^{(2)} = 653.71$; $\sigma = 3.1$			

TABLE 2 (continued)

X_i	$\overline{H}^{ex}$ (J mol^{-1})	X_i	$\overline{H}^{ex}$ (J mol^{-1})
n-Heptane (i) + acetone (j)			
0.0419	273	0.3568	1530
0.0864	525	0.3615	1538
0.0898	546	0.5271	1754
0.1761	955	0.5372	1750
0.2004	1060	0.5951	1748
0.2039	1073	0.7470	1489
0.3393	1493	0.7508	1480
0.3398	1491	0.8582	1027
$h_{ij}^{(0)} = 6950.50$; $h_{ij}^{(1)} = 1283.50$; $h_{ij}^{(2)} = 1167.50$; $\sigma = 3.4$			
Bromoform (i) + *n*-decane (j)			
0.1861	923	0.6947	1658
0.3030	1365	0.7103	1622
0.3337	1449	0.8122	1277
0.4278	1670	0.8272	1201
0.5281	1793	0.8476	1096
0.5319	1789	0.9156	687
0.6835	1688	0.9176	666
0.6860	1684	0.9560	375
$h_{ij}^{(0)} = 7080.00$; $h_{ij}^{(1)} = 1785.65$; $h_{ij}^{(2)} = 392.69$; $\sigma = 3.8$			
n-Decane (i) + acetone (j)			
0.0375	350	0.2796	1736
0.0708	635	0.2820	1750
0.0725	642	0.4274	2026
0.1324	1067	0.4311	2028
0.1505	1175	0.4711	2037
0.1639	1243	0.6281	1900
0.2570	1670	0.6611	1820
0.2715	1710	0.7876	1392
$h_{ij}^{(0)} = 8160.00$; $h_{ij}^{(1)} = -476.19$; $h_{ij}^{(2)} = 1380.95$; $\sigma = 4.5$			

which is the Redlich–Kister representation. Ternary enthalpic data are listed in Tables 3–5, with the measured values being mathematically parameterized in terms of [14]

$$\overline{H}^{ex} = X_A X_B \sum_{n=0}^{2} h_{AB}^{(n)} (X_A - X_B)^n + X_A X_C \sum_{n=0}^{2} h_{CA}^{(n)} (X_C - X_A)^n$$

$$+ X_B X_C \sum_{n=0}^{2} h_{BC}^{(n)} (X_B - X_C)^n + X_A X_B X_C \sum_{n=0}^{2} h_{ABC}^{(n)} X_A^n (X_B - X_C)^n \quad (6)$$

the three sets of $h_{ij}^{(n)}$ binary coefficients and additional $h_{ABC}^{(n)}$ ternary terms.

TABLE 3

Comparison between experimental and predicted $\overline{H}^{ex}$ values for ternary acetone (A)–bromoform (B)–cyclohexane (C) mixtures at 308.15 K

X_A	X_B	$\overline{H}^{ex}$ (J mol^{-1})				
		Exp.	Eqn. (1) [a]	Eqn. (1) [b]	Eqn. (15) [a]	Eqn. (15) [b]
0.0208	0.0798	415	426	428	424	426
0.0403	0.1546	700	739	742	734	737
0.0731	0.2800	940	1071	1078	1061	1068
0.0826	0.3169	956	1119	1126	1109	1116
0.1152	0.4420	871	1100	1101	1091	1092
0.1213	0.4654	824	1061	1061	1052	1052
0.1482	0.5688	514	740	730	735	725
0.1530	0.5874	436	654	642	650	638
0.1558	0.5956	390	609	596	606	593
0.1633	0.6267	237	441	427	439	425
0.1673	0.0434	1069	1140	1146	1133	1139
0.1761	0.6757	−52	115	102	117	104
0.1801	0.6887	−146	11	−3	13	−1
0.1920	0.7344	−490	−376	−385	−370	−379
0.2987	0.0775	1250	1452	1472	1439	1459
0.3359	0.0872	1214	1462	1484	1447	1469
0.4724	0.1226	910	1221	1255	1202	1236
0.5825	0.1512	493	735	770	715	750
0.6023	0.1564	408	619	652	600	633
0.6106	0.1585	362	570	602	551	583
0.6917	0.1796	−89	−4	15	−22	−3
0.6982	0.1813	−136	−57	−39	−75	−57
0.7088	0.1840	−210	−143	−128	−161	−146
0.7399	0.1921	−435	−418	−410	−435	−427
0.7500	0.1947	−524	−513	−508	−530	−525

$h^{(0)}_{ABC} = -10{,}757.4$; $h^{(1)}_{ABC} = 44{,}321.4$; $h^{(2)}_{ABC} = -14{,}079.80$; $\sigma = 3.6$

[a] Weighting factors approximated with molar volumes.

[b] Weighting factors calculated from binary excess enthalpy data.

Numerical values of the various ternary parameters and standard deviations are reported at the bottom of Tables 3–5.

PREDICTIONS USING MOLE FRACTION BASED ASSOCIATION CONSTANT

Application of eqn. (1) to ternary acetone–bromoform–alkane mixtures requires that the association parameters for the acetone–bromoform complex be calculable from the appropriate binary reduction. Dahiya et al. [15] have previously reported that the binary acetone–bromoform system could be reasonably (not perfectly) described by the ideal associated solution

TABLE 4

Comparison between experimental and predicted $\overline{H}^{\mathrm{ex}}$ values for ternary acetone (A)–bromoform (B)–*n*-heptane (C) mixtures at 308.15 K

X_A	X_B	$\overline{H}^{\mathrm{ex}}$ (J mol^{-1})				
		Exp.	Eqn. (1) [a]	Eqn. (1) [b]	Eqn. (15) [a]	Eqn. (15) [b]
0.0271	0.1047	570	565	556	569	560
0.0508	0.1965	919	892	865	902	875
0.0876	0.3386	1150	1111	1049	1128	1066
0.0972	0.3060	1152	1106	1044	1125	1063
0.1296	0.5011	953	912	824	932	844
0.1362	0.5267	872	831	743	851	763
0.1597	0.6127	432	442	367	461	386
0.1674	0.6473	197	249	184	267	202
0.1718	0.6644	70	139	80	156	97
0.1846	0.7083	−305	−196	−233	−180	−217
0.1857	0.7130	−337	−233	−266	−218	−251
0.1951	0.7489	−665	−538	−553	−525	−540
0.2082	0.0575	1281	1313	1290	1324	1301
0.3525	0.0973	1292	1412	1372	1426	1386
0.3897	0.1076	1242	1353	1310	1367	1324
0.5106	0.1412	975	961	924	971	934
0.5197	0.1434	968	922	886	932	896
0.5327	0.1470	935	860	827	869	836
0.6244	0.1723	494	335	317	338	320
0.6492	0.1793	311	165	150	165	150
0.6653	0.1836	172	48	36	47	35
0.7087	0.1956	−228	−296	−301	−301	−306
0.7130	0.1968	−355	−332	−336	−339	−343
0.7512	0.2073	−660	−678	−678	−689	−689

$h^{(0)}_{\mathrm{ABC}} = 5000.00$; $h^{(1)}_{\mathrm{ABC}} = -8890.56$; $h^{(2)}_{\mathrm{ABC}} = -540{,}371.33$; $\sigma = 3.9$

[a] Weighting factors approximated with molar volumes.

[b] Weighting factors calculated from binary excess enthalpy data.

(IAS) model, eqns. (1) and (2) with $B_{\mathrm{A_1B_1}} = C_{\mathrm{A_1B_1}} = 0$, although the "best" values of $\Delta\overline{H}^0_{\mathrm{AB}}$ and $\Delta\overline{V}^0_{\mathrm{AB}}$ at 298.15 K

$$\Delta\overline{H}^0_{\mathrm{AB}}\ (\mathrm{kJ\ mol^{-1}}) = -7.00 + 0.857X_{\mathrm{A}} \tag{7}$$

$$\Delta\overline{V}^0_{\mathrm{AB}}\ (\mathrm{cm^3\ mol^{-1}}) = 0.300 + 0.21X_{\mathrm{A}} + 2.076X_{\mathrm{A}}^2 \tag{8}$$

were found to vary with mole fraction composition. Since these values pertain to a lower temperature, a new standard reaction enthalpy change for AB complex formation must be determined using the experimental enthalpic data at 308.15 K given in Table 2. One possible method involves evaluating both K^x_{AB} and $\Delta\overline{H}^0_{\mathrm{AB}}$ graphically from the slope and intercept of a linear

TABLE 5

Comparison between experimental and predicted $\overline{H}^{ex}$ values for ternary acetone (A)–bromoform (B)–*n*-decane (C) mixtures at 308.15 K

X_A	X_B	$\overline{H}^{ex}$ (J mol^{-1})				
		Exp.	Eqn. (1) [a]	Eqn. (1) [b]	Eqn. (15) [a]	Eqn. (15) [b]
0.0353	0.1323	866	898	880	914	896
0.0640	0.2397	1304	1380	1326	1413	1359
0.1046	0.3918	1472	1637	1524	1686	1573
0.1136	0.4255	1427	1617	1492	1668	1543
0.1427	0.0387	1117	1148	1128	1165	1145
0.1476	0.5532	1043	1239	1101	1288	1150
0.1515	0.5674	969	1127	1028	1175	1067
0.1749	0.6551	377	542	443	580	481
0.1773	0.6643	312	459	368	496	405
0.1836	0.6878	99	234	162	267	195
0.1933	0.7239	−263	−155	−195	−129	−169
0.1940	0.7268	−300	−187	−225	−161	−199
0.1965	0.7363	−404	−298	−327	−274	−303
0.2024	0.7580	−664	−567	−580	−548	−561
0.2551	0.0692	1528	1614	1562	1648	1596
0.4093	0.1110	1567	1718	1622	1764	1668
0.4330	0.1201	1500	1672	1569	1719	1616
0.4446	0.1205	1495	1657	1555	1703	1601
0.5671	0.1538	1021	1182	1082	1219	1119
0.5805	0.1575	955	1102	1005	1138	1041
0.6634	0.1799	385	469	406	489	426
0.6719	0.1822	305	391	334	410	353
0.7271	0.1972	−225	−204	−227	−201	−224
0.7298	0.1979	−253	−237	−259	−234	−256
0.7583	0.2056	−582	−598	−604	−604	−610
0.7619	0.2066	−618	−647	−652	−654	−659

$h_{ABC}^{(0)} = -2500.10$; $h_{ABC}^{(1)} = 177{,}445.3$; $h_{ABC}^{(2)} = 10{,}039.5$; $\sigma = 4.9$

[a] Weighting factors approximated with molar volumes.

[b] Weighting factors calculated from binary excess enthalpy data.

plot of $X_A X_B/\overline{H}^{ex}$ versus $\overline{H}^{ex}$ [15]

$$\frac{X_A X_B}{\overline{H}^{ex}} = -\left[\frac{K_{AB}^x + 1}{K_{AB}^x\left(\Delta \overline{H}_{AB}^0\right)^2}\right]\overline{H}^{ex} + \frac{K_{AB}^x + 1}{K_{AB}^x\,\Delta \overline{H}_{AB}^0} \tag{9}$$

provided that the excess values are symmetrical about X_A and that the physical interactions between molecules A and B are negligible compared with the much stronger chemical interactions. Unfortunately, the enthalpic data fail to give the linear plot as suggested by eqn. (9). Significant physical contributions or the formation of a higher-order AB_2 acetone–bromoform complex will result in a nonlinear $X_A X_B/\overline{H}^{ex}$ versus $\overline{H}^{ex}$ plot. Existence of an AB_2 acetone–bromoform complex could be argued on the basis that the carbonyl oxygen on acetone possesses two lone pairs of electrons, each of which could hydrogen bond with a bromoform molecule, as is the case with acetone and chloroform [16–18]. Evaluation of two equilibrium constants and two standard reaction enthalpies is not possible with our limited number of experimental data points. Generally, such calculations require that the two equilibrium constants be determined from vapor–liquid equilibria data [16], which are not available for the binary acetone–bromoform system.

To overcome this problem, a single AB molecular complex is assumed in the present study. The equilibrium constant is assigned a numerical value of $K^x_{AB} = 2.16$, which was obtained by extrapolating two published values [15]

TABLE 6

Comparison between experimental and predicted $\bar{H}^{ex}$ values for ternary acetone (A)–bromoform (B)–*n*-hexane (C) mixtures at 308.15 K

x_A	x_B	$\bar{H}^{ex}$ (J mol^{-1})				
		Exp. [a]	Eqn. (1) [b]	Eqn. (1) [c]	Eqn. (15) [b]	Eqn. (15) [c]
0.0251	0.0943	476	504	499	506	501
0.0478	0.1793	789	857	836	861	840
0.0882	0.3311	988	1249	1187	1256	1194
0.0921	0.3455	975	1260	1195	1267	1202
0.1018	0.0281	785	817	812	819	814
0.1345	0.5033	659	1041	952	1051	962
0.1633	0.6125	152	500	430	510	440
0.1727	0.6476	−53	259	203	268	212
0.1898	0.7119	−475	−261	−284	−250	−273
0.1902	0.7133	−493	−274	−296	−262	−284
0.1914	0.0528	1148	1250	1235	1253	1238
0.1976	0.0545	1162	1269	1255	1272	1258
0.3308	0.0913	1199	1466	1438	1469	1441
0.3615	0.0998	1140	1446	1416	1449	1419
0.3658	0.1009	1130	1443	1412	1445	1414
0.4983	0.1375	735	1093	1059	1092	1058
0.5130	0.1416	668	1030	996	1029	995
0.5166	0.1426	660	1014	980	1013	979
0.6023	0.1662	255	543	518	538	513
0.6207	0.1713	146	421	396	415	390
0.6259	0.1727	126	385	362	378	355
0.6535	0.1804	−45	182	163	174	155
0.7016	0.1936	−350	−213	−222	−223	−232
0.7143	0.1971	−437	−326	−333	−336	−343
0.7394	0.2041	−625	−561	−542	−573	−554

$h^{(0)}_{ABC} = -14,300$; $h^{(1)}_{AB} = 16,147$; $h^{(2)}_{ABC} = -64,537$; $\sigma = 4.0$

---

[a] Experimental data from ref. 1.

[b] Weighting factors approximated with molar volumes.

[c] Weighting factors calculated from binary excess enthalpy data.

of $K^x_{\mathrm{AB}} = 2.38$ (NMR) and $K^x_{\mathrm{AB}} = 2.35$ (calorimetric) at 298.15–308.15 K using an average $\Delta \overline{H}^0_{\mathrm{AB}} = -6.57$ kJ mol^{-1} from eqn. (7) with $X_{\mathrm{A}} = 0.5$. Having determined K^x_{AB} in this fashion, we proceeded to calculate a $\Delta \overline{H}^0_{\mathrm{AB}}$ value at each binary composition by forcing the experimental acetone–bromoform data to fit the binary reduction of eqn. (1) with $C_{\mathrm{A_1B_1}} = 0$. An average value of $\Delta \overline{H}^0_{\mathrm{AB}} = -7.5$ kJ mol^{-1} ($\sigma = 0.570$) was then used in eqn. (1) for subsequent ternary calculations. This particular approach, while by no means perfect, is the best that can be done at the present time with the limited experimental data available.

Tables 3–6 compare experimental excess molar enthalpies of ternary acetone–bromoform–cyclohexane, acetone–bromoform–*n*-heptane, acetone–bromoform–*n*-decane and acetone–bromoform–*n*-hexane mixtures to calculated values based on eqn. (1). Weighting factors used in these predictions were either approximated with molar volumes (column 4) or evaluated from acetone–alkane and bromoform–alkane binary $\overline{H}^{\mathrm{ex}}$ data (column 5) as suggested by Bertrand and co-workers [19,20]. The $\Gamma_{\mathrm{acetone}}/\Gamma_{\mathrm{bromoform}}$ ratio was determined from the normalization condition

$$\Gamma_{\mathrm{acetone}}/\Gamma_{\mathrm{bromoform}} = \left(\Gamma_{\mathrm{acetone}}/\Gamma_{\mathrm{alkane}}\right)\left(\Gamma_{\mathrm{alkane}}/\Gamma_{\mathrm{bromoform}}\right)$$

since it could not be obtained using binary acetone–bromoform data, because $C_{\mathrm{A_1B_1}}$ was set equal to zero in the K^x_{AB} and $\Delta \overline{H}^0_{\mathrm{AB}}$ calculations. Careful examination of the fourth and fifth columns reveals that there is no clear superiority between the two different weighting factor approximations. For acetone–bromoform–*n*-decane mixtures the weighting factors are best calculated from the binary data, whereas for mixtures with *n*-heptane molar volumes appear to provide the better Γ_i values. In either case, though, significant deviations between experimental and predicted values are noted at many of the ternary compositions studied.

PREDICTIONS USING VOLUME FRACTION BASED ASSOCIATION CONSTANT

Failure of eqn. (1) could perhaps result from an incorrect description of the configurational entropic contribution and hence the wrong concentrational form of the equilibrium constant. Equation (1) is based on Raoult's law, and as a result K^x_{AC} is expressed in terms of mole fractions. For the four acetone–bromoform–alkane systems it is entirely possible that the Flory–Huggins model might provide the better description of solution ideality, in which case the Gibbs free energy of mixing should be written as

$$\mathrm{A_1} + \mathrm{B_1} \rightleftharpoons \mathrm{AB}$$

$$K^{\phi}_{\mathrm{AB}} = \frac{\hat{\phi}_{\mathrm{AB}}}{\hat{\phi}_{\mathrm{A_1}}\hat{\phi}_{\mathrm{B_1}}} = \frac{\hat{\phi}_{\mathrm{AB}}}{\left[\phi_{\mathrm{A}} - \hat{\phi}_{\mathrm{AB}}\overline{V}_A/\left(\overline{V}_{\mathrm{A}} + \overline{V}_{\mathrm{B}}\right)\right]\left[\phi_{\mathrm{B}} - \hat{\phi}_{\mathrm{AB}}\overline{V}_{\mathrm{B}}/\left(\overline{V}_{\mathrm{A}} + \overline{V}_{\mathrm{B}}\right)\right]}$$

$$
\begin{aligned}
G^{\mathrm{mix}} = RT\Big[&\hat{n}_{\mathrm{A}_1} \ln \hat{\phi}_{\mathrm{A}_1} + \hat{n}_{\mathrm{B}_1} \ln \hat{\phi}_{\mathrm{B}_1} + \hat{n}_{\mathrm{C}} \ln \hat{\phi}_{\mathrm{C}} + \hat{n}_{\mathrm{AB}} \ln \hat{\phi}_{\mathrm{AB}}\Big] \\
&+ \left(\hat{n}_{\mathrm{A}_1}\Gamma_{\mathrm{A}} + \hat{n}_{\mathrm{B}_1}\Gamma_{\mathrm{B}} + \hat{n}_{\mathrm{C}}\Gamma_{\mathrm{C}} + \hat{n}_{\mathrm{AB}}\Gamma_{\mathrm{AB}}\right)\Big[\hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{B}_1}A_{\mathrm{A}_1\mathrm{B}_1} + \hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{C}}A_{\mathrm{A}_1\mathrm{C}} \\
&+ \hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{A}_1\mathrm{AB}} + \hat{f}_{\mathrm{B}_1}\hat{f}_{\mathrm{C}}A_{\mathrm{B}_1\mathrm{C}} + \hat{f}_{\mathrm{B}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{B}_1\mathrm{AB}} + \hat{f}_{\mathrm{C}}\hat{f}_{\mathrm{AB}}A_{\mathrm{CAB}}\Big] \qquad (10)
\end{aligned}
$$

where ϕ_i is the volume fraction of component i and A_{ij} is a binary interaction parameter independent of composition. The circumflex accent ($\hat{\ }$) denotes the "true" compositions in the associated solution.

Through suitable mathematical manipulations and judicious approximation of $A_{\mathrm{A}_1\mathrm{AB}}$ and $A_{\mathrm{B}_1\mathrm{AB}}$ parameters, Acree et al. [21,22] showed that eqn. (10) can be expressed in terms of only three binary interaction parameters

$$
\begin{aligned}
G^{\mathrm{mix}} = RT\Bigg[&n_{\mathrm{A}} \ln \hat{\phi}_{\mathrm{A}_1} + n_{\mathrm{B}} \ln \hat{\phi}_{\mathrm{B}_1} + n_{\mathrm{C}} \ln \hat{\phi}_{\mathrm{C}} + n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}} \\
&- \frac{\left(n_{\mathrm{A}}\overline{V}_{\mathrm{A}} + n_{\mathrm{B}}\overline{V}_{\mathrm{B}} + n_{\mathrm{C}}\overline{V}_{\mathrm{C}}\right)}{\hat{V}_{\mathrm{soln}}}\Bigg] + \left(n_{\mathrm{A}}\Gamma_{\mathrm{A}} + n_{\mathrm{B}}\Gamma_{\mathrm{B}} + n_{\mathrm{C}}\Gamma_{\mathrm{C}}\right) \\
&\times\left[f_{\mathrm{A}}f_{\mathrm{B}}A_{\mathrm{A}_1\mathrm{B}_1} + f_{\mathrm{A}}f_{\mathrm{C}}A_{\mathrm{A}_1\mathrm{C}} + f_{\mathrm{B}}f_{\mathrm{C}}A_{\mathrm{B}_1\mathrm{C}}\right] \qquad (11)
\end{aligned}
$$

where $\Gamma_{\mathrm{AB}} = \Gamma_{\mathrm{A}} + \Gamma_{\mathrm{B}}$, $n_{\mathrm{A}} = \hat{n}_{\mathrm{A}_1} + \hat{n}_{\mathrm{AB}}$, $n_{\mathrm{B}} = \hat{n}_{\mathrm{B}_1} + \hat{n}_{\mathrm{AB}}$ and $\hat{V}_{\mathrm{soln}}$ is the molar volume of the "true" associated solution. An expression for the excess molar enthalpy is obtained by differentiating the Gibbs free energy of mixing with respect to temperature

$$
\overline{H}^{\mathrm{ex}} = r\,\Delta\overline{H}^0_{\mathrm{AB}} + \left(n_{\mathrm{A}}\Gamma_{\mathrm{A}} + n_{\mathrm{B}}\Gamma_{\mathrm{B}} + n_{\mathrm{C}}\Gamma_{\mathrm{C}}\right)\left[f_{\mathrm{A}}f_{\mathrm{B}}C_{\mathrm{A}_1\mathrm{B}_1} + f_{\mathrm{A}}f_{\mathrm{C}}C_{\mathrm{A}_1\mathrm{C}} + f_{\mathrm{B}}f_{\mathrm{C}}C_{\mathrm{B}_1\mathrm{C}}\right] \qquad (12)
$$

with r defined as $r = \hat{n}_{\mathrm{AB}}/(n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}) = \hat{\phi}_{\mathrm{AB}}(X_{\mathrm{A}}\overline{V}_{\mathrm{A}} + X_{\mathrm{B}}\overline{V}_{\mathrm{B}} + X_{\mathrm{C}}\overline{V}_{\mathrm{C}})/(\overline{V}_{\mathrm{A}} + \overline{V}_{\mathrm{B}})$. For simplicity we have assumed that all weighting factors and molar volume ratios are independent of temperature. Inherent in this particular treatment is the additional assumption that there is no excess volume of mixing.

Careful examination of eqn. (12) reveals that, for model systems obeying this model, the enthalpic properties of the two noncomplexing contributive subbinary systems would obey (per mole of binary solution)

$$
\left(\overline{H}^{\mathrm{ex}}_{\mathrm{AC}}\right)^{\star} = X^0_{\mathrm{A}}X^0_{\mathrm{C}}\,\Gamma_{\mathrm{A}}\Gamma_{\mathrm{C}}C_{\mathrm{A}_1\mathrm{C}}/\left(X^0_{\mathrm{A}}\Gamma_{\mathrm{A}} + X^0_{\mathrm{C}}\Gamma_{\mathrm{C}}\right) \qquad (13)
$$

$$
\left(\overline{H}^{\mathrm{ex}}_{\mathrm{BC}}\right)^{\star} = X^0_{\mathrm{B}}X^0_{\mathrm{C}}\Gamma_{\mathrm{B}}\Gamma_{\mathrm{C}}C_{\mathrm{B}_1\mathrm{C}}/\left(X^0_{\mathrm{B}}\Gamma_{\mathrm{B}} + X^0_{\mathrm{C}}\Gamma_{\mathrm{C}}\right) \qquad (14)
$$

where the "0" superscript indicates binary mole fractions calculated as if the third component were not present. Equation (12) can then be rearranged to the following form

$$
\begin{aligned}
\overline{H}^{\mathrm{ex}} = r\,\Delta\overline{H}^0_{\mathrm{AB}} &+ \left(X_{\mathrm{A}}\Gamma_{\mathrm{A}} + X_{\mathrm{B}}\Gamma_{\mathrm{B}} + X_{\mathrm{C}}\Gamma_{\mathrm{C}}\right)f_{\mathrm{A}}f_{\mathrm{B}}C_{\mathrm{A}_1\mathrm{B}_1} \\
&+ \left(X_{\mathrm{A}} + X_{\mathrm{C}}\right)\left(f_{\mathrm{A}} + f_{\mathrm{C}}\right)\left(\overline{H}^{\mathrm{ex}}_{\mathrm{AC}}\right)^{\star} \\
&+ \left(X_{\mathrm{B}} + X_{\mathrm{C}}\right)\left(f_{\mathrm{B}} + f_{\mathrm{C}}\right)\left(\overline{H}^{\mathrm{ex}}_{\mathrm{BC}}\right)^{\star} \qquad (15)
\end{aligned}
$$

for one mole of ternary solution. Most of the specific elements of the model eqn. (10) have been removed. Only the weighting factors required to relate f_i to the mole fraction composition of the system and a single $C_{A_1B_1}$ binary parameter remain. The two $(\overline{H}_{ij}^{ex})^{\star}$ terms correspond to actual experimentally determined excess data of the AC and BC subbinaries at X_i^0 and X_j^0.

Predictive application of eqn. (15) to the four ternary acetone–bromoform–alkane mixtures requires a prior knowledge of the acetone–bromoform association constant and standard reaction enthalpy. As before, "best" values of $K_{AB}^{\phi} = 7.5$ and $\Delta\overline{H}_{AB}^0 = -6.62$ kJ mol^{-1} are obtained by forcing the measured acetone–bromoform enthalpy data to fit the appropriate binary reduction of eqn. 15, i.e., $\overline{H}^{ex} = r\,\Delta\overline{H}_{AB}^0$. Variation of K_{AB}^{ϕ} by ± 0.5 leads to a slightly different average reaction enthalpy, but the standard deviation in $\Delta\overline{H}_{AB}^0$ remains essentially constant near the minimized value of $\sigma \approx 0.54$ kJ mol^{-1}. The two calculated association parameters do provide a fairly reasonable (but by no means perfect) description of the acetone–bromoform system, particularly in light of the many simplifying approximations made in the original derivation. Equation (15) and its mole fraction based counterpart, eqn. (1), have comparable descriptive abilities as far as the acetone–bromoform system is concerned. Readers should be aware, however, that neither equation is able to "back calculate" the binary $\overline{H}^{ex}$ values to within experimental uncertainty.

The last two columns in Tables 3–6 list calculated $\overline{H}^{ex}$ values based on eqn. (15), with weighting factors approximated by molar volumes (column 6) and evaluated from measured binary data (column 7). Inspection of all four tables reveals that there is no significant difference between the various weighting factor approximations or concentrational forms of the association constants, K_{AB}^{x} versus K_{AB}^{ϕ}. Predictions using a mole fraction association constant differ by less than about 30 J mol^{-1} from the corresponding values based on eqn. (15) and, with the exception of the acetone–bromoform–*n*-decane system, there is no a priori way of knowing which expression is more likely to give the best set of predictions. Surprisingly, for ternary mixtures containing *n*-decane cosolvent the predictions of eqn. (1) are clearly superior to those of eqn. (15). Differences between the two predictive expressions should become even more pronounced with larger hydrocarbon cosolvents. Acetone ($\overline{V} \approx 73.98$ cm^3 mol^{-1}) and bromoform ($\overline{V} \approx 87.89$ cm^3 mol^{-1}) are approximately the same size, and it is only by introducing an inert hydrocarbon cosolvent that one is able to distinguish between configurational entropic contributions based on Raoult's law or the Flory–Huggins definition of solution ideality. One would expect the Flory–Huggins model to have provided the better description of solution ideality in the acetone–bromoform–*n*-decane system, as considerable size disparity exists. Thermochemical investigations on ternary associated solutions can provide valuable information on molecular complexation which cannot be obtained via experimental measurements on the complexing binary system

At the moment we prefer not to overemphasize differences in predictive abilities of eqns. (1) and (15), as both expressions fail badly at many of the ternary compositions studied. It is entirely possible that the "apparent" superiority of eqn. (1) for the acetone–bromoform–*n*-decane system results from either neglect of nonspecific interactions in the binary acetone–bromoform system ($C_{A_1B_1} = 0$) or the formation of a higher-order AB_2 molecular complex. We believe that a re-evaluation of the equilibrium constant and standard reaction enthalpy with $C_{A_1B_1} \neq 0$ might give a more realistic set of association parameters. The predicted values depend to a large extent on the numerical values $C_{A_1B_1}$, K_{AB} and $\Delta\bar{H}^0_{AB}$ input into the calculations. Earlier solubility studies involving carbazole dissolved in binary alkane–dibutyl ether [23,24] and chloroalkane–dibutyl ether [25,26] solvent mixtures have shown that neglect of weak nonspecific interactions can have a rather dramatic effect on the calculated association parameters. The effects of the inert hydrocarbon cosolvent, the $C_{A_1B_1} = 0$ approximation and possible formation of an AB_2 molecular complex will be explored in greater detail as additional experimental data become available.

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