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THERMOCHEMICAL INVESTIGATIONS OF ASSOCIATED SOLUTIONS. 10. EXCESS ENTHALPIES AND EXCESS VOLUMES OF TERNARY ACETONE + BROMOFORM + *n*-HEXANE MIXTURES

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ABSTRACT

Excess molar volumes and excess enthalpies are reported for binary acetone + *n*-hexane, bromoform + *n*-hexane and acetone + bromoform mixtures, and for the ternary acetone + bromoform + *n*-hexane system at 308.15 K. Results of these measurements are used to test the applications and limitations of a newly derived conventional non-electrolyte associated solution model. The general model assumes that the Gibbs free energy, excess volume and excess enthalpy 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. Six binary interaction parameters are initially needed to describe all the binary non-specific interactions present. Simplifying approximations and mathematical manipulations reduces the number of binary interaction parameters to only three values.

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 non-electrolyte liquid mixtures with convenience and accuracy. The utilization of continuous dilution methods, combined with modern chromatographic head-space sampling techniques, has reduced

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the experimental time needed for the determination of excess Gibbs free 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. To address this problem researchers have turned to predictive methods as a way to generate desired quantities. Numerous equations have been derived for predicting the properties of ternary and higher-order multicomponent systems from published binary and pure component experimental data. For the most part, the predictive methods do provide fairly reasonable estimates for non-complexing systems. There still remains, however, the need to develop better predictive expressions and mixing models to describe the more non-ideal complexing systems.

Historically, the thermodynamic treatment of complexing systems can be traced back to the Ideal Associated Solution (IAS) model which attributes all solution non-ideality to the formation of new chemical species [1–4]; that is, contributions to non-ideality arising from differences in molecular shape, size and polarity (often called "physical" interactions and described using the Scatchard–Hildebrand Regular Solution approach or a similar thermodynamic model) are assumed negligible compared to chemical (specific) interactions. Neglect of the non-specific physical interactions does limit the applicability of the IAS model to systems having very strong molecular complexes and to a few select weaker associating systems such as binary triethylamine + chloroform [5–7] and *p*-dioxane + chloroform [8,9] mixtures. The underlying principles of the IAS model do provide, however, the basis for many of today's more sophisticated thermodynamic treatments.

Earlier papers in this series [10–18] have addressed the problems associated with the incorporation of both specific and non-specific interactions into various associated solution models. Expressions have been derived for the calculation of volume-fraction-based and mole-fraction-based solute–solvent association constants from the measured solute solubility as a function of solvent composition and the excess Gibbs free energy of the binary solvent mixture [10,12,15]

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

$$K_{\mathrm{AC}}^{X} = \hat{X}_{\mathrm{AC}} / \left(\hat{X}_{\mathrm{A}_1} \hat{X}_{\mathrm{C}_1} \right)$$

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

$$\begin{aligned} \ln X_{\mathrm{A}}^{\mathrm{sat}} = {} & \phi_{\mathrm{B}}^{0} \ln\left(X_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{B}} + \phi_{\mathrm{C}}^{0} \ln\left(X_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{C}} + \ln\left[1 + K_{\mathrm{AC}}^{X} X_{\mathrm{C}}^{0}\right] \\ & - \phi_{\mathrm{C}}^{0} \ln\left[1 + K_{\mathrm{AC}}^{X}\right] + \bar{V}_{\mathrm{A}} \bar{G}_{\mathrm{BC}}^{\mathrm{ex}} / RT\left(X_{\mathrm{B}}^{0} \bar{V}_{\mathrm{B}} + X_{\mathrm{C}}^{0} \bar{V}_{\mathrm{C}}\right) \end{aligned} \quad (2)$$

The superscript 0 denotes initial solvent compositions which are calculated as if the solute were not present.

McCargar and Acree [12–16] compared values for 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 iso-octane cosolvent were significantly different from values for the cyclo-octane system. In comparison, eqns. (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 both iso-octane and *t*-butylcyclohexane. The success of eqns. (1) and (2) is even more remarkable if one realizes that the carbazole mole-fraction solubilities covered a 25-fold range, and the inert cosolvents included both small (cyclohexane, *n*-hexane) and large (squalane, *n*-hexadecane) saturated hydrocarbons.

As a continuation of our studies on the thermodynamic properties of associated solutions, we have initiated a program to systematically examine the effects of inert hydrocarbons on solute–solvent association constants determined from experimental excess volume and excess enthalpy data. Two previous papers [17,18] attempted to thermodynamically model the ternary acetone + cyclohexane + chloroform system which is believed to contain 1 : 1 and 1 : 2 acetone–chloroform molecular complexes. While the derived equations did provide fairly reasonable estimates for many of the ternary compositions, a firm conclusion regarding the effect of an inert hydrocarbon cosolvent on complex formation could not be reached. The study was limited to a single cyclohexane cosolvent and there were four association parameters involved in each thermodynamic treatment. Six parameters were required to describe both excess volumes and excess enthalpies. With the hope of improving our understanding of the inert hydrocarbon effects, we have decided to return to much simpler systems with only a single molecular complex. In this paper, we report excess enthalpies and excess volumes for ternary acetone + bromoform + *n*-hexane mixtures and for the three individual sub-binary systems. The results of these measurements are compared to predicted values based on a simplified form of the Extended NIBS model.

EXPERIMENTAL

Acetone (Glaxo Lab., 99.5+%), bromoform (E. Merck, 98+%) and *n*-hexane (S.D. Fine-Chem. Pvt. Ltd., 90+%) were purchased from commer-

TABLE 1

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

Compound	Density (g cm^{-3})		
	Experimental	Literature	Ref.
Acetone	0.78512	0.78508	22
		0.78516	23
		0.78508	24
Bromoform	2.87576	2.8758	25
n-Hexane	0.65475	0.65480	26
		0.65481	27
		0.65479	28

cial sources and purified according to published methods [19–21]; purities of the final samples were checked by measuring their densities at 298.15 ± 0.01 K and these agreed to within ±0.00005 g cm^{-3} with their corresponding literature values as is shown in Table 1.

Molar excess volume, $\overline{V}^{ex}$, data at 308.15 K were measured using 2- and 3-limb dilatometers in the manner described earlier [29]. Briefly, the accurately weighed pure components were kept separated in a U-shaped dilatometer by a thread of mercury. The dilatometer was then equilibrated in a constant temperature water bath at 308.15 ± 0.01 K. After attainment of thermal equilibrium the position of both the contained liquid and reference mark in the calibrated dilatometer capillary were noted with a cathetometer which could read to ±0.001 cm. The separated pure components were then thoroughly mixed by tilting the dilatometer back and forth. To ensure a homogeneous solution, the dilatometer was temporarily removed from the water bath and cooled slightly so that most of the liquid trapped inside the capillary returned to the bulk solution. The dilatometer was returned to the water bath and this entire process was repeated three times before the dilatometer was clamped into the bath for the final thermal equilibrium and volume measurement. $\overline{V}^{ex}$ values were calculated from the change in the position of the liquid level in the dilatometer capillary and the volume per cm length. The capillary was calibrated by weighing a column of mercury thread. Estimated uncertainties in the measured $\overline{V}^{ex}$ values are believed to be in the order of ±0.5%.

Molar excess enthalpies, $\overline{H}^{ex}$, for the various binary systems at 308.15 K were determined using an LKB flow microcalorimeter LKB-2107 (M/s, LKB, Broma, Sweden) in the manner described by Monk and Wadso [30]. The precision and stability of the instrument in terms of temperature are 0.1 K and ±0.01 K/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 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 $\bar{H}^{ex}$ measurement, different calibration constants were determined according to the flow rate, the amplification

TABLE 2

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

X_i	$\bar{V}^{ex}$ (cm^3 mol^{-1})	X_i	$\bar{V}^{ex}$ (cm^3 mol^{-1})
Acetone (i) + bromoform (j)			
0.0425	−0.052	0.5652	−0.348
0.0952	−0.106	0.6251	−0.345
0.1601	−0.167	0.6623	−0.336
0.1825	−0.191	0.7052	−0.320
0.2250	−0.220	0.7535	−0.295
0.2872	−0.261	0.7997	−0.259
0.3432	−0.292	0.8501	−0.212
0.3853	−0.311	0.8831	−0.178
0.4426	−0.334	0.9105	−0.144
0.4951	−0.345	0.9612	−0.068
$v_{ij}^{(0)} = -1.3811$; $v_{ij}^{(1)} = -0.3025$; $v_{ij}^{(2)} = -0.1642$; $\sigma = 0.001$			
n-Hexane (i) + acetone (j)			
0.0325	0.121	0.5102	1.083
0.0859	0.302	0.5650	1.073
0.1264	0.425	0.6151	1.050
0.2069	0.651	0.6552	1.011
0.2421	0.736	0.6872	0.978
0.2834	0.825	0.7712	0.822
0.3051	0.861	0.8350	0.648
0.3572	0.952	0.8972	0.445
0.4003	1.001	0.9551	0.207
0.4834	1.073		
$v_{ij}^{(0)} = 4.3043$; $v_{ij}^{(1)} = 0.6035$; $v_{ij}^{(2)} = 0.0275$; $\sigma = 0.003$			
Bromoform (i) + n-hexane (j)			
0.0461	−0.074	0.5491	−0.383
0.0963	−0.142	0.5928	−0.375
0.1446	−0.197	0.5999	−0.374
0.1964	−0.248	0.6449	−0.361
0.2414	−0.284	0.6979	−0.323
0.2948	−0.322	0.7515	−0.282
0.3449	−0.345	0.8044	−0.238
0.3898	−0.362	0.8509	−0.189
0.4546	−0.381	0.9008	−0.131
0.4999	−0.385	0.9605	−0.054
$v_{ij}^{(0)} = -1.5365$; $v_{ij}^{(1)} = -0.0665$; $v_{ij}^{(2)} = 0.2135$; $\sigma = 0.001$			

TABLE 3

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
$h_{ij}^{(0)} = -6183.06$; $h_{ij}^{(1)} = 656.37$; $h_{ij}^{(2)} = 474.97$; $\sigma = 3.1$			
n-Hexane (i) + acetone (j)			
0.0958	590	0.3880	1668
0.0995	603	0.5551	1825
0.1931	1060	0.5651	1824
0.2191	1171	0.6219	1780
0.2229	1185	0.7677	1430
0.3651	1622	0.7713	1423
0.3655	1629	0.8714	943
0.3831	1659		
$h_{ij}^{(0)} = 7258.92$; $h_{ij}^{(1)} = 1111.95$; $h_{ij}^{(2)} = 631.38$; $\sigma = 3.0$			
Bromoform (i) + n-hexane (j)			
0.1158	421	0.6246	1386
0.2210	798	0.6294	1382
0.2284	817	0.7697	1087
0.3906	1264	0.7768	1062
0.4290	1328	0.8151	929
0.4344	1343	0.8985	562
0.6064	1410	0.9003	548
0.6068	1409	0.9478	300
$h_{ij}^{(0)} = 5648.61$; $h_{ij}^{(1)} = 1344.42$; $h_{ij}^{(2)} = -906.35$; $\sigma = 3.4$			

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 $\overline{H}^{\text{ex}}$ values are believed to be in the order of ±1% or better. The performance of the calorimeter has been previously checked [31] by comparing measured $\overline{H}^{\text{ex}}$ data for the binary benzene + carbon tetrachloride system with literature data [32].

Experimental excess molar volumes and enthalpies of binary acetone + n-hexane, acetone + bromoform and bromoform + n-hexane mixtures are tabulated in Tables 2 and 3, along with the coefficients and corresponding standard deviations for the Redlich–Kister representation

$$\overline{V}^{ex} = X_i X_j \sum_{n=0} v_{ij}^{(n)} (X_i - X_j)^n \tag{3}$$

$$\overline{H}^{ex} = X_i X_j \sum_{n=0} h_{ij}^{(n)} (X_i - X_j)^n \tag{4}$$

Ternary volume and enthalpy data are listed in Tables 4 and 5, with the

TABLE 4

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

X_A	X_B	$\overline{V}^{ex}$ (cm^3 mol^{-1})	Predicted $\overline{V}^{ex}$ values (cm^3 mol^{-1})		
			Eqn. (32) [a]	Eqn. (32) [b]	Eqn. (47)
0.0519	0.8105	−0.215	−0.186	−0.184	−0.220
0.0707	0.2450	−0.109	−0.043	−0.042	−0.210
0.0818	0.3238	−0.185	−0.099	−0.097	−0.223
0.0871	0.4424	−0.280	−0.189	−0.179	−0.299
0.0991	0.6537	−0.300	−0.225	−0.216	−0.305
0.1012	0.6025	−0.386	−0.223	−0.214	−0.316
0.1122	0.7570	−0.245	−0.204	−0.191	−0.253
0.1127	0.2867	−0.095	0.007	0.012	−0.146
0.1582	0.2403	0.040	0.160	0.171	−0.020
0.1606	0.6883	−0.268	−0.219	−0.196	−0.286
0.1729	0.5024	−0.255	−0.141	−0.116	−0.282
0.2549	0.5921	−0.272	−0.225	−0.184	−0.308
0.2598	0.1468	0.376	0.499	0.517	0.324
0.2667	0.5190	−0.246	−0.200	−0.120	−0.285
0.3339	0.3506	−0.065	0.062	0.116	−0.103
0.3613	0.1478	0.430	0.568	0.599	0.416
0.3936	0.4102	−0.168	−0.101	−0.039	−0.212
0.4057	0.1650	0.380	0.516	0.555	0.376
0.4560	0.2054	0.229	0.366	0.418	0.244
0.4842	0.3124	−0.054	0.025	0.088	−0.032
0.5375	0.2451	0.059	0.150	0.210	0.073
0.5651	0.1019	0.525	0.623	0.659	0.579
0.5965	0.2067	0.100	0.188	0.241	0.138
0.6524	0.1239	0.319	0.401	0.441	0.343
0.6958	0.1620	0.100	0.164	0.202	0.153
0.7078	0.2487	−0.202	−0.175	−0.155	−0.183
0.7379	0.0924	0.294	0.403	0.433	0.370
0.7472	0.1126	0.186	0.247	0.276	0.258
0.7914	0.1294	0.020	0.067	0.089	0.077
0.8120	0.0454	0.352	0.383	0.397	0.418
0.8215	0.0695	0.204	0.246	0.263	0.272
0.8295	0.0941	0.176	0.114	0.130	0.130

$v_{ABC}^{(0)} = -5.1891$; $v_{ABC}^{(1)} = 7.6432$; $v_{ABC}^{(2)} = -3.7824$; $\sigma = 0.002$

[a] Weighting factors approximated with molar volumes.

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

TABLE 5

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

X_A	X_B	$\overline{H}^{ex}$ (J mol^{-1})	Predicted $\overline{H}^{ex}$ values (J mol^{-1})		
			Eqn. (33) [a]	Eqn. (33) [b]	Eqn. (48)
0.0251	0.0943	476	504	499	530
0.0478	0.1793	789	857	836	768
0.0882	0.3311	988	1249	1187	813
0.0921	0.3455	975	1260	1195	785
0.1018	0.0281	785	817	812	664
0.1345	0.5033	659	1041	952	398
0.1633	0.6125	152	500	430	−38
0.1727	0.6476	−53	259	203	−204
0.1898	0.7119	−475	−261	−284	−537
0.1902	0.7133	−493	−274	−296	−545
0.1914	0.0528	1148	1250	1235	953
0.1976	0.0545	1162	1269	1255	964
0.3308	0.0913	1199	1466	1438	1011
0.3615	0.0998	1140	1446	1416	970
0.3658	0.1009	1130	1443	1412	965
0.4983	0.1375	735	1093	1059	595
0.5130	0.1416	668	1030	996	538
0.5166	0.1426	660	1014	980	522
0.6023	0.1662	255	543	518	124
0.6207	0.1713	146	421	396	27
0.6259	0.1727	126	385	362	−1
0.6535	0.1804	−45	182	163	−226
0.7016	0.1936	−350	−213	−222	−450
0.7143	0.1971	−437	−326	−333	−531
0.7394	0.2041	−625	−561	−542	−734

$h_{ABC}^{(0)} = -14300$; $h_{ABC}^{(1)} = 16147$; $h_{ABC}^{(2)} = -64537$; $\sigma = 3.97$

[a] Weighting factors approximated with molar volumes.

[b] Weighting factors evaluated from binary enthalpy data.

measured values being mathematically parameterized in terms of the 3 sets of $v_{ij}^{(n)}$ (and $h_{ij}^{(n)}$) binary coefficients and additional ternary $V_{ABC}^{(n)}$ (and $h_{ABC}^{(n)}$) terms [33]

$$\overline{V}^{ex} = X_A X_B \sum_{n=0}^{2} v_{AB}^{(n)} (X_A - X_B)^n + X_A X_C \sum_{n=0}^{2} v_{CA}^{(n)} (X_C - X_A)^n + X_B X_C \sum_{n=0}^{2} v_{BC}^{(n)} (X_B - X_C)^n + X_A X_B X_C \sum_{n=0} v_{ABC}^{(n)} X_A^n (X_B - X_C)^n \qquad (5)$$

$$\overline{H}^{ex} = X_A X_B \sum_{n=0}^{2} h_{AB}^{(n)} (X_A - X_B)^n + X_A X_C \sum_{n=0}^{2} h_{CA}^{(n)} (X_C - X_A)^n + X_B X_C \sum_{n=0}^{2} h_{BC}^{(n)} (X_B - X_C)^n + X_A X_B X_C \sum_{n=0} h_{ABC}^{(n)} X_A^n (X_B - X_C)^n \qquad (6)$$

Numerical values of the various ternary parameters and standard deviations are reported at the bottom of the two data tables.

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 physical and a chemical 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 physical contribution. It is often more convenient, however, to derive the corresponding expressions for the volume and enthalpy of mixing by the appropriate differentiation of the Gibbs free energy.

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

$$G^{\text{mix}}_{1,2,\ldots,N} = RT\sum_{i=1}^{N} n_i \ln X_i + \left(\sum_{i=1}^{N} n_i\Gamma_i\right)\left(\sum_{i=1}^{N}\sum_{j>i} f_i f_j A_{ij}\right) \tag{7}$$

where

$$f_i = n_i\Gamma_i \Big/ \left(\sum_{j=1}^{N} n_j\Gamma_j\right) \tag{7a}$$

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 Gibbs free energy binary interaction parameter which is independent of mixture composition. The weighting factors Γ_i represent a rough measure of the skew of the binary excess mixing property from a symmetric curve with a 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.

Application of eqn. (7) to a quaternary (A_1, B_1, C, AB) system

$$A_1 + B_1 \rightleftharpoons AB$$

$$K^{x}_{AB} = \frac{\hat{X}_{AB}}{\hat{X}_{A_1}\hat{X}_{B_1}} = \frac{r(1-r)}{(X_A - r)(X_B - r)} \tag{8}$$

yields the following expression for the Gibbs free energy of mixing

$$\begin{aligned}G^{\mathrm{mix}} = {}& RT\left(\hat{n}_{\mathrm{A}_1}\ln\hat{X}_{\mathrm{A}_1} + \hat{n}_{\mathrm{B}_1}\ln\hat{X}_{\mathrm{B}_1} + \hat{n}_{\mathrm{C}}\ln\hat{X}_{\mathrm{C}} + \hat{n}_{\mathrm{AB}}\ln\hat{X}_{\mathrm{AB}}\right)\\ &+\left(\hat{n}_{\mathrm{A}_1}\Gamma_{\mathrm{A}} + \hat{n}_{\mathrm{B}_1}\Gamma_{\mathrm{B}} + \hat{n}_{\mathrm{C}}\Gamma_{\mathrm{C}} + \hat{n}_{\mathrm{AB}}\Gamma_{\mathrm{AB}}\right)\left(\hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{B}_1}A_{\mathrm{A}_1\mathrm{B}_1} + \hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{C}}A_{\mathrm{A}_1\mathrm{C}}\right.\\ &\left.+\hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{A}_1\mathrm{AB}} + \hat{f}_{\mathrm{B}_1}\hat{f}_{\mathrm{C}}A_{\mathrm{B}_1\mathrm{C}} + \hat{f}_{\mathrm{B}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{B}_1\mathrm{AB}} + \hat{f}_{\mathrm{C}}\hat{f}_{\mathrm{AB}}A_{\mathrm{CAB}}\right)\end{aligned} \tag{9}$$

Chemical potentials of the individual components relative to the pure liquids (μ_i^0) are obtained through the appropriate differentiation

$$\begin{aligned}\hat{\mu}_{\mathrm{A}_1} - \mu_{\mathrm{A}}^0 = {}& RT\ln\hat{X}_{\mathrm{A}_1} + \Gamma_{\mathrm{A}}\left[\hat{f}_{\mathrm{B}_1}\left(1-\hat{f}_{\mathrm{A}_1}\right)A_{\mathrm{A}_1\mathrm{B}_1} + \hat{f}_{\mathrm{C}}\left(1-\hat{f}_{\mathrm{A}_1}\right)A_{\mathrm{A}_1\mathrm{C}}\right.\\ &\left.+\hat{f}_{\mathrm{AB}}\left(1-\hat{f}_{\mathrm{A}_1}\right)A_{\mathrm{A}_1\mathrm{AB}} - \hat{f}_{\mathrm{B}_1}\hat{f}_{\mathrm{C}}A_{\mathrm{B}_1\mathrm{C}} - \hat{f}_{\mathrm{B}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{B}_1\mathrm{AB}} - \hat{f}_{\mathrm{C}}\hat{f}_{\mathrm{AB}}A_{\mathrm{CAB}}\right]\end{aligned} \tag{10}$$

and

$$\begin{aligned}\hat{\mu}_{\mathrm{B}_1} - \mu_{\mathrm{B}}^0 = {}& RT\ln\hat{X}_{\mathrm{B}_1} + \Gamma_{\mathrm{B}}\left[\hat{f}_{\mathrm{A}_1}\left(1-\hat{f}_{\mathrm{B}_1}\right)A_{\mathrm{A}_1\mathrm{B}_1} + \hat{f}_{\mathrm{C}}\left(1-\hat{f}_{\mathrm{B}_1}\right)A_{\mathrm{B}_1\mathrm{C}}\right.\\ &\left.+\hat{f}_{\mathrm{AB}}\left(1-\hat{f}_{\mathrm{B}_1}\right)A_{\mathrm{B}_1\mathrm{AB}} - \hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{C}}A_{\mathrm{A}_1\mathrm{C}} - \hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{A}_1\mathrm{AB}} - \hat{f}_{\mathrm{C}}\hat{f}_{\mathrm{AB}}A_{\mathrm{CAB}}\right]\end{aligned} \tag{11}$$

and

$$\begin{aligned}\hat{\mu}_{\mathrm{C}_1} - \mu_{\mathrm{C}}^0 = {}& RT\ln\hat{X}_{\mathrm{C}} + \Gamma_{\mathrm{C}}\left[\hat{f}_{\mathrm{A}_1}\left(1-\hat{f}_{\mathrm{C}}\right)A_{\mathrm{A}_1\mathrm{C}} + \hat{f}_{\mathrm{B}_1}\left(1-\hat{f}_{\mathrm{C}}\right)A_{\mathrm{B}_1\mathrm{C}}\right.\\ &\left.+\hat{f}_{\mathrm{AB}}\left(1-\hat{f}_{\mathrm{C}}\right)A_{\mathrm{CAB}} - \hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{B}_1}A_{\mathrm{A}_1\mathrm{B}_1} - \hat{f}_{\mathrm{A}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{A}_1\mathrm{AB}} - \hat{f}_{\mathrm{B}_1}\hat{f}_{\mathrm{AB}}A_{\mathrm{B}_1\mathrm{AB}}\right]\end{aligned} \tag{12}$$

The compositions in eqns. (8)–(12) denoted by ^ refer to the quaternary system and not to the stoichiometric mole and weighted mole fractions.

For this particular association model, the true equilibrium mole fractions can be calculated from the known stoichiometric compositions and association constant

$$\hat{X}_{\mathrm{A}_1} = (X_{\mathrm{A}} - r)/(1-r) \tag{13}$$

$$\hat{X}_{\mathrm{B}_1} = (X_{\mathrm{B}} - r)/(1-r) \tag{14}$$

$$\hat{X}_{\mathrm{AB}} = r/(1-r) \tag{15}$$

$$\hat{X}_{\mathrm{C}} = X_{\mathrm{C}}/(1-r) \tag{16}$$

$$r = \hat{n}_{\mathrm{AB}}/\left(n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}\right) = \hat{n}_{\mathrm{AB}}/\left(\hat{n}_{\mathrm{A}_1} + \hat{n}_{\mathrm{B}_1} + \hat{n}_{\mathrm{C}} + 2\hat{n}_{\mathrm{AB}}\right) \tag{17}$$

Similarly, the equilibrium mole numbers of each component can be calculated from the following four expressions

$$\hat{n}_{A_1} = n_A - \hat{n}_{AB} \tag{18}$$

$$\hat{n}_{B_1} = n_B - \hat{n}_{AB} \tag{19}$$

$$\hat{n}_C = n_C \tag{20}$$

$$\hat{n}_{AB} = r(n_A + n_B + n_C) \tag{21}$$

The amount of inert cosolvent C is unchanged by the formation of the AB molecular complex.

As shown in many thermodynamic textbooks, e.g. Acree [4], the chemical potential of stoichiometric component A (and also B) is equal to the chemical potentials of the monomeric (uncomplexed) species in solution: $\hat{\mu}_{A_1} = \mu_A$ and $\hat{\mu}_{B_1} = \mu_B$. Combining eqns. (10)–(12), the Gibbs free energy of mixing of the ternary solution (A, B and C) can be written as

$$\begin{aligned} G^{\text{mix}} = RT\Big[&n_A \ln \hat{X}_{A_1} + n_B \ln \hat{X}_{B_1} + n_C \ln \hat{X}_C\Big] \\ &+ (n_A\Gamma_A + n_B\Gamma_B + n_C\Gamma_C)\Big[f_A \hat{f}_{B_1} A_{A_1B_1} \\ &+ f_A f_C A_{A_1C} + f_A \hat{f}_{AB} A_{A_1AB} + f_B f_C A_{B_1C} + \hat{f}_{A_1} f_B A_{A_1B_1} + f_B \hat{f}_{AB} A_{B_1AB} \\ &- \hat{f}_{A_1} \hat{f}_{B_1} A_{A_1B_1} - \hat{f}_{A_1} \hat{f}_{AB} A_{A_1AB} - \hat{f}_{B_1} \hat{f}_{AB} A_{B_1AB}\Big] \end{aligned} \tag{22}$$

where $\Gamma_{AB} = \Gamma_A + \Gamma_B$, $n_A = \hat{n}_{A_1} + \hat{n}_{AB}$ and $n_B = \hat{n}_{B_1} + \hat{n}_{AB}$. The A_{CAB} binary interaction parameter involving the inert cosolvent and molecular complex is 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, eqn. (22) still contains five A_{ij} terms which is far too many for practical applications. Treatment of the two remaining interaction parameters involving the AB complex in a manner similar to that employed by Bertrand [7] for the triethylamine–chloroform complex leads to

$$A_{A_1AB} = \Gamma_B^2(\Gamma_A + \Gamma_B)^{-2} A_{A_1B_1} \tag{23}$$

$$A_{B_1AB} = \Gamma_A^2(\Gamma_A + \Gamma_B)^{-2} A_{A_1B_1} \tag{24}$$

Substitution of these approximations into eqn. (22), after suitable mathematical manipulations, enables the Gibbs free energy to be expressed in terms of only three interaction parameters

$$\begin{aligned} G^{\text{mix}} = RT\Big[&n_A \ln \hat{X}_{A_1} + n_B \ln \hat{X}_{B_1} + n_C \ln \hat{X}_C\Big] \\ &+ (n_A\Gamma_A + n_B\Gamma_B + n_C\Gamma_C)\Big[f_A f_B A_{A_1B_1} + f_A f_C A_{A_1C} + f_B f_C A_{B_1C}\Big] \end{aligned} \tag{25}$$

Simplification of the general thermodynamic mixing model, eqn. (7), resulted primarily because of the judicious treatment of the binary interaction parameters. Several other methods have been proposed for treating $A_{\mathrm{A_1Complex}}$ and $A_{\mathrm{B_1Complex}}$ parameters, and in later paragraphs an alternative approach suggested by Smith and Hepler [6] will be presented. In the alternative treatment, both of the $A_{\mathrm{A_1AB}}$ and $A_{\mathrm{B_1AB}}$ parameters are arbitrarily set equal to zero.

Expressions for excess volumes and enthalpies can be obtained by differentiating eqn. (25) with respect to pressure and temperature

$$\bar{V}^{\mathrm{ex}} = r\,\Delta\bar{V}^{\ominus}_{\mathrm{AB}} + (X_{\mathrm{A}}\Gamma_{\mathrm{A}} + X_{\mathrm{B}}\Gamma_{\mathrm{B}} + X_{\mathrm{C}}\Gamma_{\mathrm{C}})\left[f_{\mathrm{A}}f_{\mathrm{B}}B_{\mathrm{A_1B_1}} + f_{\mathrm{A}}f_{\mathrm{C}}B_{\mathrm{A_1C}} + f_{\mathrm{B}}f_{\mathrm{C}}B_{\mathrm{B_1C}}\right] \tag{26}$$

$$\bar{H}^{\mathrm{ex}} = r\,\Delta\bar{H}^{\ominus}_{\mathrm{AB}} + (X_{\mathrm{A}}\Gamma_{\mathrm{A}} + X_{\mathrm{B}}\Gamma_{\mathrm{B}} + X_{\mathrm{C}}\Gamma_{\mathrm{C}})\left[f_{\mathrm{A}}f_{\mathrm{B}}C_{\mathrm{A_1B_1}} + f_{\mathrm{A}}f_{\mathrm{C}}C_{\mathrm{A_1C}} + f_{\mathrm{B}}f_{\mathrm{C}}C_{\mathrm{B_1C}}\right] \tag{27}$$

Weighting factors are assumed to be independent of both temperature and pressure: $B_{ij} = (\partial A_{ij}/\partial P)$ and $C_{ij} = \partial(A_{ij}/T)/\partial(1/T)$. The standard reaction volume and enthalpy for the formation of the AB molecular complex are denoted as $\Delta\bar{V}^{\ominus}_{\mathrm{AB}}$ and $\Delta\bar{H}^{\ominus}_{\mathrm{AB}}$, respectively. Careful examination of eqns. (26) and (27) reveals that for model systems obeying this model, the volumetric and enthalpic properties of the two non-complexing contributive binary systems would obey (per mole of binary solution)

$$(\bar{V}^{\mathrm{ex}}_{\mathrm{AC}})^{\star} = X^0_{\mathrm{A}}X^0_{\mathrm{C}}\Gamma_{\mathrm{A}}\Gamma_{\mathrm{C}}B_{\mathrm{A_1C}}/(X^0_{\mathrm{A}}\Gamma_{\mathrm{A}} + X^0_{\mathrm{C}}\Gamma_{\mathrm{C}}) \tag{28}$$

$$(\bar{H}^{\mathrm{ex}}_{\mathrm{AC}})^{\star} = X^0_{\mathrm{A}}X^0_{\mathrm{C}}\Gamma_{\mathrm{A}}\Gamma_{\mathrm{C}}C_{\mathrm{A_1C}}/(X^0_{\mathrm{A}}\Gamma_{\mathrm{A}} + X^0_{\mathrm{C}}\Gamma_{\mathrm{C}}) \tag{29}$$

and

$$(\bar{V}^{\mathrm{ex}}_{\mathrm{BC}})^{\star} = X^0_{\mathrm{B}}X^0_{\mathrm{C}}\Gamma_{\mathrm{B}}\Gamma_{\mathrm{C}}B_{\mathrm{B_1C}}/(X^0_{\mathrm{B}}\Gamma_{\mathrm{B}} + X^0_{\mathrm{C}}\Gamma_{\mathrm{C}}) \tag{30}$$

$$(\bar{H}^{\mathrm{ex}}_{\mathrm{BC}})^{\star} = X^0_{\mathrm{B}}X^0_{\mathrm{C}}\Gamma_{\mathrm{B}}\Gamma_{\mathrm{C}}C_{\mathrm{B_1C}}/(X^0_{\mathrm{B}}\Gamma_{\mathrm{B}} + X^0_{\mathrm{C}}\Gamma_{\mathrm{C}}) \tag{31}$$

where the 0 superscript indicates binary mole fractions calculated as if the third component were not present.

Equations (26) and (27) can then be rearranged to the following forms

$$\begin{aligned}\bar{V}^{\mathrm{ex}} = {} & r\,\Delta\bar{V}^{\ominus}_{\mathrm{AB}} + (X_{\mathrm{A}}\Gamma_{\mathrm{A}} + X_{\mathrm{B}}\Gamma_{\mathrm{B}} + X_{\mathrm{C}}\Gamma_{\mathrm{C}})f_{\mathrm{A}}f_{\mathrm{B}}B_{\mathrm{A_1B_1}} \\ & + (f_{\mathrm{A}} + f_{\mathrm{C}})(X_{\mathrm{A}} + X_{\mathrm{C}})(\bar{V}^{\mathrm{ex}}_{\mathrm{AC}})^{\star} + (f_{\mathrm{B}} + f_{\mathrm{C}})(X_{\mathrm{B}} + X_{\mathrm{C}})(\bar{V}^{\mathrm{ex}}_{\mathrm{BC}})^{\star}\end{aligned} \tag{32}$$

and

$$\begin{aligned}\bar{H}^{\mathrm{ex}} = {} & r\,\Delta\bar{H}^{\ominus}_{\mathrm{AB}} + (X_{\mathrm{A}}\Gamma_{\mathrm{A}} + X_{\mathrm{B}}\Gamma_{\mathrm{B}} + X_{\mathrm{C}}\Gamma_{\mathrm{C}})f_{\mathrm{A}}f_{\mathrm{B}}C_{\mathrm{A_1B_1}} \\ & + (f_{\mathrm{A}} + f_{\mathrm{C}})(X_{\mathrm{A}} + X_{\mathrm{C}})(\bar{H}^{\mathrm{ex}}_{\mathrm{AC}})^{\star} + (f_{\mathrm{B}} + f_{\mathrm{C}})(X_{\mathrm{B}} + X_{\mathrm{C}})(\bar{H}^{\mathrm{ex}}_{\mathrm{BC}})^{\star}\end{aligned} \tag{33}$$

for one mole of ternary solution. Most of the specific elements of the model eqn. (7) have been removed. Only the weighting factors required to relate f_i to the mole fraction composition of the system, and single $B_{\mathrm{A_1B_1}}$ and $C_{\mathrm{A_1B_1}}$

binary parameters remain. The two $(\overline{V}_{ij}^{\mathrm{ex}})^\star$ and $(\overline{H}_{ij}^{\mathrm{ex}})^\star$ terms correspond to actual experimental thermodynamic excess properties of the binary system at X_i^0 and X_j^0. The ternary $\overline{V}^{\mathrm{ex}}$ and $\overline{H}^{\mathrm{ex}}$ expressions are independent of the manner in which the binary data are mathematically represented.

The thermodynamic mixing model derived above resembles the Ideal Associated Solution model in many respects. Although the binary form of the IAS model assumes that all physical contributions to solution non-ideality are negligible, e.g. $B_{\mathrm{A_1B_1}} = C_{\mathrm{A_1B_1}} = 0$, the basic model contains no provisions for treating interactions involving the inert cosolvent. There is no reason to preassume that the inert cosolvent forms an ideal solution with each of the two complexing solvents. The $(\overline{V}_{ij}^{\mathrm{ex}})^\star$ and $(\overline{H}_{ij}^{\mathrm{ex}})^\star$ terms in eqns. (32) and (33) describe the non-ideality in the two sub-binary systems containing the inert cosolvent.

It should be noted that in the absence of complexation ($K_{\mathrm{AB}}^x = 0$), eqns. (25), (32) and (33) reduce to the general Nearly Ideal Binary Solvent (NIBS) mixing model [4,34–37], as $r = 0$ and the mole fractions of all uncomplexed species equal those of the stoichiometric components ($\hat{X}_{\mathrm{A_1}} = X_{\mathrm{A}}$, $\hat{X}_{\mathrm{B_1}} = X_{\mathrm{B}}$ and $\hat{X}_{\mathrm{C_1}} = X_{\mathrm{C}}$). Previous computations [38–40] using the NIBS model have shown that the "best" predictions of multicomponent thermodynamic excess properties are obtained when weighting factors are determined from experimental binary data, particularly in systems having highly skewed excess properties. Weighting factors, which provide a rough measure of the skew of the binary excess mixing property from mole fraction symmetry, can only be evaluated in a relative sense (Γ_i/Γ_j) rather than absolutely. A ratio of raw weighting factors for each binary combination is calculated from binary excess properties at mole fractions $X_i = 0.3333$ and $X_i = 0.6666$, as recommended by Bertrand, Acree and Burchfield [38]

$$\frac{\Gamma_i^{\mathrm{raw}}}{\Gamma_j^{\mathrm{raw}}} = \frac{2\left(\overline{V}_{ij}^{\mathrm{ex}}\right)_{1/3}^\star - \left(\overline{V}_{ij}^{\mathrm{ex}}\right)_{2/3}^\star}{2\left(\overline{V}_{ij}^{\mathrm{ex}}\right)_{2/3}^\star - \left(\overline{V}_{ij}^{\mathrm{ex}}\right)_{1/3}^\star} \tag{34}$$

or

$$\frac{\Gamma_i^{\mathrm{raw}}}{\Gamma_j^{\mathrm{raw}}} = \frac{2\left(\overline{H}_{ij}^{\mathrm{ex}}\right)_{1/3}^\star - \left(\overline{H}_{ij}^{\mathrm{ex}}\right)_{2/3}^\star}{2\left(\overline{H}_{ij}^{\mathrm{ex}}\right)_{2/3}^\star - \left(\overline{H}_{ij}^{\mathrm{ex}}\right)_{1/3}^\star} \tag{35}$$

To ensure that these ratios obey

$$(\Gamma_{\mathrm{A}}/\Gamma_{\mathrm{C}}) = (\Gamma_{\mathrm{A}}/\Gamma_{\mathrm{B}})(\Gamma_{\mathrm{B}}/\Gamma_{\mathrm{C}}) \tag{36}$$

the three raw ratios are combined and normalized to an average value of approximately 100 via

$$\Gamma_{\mathrm{A}} = 300/[(\Gamma_{\mathrm{A}}^{\mathrm{raw}}/\Gamma_{\mathrm{A}}^{\mathrm{raw}}) + (\Gamma_{\mathrm{B}}^{\mathrm{raw}}/\Gamma_{\mathrm{A}}^{\mathrm{raw}}) + (\Gamma_{\mathrm{C}}^{\mathrm{raw}}/\Gamma_{\mathrm{A}}^{\mathrm{raw}})] \tag{37}$$

$$\Gamma_{\mathrm{B}} = 300/[(\Gamma_{\mathrm{A}}^{\mathrm{raw}}/\Gamma_{\mathrm{B}}^{\mathrm{raw}}) + (\Gamma_{\mathrm{B}}^{\mathrm{raw}}/\Gamma_{\mathrm{B}}^{\mathrm{raw}}) + (\Gamma_{\mathrm{C}}^{\mathrm{raw}}/\Gamma_{\mathrm{B}}^{\mathrm{raw}})] \tag{38}$$

$$\Gamma_{\mathrm{C}} = 300/[(\Gamma_{\mathrm{A}}^{\mathrm{raw}}/\Gamma_{\mathrm{C}}^{\mathrm{raw}}) + (\Gamma_{\mathrm{B}}^{\mathrm{raw}}/\Gamma_{\mathrm{C}}^{\mathrm{raw}}) + (\Gamma_{\mathrm{C}}^{\mathrm{raw}}/\Gamma_{\mathrm{C}}^{\mathrm{raw}})] \tag{39}$$

These computations become meaningless if a ratio of raw weighting factors calculated from eqns. (34) or (35) has a negative value, in which case all weighting factors are approximated with molar volumes. Theoretically, the general mixing model requires that weighting factors calculated from binary $\bar{V}^{ex}$ data should equal those values based on excess molar enthalpies. In practice, this theoretical condition is rarely satisfied, and hence a different set of Γ_i values will be needed for each thermodynamic property to be predicted.

RESULTS AND DISCUSSION

Application of eqns. (32) and (33) to ternary acetone + bromoform + n-hexane mixtures requires that the association parameters for the acetone–bromoform complex be calculable from the appropriate binary reductions. Dahiya et al. [41] have previously documented that the binary acetone + bromoform system could be reasonably (not perfectly) described by the IAS model, though 'best' values of $\Delta\bar{H}^0_{AB}$ and $\Delta\bar{V}^0_{AB}$ at 298.15 K were found to vary with mole fraction composition

$$\Delta\bar{H}^{\ominus}_{AB}(\text{kJ mol}^{-1}) = -7.00 + 0.857X_A \tag{40}$$

$$\Delta\bar{V}^{\ominus}_{AB}(\text{cm}^3\text{ mol}^{-1}) = 0.300 + 0.21X_A + 2.076X_A^2 \tag{41}$$

Since these values pertain to a lower temperature, a new set of association parameters must be determined using the experimental $\bar{V}^{ex}$ and $\bar{H}^{ex}$ data at 308.15 K in Tables 2 and 3. One possible method involves evaluating all three parameters (K^X_{AB}, $\Delta\bar{V}^0_{AB}$ and $\Delta\bar{H}^{\ominus}_{AB}$) graphically from the slopes and intercepts of linear plots of $X_AX_B/\bar{V}^{ex}$ versus $\bar{V}^{ex}$ and $X_AX_B/\bar{H}^{ex}$ versus $\bar{H}^{ex}$ [42–45]

$$\frac{X_AX_B}{\bar{V}^{ex}} = -\left[\frac{K^X_{AB}+1}{K^X_{AB}\left(\Delta\bar{V}^{\ominus}_{AB}\right)^2}\right]\bar{V}^{ex} + \frac{K^X_{AB}+1}{K^X_{AB}\,\Delta\bar{V}^{\ominus}_{AB}} \tag{42}$$

$$\frac{X_AX_B}{\bar{H}^{ex}} = -\left[\frac{K^X_{AB}+1}{K^X_{AB}\left(\Delta\bar{H}^{\ominus}_{AB}\right)^2}\right]\bar{H}^{ex} + \frac{K^X_{AB}+1}{K^X_{AB}\,\Delta\bar{H}^{\ominus}_{AB}} \tag{43}$$

provided that the excess values are symmetrical about X_A and the physical interactions between molecules A and B are negligible compared to the stronger chemical interactions. This latter requirement is generally met if the measured $\bar{H}^{ex}$ value exceeds -1.5 kJ mol^{-1} at the equimolar composition of $X_A = 0.50$ [45]. Unfortunately, at 308.15 K the absolute values of $\bar{H}^{ex}$ are considerably less than 1.5 kJ mol^{-1} and neither of the two plots were linear as suggested by eqns. (42) and (43). Physical contributions undoubtedly contribute to the total non-ideality of the acetone + bromoform system.

To overcome this problem, a slightly different computational method had to be employed. The equilibrium constant was assigned a numerical value of $K_{\mathrm{AB}}^{X} = 2.16$ which was obtained by extrapolating two published values [41] of K_{AB}^{X}, -2.38 (NMR) and 2.35 (calorimetric) at 298.15, to 308.15 using an average $\Delta \overline{H}_{\mathrm{AB}}^{\ominus}$ of -6.57 kJ mol^{-1} from eqn. (40), with $X_{\mathrm{A}} = 0.50$. Having determined K_{AB}^{X} in this fashion, we proceeded to calculate r, $\Delta \overline{V}_{\mathrm{AB}}^{\ominus}$ and $\Delta \overline{H}_{\mathrm{AB}}^{0}$ values at each binary composition by forcing the experimental acetone + bromoform data to fit the IAS volumetric ($\overline{V}^{\mathrm{ex}} = r\,\Delta \overline{V}_{\mathrm{AB}}^{\ominus}$) and enthalpic ($\overline{H}^{\mathrm{ex}} = r\,\Delta \overline{H}_{\mathrm{AB}}^{\ominus}$) expressions. Average values of $\Delta \overline{V}_{\mathrm{AB}}^{\ominus} = -1.84$ cm^{3} mol^{-1} ($\sigma = 0.33$) and $\Delta \overline{H}_{\mathrm{AB}}^{\ominus} = -7.500$ kJ mol^{-1} ($\sigma = 0.570$) were then used in eqns. (32) and (33) for subsequent ternary calculations. This particular approach, while by no means perfect, is the best that can be done at present with the limited experimental data available.

Tables 4 and 5 compare the experimental ternary excess volumes and enthalpies with the calculated values based on eqns. (32) and (33). Careful examination of the middle 3 columns reveals that the predictive expressions do provide reasonable estimates of $\overline{V}^{\mathrm{ex}}$ and $\overline{H}^{\mathrm{ex}}$ at several of the ternary compositions. There is only a slight difference between predicted values calculated with molar-volume weighting factors and values based on weighting factors evaluated from acetone + *n*-hexane and bromoform + *n*-hexane binary data. The $\Gamma_{\mathrm{acetone}}/\Gamma_{\mathrm{CHBr_3}}$ weighting factor ratio could not be calculated from the measured binary properties as both $X_{\mathrm{A}}^{0} X_{\mathrm{B}}^{0} \Gamma_{\mathrm{A}} \Gamma_{\mathrm{B}} B_{\mathrm{A_1 B_1}} / (X_{\mathrm{A}}^{0} \Gamma_{\mathrm{A}} + X_{\mathrm{B}}^{0} \Gamma_{\mathrm{B}})$ and $X_{\mathrm{A}}^{0} X_{\mathrm{B}}^{0} \Gamma_{\mathrm{A}} \Gamma_{\mathrm{B}} C_{\mathrm{A_1 B_1}} / (X_{\mathrm{A}}^{0} \Gamma_{\mathrm{A}} + X_{\mathrm{B}}^{0} \Gamma_{\mathrm{B}})$ terms equal zero in the IAS model. Significant deviations are noted between experimental and predicted values for a number of ternary compositions.

Failure of eqns. (32) and (33) at several compositions could perhaps be a result of the manner in which non-specific interactions are incorporated into the basic mixing model. Smith and Hepler [6] proposed a slightly different method in their thermodynamic description of the triethylamine + chloroform + cyclohexane system. The authors calculated the heat of complex dissociation by subtracting the heat caused by triethylamine + cyclohexane and chloroform + cyclohexane interactions, $Q_{\mathrm{TEA,\,C_6H_{12}}}$ and $Q_{\mathrm{CHCl_3,\,C_6H_{12}}}$, from the measured heat of dilution

$$Q^{\mathrm{diss}} = \Delta \hat{n}_{\mathrm{AB}}\, \Delta \overline{H}_{\mathrm{AB}}^{\ominus} = Q^{\mathrm{exp}} - Q_{\mathrm{TEA,\,C_6H_{12}}} - Q_{\mathrm{CHCl_3,\,C_6H_{12}}} \tag{44}$$

The last two terms in eqn. (44) were evaluated for the two sub-binaries from expressions of the form

$$Q_{\mathrm{TEA,\,C_6H_{12}}} = 2\hat{X}_{\mathrm{TEA}} \hat{X}_{\mathrm{C_6H_{12}}} (\hat{n}_{\mathrm{TEA}} + \hat{n}_{\mathrm{C_6H_{12}}}) h_{\mathrm{TEA,\,C_6H_{12}}} \tag{45}$$

$$Q_{\mathrm{CHCl_3,\,C_6H_{12}}} = 2\hat{X}_{\mathrm{CHCl_3}} \hat{X}_{\mathrm{C_6H_{12}}} (\hat{n}_{\mathrm{CHCl_3}} + \hat{n}_{\mathrm{C_6H_{12}}}) h_{\mathrm{CHCl_3,C_6H_{12}}} \tag{46}$$

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 non-specific 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 AB complex in solution should be similar in nature to those between the cosolvent and two complexing solvents.

Extension of this latter approach to integral thermodynamic excess properties should give the following predictive expressions for the acetone + bromoform + n-hexane system

$$\bar{V}^{\mathrm{ex}} = r\,\Delta\bar{V}^{\ominus}_{\mathrm{AB}} + \frac{2\hat{X}_{\mathrm{A_1}}\hat{X}_{\mathrm{C}}(\hat{n}_{\mathrm{A_1}} + \hat{n}_{\mathrm{C}})v_{\mathrm{A_1C}}}{n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}} + \frac{2\hat{X}_{\mathrm{B_1}}\hat{X}_{\mathrm{C}}(\hat{n}_{\mathrm{B_1}} + \hat{n}_{\mathrm{C}})v_{\mathrm{B_1C}}}{n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}} \tag{47}$$

and

$$\bar{H}^{\mathrm{ex}} = r\,\Delta\bar{H}^{\ominus}_{\mathrm{AB}} + \frac{2\hat{X}_{\mathrm{A_1}}\hat{X}_{\mathrm{C}}(\hat{n}_{\mathrm{A_1}} + \hat{n}_{\mathrm{C}})h_{\mathrm{A_1C}}}{n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}} + \frac{2\hat{X}_{\mathrm{B_1}}\hat{X}_{\mathrm{C}}(\hat{n}_{\mathrm{B_1}} + \hat{n}_{\mathrm{C}})h_{\mathrm{B_1C}}}{n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}}} \tag{48}$$

It should be noted that eqns. (47) and (48) are strictly empirical as we are unable to rigorously derive either expression from basic thermodynamic principles. Furthermore, the fact that the physical contributions are expressed in terms of true mole fractions, rather than stoichiometric compositions, will result in a fairly complicated expression for the Gibbs free energy of mixing: remember that $\bar{V}^{\mathrm{ex}}$ and $\bar{H}^{\mathrm{ex}}$ are obtained by differentiating $\bar{G}^{\mathrm{mix}}$ with respect to pressure and temperature, respectively.

As shown in the last column in Tables 4 and 5, eqns. (47) and (48) provide a reasonable mathematical description of the volumetric and enthalpic properties at many of the ternary compositions. Deviations between measured and calculated values are substantially reduced. For this particular ternary system, one must conclude that eqns. (47) and (48) are far superior to eqns. (32) and (33). The applications and limitations of both mixing models still need to be more thoroughly tested using $\bar{V}^{\mathrm{ex}}$ and $\bar{H}^{\mathrm{ex}}$ data for additional ternary acetone + bromoform + alkane mixtures. It should be noted that there are a few compositions for which eqns. (47) and (48) fail. At present, we are unable to explain the few large deviations. We do believe, however, that a re-evaluation of the equilibrium constant and standard reaction enthalpy and volume with $C_{\mathrm{A_1B_1}} \neq 0$ and $B_{\mathrm{A_1B_1}} \neq 0$ might give a more realistic set of association parameters. The predicted values do depend on the numerical values of K^{X}_{AB}, $\Delta\bar{V}^{\ominus}_{\mathrm{AB}}$ and $\Delta\bar{H}^{\ominus}_{\mathrm{AB}}$ used in the calculations. Earlier solubility studies involving carbazole dissolved in binary alkane + dibutyl ether [12,13] and chloroalkane + dibutyl ether [14,46] solvent mixtures have shown that neglect of weak non-specific interactions can have a rather dramatic effect on the calculated association parameters. In closing, readers are reminded that the present study is the beginning of a systematic study of the thermodynamic excess properties of ternary acetone +

bromoform + alkane systems. The effect of the inert hydrocarbon cosolvent, and the $B_{A_1B_1} = C_{A_1B_1} = 0$ approximations will be explored in much greater detail in subsequent papers.

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
C_{ij}	binary interaction parameter for components i and j used in 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
G^{mix}	Gibbs free energy of mixing
$\bar{G}_{ij}^{\mathrm{ex}}$	excess molar Gibbs free energy of the ij binary mixture based on Raoult's Law
$\bar{G}_{ij}^{\mathrm{fh}}$	excess molar Gibbs free energy of the ij binary mixture based on the Flory–Huggins model for solution ideality
$\bar{H}^{\mathrm{ex}}$	excess molar enthalpy
$\Delta \bar{H}_{\mathrm{AB}}^{\ominus}$	standard reaction enthalpy for the formation of the AB molecular complex
$(\bar{H}_{ij}^{\mathrm{ex}})^{\star}$	excess molar enthalpy of the ij binary system at mole fraction compositions X_i^0 and X_j^0
K_{AB}^{X}	mole-fraction-based equilibrium constant for the formation of the AB molecular complex
K_{AC}^{ϕ}	volume-fraction-based equilibrium constant for the formation of the AC molecular complex
n_i	stoichiometric number of moles of component i
$\hat{n}_i$	true number of moles of component i in the associated solution
$\bar{V}_{\mathrm{i}}$	molar volume of component i
$\bar{V}^{\mathrm{ex}}$	excess molar volume
$\Delta \bar{V}_{\mathrm{AB}}^{\ominus}$	standard reaction volume for the formation of the AB molecular complex
$(\bar{V}_{ij}^{\mathrm{ex}})^{\star}$	excess molar volume of the ij binary system at mole fraction compositions X_i^0 and X_j^0
X_i	stoichiometric mole fraction of component i
$\hat{X}_i$	mole fraction of component i, calculated assuming an 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
$X_{\mathrm{A}}^{\mathrm{sat}}$	mole fraction solubility of solute

Greek letters

Γ_i	weighting factor of component *i*
ϕ_i	ideal volume fraction of component *i*
ϕ_i^0, ϕ_j^0	ideal volume-fraction composition of the *ij* binary mixture, calculated as if the third component were not present

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