Thermodynamic Properties of Ternary Non-electrolyte Solutions

Part 3.—Excess Molar Volumes of 2-Propanone–Tribromomethane–Alkane Mixtures

Prem P. Singh, Renu Malik and S. Maken

Department of Chemistry, Maharshi Dayanand University, Rohtak-124001, India

William E. Acree Jr*

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

Excess molar volumes are reported for ternary 2-propanone–tribromomethane–cyclohexane, 2-propanone–tribromomethane–n-heptane and 2-propanone–tribromomethane–n-decane mixtures at 308.15 K, as well as volumetric data for the seven sub-binary systems. Results of these measurements are used to test the applications and limitations of two previously derived associated solution models. For the most part, experimental and predicted values were in reasonably good agreement. Large deviations were noted for a few ternary compositions studied, however, suggesting that non-specific interactions are important in the binary 2-propanone–tribromomethane system and should be included in any subsequent re-evaluation of the equilibrium constant and standard reaction volume.

As part of a continuing study on the thermochemical behaviour of ternary associated non-electrolyte solutions, we have previously derived expressions for predicting excess molar enthalpies (H_m^E) and excess molar volumes (V_m^E) of systems containing a single AB molecular complex¹

$$\begin{aligned} A_1 + B_1 &\rightleftharpoons AB; \quad K_{AB}^* = \hat{X}_{AB}/(\hat{X}_{A_1}\hat{X}_{B_1}) \\ V_m^E &= \frac{\hat{X}_{A_1}\hat{X}_{B_1}K_{AB}^*\Delta_r V_{AB}^0}{1 + K_{AB}^*\hat{X}_{A_1}\hat{X}_{B_1}} \\ &+ (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C)f_A f_B B_{A_1B_1} \\ &+ (X_A + X_C)f_A + f_C(V_{mAC}^E)^* \\ &+ (X_B + X_C)f_B + f_C(V_{mBC}^E)^* \end{aligned} \quad (1)$$

and both AB and AB₂ molecular complexes^{2,3}

$$\begin{aligned} A_1 + B_1 &\rightleftharpoons AB; \quad K_{AB}^* = \hat{X}_{AB}/(\hat{X}_{A_1}\hat{X}_{B_1}) \\ A_1 + 2B_1 &\rightleftharpoons AB_2; \quad K_{AB_2}^* = \hat{X}_{AB_2}/(\hat{X}_{A_1}\hat{X}_{B_1}^2) \\ V_m^E &= \frac{\hat{X}_{A_1}\hat{X}_{B_1}(K_{AB}^*\Delta_r V_{AB}^0 + K_{AB_2}^*\Delta_r V_{AB_2}^0\hat{X}_{B_1})}{1 + \hat{X}_{A_1}\hat{X}_{B_1}(K_{AB}^* + 2\hat{X}_{B_1}K_{AB_2}^*)} \\ &+ (X_A + X_C)f_A + f_C(V_{mAC}^E)^* \\ &+ (X_B + X_C)f_B + f_C(V_{mBC}^E)^* \\ &+ (X_A\Gamma_A + X_B\Gamma_B + X_C\Gamma_C)f_A f_B B_{A_1B_1} \end{aligned} \quad (2)$$

from measured binary (V_{mij}^E)^{*} data, which are determined at mole fraction compositions $X_i^* = 1 - X_j^* = X_i/(X_i + X_j)$. In eqn (1) and (2) $\Delta_r V_{AB_i}^0$ refer to the standard molar volumes for AB_i complex formation, $B_{A_1B_1}$ denotes volumetric binary interaction parameter for the AB sub-binary system, and f_i is the weighted mole-fraction composition of component i , i.e. $f_i = X_i\Gamma_i/(\sum X_j\Gamma_j)$. (‘^{*}’) indicates that the compositions refer to the associated solution, rather than the stoichiometric concentrations. (The H_m^E expressions are identical to eqn (1) and (2) in mathematical form, with the standard reaction volume being replaced by the corresponding reaction enthalpy.) The weighting factors (Γ_i) are used in describing the probability that two molecules interact in solution, and represent a rough measure of the skew of the binary excess 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 weigh-

ting factors must be regarded as approximations of these ‘true’ weighting factors. Replacement of weighting factors with molar volumes requires that the values are referred to a specified condition, such as 25°C and 1 atm, or to an extrapolated state such as ‘close-packed’ volume.

Past studies¹⁻³ have documented that eqn (1) and (2) with $B_{A_1B_1} = 0$ provide fairly reasonable estimates of H_m^E and V_m^E values for 2-propanone–tribromomethane–n-hexane (AB complex only) and 2-propanone–trichloromethane–cyclohexane (AB and AB₂ complexes) 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 eqn (1) and (2) could result from an incorrect description of physical interactions (e.g. $B_{A_1B_1} \neq 0$), or from the formation of a higher-order molecular complex, as might be the case for propanone and tribromomethane as 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. Both equations were originally derived by differentiating an expression for the Gibbs free energy of mixing with respect to pressure. These concerns can be addressed in part by studying how the size and shape of the inert hydrocarbon cosolvent affects the calculated association parameters for complex formation. To examine this effect further, we report excess molar volumes of ternary 2-propanone–tribromomethane–cyclohexane, 2-propanone–tribromomethane–n-heptane and 2-propanone–tribromomethane–n-decane mixtures at 308.15 K, plus volumetric data for the seven contributing sub-binary systems. Results of these measurements are used to test further the limitations and applications of eqn (1).

Experimental

2-Propanone (Glaxo Lab., 99.5+ %), tribromomethane (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 purified according to published methods.⁴⁻⁸ 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 shown in table 1.

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	
2-propanone	0.78512	0.78508 0.78516 0.78508	24 25 26
tribromomethane	2.87576	2.8758	27
cyclohexane	0.77392	0.77389 0.77392	28 29
n-heptane	0.67954	0.67958 0.67955	30 31
		0.67952	32
n-decane	0.72611	0.72608	33

Molar excess volume, V_m^E , data at 308.15 K were measured using two- and three-limb dilatometers in the manner described earlier.⁹ 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 the contained liquid and reference mark in the calibrated dilatometer capillary were noted with a cathetometer which could read to within ± 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 of 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 equilibration and volume measurement. From the change in the position of the liquid level in the dilatometer capillary and the volume per cm length, V_m^E values were calculated. The capillary was calibrated by weighing a column of mercury thread. Estimated uncertainties in the measured V_m^E values are believed to be of the order of $\pm 0.5\%$.

Results and Discussion

Experimental excess molar volumes of the seven sub-binary systems are tabulated in table 2, along with the coefficients and corresponding standard deviations for the Redlich-Kister representation

$$V_m^E = X_i X_j \sum_{n=0}^2 v_{ij}^{(n)} (X_i - X_j)^n \quad (3)$$

Experimental values for the binary systems at 308.15 K could not be found in the chemical literature. Ternary volumetric data are listed in tables 3–5, with the measured values being mathematically parametrized in terms of the three sets of $v_{ij}^{(n)}$ binary coefficients and additional $v_{ABC}^{(n)}$ ternary terms¹⁰

$$V_m^E = X_A X_B \sum_{n=0}^2 v_{AB}^{(n)} (X_A - X_B)^n + X_A X_C \sum_{n=0}^2 v_{AC}^{(n)} (X_C - X_A)^n + X_B X_C \sum_{n=0}^2 v_{BC}^{(n)} (X_B - X_C)^n + X_A X_B X_C \sum_{n=0}^2 v_{ABC}^{(n)} X_A^n (X_B - X_C)^n \quad (4)$$

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

Table 2. Experimental V_m^E data at 308.15 K for the various binary mixtures as a function of mole-fraction composition

X_i	$V_m^E/\text{cm}^3 \text{mol}^{-1}$	X_i	$V_m^E/\text{cm}^3 \text{mol}^{-1}$
2-propanone (i)–tribromomethane (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

$$v_{ij}^{(0)} = -1.3811; v_{ij}^{(1)} = -0.3025; v_{ij}^{(2)} = -0.1642; \sigma = 0.001$$

tribromomethane (i)–cyclohexane (j)

0.0409	0.064	0.5480	0.289
0.0868	0.123	0.5941	0.277
0.1561	0.199	0.6576	0.245
0.1887	0.226	0.6929	0.227
0.2478	0.266	0.7449	0.196
0.2868	0.283	0.8048	0.152
0.3509	0.302	0.8477	0.124
0.4008	0.311	0.8949	0.086
0.4448	0.309	0.9542	0.039
0.4973	0.304		

$$v_{ij}^{(0)} = 1.2138; v_{ij}^{(1)} = -0.4037; v_{ij}^{(2)} = 0.0203; \sigma = 0.001$$

cyclohexane (i)–2-propanone (j)

0.0469	0.197	0.4751	1.253
0.1001	0.412	0.5062	1.261
0.1372	0.553	0.5513	1.251
0.1525	0.608	0.6006	1.221
0.1927	0.741	0.6401	1.170
0.2478	0.896	0.6951	1.074
0.2775	0.972	0.7524	0.942
0.3105	1.045	0.8027	0.800
0.3625	1.141	0.8579	0.607
0.4327	1.233	0.9451	0.258

$$v_{ij}^{(0)} = 5.0507; v_{ij}^{(1)} = 0.2441; v_{ij}^{(2)} = -0.4097; \sigma = 0.003$$

tribromomethane (i)–n-heptane (j)

0.0769	−0.015	0.5479	−0.073
0.1229	−0.024	0.5986	−0.076
0.1749	−0.030	0.6478	−0.080
0.2048	−0.034	0.6947	−0.080
0.2449	−0.041	0.7549	−0.076
0.2988	−0.047	0.7951	−0.073
0.3398	−0.050	0.8348	−0.067
0.3925	−0.057	0.8848	−0.052
0.4348	−0.061	0.9299	−0.037
0.4841	−0.069	0.9598	−0.023

$$v_{ij}^{(0)} = -0.2765; v_{ij}^{(1)} = -0.1954; v_{ij}^{(2)} = -0.1518; \sigma = 0.001$$

n-heptane (i)–2-propanone (j)

0.0497	0.206	0.5491	0.983
0.0894	0.352	0.6024	0.951
0.1269	0.470	0.6549	0.894
0.1799	0.620	0.6965	0.835
0.2595	0.795	0.7541	0.733
0.3141	0.885	0.8148	0.602
0.3548	0.929	0.8527	0.502
0.4099	0.979	0.8991	0.360
0.4573	0.997	0.9418	0.218
0.4996	1.002		

$$v_{ij}^{(0)} = 3.9993; v_{ij}^{(1)} = -0.1835; v_{ij}^{(2)} = 0.2217; \sigma = 0.002$$

(continued)

Table 2—continued

X_i	$V_m^E/\text{cm}^3 \text{ mol}^{-1}$	X_i	$V_m^E/\text{cm}^3 \text{ mol}^{-1}$
tribromomethane (i)-n-decane (j)			
0.0479	0.096	0.5270	0.574
0.0950	0.187	0.5659	0.559
0.1349	0.256	0.6349	0.521
0.1768	0.321	0.6750	0.489
0.2350	0.401	0.7349	0.429
0.2679	0.444	0.7580	0.399
0.3379	0.514	0.8269	0.306
0.3750	0.536	0.8679	0.240
0.4380	0.563	0.9350	0.120
0.4899	0.575		
$v_{ij}^{(0)} = 2.2987$; $v_{ij}^{(1)} = -0.0668$; $v_{ij}^{(2)} = -0.3102$; $\sigma = 0.002$			
n-decane (i)-2-propanone (j)			
0.0721	0.346	0.5500	1.294
0.1215	0.573	0.6260	1.208
0.1565	0.699	0.6671	1.146
0.2330	0.940	0.7050	1.061
0.2621	1.027	0.7450	0.960
0.3200	1.147	0.8321	0.700
0.3650	1.227	0.8500	0.630
0.4131	1.280	0.9150	0.384
0.4671	1.309	0.9451	0.249
0.5320	1.297		
$v_{ij}^{(0)} = 5.2358$; $v_{ij}^{(1)} = -0.2126$; $v_{ij}^{(2)} = -0.2321$; $\sigma = 0.004$			

Table 3. Comparison between experimental and predicted V_m^E values for ternary 2-propanone (A)-tribromomethane (B)-cyclohexane (C) mixtures at 308.15 K

X_A	X_B	$V_m^E/\text{cm}^3 \text{ mol}^{-1}$	predicted V_m^E values/ $\text{cm}^3 \text{ mol}^{-1}$		
			eqn (1) ^a	eqn (1) ^b	eqn (11)
0.0413	0.6452	0.214	0.248	0.217	0.198
0.0707	0.2487	0.395	0.450	0.390	0.258
0.0724	0.8049	0.039	0.057	0.037	0.028
0.0894	0.3343	0.392	0.467	0.388	0.236
0.0899	0.7016	0.113	0.153	0.110	0.068
0.0926	0.2486	0.422	0.497	0.422	0.266
0.0978	0.7955	0.009	0.022	-0.001	-0.019
0.1297	0.2565	0.464	0.564	0.465	0.273
0.1336	0.8180	-0.088	-0.091	-0.101	-0.115
0.2119	0.6038	0.072	0.105	0.037	-0.086
0.2396	0.1808	0.615	0.782	0.658	0.437
0.2303	0.3790	0.364	0.493	0.359	0.113
0.2854	0.4475	0.226	0.301	0.189	-0.032
0.2786	0.5791	0.002	0.010	-0.048	-0.173
0.2825	0.5465	0.056	0.077	0.005	-0.145
0.2985	0.4778	0.153	0.205	0.109	-0.089
0.3217	0.5016	0.076	0.096	0.001	-0.150
0.3494	0.4924	0.045	0.055	-0.015	-0.178
0.3707	0.5480	-0.131	-0.156	-0.189	-0.280
0.4228	0.3139	0.320	0.417	0.302	0.076
0.4311	0.3178	0.300	0.389	0.277	0.058
0.4241	0.3902	0.142	0.174	0.088	-0.102
0.5411	0.1520	0.593	0.750	0.651	0.516
0.5850	0.1031	0.703	0.850	0.771	0.689
0.6504	0.1773	0.353	0.388	0.324	0.246
0.6952	0.2051	0.078	0.119	0.083	0.019
0.7124	0.1092	0.434	0.511	0.463	0.337
0.7732	0.2151	-0.226	-0.202	-0.206	-0.210
0.8249	0.1129	0.065	0.106	0.092	0.092
0.8469	0.1056	0.020	0.062	0.052	0.053
0.8825	0.0099	0.420	0.428	0.425	0.462
$v_{ABC}^{(0)} = -4.4929$; $v_{ABC}^{(1)} = 18.5291$; $v_{ABC}^{(2)} = -60.6016$; $\sigma = 0.003$					

^a Weighting factors approximated with molar volumes. ^b Weighting factors calculated from binary excess volume data.

Table 4. Comparison between experimental and predicted V_m^E values for ternary 2-propanone (A)-tribromomethane (B)-n-heptane (C) mixtures at 308.15 K

X_A	X_B	$V_m^E/\text{cm}^3 \text{ mol}^{-1}$	predicted V_m^E values/ $\text{cm}^3 \text{ mol}^{-1}$		
			eqn (1) ^a	eqn (1) ^b	eqn (11)
0.0345	0.6021	-0.077	-0.045	-0.010	-0.085
0.0898	0.7519	-0.117	-0.087	-0.028	-0.125
0.1006	0.1096	0.236	0.279	0.298	0.190
0.1425	0.6149	0.096	-0.043	0.072	-0.157
0.1715	0.5024	-0.040	0.044	0.165	-0.134
0.1965	0.5981	-0.104	-0.065	0.069	-0.194
0.2073	0.3458	0.096	0.219	0.323	-0.020
0.2075	0.7319	-0.184	-0.201	-0.122	-0.234
0.2088	0.2898	0.158	0.286	0.377	0.050
0.2113	0.2792	0.168	0.303	0.390	0.066
0.2149	0.7059	-0.179	-0.190	-0.123	-0.238
0.2075	0.7319	-0.180	-0.201	-0.145	-0.234
0.2269	0.4498	-0.005	0.089	0.224	-0.127
0.2556	0.4048	0.039	0.141	0.276	-0.095
0.3004	0.4356	-0.003	0.056	0.213	-0.168
0.3202	0.6406	-0.241	-0.288	-0.224	-0.322
0.3513	0.1439	0.454	0.607	0.674	0.419
0.3858	0.3602	0.059	0.132	0.278	-0.094
0.4205	0.2049	0.323	0.469	0.572	0.248
0.4870	0.0308	0.850	0.912	0.931	0.864
0.5291	0.1504	0.415	0.546	0.628	0.380
0.5864	0.1216	0.456	0.576	0.645	0.443
0.6607	0.1408	0.305	0.390	0.459	0.373
0.6709	0.1740	0.174	0.242	0.315	0.131
0.7031	0.2503	-0.153	-0.138	-0.094	-0.183
0.7148	0.1658	0.112	0.170	0.230	0.083
0.7223	0.1060	0.327	0.396	0.447	0.309
0.7415	0.1978	-0.082	-0.036	0.007	-0.087
0.7721	0.0506	0.463	0.514	0.539	0.456
0.8125	0.0914	0.174	0.222	0.251	0.171
0.8315	0.0721	0.214	0.254	0.278	0.209
$v_{ABC}^{(0)} = -3.9442$; $v_{ABC}^{(1)} = 15.6366$; $v_{ABC}^{(2)} = -16.9744$; $\sigma = 0.002$					

^a Weighting factors approximated with molar volumes. ^b Weighting factors calculated from binary excess volume data.

Application of eqn (1) to ternary 2-propanone-tribromomethane-alkane mixtures requires that the association parameters for the propanone-tribromomethane complex be calculable from the appropriate binary V_m^E binary reduction. Dahiya and coworkers¹¹ have previously documented that the binary 2-propanone-tribromomethane system could be reasonably (not perfectly) described by the 'ideal associated solution' (IAS) model, eqn (1) with $B_{A_1B_1} = 0$, though the best values of $\Delta_r H_{AB}^0$ and $\Delta_r V_{AB}^0$ at 298.15 K were found to vary with mole-fraction composition

$$\Delta_r H_{AB}^0 (\text{kJ mol}^{-1}) = -7.00 + 0.857X_A \quad (5)$$

$$\Delta_r V_{AB}^0 (\text{cm}^3 \text{ mol}^{-1}) = 0.300 + 0.21X_A + 2.076X_A^2 \quad (6)$$

Since these values pertain to a lower temperature, a new standard reaction volume for AB-complex formation must be determined using the experimental volumetric data at 308.15 K given in table 2. One possible method involves evaluating both K_{AB}^* and $\Delta_r V_{AB}^0$ graphically from the slope and intercept of a linear plot of $X_A X_B / V_m^E$ vs. V_m^E ¹¹

$$\frac{X_A X_B}{V_m^E} = - \left(\frac{K_{AB}^* + 1}{K_{AB}^* (\Delta_r V_{AB}^0)^2} \right) V_m^E + \frac{K_{AB}^* + 1}{K_{AB}^* \Delta_r V_m^E} \quad (7)$$

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. Unfortunately, the volumetric data fail to give the linear plot as suggested by eqn (7). Significant physical contributions or

Table 5. Comparison between experimental and predicted V_m^E values for ternary 2-propanone (A)–tribromomethane (B)–n-decane (C) mixtures at 308.15 K

X_A	X_B	$V_m^E/\text{cm}^3 \text{ mol}^{-1}$	predicted V_m^E values/ $\text{cm}^3 \text{ mol}^{-1}$		
			eqn (1) ^a	eqn (1) ^b	eqn (11)
0.0291	0.8041	0.280	0.294	0.275	0.266
0.0541	0.7254	0.355	0.388	0.347	0.289
0.1069	0.2495	0.601	0.714	0.639	0.416
0.1354	0.4906	0.571	0.657	0.551	0.284
0.1632	0.7809	-0.025	-0.040	-0.053	-0.098
0.1925	0.4695	0.558	0.646	0.524	0.182
0.2156	0.6215	0.230	0.243	0.178	-0.030
0.2359	0.0976	0.708	0.945	0.883	0.690
0.2442	0.4240	0.570	0.672	0.540	0.142
0.2753	0.5109	0.365	0.393	0.298	-0.025
0.2931	0.4921	0.379	0.400	0.427	-0.033
0.3125	0.3773	0.575	0.675	0.543	0.114
0.3419	0.4779	0.286	0.300	0.221	-0.100
0.3471	0.2053	0.675	0.990	0.864	0.472
0.3661	0.4551	0.291	0.304	0.225	-0.049
0.3875	0.1506	0.691	1.072	0.965	0.639
0.3974	0.1192	0.734	1.118	1.026	0.756
0.4145	0.0301	1.032	1.233	1.205	1.131
0.4290	0.4559	0.075	0.075	0.033	-0.209
0.4561	0.0409	0.981	1.241	1.203	1.099
0.4916	0.3520	0.281	0.283	0.221	-0.077
0.5249	0.2051	0.610	0.770	0.675	0.352
0.5615	0.2409	0.471	0.528	0.455	0.166
0.6249	0.3354	-0.182	-0.175	-0.179	-0.262
0.6520	0.3049	-0.147	-0.135	-0.141	-0.226
0.6771	0.2512	0.026	0.039	0.023	-0.096
0.6973	0.2054	0.179	0.202	0.150	0.038
0.7085	0.1902	0.210	0.233	0.208	0.077
0.7285	0.2341	-0.116	-0.095	-0.099	-0.158
0.7681	0.1004	0.403	0.471	0.445	0.351
0.7840	0.1407	0.150	0.182	0.169	0.094
0.8015	0.0509	0.527	0.597	0.578	0.524

$$v_{ABC}^{(0)} = -1.8000; v_{ABC}^{(1)} = 45.000; v_{ABC}^{(2)} = -300.00; \sigma = 0.003$$

^a Weighting factors approximated with molar volumes. ^b Weighting factors calculated from binary excess volume data.

the formation of a higher-order AB_2 propanone-tribromomethane complex will result in a non-linear $X_A X_B / V_m^E$ vs. V_m^E plot. Existence of an AB_2 propanone-tribromomethane complex could be argued on the basis that the carbonyl oxygen on propanone does have two lone pairs of electrons, each of which could hydrogen bond with a tribromomethane as is the case with propanone and trichloromethane.¹²⁻¹⁴ Evaluation of two equilibrium constants and standard reaction volumes is not possible with our limited number of experimental data points. Generally, such computations require that the two equilibrium constants be determined from vapour-liquid equilibria data,¹² which are not available for the binary 2-propanone-tribromomethane system.

To overcome this problem, a single AB molecular complex is assumed. The equilibrium constant is assigned a numerical value of $K_{AB}^* = 2.16$ which was obtained by extrapolating two published values¹¹ of $K_{AB}^* = 2.38$ (NMR) and $K_{AB}^* = 2.35$ (calorimetric) at 298.15 to 308.15 K using an average $\Delta_r H_{AB}^0 = -6.57 \text{ kJ mol}^{-1}$ from eqn (5) with $X_A = 0.5$. Having determined K_{AB}^* in this fashion, we proceeded to calculate a $\Delta_r V_{AB}^0$ value at each binary composition by forcing the experimental 2-propanone-tribromomethane data to fit the binary reduction of eqn (1) with $B_{A_1B_1} = 0$. An average value of $\Delta_r V_{AB}^0 = -1.84 \text{ cm}^3 \text{ mol}^{-1}$ ($\sigma = 0.33$) was then used in eqn (1) for subsequent ternary calculations. This particular approach, while by no means perfect, is the best possible at present with the limited experimental data available.

Tables 3-5 compare experimental excess molar volumes of ternary 2-propanone-tribromomethane-cyclohexane, 2-propanone-tribromomethane-n-heptane and 2-propanone-tribromomethane-n-decane 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 2-propanone-alkane and tribromomethane-alkane binary V_m^E data (column 5) as suggested by Bertrand *et al.*^{15,16} The $\Gamma_{(CH_3)_2CO}/\Gamma_{CHBr_3}$ ratio was determined from the normalization condition

$$\Gamma_{(CH_3)_2CO}/\Gamma_{CHBr_3} = (\Gamma_{(CH_3)_2CO}/\Gamma_{\text{alkane}})(\Gamma_{\text{alkane}}/\Gamma_{CHBr_3})$$

since it could not be obtained using binary 2-propanone-tribromomethane data because $B_{A_1B_1}$ was set equal to zero in the K_{AB}^* and $\Delta_r V_{AB}^0$ computations. Careful examination of the fourth and fifth columns reveals that there is no clear superiority between the two different weighting-factor approximations. For 2-propanone-tribromomethane-cyclohexane 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. Average absolute deviations between experimental and calculated values ($\Gamma_i = \bar{V}_i$) for mixtures containing cyclohexane and n-decane, $0.056 \text{ cm}^3 \text{ mol}^{-1}$ vs. $0.091 \text{ cm}^3 \text{ mol}^{-1}$, suggest that eqn (1) may not properly describe systems having large differences in molar volumes. In deriving eqn (1) and (2) we based the configurational entropic contributions on Raoult's law, rather than on the Flory-Huggins model. Raoult's law gives rise to a mole-fraction-based equilibrium constant. It is entirely conceivable that as eqn (1) is applied to additional ternary systems, we may learn that the association constant is best defined in terms of volume fractions. At this point in time we have measured V_m^E data for only four ternary 2-propanone-tribromomethane-alkane mixtures and H_m^E data for only the 2-propanone-tribromomethane-n-hexane system.¹ It is still much too early for us to reach a firm conclusion regarding the appropriate concentrational form of the association constant.

Significant deviations are noted between experimental and predicted values for a number of ternary compositions. Failure of eqn (1) 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 Hepler¹⁷ proposed a slightly different method in their thermodynamic treatment of the triethylamine-trichloromethane-cyclohexane system. The authors calculated the heat of complex dissociation by subtracting the heat caused by triethylamine-cyclohexane and trichloromethane-cyclohexane interactions, $Q_{TEA, C_6H_{12}}$ and $Q_{CHCl_3, C_6H_{12}}$, from the measured heat of dilution

$$Q^{dil} = \Delta n_{AB} \Delta_r H_{AB}^0 = Q^{exp} - Q_{TEA, C_6H_{12}} - Q_{CHCl_3, C_6H_{12}} \quad (8)$$

The last two terms in eqn (8) were evaluated for the two sub-binaries from expressions of the form:

$$Q_{TEA, C_6H_{12}} = 2\bar{X}_{TEA} \bar{X}_{C_6H_{12}} (\hat{n}_{TEA} + \hat{n}_{C_6H_{12}}) h_{TEA, C_6H_{12}} \quad (9)$$

$$Q_{CHCl_3, C_6H_{12}} = 2\bar{X}_{CHCl_3} \bar{X}_{C_6H_{12}} (\hat{n}_{CHCl_3} + \hat{n}_{C_6H_{12}}) h_{CHCl_3, C_6H_{12}} \quad (10)$$

where $2\bar{X}_i \bar{X}_j$ represents the probability of an i - j interaction in a random mixture of the two components and h_{ij} is an interactional 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. 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 excess molar volumes should give the following predictive expression for 2-propanone + tribromomethane + alkane mixtures

$$V_m^E = \frac{\bar{X}_A \bar{X}_B K_{AB}^* \Delta_r V_{AB}^0}{1 + K_{AB}^* \bar{X}_A \bar{X}_B} + \frac{2\bar{X}_A \bar{X}_C (\hat{n}_A + \hat{n}_C) v_{A,C}}{n_A + n_B + n_C} + \frac{2\bar{X}_B \bar{X}_C (\hat{n}_B + \hat{n}_C) v_{B,C}}{n_A + n_B + n_C} \quad (11)$$

Note that eqn (11) is empirical in nature in that we are unable to derive it rigorously 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 V_m^E is obtained by differentiating G^{mix} with respect to pressure.

As shown in the last columns of tables 3–5, eqn (11) provides a fairly reasonable mathematical description of the volumetric properties of the 2-propanone–tribromomethane–n-heptane system at many of the compositions studied. Deviations between observed and predicted values are substantial, however, for the remaining two ternary systems. In the case of the 2-propanone–tribromomethane–n-decane mixtures, eqn (11) erroneously underestimates many of the large positive excess volumes, missing the sign on V_m^E on eight separate occasions. Many of the larger deviations correspond to compositions where appreciable complexation occurs. Failure of eqn (11) appears to result from neglect of non-specific interactions between the inert cosolvent and AB molecular complex. Calculated physical contributions are much too small as the three binary 2-propanone–alkane systems have V_m^E values ranging as high as $1.25 \text{ cm}^3 \text{ mol}^{-1}$. Based on our calculations, we feel that eqn (1) provides a better description of the physical interactions in these three ternary systems.

At the present time we are unable to explain adequately the few large deviations between experimental V_m^E data and predictions based on eqn (1). We do believe that a re-evaluation of the equilibrium constant and standard reaction volume with $B_{A,B_1} \neq 0$ might give a more realistic set of association parameters. The predicted values do depend on the numerical values of K_{AB}^* and $\Delta_r V_{AB}^0$ used in the calculations. Earlier solubility studies involving carbazole dissolved in binary alkane–dibutyl ether^{18–21} and chloroalkane–dibutyl ether^{22,23} mixtures have shown that neglect of weak non-specific interactions can have a rather dramatic effect on the calculated association parameters. Also, the possible formation of an AB_2 molecular complex needs to be examined when liquid–vapour equilibria data become available for 2-propanone–tribromomethane mixtures. In closing, readers are reminded that the present study is the second in a series of papers devoted to the thermodynamic excess properties of ternary 2-propanone–tribromomethane–alkane systems. The effects of the inert

hydrocarbon cosolvent and the $B_{A,B_1} = 0$ approximation will be explored in much greater detail in subsequent papers.

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