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THERMODYNAMICS OF CHLOROFORM AND *n*-PROPANOL MIXTURES

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ABSTRACT

Heats of mixing and vapour pressures of chloroform (A) + *n*-propanol (B_n) as a function of concentration have been determined at 303.15 K. The excess Gibbs free energy of mixing, G^E values, have been obtained from the measured vapour pressure data. The heats of mixing values are negative for solutions rich in *n*-propanol but they become positive for solutions rich in chloroform. On the other hand, G^E values are positive for all the *n*-propanol mole fractions and $G^E > H^E$. The results have been analysed in terms of Barker and the ideal associated model theory of non-electrolyte solutions. The analyses have revealed that only the ideal associated model approach (which here assumes the presence of A_mB ($m = 1,2$), AB_K ($K = 2$) and B_l ($l = 1$) molecular species) well describes the general behaviour of H^E with x_A over the entire chloroform concentration range for this mixture. The equilibrium constants for the various association reactions along with the enthalpy of formation of the various molecular species have also been calculated.

INTRODUCTION

Following Frank and Wen's model[1] of liquid water, it was believed that lower alcohols should also possess a similar type of co-operativity in the formation of hydrogen-bonded polymers. But there is considerable disagreement as to the identity of the predominant associated species[2-6]. Again, while the solution hetero-association data[7, 8] have been limited to calculation of equilibrium constants for 1:1 and 2:1 complexes only, Tucker and Christian[9] have interpreted the results of their distribution studies to indicate that lower alkanols contain monomers, dimers and higher polymers. The present work describes interactions in chloroform + *n*-propanol mixtures.

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EXPERIMENTAL

Materials and method

n-Propanol (B.D.H. Analar) was treated with anhydrous potassium carbonate overnight in the manner suggested by Vogel[10]. 50–75 ml of *n*-propanol, 5.0 g of Mg and 0.5 g of iodine were placed in a round-bottomed flask. The mixture was warmed on a water bath until iodine disappeared and *n*-propoxide formed; 900 ml of *n*-propanol were added, the mixture boiled under reflux and then finally distilled. Chloroform (B.D.H. Analar) was shaken, as suggested by Vogel[10], several times with about half of its volume of water, dried over anhydrous calcium chloride and finally distilled. The purity of the final samples was checked by density determinations at 298.15 ± 0.01 K, which agreed to within 0.00005 g ml^{-1} with the literature values[11,12].

Heats of mixing measurements at 303.15 ± 0.01 K were made in an adiabatic calorimeter similar in design to that of Fernandez-Garcia and Boissonas[13] and has been described elsehwere[14]. The performance of the calorimeter was tested by determining the heats of mixing of benzene and cyclohexane at 298.15 ± 0.01 K and these agreed to within 0.3% (over the central range of concentration) with the corresponding literature values[15].

Vapour pressures of the chloroform + *n*-propanol mixtures were determined by a static method described previously[16]. The apparatus (excluding the manometric part) was placed in a water thermostat which in turn was placed in another thermostat. The temperature of the outer thermostat was controlled to better than ±0.01 K and the temperature drift in the inner thermostat was of the order of ±0.002 K. The mercury heights in the manometer were read by a cathetometer which could read to ±0.001 cm. All vapour pressure measurements were reproducible to better than ±0.02 torr.

The measured vapour pressure (29.58 torr) of *n*-propanol at 303.15 K agreed within 0.3% with that at 303.15 K obtained by Richardson[17] (29.50 torr). The measured vapour pressure of chloroform (241.15 torr) also compared well with that reported in the literature[18] (239.00 torr).

RESULTS

The molar heats of mixing, H^E, and the measured vapour pressure data at 303.15 K for chloroform + *n*-propanol are recorded in Tables 1 and 2, respectively. The H^E, G^E and TS^E data are plotted in Figs. 1 and 2.

The H^E data (Table 1) were fitted to the expression

$$\frac{H^E}{x_A(1-x_A)} = [h_0 + h_1(2x_A - 1) + h_2(2x_A - 1)^2] \tag{1}$$

where x_A is the mole fraction of chloroform, the parameters h_0, h_1 and h_2, evaluated by fitting $H^E/[x_A(1-x_A)]$ to expression (1) by the method of least squares, are given together with the standard deviation of the molar heats of mixing, $\sigma(H^E)$, in Table 3.

TABLE 1

MEASURED MOLAR HEATS OF MIXING FOR DIFFERENT MOLE FRACTIONS x_A OF CHLOROFORM FOR CHLOROFORM (A) + n-PROPANOL (B) MIXTURE AT 303.15 K

x_A	H^E ($J\ mole^{-1}$)	x_A	H^E ($J\ mole^{-1}$)
0.0698	−165.07	0.5552	346.94
0.1201	−221.23	0.6098	436.47
0.1753	−235.17	0.6503	486.55
0.2803	−152.82	0.7100	535.79
0.3699	− 10.81	0.7702	541.96
0.4452	136.35	0.8397	482.15
0.4897	225.09	0.8801	410.58
0.5101	264.75	0.9099	338.25

TABLE 2

MEASURED TOTAL VAPOUR PRESSURE P; ACTIVITY COEFFICIENT, γ; RESIDUAL VAPOUR PRESSURE $R = P_{exp} - P_{calc}$; MOLAR EXCESS FREE ENERGIES, G^E AND TS^E FOR DIFFERENT MOLE FRACTIONS x_A OF CHLOROFORM FOR CHLOROFORM (A) + n-PROPANOL (B) MIXTURE AT 303.15 K

x_A	P (torr)	γ_A	γ_B	P_A (torr)	P_B (torr)	$R = P_{exp} - P_{calc}$	G^E ($J\ mole^{-1}$)	TS^E ($J\ mole^{-1}$)
0.0000	29.58	1.6398	1.0000	0.00	29.58	0.00	0.00	0.00
0.0799	58.53	1.6353	1.0066	31.22	27.44	−0.13	124.12	−301.41
0.1800	94.52	1.6201	1.0183	69.82	24.80	−0.10	244.14	−478.26
0.2402	115.94	1.6084	1.0215	92.62	23.08	0.22	309.03	−509.18
0.3697	158.49	1.5705	1.0231	139.54	19.23	−0.28	445.97	−457.66
0.4502	182.95	1.5296	1.0352	165.74	16.99	−0.20	528.30	−383.27
0.5598	209.26	1.4423	1.1021	194.62	14.51	0.11	621.55	−264.16
0.6703	225.57	1.3180	1.2986	213.17	12.82	−0.42	662.82	−153.61
0.7500	231.53	1.2158	1.6063	220.10	12.02	−0.60	634.95	− 88.25
0.8301	235.48	1.1168	2.2051	223.82	11.22	0.42	536.51	− 39.40
0.9203	239.55	1.0307	3.6497	229.06	8.71	1.76	315.41	− 6.52
1.0000	241.51	1.0000	6.5933	241.51	0.00	0.00	0.00	0.00

The vapour pressure data were used to evaluate the molar excess Gibbs free energy, G^E, by Barker's method[19]. The form of the function used for G^E, following Redlich and Kister[20] is

$$\frac{G^E}{RT} = x_A(1 - x_A)\left[G_0 + G_1(2x_A - 1) + G_2(2x_A - 1)^2 + G_3(2x_A - 1)^3\right] \qquad (2)$$

where G_0, G_1, G_2 and G_3 are adjustable parameters. These parameters are recorded in Table 3. The second virial coefficients of n-propanol and chloroform were evaluated

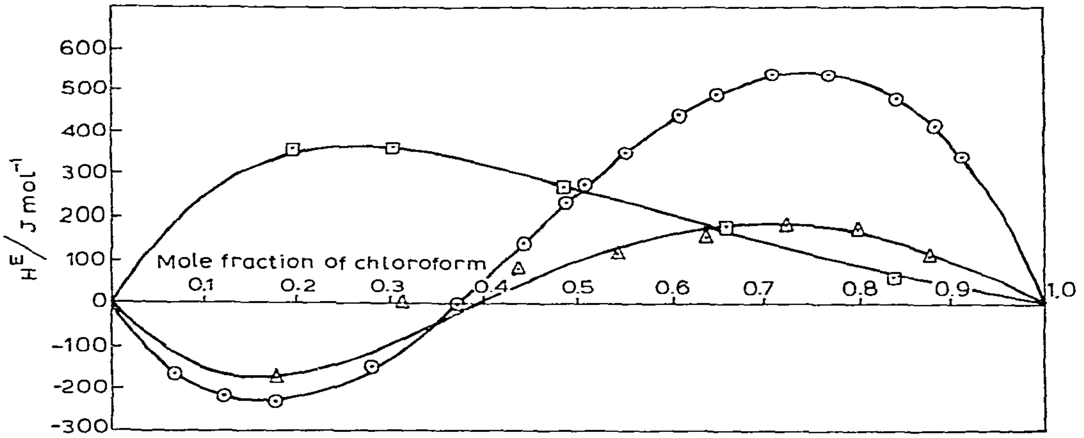

Fig. 1. Enthalpies of mixing, H^E, for chloroform (A) + n-propanol (B) at 303.15 K. ○, Experimental H^E; △ calculated H^E according to ideal associated model that assumes the presence of AB, AB_2, A_2B and B molecular species; ⊡, calculated H^E according to ideal associated model that assumes the presence of AB, AB_2, AB_3 and B molecular species ($K_{1,0.5} = 0.55$, $\Delta H_{AB} = -1.0$ kJ mole^{-1}; $K_{0.5} = 0.04$, $\Delta H_B = 2.5$ kJ mole^{-1}; $K_{1,1} = 0.40$, $\Delta H_{AB_2} = -2.5$ kJ mole^{-1}; $K_{1,1.5} = 0.05$, $\Delta H_{AB_3} = -1.0$ kJ mole^{-1}).

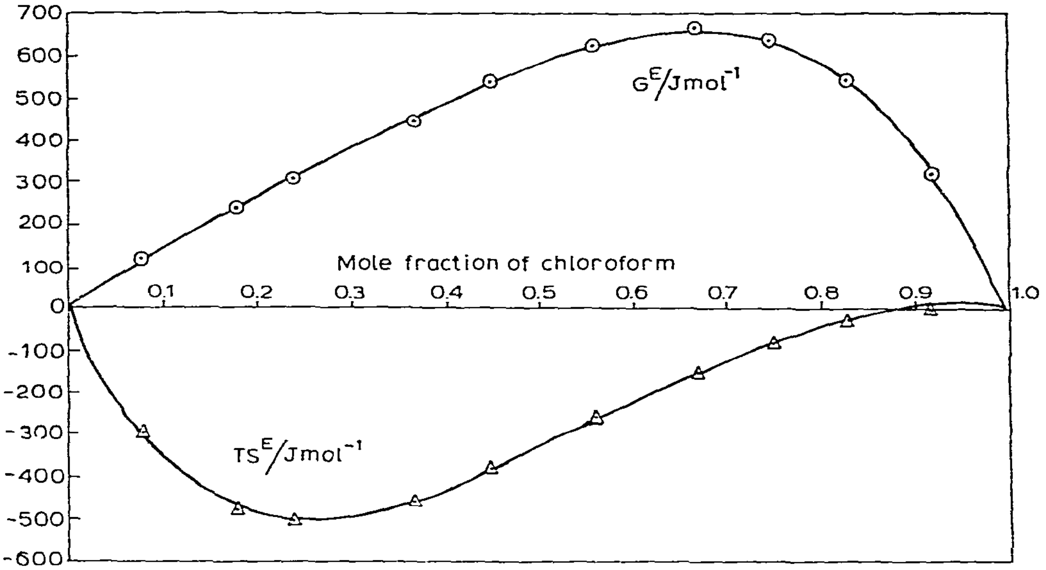

Fig. 2. Excess functions for chloroform (A) + n-propanol (B) at 303.15 K. ○, G^E; △ TS^E.

TABLE 3

PARAMETERS X_m ($X = h$ OR G) OF EQNS. (1 AND 2), STANDARD DEVIATION OF PRESSURE $\sigma(P)$ ALONG WITH THE STANDARD DEVIATION OF H^E, $\sigma(H^E)$ FOR CHLOROFORM (A) + n-PROPANOL (B) MIXTURE AT 303.15 K

	m				$\sigma(H^E)$	$\sigma(P)$
	0	*1*	*2*	*3*	*(J mole^{-1})*	*(torr)*
h_m	980.40	3931.96	−122.45		1.77	
G_m	0.9121	0.6957	0.3904	−0.1123		0.83

from the Berthelot relation[21] using critical constant data[22, 23]. The cross virial coefficients were taken as $(B_{11} + B_{22})/2$. The thermodynamic consistency of the data was tested[20] by plotting $\ln(\gamma_A/\gamma_B)$ vs. x_A. The positive and negative areas bounded by the curve $\ln(\gamma_A/\gamma_B)$ vs. x_A and the x-axis agreed to better than 0.2%.

DISCUSSION

We are unaware of any H^E or G^E data for chloroform + *n*-propanol with which to compare our results.

Heats of mixing for chloroform (A) + *n*-propanol (B) are negative for solutions rich in *n*-propanol but they become positive for solutions rich in chloroform. The S-shaped H^E curve attains a maximum negative value of 235.0 mole^{-1} at $x_{n\text{-propanol}} = 0.83$ and a maximum positive value of 541.0 J mole^{-1} at $x_{n\text{-propanol}} = 0.24$. Further, TS^E is negative at all the *n*-propanol mole fractions for which the experimental data are available and the curve of TS^E vs. $x_{n\text{-propanol}}$ is highly unsymmetrical about $x_{n\text{-propanol}}$.

At the simplest qualitative level the observed H^E data for this mixture may be accounted for if we assume that (i) *n*-propanol is self-associated and there is a change (decrease) in its self-association when mixed with chloroform (ii) there is a hydrogen-bonded interaction between the hydroxyl oxygen of *n*-propanol and the chloroform hydrogen, and (iii) there is specific interaction between the hydroxyl hydrogen of *n*-propanol with the chlorine of chloroform. The negative values of H^E for high *n*-propanol concentrations are then due essentially to factor (ii). This is because while interactions due to factor (ii) can occur without breaking the alcohol–alcohol hydrogen bond, the same is not true of interactions due to factor (iii). Again, the hydrogen-bonded interaction due to factor (ii) limits the orientational freedom of the chloroform molecules, thus making TS^E strongly negative so that G^E should be (and indeed is) positive. The positive values of H^E at high chloroform, concentrations are due to the rupture of alcohol–alcohol hydrogen bonds followed by their subsequent hydrogen-bonded interaction with chloroform molecules. This in turn would require the TS^E at high chloroform concentrations to be considerably more positive than that at low chloroform concentrations and thus explains the unsymmetrical nature of TS^E vs. $x_{n\text{-propanol}}$.

We examined our results using Barker's theory[24]. It was assumed that chloroform (A) and *n*-propanol (B) have the geometrical parameters lattice $Z = 4$; chloroform molecules (A) $r_A = 3$, $Q^A_{H'} = 1$, $Q^A_{R'} = 7$; and *n*-propanol molecules (B) $r_B = 2$; $Q^B_O = 2$; $Q^B_H = 1$; $Q^B_R = 3$ where O, H and R represent, respectively, hydroxyl oxygen, hydrogen and hydrocarbon surfaces of *n*-propanol, and H′ and R′ represent the hydrogen and chlorine surfaces of chloroform. The interactions first considered were a specific (O ⋯ H′) interaction of strength U_3 between the hydroxyl oxygen of *n*-propanol and the hydrogen of chloroform, a specific (O ⋯ H) interaction of strength U_2 between the hydroxyl oxygen and hydroxyl hydrogen of *n*-propanol, and a non-specific interaction for all the remaining contact points. For the sake of simplicity

TABLE 4

COMPARISON OF H^E VALUES CALCULATED ACCORDING TO BARKER'S THEORY WITH VALUES INTERPOLATED FROM THE MEASURED VALUES AT THREE MOLE FRACTIONS OF THE COMPONENT (A) AND THE INTERACTION ENERGIES OF CHLOROFORM (A) + n-PROPANOL (B) AT 303.15 K

Property ($J\,mole^{-1}$)	*Mole fraction of component (A)*			*Interaction energies ($J\,mole^{-1}$)*
	0.3	*0.5*	*0.7*	
H_{exp}^E	-130.00	250.00	530.00	
$H^{E(1)}$	119.73	117.67	118.07	$U_1^{(1)} = 51.08$, $U_2^{(1)} = -2408.72$, $U_3^{(1)} = -2309.48$
$H^{E(2)}$	28.69	38.00	24.71	$U_1^{(2)} = 51.08$, $U_2^{(2)} = -2408.72$, $U_3^{(2)} = -2503.91$, $U_4^{(2)} = -1481.80$
$H^{E(3)}$	-32.01	-52.95	-22.65	$U_1^{(3)} = 51.08$, $U_2^{(3)} = -1618.18$, $U_3^{(3)} = -1337.28$, $U_4^{(3)} = -1618.18$

these non-specific interactions for all the remaining contact points were considered to have the same strength U_1. Excess energy of mixing at constant volume U_V^E, values at $x_A = 0.3$, 0.5 and 0.7 were then calculated[24] from this theory and they did not reproduce the corresponding experimental H^E values. It is customary while testing a lattice theory to convert U_V^E values to measurements at constant pressure, H^E, using the relation $U_V^E = H^E - TV^E\alpha_m/(K_T)_m$ where α_m, $(K_T)_m$ and V^E are, respectively, the expansivity, isothermal compressibility and excess volume of the mixture. However, since V^E is small (V^E for an equimolar mixture is -0.002 cm^3 mole^{-1}), contribution of the $TV^E\alpha_m/(K_T)_m$ term would be negligibly small and for the present analysis we have assumed $U_V^E \approx H^E$. The best values of U_1, U_2, U_3 designated as $U_i^{(1)}$ (i = 1–3) and the corresponding H^E values designated as $H^{E(1)}$ are recorded in Table 4.

We next considered a slightly different model in which in addition to the above interactions, one of the chlorines of chloroform was assumed to be involved in a specific (H ··· Cl) interaction of strength U_4 with the hydroxyl hydrogen of n-propanol. The chloroform was considered to have the geometrical parameters $r_A = 3$; $Q_{Cl'}^A = 1$; $Q_{H'}^A = 1$, and $Q_{R'}^A = 6$. The theoretical H^E values are now positive throughout the entire chloroform concentration range. The experimental H^E values for this mixture on the other hand are negative for $x_A \leqslant 0.37$ only. (The values of U_i (i = 1–4) and H^E are designated as $U_i^{(2)}$ and $H^{E(2)}$ in Table 4.) Models of chloroform molecules with two and higher hydrogen contact points were also considered but they failed to explain the overall behaviour of H^E with x_A for this mixture. The reason for the failure of the theory may be the simplicity of the models considered. Perhaps associated complexes of the general formula A_iB_j and B_n are present in these mixtures. H^E and G^E data for this mixture were analysed in terms of the ideal associated model[25, 26].

It is assumed that in a binary solution of chloroform (A) and n-propanol (designated as B_n since n-propanol is self-associated) mutual equilibrium of the species A_mB, AB_k and B_l ($l = 1, 2, 3 \cdots l$; $k = 1, 2, 3 \cdots k$; $n = 1, 2, 3 \cdots n$; $m = 2, 3 \cdots m$) exist according to the reactions

$$mA + B_n \rightleftharpoons A_mB + AB_k + B_l \tag{3}$$

so that the equilibrium constants for the various association reactions represented by eqn. (3) are

$$K_{m,1/n} = \frac{a_{A_mB}}{a_A^m a_{B_n}^{1/n}} \tag{4}$$

$$K_{1,k/n} = \frac{a_{AB_k}}{a_A a_{B_n}^{k/n}} \tag{5}$$

and

$$K_{1/n} = \frac{a_{B_1}}{a_{B_n}^{1/n}} \tag{6}$$

where a denotes activities. If the activity coefficients of the various species represented in eqn. (3) are assumed to be unity[25-28] the material balance equation for the system can be written as

$$a_A + a_{B_n} + \sum_m K_{m,1/n}\, a_A^m\, a_{B_n}^{1/n} + \sum_k K_{1,k/n}\, a_A\, a_{B_n}^{k/n} + \sum_1 K_{1/n}\, a_{B_n}^{1/n} = 1 \tag{7}$$

Two simple cases were next considered. Case (i) $m = 1, 2 \cdots m$; $n = 2$; $k = 2, 3 \cdots k$; $l = 1$ so that eqn. (7) reduces to

$$a_A + a_{B_2} + \sum_m K_{m,0.5}\, a_A^m\, a_{B_2}^{1/2} + \sum_k K_{1,k/2}\, a_A\, a_{B_2}^{k/2} + K_{0.5}\, a_{B_2}^{1/2} = 1 \tag{8}$$

Case (ii) $m = 1$; $n = 2$; $k = 2, 3 \cdots k$; $l = 1$ so that eqn. (7) yields

$$a_A + a_{B_2} + K_{1,0.5}\, a_A\, a_{B_2}^{1/2} + \sum_k K_{1,k/2}\, a_A\, a_{B_2}^{k/2} + K_{0.5}\, a_{B_2}^{1/2} = 1 \tag{9}$$

Algebraic manipulation of eqns. (8) and (9) yields

$$\left[\sum_m K_{m,0.5}\, a_A^m + \sum_k K_{1,k/2}\, a_A\, a_{B_2}^{(k-1)/2} + K_{0.5}\right] = \frac{1 - a_A - a_{B_2}}{a_{B_2}^{1/2}} \tag{10}$$

and

$$\left[K_{1,0.5}\, a_A + \sum_k K_{1,k/2}\, a_A\, a_{B_2}^{(k-1)/2} + K_{0.5}\right] = \frac{1 - a_A - a_{B_2}}{a_{B_2}^{1/2}} \tag{11}$$

respectively.

In order to evaluate the various K-values in eqns. (10) and (11) the observed activities of the components of these binary mixtures were corrected[29-31] for

TABLE 5

THE EQUILIBRIUM CONSTANTS (MOLE FRACTION SCALE) FOR THE VARIOUS COMPLEXING REACTIONS TOGETHER WITH THE ENTHALPIES OF FORMATION OF VARIOUS MOLECULAR SPECIES AND THE VARIANCE OF THE FIT σ_D^2 AT 303.15 K

Equilibrium constant	*Reaction of chloroform with n-propanol*	*Parameter*	*Mixtures of n-propanol (B) with chloroform (A)*
$K_{1,0.5}$	0.60	ΔH_{AB} (kJ mole^{-1})	−1.01
$K_{2,0.5}$	0.05	ΔH_{A_2B} (kJ mole^{-1})	−1.00
$K_{1,1}$	0.40	ΔH_{AB_2} (kJ mole^{-1})	−2.50
$K_{0.5}$	0.04	ΔH_B (kJ mole^{-1})	2.50
		$\sigma_{D_{10}}^2$	0.088
		$\sigma_{D_{11}}^2$	0.079

dispersion contributions by expressing

$$a_A = \frac{\gamma_A x_A}{\gamma_A^*}$$

$$a_{B_2} = \frac{\gamma_{B_2} x_{B_2}}{\gamma_{B_2}^*}$$

where γ_A^* and $\gamma_{B_2}^*$ are the activity coefficients of a reference mixture. Since cyclohexane has nearly the same molar volume as chloroform, cyclohexane (A) + methanol (B) was taken as a reference system for the present analysis. Further, as the G^E data[32] for cyclohexane + methanol is available at 304.15 K, we assumed $G^E_{304.15\,K} \approx G^E_{304.15\,K}$ in order to evaluate the activity coefficient data for the components of this reference mixture at the various experimental mole fractions of *n*-propanol. A series of values were next assumed for the various *K*-values in eqns. (10) and (11) and the process was repeated until a set of *K*-values was obtained which yielded

$$\frac{(1 - a_A - a_{B_2})}{a_{B_2}^{1/2}} = D$$

values that correspond very closely to those obtained from the experimental a_A and a_{B_2} values. It was observed that eqn. (10) with a set of *K*-values ($K_{1,0.5}$, $K_{2,0.5}$, $K_{1,1}$, $K_{0.5}$) and eqn. (11) with a set of *K*-values ($K_{1,0.5}$, $K_{1,1}$, $K_{1,1.5}$, $K_{0.5}$) yielded *D*-values that reproduce equally well the corresponding values obtained from experimental values for this system.

The criterion of effectiveness was the variance of the fit σ_D^2 defined by

$$\sigma_D^2 = \frac{\sum_i [D_{(calc)} - D_{(exp)}]^2}{(q - p)} \tag{12}$$

where q is the number of points used in the fit and p is the number of adjustable parameters. The various K and σ_D^2 for eqns. (10) and (11) are recorded in Table 5. $\sigma_{D_{10}}^2$ and $\sigma_{D_{11}}^2$ in Table 5 represent σ_D^2 for the activity data analysed in terms of eqns. (10) and (11), respectively. Since both eqns. (10 and 11) represent the corresponding D-values obtained from experimental data equally well, the analysis of the activity coefficient data described above suggests that these mixtures may be assumed to have either AB, A_2B, AB_2 and B or AB, AB_2, AB_3 and B molecular species in solution. We next considered our H^E data.

The H^E data of this mixture were examined in terms of models that involved consideration of (i) AB, A_2B, AB_2 and B, and (ii) AB, AB_2, AB_3 and B molecular species. Consequently, H^E was expressed as

$$H^E = \frac{\left(\sum_{m=1}^{2} n_{AB_m}\,\Delta H_{AB_m} + n_{A_2B}\,\Delta H_{A_2B} + n_B\,\Delta H_B\right)}{(N_A + N_{B_2})} \tag{13}$$

and

$$H^E = \frac{\left(\sum_{m=1}^{3} n_{AB_m}\,\Delta H_{AB_m} + n_B\,\Delta H_B\right)}{(N_A + N_{B_2})} \tag{14}$$

where n_{AB_m} represents the amount of species AB_m at equilibrium in the solution and N_A and N_{B_2} the stoichiometric amounts of A and B_2. If the equilibrium mole fractions of A, B_2, B, AB_m ($m = 1, 2$) and A_2B are represented by Z_A, Z_{B_2}, Z_B, Z_{AB_m} and Z_{A_2B}, then for an ideal associated mixture A + B_2, containing AB, A_2B, AB_2 and B molecular species

$$Z_A + Z_{B_2} + \sum_{m=1}^{2} Z_{A_mB} + Z_{AB_2} + Z_B = 1 \tag{15}$$

where

$$Z_{A_mB} = K_{m,0.5}\, Z_A^m\, Z_{B_2}^{1/2},\ Z_{AB_2} = K_{1,1}\, Z_A Z_{B_2} \text{ and } Z_B = K_{0.5}\, Z_{B_2}^{1/2}$$

The experimental H^E-values were again corrected for dispersion contributions by subtracting from H^E_{exp} the H^E-values[33] at 298.15 K for cyclohexane + methanol. Consequently, in eqns. (13) and (14)

$$H^E = H^E_{exp} - H^E_{cyclohexane+methanol} \tag{15a}$$

Algebraic manipulation of eqns. (13) and (14) and the material balance equations

$$N_A = n_A + \sum_{m=1}^{2} n_{AB_m} + 2\, n_{A_2B} \tag{16}$$

$$N_{B_2} = n_{B_2} + 1/2 \sum_{m=1}^{2} n_{A_mB} + n_{AB_2} + 1/2\, n_B \tag{17}$$

lead to

$$jH^{E} = \sum_{m=1}^{2} K_{m,0.5}\, Z_{A_m}^{m}\, \Delta H_{A_mB} + Z_{B_2}^{1/2}\, Z_A\, K_{1,1}\, \Delta H_{AB_2} + K_{0.5}\, \Delta H_B \tag{18}$$

where

$$j = \frac{(Z_{B_2}^{1/2} + 0.5\, K_{1,0.5}\, Z_A + K_{1,1}\, Z_{B_2}^{1/2}\, Z_A + 0.5\, K_{2,0.5}\, Z_A^2 + 0.5\, K_{0.5})}{x_{B_2}}$$

Further combination of eqns. (15–17) yields

$$x_{B_2} = \frac{0.5\, K_{1,0.5}\, Z_A\, Z_{B_2}^{1/2} + K_{1,1}\, Z_A\, Z_{B_2} + 0.5\, K_{0.5}\, Z_{B_2}^{1/2} + 0.5\, K_{2,0.5}\, Z_A^2\, Z_{B_2}^{1/2} + Z_{B_2}}{Z_A + Z_{B_2} + 1.5\, K_{1,0.5}\, Z_A\, Z_{B_2}^{1/2} + 2\, K_{1,1}\, Z_A\, Z_{B_2} + 2.5\, K_{2,0.5}\, Z_A^2\, Z_{B_2}^{1/2} + 0.5\, K_{0.5}\, Z_{B_2}^{1/2}} \tag{19}$$

where

$$Z_{B_2}^{1/2} = \frac{-Y \pm \sqrt{Y^2 - 4(Z_A - 1)(1 + K_{1,1}\, Z_A)}}{2(1, K_{1,1}\, Z_A)}$$

$$Y = K_{1,0.5}\, Z_A + K_{2,0.5}\, Z_A^2 + K_{0.5}$$

Using the various K-values described above for a solution containing AB, A_2B, AB_2 and B species, we calculated x_{B_2} from eqn. (19) for various values of Z_A and assigned various values to ΔH_{A_mB}, ΔH_{AB_2} and ΔH_B until they gave H^E-values (from eqns. 15a and 18) that compared well with the corresponding experimental values. The various ΔH values are recorded in Table 5 and the calculated H^E-values are plotted in Fig. 1. It is evident from Fig. 1 that the theoretical H^E-values well describe the general behaviour of H^E with x_A for chloroform (A) + *n*-propanol (B_2) mixture.

A similar process was applied to the case when the mixture contains AB_m (m = 1–3) and B molecular species. The final expressions were

$$j'H^{E} = K_{1,0.5}\, Z_A\, \Delta H_{AB} + K_{1,1}\, Z_A\, \Delta H_{AB_2} + K_{1,1.5}\, Z_A\, Z_{B_2}^{3/2}\, \Delta H_{AB_3} + K_{0.5}\, \Delta H_B \tag{20}$$

where

$$j' = \frac{Z_{B_2}^{1/2} + 0.5\, K_{1,0.5}\, Z_A + K_{1,1}\, Z_A\, Z_{B_2}^{1/2} + 1.5\, K_{1,1.5}\, Z_A\, Z_{B_2}^{2} + K_{0.5}\, Z_{B_2}^{1/2}}{x_{B_2}}$$

$$x_{B_2} = \frac{Z_{B_2} + 0.5\, K_{0.5}\, Z_{B_2}^{1/2} + 0.5\, K_{1,0.5}\, Z_A\, Z_{B_2}^{1/2} + K_{1,1}\, Z_A\, Z_{B_2} + 1.5\, K_{1,1.5}\, Z_A\, Z_{B_2}^{3/2}}{Z_A + Z_{B_2} + 0.5\, K_{0.5}\, Z_{B_2}^{1/2} + 1.5\, K_{1.0.5}\, Z_A\, Z_{B_2}^{1/2} + 2\, K_{1,1}\, Z_A\, Z_{B_2} + 2.5\, K_{1,1.5}\, Z_A\, Z_{B_2}^{3/2}}$$

and

$$Z_A = \frac{(1 - K_{0.5}\, Z_{B_2}^{1/2} - Z_{B_2})}{(1 + K_{1,0.5}\, Z_{B_2}^{1/2} + K_{1,1}\, Z_{B_2} + K_{1,1.5}\, Z_{B_2}^{3/2}}$$

where

$$Z_{AB_m} = K_{1,m/2}\, Z_A\, Z_{B_2}^{m/2} \qquad m = 1, 2, 3$$

$$Z_B = K_{0.5}\, Z_{B_2}^{1/2}$$

However, no values of ΔH_{AB_m} (m = 1–3) and ΔH_B could yield H^E-values that described the experimental behaviour of H^E with x_A for this mixture. The calculated H^E-values are either positive or negative throughout the entire chloroform concentration range. Furthermore, the quantitative agreement is not good. (See Fig. 1 where only those ΔH_{AB_m} and ΔH_B-values are considered that render H^E_{calc} positive throughout the entire chloroform concentration range.)

The analysis of H^E and activity coefficient data for chloroform + n-propanol mixtures thus suggests that this mixture is characterized by the presence of AB, AB_2, A_2B and B molecular species in solution.

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