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TOPOLOGICAL STUDIES OF THE MOLECULAR SPECIES THAT CHARACTERIZE LOWER ALKANOL + METHYLENE BROMIDE MIXTURES: MOLAR EXCESS VOLUMES AND MOLAR EXCESS ENTHALPIES

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ABSTRACT

Molar excess volumes, V^E, and molar excess enthalpies, H^E, have been determined at 298.15 and 308.15 K for the binary mixtures of methanol (A) or ethanol (A) with methylene bromide (B). The V^E data for these mixtures have been analysed in terms of an approach that employs the graph theoretical connectivity parameters of the third degrees of the A and the B molecular entities to show, for the first time, that (i) in the pure states while methanol exists mainly as cyclic dimers (with perhaps open chain dimers and trimers), ethanol exists mainly as open chain trimers, and that (ii) in the (A + B) mixtures A ($= a_n (n = 1$ and/or 2))B molecular species characterize these mixtures. The H^E data of these (A + B) mixtures have been utilized to understand the energetics of the various interactions that characterize these binary mixtures. These conclusions have further been substantiated with an analysis of the V^E and the H^E data of ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CHX_3 (B) (X = Cl or Br) mixtures.

INTRODUCTION

Following Frank and Wen's model [1] of liquid water, it was believed that alkanols should also have a similar type of hydrogen-bonded structure. A number of studies [2-4] have indeed indicated that alkanols are self-associated through hydrogen-bonded linear chains (with restricted rotation about the hydrogen bond) into a variable degree of polymerization. There is, however, considerable disagreement [5-11] as to the identification of predominant associated species present in these alkanols. Thus, while a number of investigations [5-8] on alkanol self-association have been interpreted in terms of monomer-dimer equilibria, results from other studies [8-11] have indicated that associated species larger than dimers are important in all but the dilute solutions. Liddel and Backer [12], on the other hand, maintain

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that methanol contains both cyclic as well as chain dimers in solution. It appears that the state of aggregation of alkanols in binary solutions is dictated primarily by the other component. Since the suggestion that the structural formula of chemicals is actually a kind of "molecular graph", a number of workers [13–18] have shown that this "molecular graph", which describes the topology of molecules, gives valuable information about a molecule. Since the state of association of alkanols in pure as well as in binary solutions may or may not be the same, it follows that this must be reflected in their corresponding "molecular graph". Thus the topological aspect of these alkanols may provide valuable insight into the state of aggregation of these alkanols. In the present investigation we have combined the graph theoretical concept of the connectivity parameter of the third degrees of A and B with molar excess volume, V^E, and molar excess enthalpy, H^E, data of methanol (A) + methylene bromide (B) and ethanol (A) + methylene bromide (B) mixtures to understand the state of aggregation of these alkanols in the pure state and in (A + B) mixtures.

EXPERIMENTAL

Materials and method

Methanol and ethanol (BDH, AR Grade), were purified by standard procedures [19–21]. Methylene bromide, however, was obtained from two different sources. One sample (Sojuzchimexport, Moscow) was purified by shaking with 5% sodium carbonate solution, followed by washing with distilled water, drying over anhydrous calcium chloride followed by fractional distillation. The other sample of methylene bromide was synthesized from bromoform in the manner suggested by Vogel [22], and was finally purified by the same method as that described above. These two samples of methylene bromide were stored in two separate amber coloured bottles for subsequent use. The purity of the purified samples was checked by measuring their densities at 298.15 ± 0.01 K, and these agreed within ±0.00005 g cm^{-1} with their corresponding literature values [23–25].

Molar excess volumes, V^E, for the various binary mixtures were determined in a V-shaped dilatometer in the manner described earlier [26]. The temperature of the water bath was controlled to within less than ±0.01 K by means of a toluene regulator and the change in level of the liquid in the dilatometer capillary was measured with a cathetometer that could be read to ±0.001 cm. The uncertainty in the measured V^E values is about 0.5%.

Molar excess enthalpies, H^E, for the various binary mixtures were measured calorimetrically by a method described elsewhere [27]. The temperature of the bath was controlled to ±0.01 K by means of a toluene regulator and the uncertainty in the measured H^E values is about 1%.

TABLE 1

Measured V^E and H^E values at 298.15 and 308.15 K of various (A + B) binary mixtures as a function of the mole fraction of component A

x_A	V^E (cm^3 mol^{-1})	H^E (J mol^{-1})	x_A	V^E (cm^3 mol^{-1})	H^E (J mol^{-1})
Methanol (A) + methylene bromide (B) at 298.15 K					
0.0632	–	255.7	0.5852	–	602.0
0.0766	0.106	–	0.6258	0.334	–
0.1138	–	418.9	0.6624	0.325	–
0.1253	0.161	–	0.6804	–	461.3
0.1642	0.197	–	0.7016	0.308	–
0.1950	–	606.8	0.7254	–	392.1
0.2618	0.268	–	0.7268	0.297	–
0.2852	–	723.8	0.7710	0.269	–
0.3100	–	742.0	0.8170	0.238	–
0.3549	–	758.1	0.8299	–	226.2
0.4368	0.337	–	0.8651	0.190	–
0.4488	–	735.3	0.8791	–	151.3
0.4892	0.343	–	0.9250	0.117	–
0.5002	–	695.2	0.9322	–	79.2
0.5301	0.346	–	0.9750	0.041	–
At 308.15 K					
0.0672	0.044	–	0.5367	0.180	–
0.0751	–	175.5	0.5536	–	748.1
0.1152	–	272.7	0.6195	0.170	–
0.1268	0.077	–	0.6500	–	621.7
0.1700	–	402.9	0.7110	0.149	–
0.1900	0.108	–	0.7197	–	494.6
0.2450	–	562.7	0.7557	0.134	–
0.2516	0.135	–	0.7750	–	385.2
0.3068	–	670.0	0.8096	–	310.1
0.3072	0.151	–	0.8099	0.111	–
0.4001	–	770.1	0.8533	0.090	–
0.4369	–	780.9	0.8767	0.078	–
0.4727	0.179	–	0.9215	–	91.2
0.4788	–	786.3	0.9399	0.043	–
0.5150	–	773.3	0.9538	–	43.4
Ethanol (A) + methylene bromide (B) at 298.15 K					
0.0665	0.090	–	0.4602	0.313	–
0.0816	–	449.8	0.4851	0.311	–
0.1158	0.143	–	0.5221	0.305	–
0.1329	–	653.6	0.5350	–	876.3
0.1644	–	740.2	0.5419	0.302	–
0.1875	0.211	–	0.5747	–	834.1
0.1903	–	803.0	0.6250	–	775.1
0.2196	–	865.1	0.6728	–	699.5
0.2476	0.253	–	0.6846	–	680.0
0.2860	–	952.1	0.7190	0.230	–
0.3050	–	973.0	0.7534	–	572.1

TABLE 1 (continued)

x_A	V^E (cm^3 mol^{-1})	H^E (J mol^{-1})	x_A	V^E (cm^3 mol^{-1})	H^E (J mol^{-1})
0.3328	0.291	–	0.8462	0.139	–
0.3627	0.301	–	0.8627	0.127	–
0.3929	0.306	–	0.8690	–	345.3
0.4448	–	959.2	0.8840	0.107	–
At 308.15 K					
0.0663	0.128	–	0.5437	0.408	–
0.1438	0.242	–	0.5804	–	1006.9
0.1568	–	527.4	0.6204	–	944.3
0.1789	0.285	–	0.6475	–	885.9
0.1880	–	633.4	0.6904	0.318	–
0.2233	–	731.8	0.7310	–	670.2
0.2333	0.340	–	0.7403	0.277	–
0.2744	–	870.2	0.7568	–	601.8
0.2800	0.376	–	0.7902	0.229	–
0.3659	0.417	–	0.8370	0.182	370.4
0.3678	–	1040.0	0.8468	0.171	–
0.4564	–	1095.9	0.8672	–	282.6
0.4741	0.424	–	0.8937	0.121	–
0.5356	–	1061.3	0.9257	–	134.9
0.5398	0.407	–			

RESULTS

The measured V^E and H^E data at 298.15 and 308.15 K for methanol (A) + methylene bromide (B) and ethanol (A) + methylene bromide (B) mixtures (recorded in Table 1) were fitted to the expression

$$X^E(X = V \text{ or } H) = x_A x_B \sum_{n=0}^{2} x^n (2x_A - 1)^n \tag{1}$$

where X^n ($n = 0$–2) are adjustable parameters and x_A is the mole fraction of component A in the binary mixture. These parameters were evaluated by fitting X^E ($X = H$ or V)/$x_A x_B$ to eqn. (1) by the method of least squares and are recorded, together with the standard deviations, $\sigma(X^E)$ or X^E ($X = H$ or V) defined by

$$\sigma(x^E) = \left[\frac{\sum\left(X^e_{\text{expt.}} - X^E_{\text{calc.eqn.1}}\right)^2}{m - t}\right]^{0.5} \tag{2}$$

(where m is the number of data points and t is the number of adjustable parameters in eqn. 1) in Table 2.

The V^E and H^E data of binary mixtures of methanol (A) and ethanol (A) with methylene bromide (B) may be explained if it is assumed that:

(i) these alkanols (A) are self-associated as A ($= a_n$) and their mixing with

B establishes A (a_n)–B interactions between the A ($=a_n$) and the B molecular entities of the (A + B) mixtures;

(ii) the A (a_n)–B interactions cause rupture of the self-association of A to form monomers, a, and other A (a_{n-1}) entities;

(iii) the a_{n-1} and the monomers a of A then interact specifically with the B moiety of the (A + B) mixture.

Since V^E and H^E data at 295.15 and 308.15 K are positive for the binary mixtures of methanol (A) and ethanol (A) with methylene bromide (B), it follows that in these mixtures contributions due to factor (ii) always outweigh those due to factor (iii). In this connection it would be interesting to compare the general trend in V^E and H^E data of these mixtures at 298.15 and 308.15 K with the available V^E and H^E data [8,28,29] at 303.15 K of binary mixtures of methanol (A) and ethanol (A) with chloroform (B) and bromoform (B). Thus, while V^E and H^E data at 298.15 and 308.15 K are positive for the binary mixtures of methanol (A) and ethanol (A) with methylene bromide (B) throughout the entire x_A range, V^E at 303.15 K are negative for the binary mixtures of methanol (A) with chloroform (B) and bromoform (B) throughout the entire x_A range, but V^E values at 303.15 K are negative in the range $0 < x_A < 0.7$ and positive over the rest of the x_A range for C_2H_5OH (A) + $CHCl_3$ (B) and C_2H_5OH (A) + $CHBr_3$ (B) mixtures. For CH_3OH (A) + $CHCl_3$ (B), CH_3OH (A) + $CHBr_3$ (B), C_2H_5OH (A) + $CHCl_3$ (B) and C_2H_5OH (A) + $CHBr_3$ (B) mixtures, H^E data at 303.15 K change sign with x_A; H^E is negative for low x_B (i.e. $x_B \leqslant 0.25$–0.4) and is positive over the rest of the x_B composition range. This then suggests that when $CHCl_3$ (B) and $CHBr_3$ (B) replace CH_2Br_2 (B) in their binary mixtures with CH_3OH (A) and C_2H_5OH (A), the contributions due to factors (ii) and (iii) depend markedly on x_A so that V^E and H^E data change sign with x_A. This suggests that the state of aggregation (or topology) of CH_3OH (A) and C_2H_5OH (A) may or may not be the same after mixing with B.

It would thus be worthwhile to analyse V^E data of the binary mixtures of CH_3OH (A) and C_2H_5OH (A) with CH_2Br_2 (B) in terms of the approach [30] that employs the graph theoretical concept of the connectivity parameters of the third degree, $^3\xi$, of both A and B. Since the $^3\xi$ of A may or may not be the same in the pure (A) and (A + B) mixture, we denote it, respectively, as $(^3\xi_A)$ and $(^3\xi_A)_m$, and express V^E according to this approach [30] by

$$V^E = \alpha_{AB}\left[\frac{1}{x_A(^3\xi_A)_m + x_B(^3\xi_B)} - \frac{x_A}{^3\xi_A} - \frac{x_B}{^3\xi_B}\right] \tag{3}$$

where $^3\xi_A$, etc., are defined [30] by

$$^3\xi_A = \sum_{1<m} \sum_{m<n} \sum_{n<0} (\delta_1\delta_m\delta_n\delta_0)^{-0.5} \tag{4}$$

TABLE 2

Comparison of V^E and H^E values calculated at different temperatures and at various x_A values from eqns. (3) and (18) with their corresponding experimental values for the various (A + B) mixtures. Also listed are the parameters of eqn. (1) along with the standard deviations $\sigma(V^E)$ of V^E and $\sigma(H^E)$ of H^E for methanol (A) or ethanol (A) + methylene bromide (B) mixtures at 298.15 and 308.15 K. Also recorded are the various interaction energies χ_{12}, χ_{ii} and χ_{iii} that characterize the various ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CH_2Br_2 (B) or CHX_3 (B) (X = Cl or Br) mixtures.

Mixture	Temp. (K)	V^E (cm^3 mol^{-1})	H^E (J mol^{-1})	x_A = 0.1	0.2	0.3	0.7	0.8	0.9
(1) Methanol (A) + methylene bromide (B)	298.15	Calc.	–	0.112	0.203	0.274	0.307	0.242	0.140
		Expt.	–	0.133	0.227	0.290	0.310	0.250	0.150
		–	Calc.	418.0	660.6	765.6	413.7	257.0	113.5
		–	Expt.	379.8	617.6	735.0	432.6	214.4	120.6

V^E (cm^3 mol^{-1}) = $x_Ax_B[1.38+0.1185(x_A-x_B)+0.3038(x_A-x_B)^2]$; $\sigma(V^E)$ (cm^3 mol^{-1}) = 0.002;
H^E (J mol^{-1}) = $x_Ax_B[2780.01-1800.0(x_A-x_B)]$; $\sigma(H^E)$ (J mol^{-1}) = 2.0; $^3\xi_A = 0.75$; $(^3\xi_A)_m = 0.75$; $^3\xi_B = 1.0$; χ_{12} (J mol^{-1}) = 2414.7;
χ_{ii} (J mol^{-1}) = 1481.05; χ_{iii} (J mol^{-1}) = -1481.05

Mixture	Temp. (K)	V^E (cm^3 mol^{-1})	H^E (J mol^{-1})	x_A = 0.1	0.2	0.3	0.7	0.8	0.9
	308.15	Calc.	–	0.058	0.105	0.141	0.154	0.120	0.069
		Expt.	–	0.064	0.114	0.150	0.152	0.116	0.065
		–	Calc.	343.2	532.2	684.9	636.1	476.3	262.4
		–	Expt.	235.5	471.7	660.0	535.0	328.9	128.3

V^E (cm^3 mol^{-1}) = $x_Ax_B[0.72+0.0119(x_A-x_B)-0.0059(x_A-x_B)^2]$; $\sigma(V^E)$ (cm^3 mol^{-1}) = 0.001;
H^E (J mol^{-1}) = $x_Ax_B[3120.01-744.08(x_A-x_B)-1717.31(x_A-x_B)^2]$; $\sigma(H^E)$ (J mol^{-1}) = 2.1; $^3\xi_A = 0.8$; $(^3\xi_A)_m = 0.8$; $^3\xi_B = 1.0$;
χ_{12} (J mol^{-1}) = 2826.0; χ_{ii} (J mol^{-1}) = -53.33; χ_{iii} (J mol^{-1}) = 53.33

Mixture	Temp. (K)	V^E (cm^3 mol^{-1})	H^E (J mol^{-1})	x_A = 0.1	0.2	0.3	0.7	0.8	0.9
(2) Ethanol (A) + methylene bromide (B)	298.15	Calc.	–	0.156	0.252	0.304	0.228	0.164	0.087
		Expt.	–	0.140	0.230	0.280	0.240	0.175	0.094
		–	Calc.	432.3	835.0	848.3	672.3	510.2	150.8
		–	Expt.	520.0	828.0	960.0	660.0	480.0	271.8

V^E (cm^3 mol^{-1}) = $x_Ax_B[1.24-0.238(x_A-x_B)-0.0118(x_A-x_B)^2]$; $\sigma(V^E)$ (cm^3 mol^{-1}) = 0.002;
H^E (J mol^{-1}) = $x_Ax_B[3660.0-1785.72(x_A-x_B)+1232.14(x_A-x_B)^2]$; $\sigma(H^E)$ (J mol^{-1}) = 3.5; $^3\xi_A = 2.10$; $(^3\xi_A)_m = 2.10$; $^3\xi_B = 1.0$;
χ_{12} (J mol^{-1}) = 5612.0; χ_{ii} (J mol^{-1}) = 4689.23; χ_{iii} (J mol^{-1}) = -4689.23

	308.15	Calc.	–	0.213	0.342	0.410	0.306	0.214	0.116
		Expt.	–	0.189	0.309	0.405	0.311	0.220	0.114
		–	Calc.	403.1	709.1	919.4	855.1	633.6	344.2
		–	Expt.	337.7	666.9	925.5	782.9	505.0	193.7

V^E (cm^3 mol^{-1}) $= x_A x_B[1.68 - 0.4643(x_A - x_B) - 0.0714(x_A - x_B)^2]$; $\sigma(V^E)$ (cm^3 mol^{-1}) $= 0.002$; H^E (J mol^{-1}) $= x_A x_B[4360.0 - 1000.02(x_A - x_B) - 2200.0(x_A - x_B)^2]$; $\sigma(H^E)$ (J mol^{-1}) $= 3.2$; ${}^3\xi_A = 2.15$; $({}^3\xi_A)_m = 2.15$; ${}^3\xi_B = 1.0$; χ_{12} (J mol^{-1}) $= 6690.83$; χ_{ii} (J mol^{-1}) $= 3033.0$; χ_{iii} (J mol^{-1}) $= -3033.0$

(3) Methanol (A) + chloroform (B)	303.15	Calc.	–	−0.048	−0.086	−0.116	−0.127	−0.099	−0.057
		Expt.	–	−0.030	−0.067	−0.090	−0.140	−0.110	−0.067
		–	Calc.	294.9	360.8	299.0	−326.7	−425.4	−290.4
		–	Expt.	298.4	358.4	304.5	−377.8	−400.1	−284.7

${}^3\xi_A = 0.8$; $({}^3\xi_A)_m = 0.8$; ${}^3\xi_B = 1.0$; χ_{12} (J mol^{-1}) $= -237.6$; χ_{ii} (J mol^{-1}) $= 3655.36$; χ_{iii} (J mol^{-1}) $= -3655.36$

(4) Methanol (A) + bromoform (B)	303.15	Calc.	–	−0.067	−0.121	−0.163	−0.178	−0.139	−0.080
		Expt.	–	−0.034	−0.075	−0.120	−0.225	−0.190	−0.117
		–	Calc.	375.4	540.9	551.6	−14.1	−107.3	−112.4
		–	Expt.	310.0	461.5	480.1	−20.1	−130.0	−132.3

${}^3\xi_A = 0.8$; $({}^3\xi_A)_m = 0.8$; ${}^3\xi_B = 1.0$; χ_{12} (J mol^{-1}) $= 1098.0$; χ_{ii} (J mol^{-1}) $= 2902.5$; χ_{iii} (J mol^{-1}) $= -2902.5$

(5) Ethanol (A) + chloroform (B)	303.15	Calc.	–	0.057	0.050	0.021	−0.326	−0.453	−0.593
		Expt.	–	0.058	0.058	0.094	−0.196	−0.180	−0.110
		–	Calc.	218.4	307.1	280.0	−487.8	−610.2	−516.2
		–	Expt.	310.0	505.0	410.0	−420.0	−400.0	−322.0

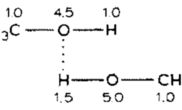
$\xi_A = 2.69$; $({}^3\xi_A)_m = 1.80$; ${}^3\xi_B = 1.0$; χ_{12} (J mol^{-1}) $= -295.24$; χ_{ii} (J mol^{-1}) $= 8010.0$; χ_{iii} (J mol^{-1}) $= -8010.0$

(6) Ethanol (A) + bromoform (B)	303.15	Calc.	–	−0.0043	−0.0254	−0.061	−0.305	−0.385	−0.471
		Expt.	–	0.037	0.030	−0.025	−0.257	−0.242	−0.118
		–	Calc.	307.5	406.7	575.0	98.7	−72.8	−148.3
		–	Expt.	310.0	460.0	638.0	135.0	10.0	−41.0

${}^3\xi_A = 2.69$; $({}^3\xi_A)_m = 1.65$; $({}^3\xi_B) = 1.0$; χ_{12} (J mol^{-1}) $= 3340.87$; χ_{ii} (J mol^{-1}) $= 6582.93$; χ_{iii} (J mol^{-1}) $= -6582.93$

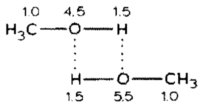
and δ_m, etc., denote the degrees of the m-th, etc., vertices of the molecular graph of A. α_{AB} is a constant characteristic of the (A + B) mixture. Following our earlier convention [30], we assumed ${}^3\xi_B = 1$ for CH_2Br_2 (B), and then varied $({}^3\xi_A)_m$ and $({}^3\xi_A)$ so that expression (3) best reproduced the experimental V^E data of the binary mixtures of CH_3OH (A) and C_2H_5OH (A) with CH_2Br_2 (B). $({}^3\xi_A)_m$ and ${}^3\xi_A$ for ROH (A) (R = $-CH_3$ or $-C_2H_5$) in their binary mixtures with CHX_3 (B) (X = Cl or Br) were also evaluated in a similar manner using ${}^3\xi_B = 1$. Such $({}^3\xi_A)_m$ and ${}^3\xi_A$ values for ROH (A) (R = $-CH_3$ or $-C_2H_5$) are recorded in Table 2 and show that whereas $({}^3\xi_A)_m = {}^3\xi_A$ for CH_3OH (A) in its binary mixtures with CH_2Br_2 (B) and CHX_3 (B) (X = Cl or Br) and for C_2H_5OH (A) with CH_2Br_2 (B), the same is not true of C_2H_5OH (A) in its binary mixtures with CHX_3 (B) (X = Cl or Br). The V^E values obtained in this manner from eqn. (3) for the various binary mixtures at various x_A are recorded in Table 2 and are also compared with their corresponding experimental values. Since the agreement between the experimental and the calculated V^E values is reasonably good, $({}^3\xi_A)_m$ and ${}^3\xi_A$ values so obtained can be relied upon to understand the state of aggregation of A in both the pure and the (A + B) state.

As alkanols are known to be self-associated through hydrogen bonding, they may exist as r-mers in solution. If we assume that ROH (A) (R = $-CH_3$ or $-C_2H_5$) exist in solution as dimers or as trimers, in the pure state, while CH_3OH (A) may exist as



(α)

or



(β)

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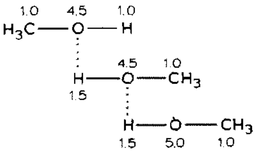
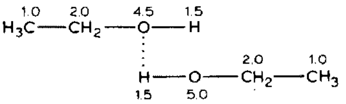


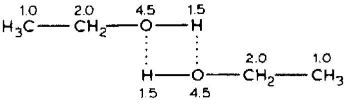
(β')

C_2H_5OH (A) may exist as



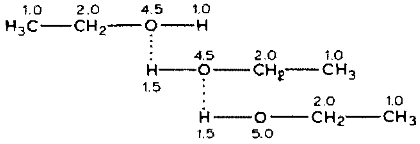
(γ)

or



(ϕ)

and / or



(ϕ')

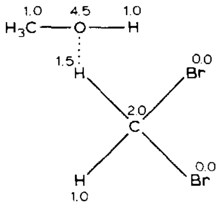
In these states of CH_3OH (A) and C_2H_5OH (A), following Kier [31], the degree of vertex of the oxygen atom involved in hydrogen-bonded interaction would be more than 4 but less than 5. Similarly, the degree of vertex of the hydrogen atom involved in hydrogen-bonded interaction would be more than one but evidently less than 2. Since no method is available to assign unambiguously the degree of vertices of the oxygen and the hydrogen atoms that are involved in hydrogen-bonded interactions, we have arbitrarily assigned $\delta(\text{oxygen}) = 4.5$ and $\delta(\text{hydrogen}) = 1.5$ to these atoms in these interactions. The hydrogen atom not involved in O- - -H interactions has been assigned $\delta = 1$ while the δ values for the carbon atoms in CH_2– and CH_3– were taken to be 2 and 1, respectively. The degrees of various vertices in the molecular graph of CH_3OH (A) are shown in the configurations α, β and β' while those of C_2H_5OH (A) are shown in the configurations γ, ϕ and ϕ'.

The ${}^3\xi_A$ values for the α, β and β' configurations of CH_3OH would then be 0.52, 0.61 and 1.08, respectively. Since ${}^3\xi_A$ for CH_3OH, as obtained from an analysis of its V^E data of its binary mixtures with CH_2Br_2 (B), $CHCl_3$ (B) and $CHBr_3$ (B) in terms of eqn. (3), has been found to be 0.75, it follows that in the pure state CH_3OH (A) exists mainly in the cyclic dimer configuration, β; a small amount of the α and β' configurations may also be present, or alternatively it may exist as an equilibrium mixture of all three (α, β and β') configurations (each present in 1 : 1 : 1 proportion thereby yielding ${}^3\xi_A = 0.73$).

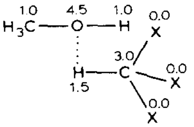
On the other hand, the ${}^3\xi_A$ values for the γ, ϕ and ϕ' configurations of C_2H_5OH (A) would be 1.05, 1.24 and 2.03, respectively. As ${}^3\xi_A$ for C_2H_5OH (A) has been found to be 2.1 in the present analysis of its V^E data with CH_2Br_2 (B) and CHX_3 ($X = Cl$ or Br), it follows that in the pure state C_2H_5OH (A) exists mainly in the ϕ' configuration.

Again $({}^3\xi_A)_m = {}^3\xi_A$ for CH_3OH (A) in its binary mixtures with CH_2Br_2 (B) and CHX_3 (B) ($X = Cl$ or Br) and while V^E data at 298.15 and 308.15 K are positive for the CH_3OH (A) + CH_2Br_2 (B) mixture, it is negative for $CH_3OH + CHX_3$ (B) ($X = Cl$ or Br) mixtures. Since the replacement of CH_2Br_2 (B) by $CHBr_3$ (B) in its binary mixtures with CH_3OH (A) causes V^E data to change from positive to negative values, this suggests that the addition of B to A causes rupture of the self-association in A to form monomers and other entities which then undergo specific interactions with B.

In these (A + B) solutions, CH_3OH (A) may then exist as θ, θ' and/or θ^* entities. It is now reasonable to assume that the major portion of the molar volumes of CH_2Br_2 (B) and CHX_3 (B) ($X = Cl$ or Br) is due to their X atoms. Since both CH_2Br_2 (B) and CHX_3 (B) are involved in hydrogen-bonded interaction with A in these structures, only those molecules of B should be deemed to contribute to the molar volume of A in these (A + B) mixtures that are involved in these hydrogen-bonded interactions. In other words, so far as expression (3) is concerned, the contributions that X of CH_2Br_2 (B) or CHX_3 (B) make to the molar volume of A in these (A + B)



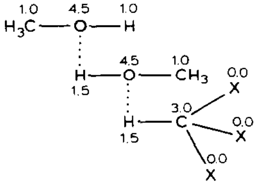
(θ)



(θ′)

(X = Cl or Br)

OR

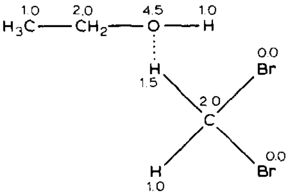


(X = Cl or Br)

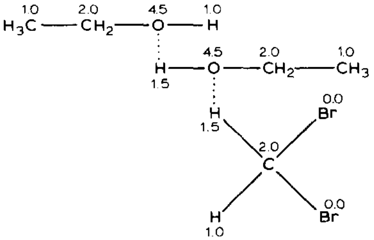
(θ*)

mixtures would be very small so that it would be reasonable to assume that $\delta = 0$ for all the X atoms. ${}^3\xi$ of the θ, θ^* and θ' species would then be 0.81, 0.88 and 0.77, respectively. (The degrees of various vertices are shown in these configurations.) Since the ${}^3\xi$ values for the θ and θ' species are closer to the (${}^3\xi_A$) value evaluated for CH_3OH (A) in the (A + B) state, it follows that θ and θ' (and perhaps θ^*) might be present in CH_3OH (A) + CH_2Br_2 (B) and CH_3OH (A) + CHX_3 (B) (X = Cl or Br) mixtures, respectively. In fact it has actually been shown [8,28,29] (from an analysis of H^E and activity coefficient data at 308.15 K of CH_3OH (A) + CHX_3 (B) (X = Cl or Br) in terms of the ideal associated model) that CH_3OH (A) exists as a dimer in the pure state and that in the (A + B) mixture it forms, among other species, an A ($= a_n(n = 1)$) B molecular species.

Similar treatment would then yield ${}^3\xi = 1.45$ for C_2H_5OH (A) in its binary mixtures with CH_2Br_2 corresponding to the species θ^{11}. This value of ${}^3\xi$ for C_2H_5OH (A) is about 50% lower than that obtained from an analysis of its V^E data (with CH_2Br_2) in terms of eqn. (3). One way to account for this

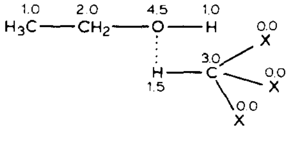


(θ^{II})



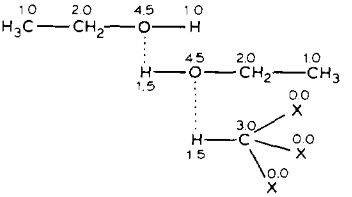
(θ^{III})

would be to assume that in the C_2H_5OH (A) + CH_2Br_2 (B) mixture, another molecular species, θ^{III}, may be present. This would yield $^3\xi = 2.52$ which is closer to the $^3\xi_A$ value that has been obtained for C_2H_5OH in $C_2H_5OH + CH_2Br_2$. The present analysis of the V^E data of C_2H_5OH (A) + CH_2Br_2 (B) would then suggest that C_2H_5OH exists as open chain trimers in the pure state and that in the (A + B) mixture an A ($= a_n(n = 2)$)B molecular species is present in this mixture. In order to further substantiate these conclusions, we next assume that in the C_2H_5OH (A) + CHX_3 (B) (X = Cl or Br) mixtures, the following species may be present:



(X = Cl or Br)

(θ^{IV})



(X = Cl or Br)

(θ^{V})

The $^3\xi$ values for the θ^{IV} and θ^{V} species would then be 0.93 and 2.84, respectively. But while the $^3\xi_A$ for C_2H_5OH (A) in the C_2H_5OH (A) + $CHCl_3$ (B) mixture is 1.80, it is 1.65 in the C_2H_5OH (A) + $CHBr_3$ (B) mixture. If it is assumed that both the θ^{IV} and the θ^{V} species are present in 1 : 1 proportion in C_2H_5OH (A) + CHX_3 (B) (X = Cl or Br) mixtures, then the resulting $^3\xi_A$ value would be 1.89. This $^3\xi_A$ value is very close to the value (1.8) obtained for C_2H_5OH (A) (from eqn. 3) in C_2H_5OH (A) + CHX_3 (B) (X = Cl or Br) mixtures.

The present analysis of V^E data for C_2H_5OH (A) + CHX_3 (B) (X = Cl or Br) mixtures in terms of eqn. (3) thus reveals that an A ($= a_n$ ($n = 2$))B molecular species may be present in these mixtures. This has actually been inferred [8,28,29] from an analysis of H^E and activity coefficient data of these mixtures in terms of the ideal associated model.

We now undertake to study the energetics of the various interactions that characterize these (A + B) mixtures. For this purpose we utilized H^E data of ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CH_2Br_2 (B) mixtures. H^E data at 303.15 K of ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CHX_3 (B) (X = Cl or Br) mixtures were taken from the literature [8,28,29].

So far it has been assumed that when component B is added to component A to yield an (A + B) mixture, component B first mixes with A to establish A ($= a_n$ ($n = 2$))–B contacts. These A ($= a_n$ ($n = 2$))–B contacts then cause rupture of the self-association in A ($= a_n$ ($n = 2$)) to yield monomers, a, and a_{n-1} entities of A which then interact with the component B. The measured molar excess enthalpy of these (A + B) mixtures at any temperature T and composition x_A, H^E (T_1x_A), would then be composed of contributions due to these factors. Now if χ_{12} is the energy per A ($= a_n$ ($n = 2$))–B contact and if V_A and V_B are the molar volumes of A

($= a_n$) and B, respectively, then the molar enthalpy change, ΔH_i, due to A ($= a_n$ ($n = 2$))–B mixing would be given by [32,33]

$$\Delta H_i = x_A S_B \chi_{12} \tag{5}$$

where S_B is the surface fraction of B defined [32] by

$$S_B = x_B V_B / \sum_{i=A,B} (x_i V_i) \tag{6}$$

so that

$$\Delta H_i = x_A x_B \chi_{12} / \left[\sum_{i=A,B} (x_i V_i) \right] \tag{7}$$

The variation of the H^E data [8,28,29] of ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CHX_3 (B) (X = Cl or Br) mixtures with x_A clearly point out that the molecules of B that are involved in A ($= a_n$)–B interactions cause rupture of the self-association of A ($= a_n$) to yield a_{n-1} and monomers, a. Consequently, if χ_{ii} is the energy per mole required to form monomers a and the a_{n-1} entities of A via rupture of the self-association of A, then the enthalpy change, ΔH_{ii}, accompanying this process would be given by an expression identical to expression (5), i.e. by

$$\Delta H_{ii} = x_A \chi_{ii} S'_B \tag{8}$$

where S'_B is the surface fraction of B that brings about this change in A ($= a_n$). But S'_B would depend on the mole fraction of A ($= a_n$) and on the surface fraction of B in the A ($= a_n$) + B mixture

$$S'_B \propto x_A S_B$$

or

$$S'_B \propto x_A x_B V_B / \left(\sum x_i V_i \right) \tag{9}$$

Hence

$$\Delta H_{ii} = k x_A^2 x_B v_B \chi_{ii} / \left(\sum x_i V_i \right) \tag{10}$$

where k is a constant of proportionality.

On the other hand, if χ_{iii} is the energy per a_n ($n = 1$ or 2)–B contact to yield aB and/or a_2B species then the molar enthalpy change, ΔH_{iii}, due to this process would likewise be given by

$$\Delta H_{iii} = x_A S''_B \chi_{iii} \tag{11}$$

where S''_B is the surface fraction of B that is involved in this process. Now S''_B would evidently depend on the surface fraction, S_B, of B in the A ($= a_n$) + B mixture and the mole fractions of B

$$S''_B \propto x_B S_B \tag{12}$$

$$\text{or } \Delta H_{iii} \propto x_A x_B S_B \chi_{iii} \tag{13}$$

or

$$\Delta H_{iii} = k' x_A x_B^2 \chi_{iii} / \left(\sum x_i V_i \right) \tag{14}$$

where k' is another constant of proportionality. Hence

$$\begin{aligned} H^E(T, x_A) &= \Delta H_i + \Delta H_{ii} + \Delta H_{iii} \\ &= \left(x_A x_B V_B / \left(\sum x_i V_i \right) \right) \left(\chi_{12} + k x_A \chi_{ii} + k' x_B \chi_{iii} \right) \end{aligned} \tag{15}$$

Now if $k\chi_{ii} = -k'\chi_{iii} = \chi$, then

$$H^E(T, x_A) = \left(x_A x_B V_B / \sum x_i V_i \right) \left[\chi_{12} + (x_A - x_B)\chi \right] \tag{16}$$

But it has been shown [30] that

$$V_B / V_A = \left({}^3\xi_A / {}^3\xi_B \right)_{\text{pure state}} \tag{17}$$

$$H^E(T, x_A) = \frac{x_A x_B \left({}^3\xi_A / {}^3\xi_B \right)_{\text{pure state}}}{x_A + x_B \left({}^3\xi_A / {}^3\xi_B \right)_{\text{pure state}}} \left[\chi_{12} + (x_A - x_B)\chi \right] \tag{18}$$

Evaluation of χ_{12} and χ (and hence χ_{ii} and χ_{iii}) interaction energies thus requires a knowledge of H^E data of the A ($= a_n$) + B mixture. For this purpose we utilized H^E data at 298.15 and 308.15 K for ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CH_2Br_2 (B) mixtures at $x_A = 0.5$ and 0.4 and coupled them with ${}^3\xi_A$ values of A, (obtained from an analysis of the V^E data at these temperatures in terms of expression 3), to evaluate χ_{12} and χ for these mixtures. Such χ_{12} and χ interaction energies are recorded in Table 2. These χ_{12} and χ interaction energy values were further used to evaluate H^E for the A ($= a_n$) + B mixtures at various x_A. Such H^E values are recorded in Table 2 and they compare well with their corresponding experimental values: χ_{12} and χ and, hence H^E for ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CHX_3 (B) (X = Cl or Br) mixtures at 303.15 K were also similarly computed; these H^E values are also recorded in Table 2 and are also compared with their corresponding experimental values.

Examination of Table 2 clearly reveals that the H^E values evaluated at 303.15 K for ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CHX_3 (B) (X = Cl or Br) or CH_2Br_2 (B) mixtures in the manner described above reproduce reasonably well the general shape of the experimental H^E versus x_A curves for these mixtures. A heartening feature of this study is that it has been able to reproduce reasonably well the change in sign of H^E with x_A for ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CHX_3 (B) (X = Cl or Br) mixtures even though it has been assumed that the interaction energies in the A ($= a_n$ ($n = 1$ or 2))B molecular species are the same. The quantitative agreement between the calculated and the experimental H^E values may have been improved by assuming that the A ($= a_n$ ($n = 1$ or 2))B molecular species that characterize these (A + B) mixtures have different interaction energies but the approach would lose its simplicity in that case.

Table 2 further shows that whereas χ_{12} at 303.15 K is negative for $CHCl_3$ (B) + ROH (A) (R = $-CH_3$ or $-C_2H_5$) mixtures, and varies for $\chi_{12}(CHCl_3$ (B) + CH_3OH (A)) > $\chi_{12}(CHCl_3$ (B) + C_2H_5OH (A)) mixtures, it is positive for ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CH_2Br_2 (B) or $CHBr_3$ (B) mixtures and varies for $\chi_{12}(CHCl_3$(B) or $CHBr_3$ (B) + CH_3OH (A)) < $\chi_{12}(CH_2Br_2$ (B) or $CHBr_3$ (B) + C_2H_5OH (A)) mixtures. This would then mean that when C_2H_5OH (A) replaces CH_3OH (A) in its binary mixtures with $CHCl_3$, compared to CH_3OH, C_2H_5OH (A) has greater affinity for the molecules of $CHCl_3$. This is perfectly understandable. The inductive effect of the $-C_2H_5$ group is more than that of the $-CH_3$ group so that more charge is centered on the oxygen atom of the O–H group in C_2H_5OH than that in CH_3OH. Such a scheme of molecular interactions would require that in the ROH (A) (R = $-CH_3$ or $-C_2H_5$) + $CHCl_3$ (B) mixtures not only should the energy released when A ($= a_n$ ($n = 1$ or 2))B molecular species are formed in C_2H_5OH (A) + $CHCl_3$ (B) mixtures be more than that in the CH_3OH (A) + $CHCl_3$ (B) mixtures, but H^E should also be negative over the entire x_A range in these mixtures. The χ_{iii} values and the expt. H^E data in Table 2 actually support this idea.

On the other hand, χ_{12} is positive for ROH (A) (R = $-CH_3$ or $-C_2H_5$) + $CHBr_3$ (B) or CH_2Br_2 (B) mixtures and vary according to $\chi_{12}(C_2H_5OH)$ > $\chi_{12}(CH_3OH)$ when these alkanols are mixed with $CHBr_3$ (B) or CH_2Br_2 (B). This would then suggest that in ROH (A) (R = $-CH_3$ or $-C_2H_5$) + $CHBr_3$ (B) mixtures, compared to C_2H_5OH, CH_3OH (A) has greater affinity for the $CHBr_3$ molecules so that comparatively more energy should be released when the A ($= a_n$ ($n = 1$ or 2))B molecular species are formed in the CH_3OH (A) + $CHBr_3$ (B) than that in the C_2H_5OH (A) + $CHBr_3$ (B) mixtures. The χ_{iii} values in Table 2 support this conjecture. Similar arguments would also apply to χ_{12}, χ_{ii} and χ_{iii} values in the ROH (A) (R = $-CH_3$ or $-C_2H_5$) + CH_2Br_2 (B) mixtures.

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