

Topological investigations of molecular interactions in mixtures containing 1,4-dioxane and alkanols

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Abstract

Molar excess volumes, V^E , and molar excess enthalpies, H^E , of 1,4-dioxane (i) + propan-1-ol, or + propan-2-ol, or + butan-1-ol, or + butan-2-ol (j) binary mixtures have been measured dilatometrically and calorimetrically as a function of composition at 308.15 K. The data have been analysed in terms of the graph theoretical approach (which involves the topology of the components of the mixture) to extract information about the state of components in pure and mixture states. The analysis of V^E data by the graph approach has revealed that while propan-1-ol and propan-2-ol exist as associated molecular entities; 1,4-dioxane and butan-2-ol exist as monomers and these ($i+j$) mixtures contain a 1:1 molecular complex. The IR spectral studies of the ($i+j$) mixture lend additional support to the nature and extent of interaction for the proposed molecular entity in the mixtures. The energetic of the mixtures have also been studied. The V^E and H^E values predicated by graph approach compare well with their corresponding experimental values. The observed data have also been analyzed in terms of Flory and Lacombe and Sanchez theory. © 2004 Published by Elsevier B.V.

Keywords: 1,4-Dioxane; Alkanols; Connectivity parameter; Flory theory; Lacombe and Sanchez theory

1. Introduction

The physical properties of the solution depends upon the manner in which the constituents of the solution are associated with one another. Recent studies [1,2] have shown that in a binary ($i+j$) mixtures, ($i-i$) and ($j-j$) contacts are replaced by $i-j$ contacts and so the topology of the molecules also changes. The graph theoretical approach based on the topology of the molecules could be utilized to extract information about the state of components in pure as well as in mixed states and also about the nature and extent of interaction between them. Alcohols are known to be associated entities in the pure state through hydrogen bonding. Further, 1,4-dioxane molecule contains two oxygen atoms with two free lone pairs of electrons on each, in its structure. Thus the addition of 1,4-dioxane to alcohols may lead to disruption of alkanol–alkanol interactions which lead to change in

their topology. This prompted us to measure molar excess volumes, V^E and molar excess enthalpies, H^E of 1,4-dioxane (i) + propan-1-ol, +propan-2-ol, +butan-1-ol and +butan-2-ol (j) binary mixtures.

2. Experimental

1,4-Dioxane (D) (Fluka), propan-1-ol, propan-2-ol, butan-1-ol and butan-2-ol were purified by standard methods [3]. The purities of the purified liquids were then checked by measuring their densities at 298.15 ± 0.01 K and these agreed to within $\pm 5 \times 10^{-5}$ g cm⁻³ with their values reported in literature [3,4].

Molar excess volumes V^E , for the studied binary mixtures were determined as a function of composition at 308.15 K in a V-shaped dilatometer in the manner as described elsewhere [5]. The temperature of the water thermostat was controlled to ± 0.01 K by toluene regulator and change in liquid level of the dilatometer capillary was measured with a cathetometer that could read to ± 0.001 cm. The uncertainties in the measured V^E values are about 0.5%.

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Molar excess enthalpies, H^E for binary mixtures were measured as a function of composition at 308.15 K in a flow microcalorimeter (LKB Broma, Sweden) that has been described elsewhere [6]. The uncertainties in the measured H^E values are $\pm 1\%$.

Samples for IR studies were prepared by mixing (i) and (j) components in 1:1 (w/w) ratio and their IR spectra were recorded on a Beckman spectrophotometer (Model 4250) using sodium chloride optics.

3. Results

The measured molar excess volumes V^E , and molar excess enthalpies, H^E data for D (i) + propan-1-ol, propan-2-ol, +butan-1-ol and butan-2-ol (j) binary mixtures (recorded in (Tables 1 and 2) and plotted in Figs. 1 and 2 were fitted to Eq. (1)

$$X^E(X = V \text{ or } H) = x_i x_j [X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2] \quad (1)$$

where x_i is the mole fraction of (i) in the ($i+j$) mixture and $X^{(n)}$ ($n=0-2$) are parameters characteristic of ($i+j$) binary mixtures. These parameters were evaluated by fitting experimental X^E data to Eq. (1) by least square method. Such parameters along with the standard deviation $\sigma(X^E)$, defined by

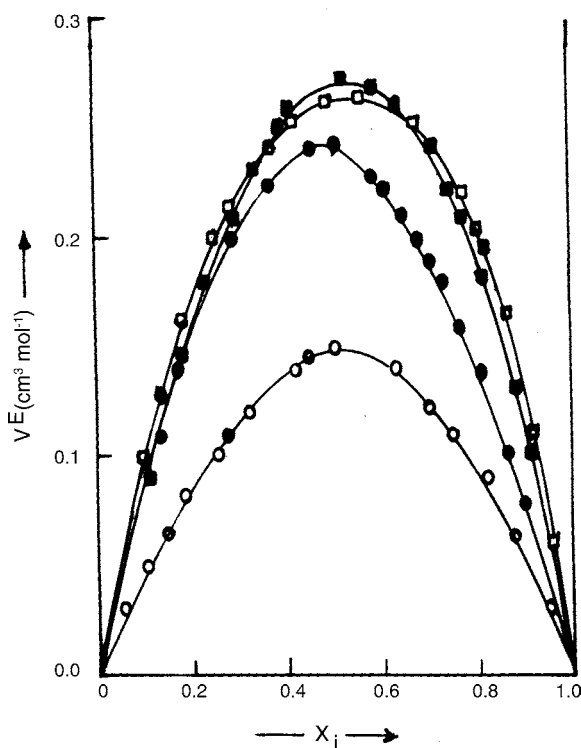


Fig. 1. Molar excess volumes, V^E , for 1,4-dioxane (i) + propan-1-ol (j), \circ ; 1,4-dioxane (i) + butan-2-ol (j), \bullet ; 1,4-dioxane (i) + propan-2-ol (j), \square ; 1,4-dioxane (i) + butan-1-ol (j), \blacksquare ; at 308.15 K.

Table 1

Measured V^E values at 308.15 K for the various ($i+j$) mixtures as a function of x_i , the mole fraction of component i ; also included are the various $V^{(n)}$ ($n=0-2$) parameters alongwith standard deviation $\sigma(V^E)$

x_i	V^E ($\text{cm}^3 \text{mol}^{-1}$)	x_i	V^E ($\text{cm}^3 \text{mol}^{-1}$)
1,4-dioxane (i) + propan-1-ol (j)			
0.0500	0.030	0.4502	0.143
0.1010	0.054	0.4920	0.145
0.1802	0.086	0.5010	0.146
0.2201	0.100	0.6301	0.138
0.2501	0.108	0.7010	0.124
0.2802	0.112	0.7520	0.112
0.3201	0.125	0.8210	0.089
0.4201	0.140	0.9510	0.030
$V^{(0)} = 0.6858$	$V^{(1)} = 0.2174$	$V^{(2)} = 0.0326$	$\sigma(V^E) = 0.002 \text{ cm}^3 \text{ mol}^{-1}$
1,4-dioxane (i) + propan-2-ol (j)			
0.0901	0.098	0.5601	0.266
0.1695	0.158	0.6801	0.255
0.2601	0.204	0.7220	0.245
0.2857	0.214	0.7802	0.222
0.3890	0.245	0.8106	0.205
0.4010	0.248	0.8920	0.142
0.4601	0.258	0.9201	0.112
0.4811	0.260	0.9621	0.059
$V^{(0)} = 1.0434$	$V^{(1)} = 0.1857$	$V^{(2)} = 0.4176$	$\sigma(V^E) = 0.002 \text{ cm}^3 \text{ mol}^{-1}$
1,4-dioxane (i) + butan-1-ol (j)			
0.1102	0.094	0.5221	0.275
0.1920	0.154	0.5820	0.273
0.2302	0.178	0.6421	0.262
0.2806	0.205	0.6902	0.249
0.3320	0.230	0.7120	0.240
0.3612	0.240	0.7616	0.215
0.4102	0.257	0.8820	0.128
0.4426	0.265	0.9126	0.099
$V^{(0)} = 1.0838$	$V^{(1)} = 0.1738$	$V^{(2)} = -0.0231$	$\sigma(V^E) = 0.003 \text{ cm}^3 \text{ mol}^{-1}$
1,4-dioxane (i) + butan-2-ol (j)			
0.1350	0.115	0.6510	0.216
0.1726	0.140	0.6802	0.206
0.2960	0.200	0.7020	0.194
0.3002	0.206	0.7328	0.184
0.4605	0.242	0.7910	0.154
0.5010	0.243	0.8102	0.142
0.5912	0.232	0.8620	0.108
0.6106	0.226	0.9001	0.082
$V^{(0)} = 0.9605$	$V^{(1)} = -0.0448$	$V^{(2)} = -0.0408$	$\sigma(V^E) = 0.002 \text{ cm}^3 \text{ mol}^{-1}$

Eq. (2)

$$\sigma(X^E; X = V \text{ or } H) = \left[\sum (X_{\text{expt}}^E - X^E \text{ calc. Eq. [1]})^2 / (m - p) \right]^{0.5} \quad (2)$$

where m is the number of data points and p the number of adjustable parameters of Eq. (1) are recorded in (Tables 1 and 2).

3.1. Discussion

The H^E data for D (i) + propan-1-ol, +propan-2-ol (j) at 298.15 K and for D (i) + butan-1-ol, +butan-2-ol (j) binary

Table 2
measured H^E Values at 308.15 K for various ($i+j$) mixtures as a function of x_i , the mole fraction of component i ; also included the various $H^{(n)}$ ($n=0-2$) parameters along with standard deviation $\sigma(H^E)$

x_i	H^E (J mol ⁻¹)	x_i	H^E (J mol ⁻¹)
1,4-dioxane (i) + propan-1-ol (j)			
0.0695	513	0.5320	1923
0.1416	975	0.5990	1865
0.1720	1110	0.6326	1813
0.2386	1406	0.7020	1646
0.3102	1648	0.7426	1516
0.3720	1795	0.8102	1235
0.4210	1873	0.9120	662
0.4961	1926	0.9812	158
$H^{(0)} = 7690.8$	$H^{(1)} = 210.03$	$H^{(2)} = 476.9$	$\sigma(H^E) = 5.3 \text{ J mol}^{-1}$
1,4-dioxane (i) + propan-2-ol (j)			
0.1321	1151	0.6420	2031
0.1926	1502	0.7126	1849
0.2260	1658	0.7728	1625
0.3320	2003	0.8010	1495
0.4102	2135	0.8621	1155
0.4926	2180	0.9020	200
0.5120	2178	0.9726	280
0.5521	2157	0.9810	200
$H^{(0)} = 8705.4$	$H^{(1)} = -200.9$	$H^{(2)} = 2140.2$	$\sigma(H^E) = 4.4 \text{ J mol}^{-1}$
1,4-dioxane (i) + butan-1-ol (j)			
0.0891	628	0.5102	1896
0.1102	756	0.5960	1838
0.1706	1083	0.6320	1780
0.2102	1265	0.6710	1697
0.2961	1580	0.7326	1518
0.3421	1705	0.8102	1207
0.3989	1804	0.8828	824
0.4102	1830	0.9320	511
$H^{(0)} = 7569.05$	$H^{(1)} = 169.5$	$H^{(2)} = 394.7$	$\sigma(H^E) = 4.6 \text{ J mol}^{-1}$
1,4-dioxane (i) + butan-2-ol (j)			
0.0269	245	0.4420	2150
0.1326	1066	0.5561	2112
0.1926	1420	0.6102	2020
0.2421	1660	0.6920	1790
0.2762	1790	0.7512	1562
0.3302	1976	0.8102	1270
0.3716	2060	0.8892	812
0.3965	2100	0.9610	310
$H^{(0)} = 8657.8$	$H^{(1)} = -691.3$	$H^{(2)} = 172.0$	$\sigma(H^E) = 5.3 \text{ J mol}^{-1}$

mixtures at 298.15 and 313.15 K have been reported in literature [7,8]. For D (i) + propan-1-ol and propan-2-ol, our H^E values at $x_i = 0.5$ are 70–90 J mol⁻¹ higher than those reported in the literature [7]. Also for D (i) + butan-1-ol and butan-2-ol (j) binary mixtures our H^E values lie between H^E values [8] at 298.15 and 313.15 K. The general shape of curves for all these ($i+j$) binary mixtures are the same. The V^E data for these binary mixtures have also been reported at 303.15 K in literature [9]. Our V^E values (at $x_i = 0.5$) are about 0.02 cm³ mol⁻¹ more than those reported in literature [9].

V^E and H^E data for the studied binary mixtures are positive over the whole composition range. While V^E data for an equimolar composition vary as butan-1-ol \cong butan-2-

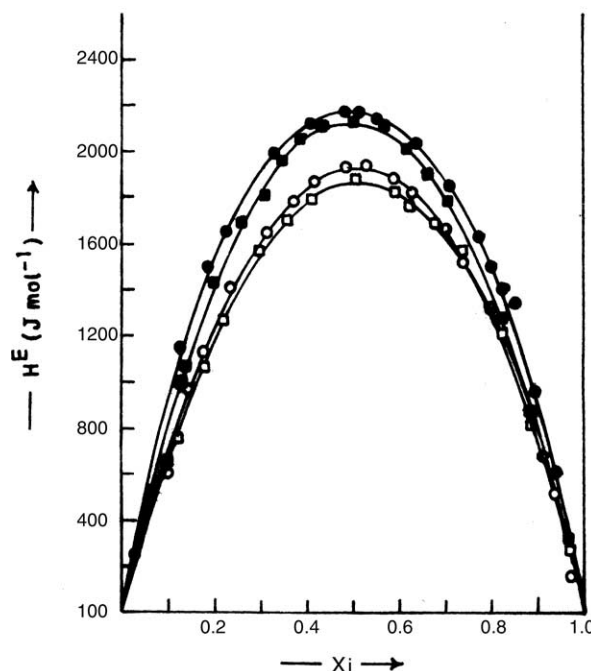


Fig. 2. Molar excess enthalpies, H^E , for 1,4-dioxane (i) + n -butan-ol (j), \square ; 1,4-dioxane (i) + n -propan-ol (j), \circ ; 1,4-dioxane (i) + butan-2-ol (j), \blacksquare ; 1,4-dioxane (i) + propan-2-ol (j), \bullet ; at 308.15 K.

ol \cong propan-2-ol > propan-1-ol; H^E data vary in the order: propan-2-ol \cong butan-2-ol > propan-1-ol > butan-1-ol.

The observed H^E data for these mixtures can qualitatively be explained if it be assumed that: (1) alcohols are associated entities; (2) there is interaction between etheral oxygen atoms and hydrogen atom of alcohols; (3) interactions between (i) and (j) then weaken $j-j$ interactions which leads to depolymerisation of j ; (4) monomers of (i) then undergoes interaction with monomers of j to form $i:j$ molecular complex; (5) there is a steric repulsion between D (i) and propan-2-ol or butan-2-ol (j) molecules due to the presence of bulky-CH₃ groups. The positive values of H^E for D (i) + propan-2-ol and butan-2-ol mixtures suggest that contributions to the factor (3) (which results in the net breaking of interactions in alcohols) far outweigh the contribution due to the factors (2) and (4) so that overall H^E values for these mixtures are positive. However, lower values of H^E for D (i) + propan-1-ol and butan-1-ol (j) mixtures than those for D (i) propan-2-ol and + butan-2-ol (j) mixtures are due to the absence of bulky CH₃ groups.

4. Conceptual aspects of Graph approach and results

According to mathematical discipline of graph theory, if atoms in the structural formula of a molecule are represented by letters and the bonds joining them by lines, the resulting graph then provides the information contained in that molecule [10–13]. In order to further extract the information contained in the molecular graph of molecule, Kier et al. [14]

suggested the use of molecular connectivity index of the first, second and third degree of the molecule defined by

$${}^1\xi = \sum_{l < m} (\delta_l \delta_m)^{-0.5} \quad (3)$$

$${}^2\xi = \sum_{l < m < n} (\delta_l \delta_m \delta_n)^{-0.5} \quad (4)$$

$${}^3\xi = \sum_{l < m < n < o} (\delta_l \delta_m \delta_n \delta_o)^{-0.5} \quad (5)$$

where δ_l etc. denotes the degree of 'l' etc. vertices of the graph of a molecule. Kier [15] further advocated the use of δ^v values reflecting explicitly the valency of the atoms forming the bonds ($\delta^v = \text{valence } \delta$) and δ^v can be determined from Eq. (6).

$$\delta^v = Z_m - h \quad (6)$$

where Z_m denotes the maximum valency of atoms and h the number of hydrogen atoms linked to atom. Accordingly $\delta^v(c)$ in CH_3 fragment of a molecule would be $4 - 3 = 1$.

Singh et al. [16] have suggested that $1/{}^3\xi$ of a molecule represent a measure of the probability that surface area interacts effectively with the surface area of other molecules and determined [17] ${}^3\xi$ by Eq. (7).

$${}^3\xi = \sum_{l < m < n < o} (\delta_l^v \delta_m^v \delta_n^v \delta_o^v)^{-0.5} \quad (7)$$

Molar excess volumes, V^E is a packing effect and molar excess enthalpies, H^E of $(i+j)$ mixtures are due to the replace-

ment of $i-i$ or $j-j$ contact in the pure state by $i-j$ contacts in the mixture and these number of contacts depend on the surface areas of the i and j components that come into effective $i-j$ interaction. Thus V^E and H^E of mixtures would be influenced by the change in topology of the molecules that undergo these interactions. It would, therefore, be of interest to analyse V^E and H^E data of $(i+j)$ mixtures in terms of graph theory. According to this theory [16,17], V^E is given by

$$V^E = \alpha_{ij} [1/x_i ({}^3\xi_i)_m + x_j ({}^3\xi_j)_m - x_i/{}^3\xi_i - x_j/{}^3\xi_j] \quad (8)$$

where α_{ij} is the constant characteristic of $(i+j)$ mixtures and $({}^3\xi_i)$ ($i=i$ or j), $({}^3\xi_j)_m$ ($i=i$ or j), etc. are the connectivity parameters of components (i) and (j) in pure and mixtures state.

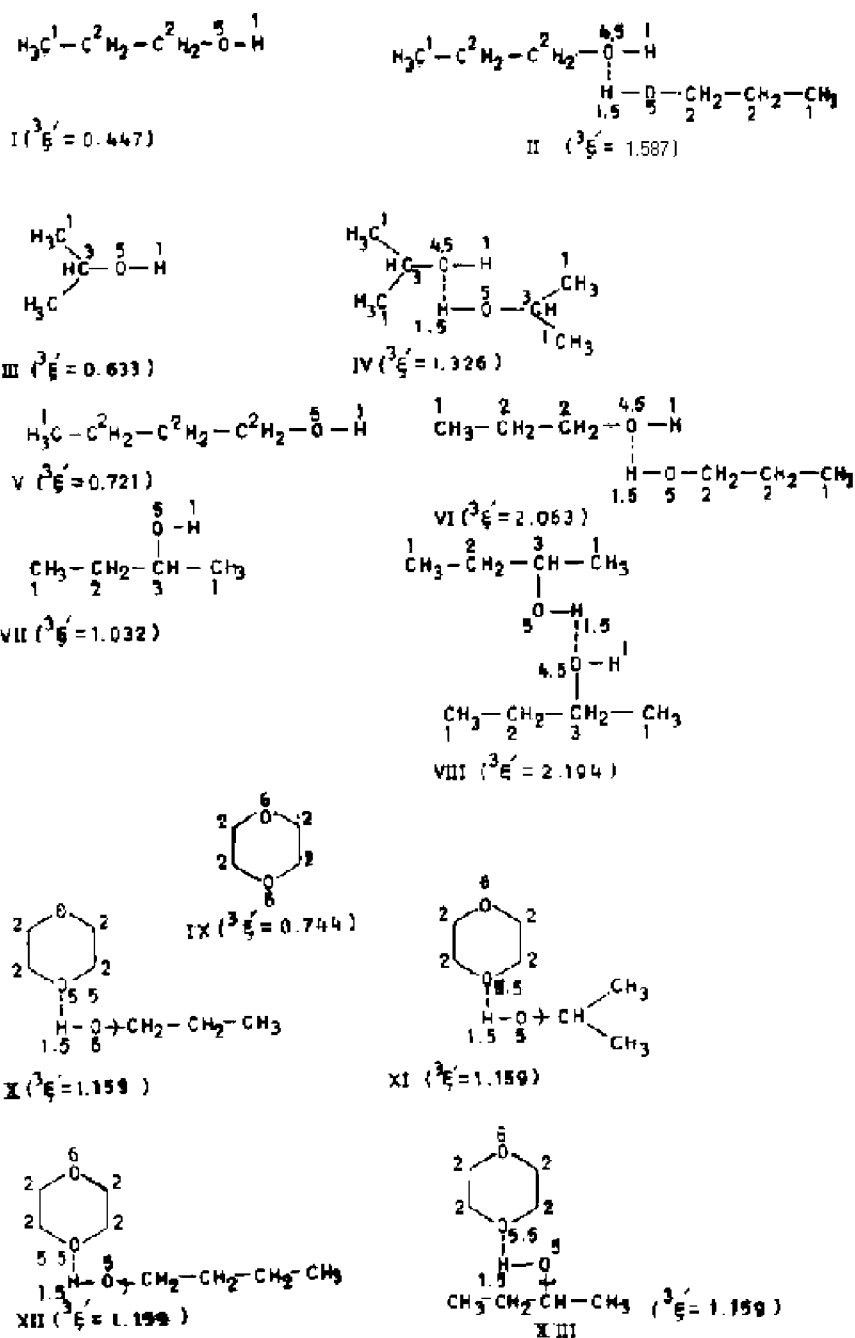
As the degree of association of i and j is not known in pure and mixture state, we regarded ${}^3\xi_i$ ($i=i$ or j) and $({}^3\xi_i)_m$ ($i=i$ or j) as adjustable parameters. These parameters were evaluated by fitting experimental V^E data to Eq. (8). Only those ${}^3\xi_i$ and $({}^3\xi_i)_m$, etc. values were retained that best reproduced the experimental V^E data. These parameters along with the V^E values calculated via Eq. (8) at various values of mole fraction (x_i) are recorded in (Table 3). Examination of (Table 3) reveals that calculated V^E values compare well with their experimental values and thus ${}^3\xi$ values for various components can be relied upon to extract information about their state in pure and mixture state.

A number of structures were then assumed for D (i), propan-1-ol, butan-1-ol, propan-2-ol and butan-2-ol and their ${}^3\xi'$ values were evaluated from structural considerations via Eq. (7). These values were then compared with ${}^3\xi$ values

Table 3

Comparison of V^E and H^E value calculated from appropriate equations with the corresponding experimental values at 308.15 K for the various $(i+j)$ mixtures as a function of x_i , mole fraction of component i ; also included are the various interaction energies χ_{ij}^{**} , χ_{ij}'' , etc.

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1,4-dioxane (i) + propan-1-ol									
V^E (exptl)	0.051	0.091	0.119	0.136	–	0.138	0.122	0.094	0.054
V^E (graph)	0.054	0.099	0.126	0.141	–	0.138	0.121	0.089	0.052
V^E (Sanchez)	0.168	0.091	0.118	0.136	–	0.138	0.123	0.093	0.124
V^E (Flory)	0.129	0.251	0.366	0.475	–	0.677	0.772	0.861	0.948
$({}^3\xi_i) = ({}^3\xi_i)_m = 0.801$, $({}^3\xi_j) = ({}^3\xi_j)_m = 0.701$, $\alpha_{ij} = -24.6671$, $\chi_{ij}^{**} = 1051.104$, $\chi_{ij}'' = 118.721$									
1,4-dioxane (i) + propan-2-ol									
V^E (exptl)	0.104	0.173	0.217	0.245	–	0.263	0.248	0.208	0.130
V^E (graph)	0.086	0.158	0.210	0.244	–	0.252	0.224	0.272	0.101
V^E (Sanchez)	0.165	0.300	0.303	0.379	–	0.341	0.383	0.294	0.230
V^E (Flory)	0.888	0.998	0.976	0.908	–	0.713	0.602	0.485	0.363
$({}^3\xi_i) = ({}^3\xi_i)_m = 0.750$, $({}^3\xi_j) = ({}^3\xi_j)_m = 0.902$, $\alpha_{ij} = -25.6078$, $\chi_{ij}^{**} = 1119.295$, $\chi_{ij}'' = 137.068$									
1,4-dioxane (i) + butan-1-ol									
V^E (exptl)	0.083	0.155	0.212	0.251	–	0.268	0.242	0.190	0.108
V^E (graph)	0.090	0.163	0.216	0.252	–	0.265	0.236	0.183	0.105
V^E (Sanchez)	0.083	0.088	0.170	0.166	–	0.273	0.565	0.990	1.545
V^E (Flory)	0.363	0.485	0.520	0.515	–	0.443	0.391	0.333	0.270
$({}^3\xi_i) = ({}^3\xi_i)_m = 0.744$, $({}^3\xi_j) = ({}^3\xi_j)_m = 0.901$, $\alpha_{ij} = -24.423$, $\chi_{ij}^{**} = 986.963$, $\chi_{ij}'' = 10.248$,									
1,4-dioxane (i) + butan-2-ol									
V^E (exptl)	0.087	0.155	0.204	0.232	–	0.227	0.196	0.147	0.080
V^E (graph)	0.050	0.147	0.198	0.234	–	0.224	0.177	0.177	0.103
V^E (Sanchez)	0.088	0.102	0.127	0.233	–	0.429	0.454	0.803	0.990
V^E (Flory)	0.030	0.059	0.085	0.109	–	0.153	0.174	0.192	0.211
$({}^3\xi_i) = ({}^3\xi_i)_m = 0.801$, $({}^3\xi_j) = ({}^3\xi_j)_m = 1.110$, $\alpha_{ij} = -9.304$, $\chi_{ij}^{**} = 1036.866$, $\chi_{ij}'' = 124.302$									



Scheme 1. Connectivity parameters of various molecular entities.

determined from Eq. (8). Any structure or combinations of structures that give ${}^3\xi'$ values which compared well with ${}^3\xi'$ values were taken to be a good representation of the structures of that component. For the analysis of the studied mixtures, we assumed that propan-1-ol, propan-2-ol, butan-1-ol and butan-2-ol exist as I–II, III–IV, V–VI, VII–VIII, molecular entities (Scheme 1). The ${}^3\xi'$ values for the entities I–VIII were then calculated to be 0.447, 1.586, 0.633, 1.326, 0.721, 2.063, 1.032 and 2.194, respectively. ${}^3\xi'$ values 0.701, 0.902, 0.901 and 1.110 (Table 3) of propan-1-ol, propan-2-ol, butan-1-ol and butan-2-ol suggest that while propan-1-ol, propan-

2-ol and butan-1-ol exist as an mixture of monomer and dimer (${}^3\xi' = 1.01, 0.980, 0.877$); butan-2-ol exist as monomer (${}^3\xi' = 1.032$). Further ${}^3\xi'$ values of 0.801, 0.750, 0.744 and 0.801 for D (i) in these mixtures suggest that D (i) exist as molecular entity IX; (${}^3\xi' = 0.744$).

(${}^3\xi'_j$)_m values were next evaluated (via Eq. (7)) to understand the state in which various alkanols exist in D (i). It was assumed that studied (i + j) mixtures may contain molecular entities X–XIII and are characterised by interaction between oxygen atoms of D (i) and hydrogen atom of alcoholic group of alkanols. In calculating (${}^3\xi'_j$)_m values for these molecu-

lar entities, it was assumed further that only O–H edge of alkanol is involved in hydrogen bond interaction with two oxygen atoms of D (*i*). The $({}^3\xi'_j)_m$ values for molecular entities X–XIII were then calculated to be 1.159 $({}^3\xi_j)_m$ values of 0.701, 0.902, 0.901 and 1.110 (Table 3) suggest the presence of molecular entities X–XIII in the studied mixtures. The presence of molecular entities X–XIII suggest that addition of *j* to *i* should have influenced the cyclic ether oxygen vibrations in D (*i*) and O–H vibrations in alkanols. To substantiate this, we analysed IR spectral data of pure D (*i*), propan-1-ol and equimolar mixture of D (*i*) + propan-1-ol. It was observed that cyclic ether oxygen vibrations and O–H vibrations in pure D (*i*) occur [18] at 1134 and 3170 cm^{-1} . On the other hand, IR spectra of D (*i*) + propan-1-ol (*j*) mixtures showed characteristic absorption at 1160 and 3145 cm^{-1} . The IR spectra data of D (*i*) + propan-1-ol mixture thus suggest that addition of *j* to *i* does influence cyclic ether oxygen vibrations of D (*i*) and O–H vibrations of alkanols and thus lends additional support to the assumption in calculating $({}^3\xi'_j)_m$ values and also for the existence of molecular entities X–XIII.

In order to understand the energetics of various interactions that characterize these mixtures, we assumed that mixture formation in these mixtures involves: (1) the establishment of unlike contact formation between D (*i*) and alkanols (*j*); (2) the establishment of D (*i*) and alkanol contacts then influences alkanol–alkanol interactions which yields their respective monomers; (3) the monomers of (*i*) undergo interactions with monomers of (*j*) to form *i*:*j* molecular entity; (4) steric repulsion between D (*i*) and propan-2-ol or butan-2-ol due to the presence of bulky- CH_3 groups.

Consequently, if χ_{ij} , χ_{ji} are molar interaction energies for *i*–*j*, *j*–*j* contact and χ_{12} is the molar interaction energy due to specific interaction between D (*i*) and alkanol (*j*), then molar enthalpy change due to processes (i)–(iii) would be given [19–21] by

$$\Delta H_1 = x_i x_j \chi_{ij} v_j / \sum x_i v_i \quad (9)$$

$$\Delta H_2 = x_i^2 x_j \chi_{jj} v_j / \sum x_i v_i \quad (10)$$

and

$$\Delta H_3 = x_i x_j^2 \chi_{12} v_j / \sum x_i v_i \quad (11)$$

where v_i etc. represent the molar volume of component (*i*). The overall change in molar enthalpy due to processes (1)–(3) then can be expressed by

$$H^E = \sum_{i=1}^3 \Delta H_i = \left[x_i x_j v_j / \sum x_i v_i \right] [\chi_{ij} + x_i \chi_{jj} + x_j \chi_{12}] \quad (12)$$

For the present mixtures it would be reasonable to assume $\chi_{ij} = \chi_{ji} \cong \chi'_{ij}$ so that Eq. (12) is expressed as

$$H^E = \left[x_i x_j v_j / \sum x_i v_i \right] [(1 + x_j) \chi'_{ij} + x_j \chi_{12}] \quad (13)$$

Since $v_j/v_i = {}^3\xi_i/{}^3\xi_j$, then Eq. (13) reduces to Eq. (14)

$$H^E = [x_i x_j ({}^3\xi_i/{}^3\xi_j)/x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [(1 + x_i) \chi'_{ij} + x_j \chi_{12}] \quad (14)$$

For D (*i*) + butan-2-ol mixture, the overall change in enthalpy would be only due to processes (i) and (iii) consequently H^E for this mixture can be expressed by Eq. (13)

$$H^E = [x_i x_j ({}^3\xi_i/{}^3\xi_j)/x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [\chi'_{ij} + \chi_{12}] \quad (15)$$

Eqs. (14) and (15) contains two unknown parameters (χ'_{ij} , χ_{12}) and these parameters were calculated by employing H^E data at two arbitrary compositions ($x_i = 0.4$ and 0.5). The calculated parameters were subsequently utilized to evaluate H^E values at other values of x_i . Such H^E values along with these parameters are recorded in (Table 4) and are also compared with their corresponding experimental values.

V^E and H^E data for the studied binary mixtures were next analysed in terms of Lacombe and Sanchez theory and Flory theory. According to Lacombe and Sanchez theory [22,23], V^E for a binary mixtures is given by

$$V^E = r_{\text{mix}} v_{\text{mix}} \left[\bar{v}_{\text{mix}} - \sum_{i=1}^j \phi_i \bar{v}_i \right] \quad (16)$$

$$H^E = 2\phi_i \phi_j r_{\text{mix}} \bar{\rho}_{\text{mix}} \chi_{ij}^{**} + RT_{\text{mix}} \sum [(\phi_i \bar{\rho}_i - \bar{\rho}_{\text{mix}} \phi_i) / \bar{T}] \quad (17)$$

$$\phi_i = m_i (\rho_i^*)^{-1} \left[\sum_{i=1}^j (m_i \rho_i^*)^{-1} \right] \quad (18)$$

$$m_i = x_i m_i \left[\sum_{i=1}^j (x_i m_i)^{-1} \right] \quad (19)$$

$$r_{\text{mix}} = \sum_{i=1}^j x_i r_i \quad (20)$$

$$r_i = r_i [v_i^* (v_{\text{mix}}^*)^{-1}] \quad (21)$$

$$v_{\text{mix}}^* = \sum_{i=1}^j \phi_i^* v_i^* \quad (22)$$

$$\bar{v}_{\text{mix}} = 1/\bar{\rho}_{\text{mix}} \quad (23)$$

$$\phi_i = m_i (\rho_i^* v_i^*)^{-1} \left[\sum_{i=1}^j (m_i / \rho_i v_i^*) \right]^{-1} \quad (24)$$

where \bar{v} , $\bar{\rho}$, v^* , T^* , ϕ_i are reduced volume, reduced density, characteristic volume, characteristic temperature and volume fraction and have the same significance as described elsewhere [22,23].

Table 4

Comparison of H^E values calculated from appropriate equation with the corresponding experimental values at 308.15 K for the various ($i+j$) mixtures as a function of x_i , mole fraction of i ; also included are the various interaction energies χ_{ij}^* , χ_{12} parameter

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1,4-dioxane (i) + propan-1-ol									
H^E (exptl)	704	1237	1613	–	–	1860	1648	1416	734
H^E (graph)	636	1154	1546	–	–	1883	1682	1309	838
H^E (Sachez)	1443	2210	2447	2307	–	1411	874	406	88
H^E (Flory)	385	777	1154	–	–	2305	2688	3070	3456
$(^3\xi_i) = (^3\xi_i)_m = 0.801$, $(^3\xi_j) = (^3\xi_j)_m = 0.701$, $\chi_{ij}^* = 3739.1$; $\chi_{12} = 3183.2$									
1,4-dioxane (i) + propan-2-ol									
H^E (exptl)	921	1535	1916	–	–	–2100	1883	1496	892
H^E (graph)	766	1375	1819	–	–	2128	1875	1438	814
H^E (Sachez)	1599	2453	2745	2621	–	1687	1100	573	179
H^E (Flory)	411	833	1269	1717	–	2641	3110	3582	4053
$(^3\xi_i) = (^3\xi_i)_m = 0.750$, $(^3\xi_j) = (^3\xi_j)_m = 0.902$, $\chi_{ij}^* = 5460.6$; $\chi_{12} = 2978.7$									
1,4-dioxane (i) + butan-1-ol									
H^E (exptl)	691	1217	1588	–	–	1828	1617	1250	716
H^E (graph)	766	1211	1604	–	–	1876	1654	1269	718
H^E (Sachez)	1123	1826	2149	2152	–	1465	937	422	69
H^E (Flory)	373	748	1126	1507	–	2278	2667	3058	3449
$(^3\xi_i) = (^3\xi_i)_m = 0.744$, $(^3\xi_j) = (^3\xi_j)_m = 0.901$, $\chi_{ij}^* = 4856.6$; $\chi_{12} = 2577.3$									
1,4-dioxane (i) + butan-2-ol									
H^E (exptl)	838	1461	1881	–	–	2046	1765	1328	739
H^E (graph)	831	1457	1886	–	–	1998	1799	1356	755
H^E (Sachez)	1252	2043	2418	2430	–	1718	1125	557	129
H^E (Flory)	433	866	1298	1731	–	2596	3028	3460	3891
$(^3\xi_i) = (^3\xi_i)_m = 0.801$, $(^3\xi_j) = (^3\xi_j)_m = 1.110$, $\chi_{ij} = 11430.2$; $\chi_{12} = 2056.3$, χ_{ij} , χ_{12} , χ_{ij}^{**} , etc., in J mol^{-1}									

Evaluation of V^E via Eqs. (16)–(24) requires a knowledge of reduced density, ρ_{mix} of ($i+j$) mixture which in turn can be evaluated from the equation of state of the mixture i.e. Eq. (25).

$$(\bar{\rho}_{\text{mix}})^2 + \bar{P} + [RT/\epsilon_{\text{mix}}^*][\ln[1 - \bar{\rho}_{\text{mix}}] + [1 - [r_{\text{mix}}]^{-1}][\bar{\rho}_{\text{mix}}] = 0 \quad (25)$$

where

$$\epsilon_{\text{mix}}^* = \left[\sum_{i=i}^j \phi_i^2 \epsilon_{ii} - \phi_i \phi_j \chi_{ij}^{**} \right] \quad (26)$$

χ_{ij}^{**} etc. are the interaction energy parameters for the various binary mixtures and were evaluated by employing their H^E value (at $x_i = 0.5$) via Eq. (27).

$$H^E = 2\phi_i \phi_j \bar{\rho}_{\text{mix}} \chi_{ij}^{**} + RT r_{\text{mix}} \left[\sum (\phi_i^0 \bar{\rho}_i - \bar{\rho}_{\text{mix}} \phi_i) (\bar{T}_i)^{-1} \right], \quad (27)$$

where \bar{T} is the reduced temperature. Since the studied binary mixtures do not satisfy equation of state i.e. Eq. (25). We utilized their V^E and H^E data at $x_i = 0.5$ to evaluate $\bar{\rho}_{\text{mix}}$ and ϵ_{mix}^* . These values were then subsequently used to see how far these mixtures deviate from Eq. (25). It was observed that right hand side of Eq. (25) for the present mixtures varied from -0.045 to -0.055 . Once the equation of state for the mixture was established, it was solved to predict the reduced density of the mixture. These values of $\bar{\rho}_{\text{mix}}$ were then utilized to predict V^E and H^E values at $x_i = 0.1, 0.2, \dots, 0.9$.

Such V^E and H^E values for various mixtures along with χ_{ij}^{**} are recorded in (Table 3) and are also compared with their experimental values.

According to Flory theory, V^E and H^E for a binary mixture is given [24,25] by:

$$V_{ij}^E = \bar{V}_{\text{cal}}^E \left[\sum_{i=i}^j x_i v_i^* \right] \quad (28)$$

$$H^E = \sum x_i P_i^* (\bar{v}_i^{-1} - \bar{v}_{\text{cal}}^{-1}) + x_i v_i^* \theta_j \chi_{ij}'' \bar{v}_{\text{cal}}^{-1} \quad (29)$$

$$\bar{v}_i = [1 + \alpha_i(T/3)/(1 + \alpha_i T)^3]^3 \quad (30)$$

$$\bar{V}_{\text{cal}}^E = \bar{v}_0^{7/3} [(4/3) - (\bar{v}_0)^{1/3}]^{-1} [\bar{T} - \bar{T}_0] \quad (31)$$

$$\bar{V}_{\text{cal}} = \bar{v}_0 + \bar{V}_{\text{cal}}^E \quad (32)$$

$$\bar{T}_0 = (\bar{v}_0^{1/3} - 1)/\bar{v}_0^{4/3} \quad (33)$$

$$\bar{v}_i^* = v_i/\bar{v}_i \quad (34)$$

$$\bar{v}_0 = \sum \phi_i v_i^* \quad (35)$$

$$\bar{T} = \left[\sum \phi_i P_i^* \bar{T}_i / \sum \phi_i P_i^* \right] \times \left[1 - (\phi_i \theta_j \chi_{ij}'') (\sum \phi_i P_i^*)^{-1} \right]^{-1} \quad (36)$$

$$\bar{T}_i = (\bar{v}_i^{1/3} - 1)/\bar{v}_i^{4/3} \quad (37)$$

$$P^* = \sum \phi_i P_i^* - \sum \phi_i^* \theta_j \chi_{ij}'' \quad (38)$$

$$P_i^* = \alpha_i T \bar{v}_i^2 [(K_T)_i]^{-1} \quad (39)$$

where x_i , v_i^* , P_i^* , \bar{T} , \bar{v} denotes, respectively the mole fraction and characteristic volume, characteristic pressure, reduced temperature, reduced volume of component (i) and have the same significance as described elsewhere [24,25]. Evaluation of V^E and H^E by Flory theory requires a knowledge of reduced temperature, \bar{T} , which in turn depends upon adjustable parameters $\theta_j \chi_{ij}''$, etc. of binary mixtures. These parameters were determined by fitting their H^E value at $x_i = 0.5$ to Eq. (39).

$$H^E = \sum x_i P_i^* (\bar{v}_i^{-1} - \bar{v}_{cal}^{-1}) + x_i v_i^* \theta_j \chi_{ij}'' \bar{v}_{cal}^{-1} \quad (40)$$

Various parameters of pure components were determined using isothermal compressibility (K_T) reported in literature [26]. K_T values for those liquids which were not available in the literature were calculated by employing ΔH_V values in the manner as suggested by Hildebrand [27]. Such V^E and H^E values evaluated via Eqs. (28)–(37) by employing Flory theory along with χ_{ij}'' , etc. are recorded in (Table 3) and also compared with their experimental values.

Examination of data in (Table 4) reveals that H^E values calculated by employing graph theory compare well with their corresponding experimental values. This lends additional support to the qualitative analysis of H^E data and also to the assumptions made in deriving Eqs. (14) and (15). However, V^E and H^E values calculated by Flory and Lacombe and Sanchez theory are of the same sign but the quantitative agreement is poor.

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