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Topological investigations of binary and ternary mixtures: excess isentropic compressibilities

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Abstract

The speed of sound, U_{ij} 1,3-dioxolane (D) in binary mixtures (ij) with benzene, cyclohexane, n-hexane or n-heptane and U_{ijk} for 1,3-dioxolane in ternary mixtures (ijk) with the same hydrocarbons have been measured as a function of composition at 298.15 K. The observed data have been utilised to evaluate excess isentropic compressibility of binary, $(\kappa_s^E)_{ij}$ and ternary $(\kappa_s^E)_{ijk}$ mixtures using density and speed of sound values of the binary and ternary mixtures. The Moelyn-Huggins concept of interaction between the molecular surfaces of the components of a binary mixture [Polymer 12 (1971) 389] has been extended to evaluate excess isentropic compressibility of the studied binary and ternary mixtures. It has been observed that κ_s^E values predicted by a graph–theoretical approach using connectivities of third degree for binary mixtures compare reasonably well with their corresponding experimental values and κ_s^E for ternary mixtures are of the same sign and order of magnitude.

Keywords: 1,3-Dioxolane; Binary and ternary mixtures; Topological indices

1. Introduction

Topological indices have found use in chemical and biological applications and chemical graph theory has important conceptual and quantitative contributions to chemistry [1,2]. Topological indices are structural invariants based on modelling of chemical structures by molecular graphs, and in numerical form they express the topology of the chemical species. The investigation of topological indices that may characterise molecular topology are one of the main directions of graph theory [3]. In the last few years, we have made an attempt to evaluate molar excess volumes and enthalpies of binary [4,5] as well as ternary mixtures [6,7] of non-electrolytes by graph theory which involves the topology of the constituents of the mixture. In the present study, an attempt has been made to evaluate molar excess isentropic compressibilities of 1,3-dioxolane in binary and ternary mixtures with cyclochexane, n-hexane or n-heptane.

2. Experimental

1,3-Dioxolane (D) (Fluka), benzene, cyclohexane, n-hexane and n-heptane (AR Grade) were purified by standard methods [8]. The purities of the purified samples were checked by measuring their densities by pycnometer at 298.15 ± 0.01 K which agreed to within $\pm 0.05\ \mathrm{kg\,m^{-3}}$ with their corresponding literature values [7,9].

The speed of sound at frequency 2 MHz was determined using a quartz crystal interferometer (Mittal Enterprises, New Delhi, India). The measuring cell was a specially designed double-walled cell in which water was circulated to maintain the temperature at (298.15 ± 0.01 K). The uncertainty in speed of sound measurement is ± 0.05%.

3. Results and discussion

The speed of sound (U_{ij}) data of binary mixtures (ij): D + benzene, D + n-hexane, D + n-heptane or D + cyclohexane; and ternary mixtures (ijk): D + benzene + cyclohexane, D + benzene + n-hexane, D + benzene + n-heptane over the entire range of composition at 298.15 K

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Table 1
Ultrasonic speed U_{ij}, excess isentropic compressibility (κ_S^E) for the various ($i + j$) mixtures as functions of x_i, the mole fraction of component i

x_i	U (ms^{-1})	κ_S^E (TPa^{-1})	x_i	U (ms^{-1})	κ_S^E (TPa^{-1})
1,3-Dioxolane (i) + benzene (j)					
0.0655	1305	−3.1	0.4825	1322	−12.7
0.1287	1307	−5.7	0.5436	1324	−12.6
0.1863	1310	−7.7	0.6211	1326	−11.9
0.2394	1312	−9.2	0.6978	1329	−10.7
0.3009	1315	−10.6	0.7694	1331	−9.0
0.3521	1317	−11.5	0.8527	1334	−6.3
0.4108	1319	−12.3	0.9609	1337	−1.9
$\kappa_S^0 = -50.817$; $\kappa_S^1 = -6.506$; $\kappa_S^2 = -1.090$; $\sigma(\kappa_S^E) = 0.1$					
1,3-Dioxolane (i) + n-hexane (j)					
0.0543	1079	−6.3	0.4681	1127	−53.2
0.1192	1084	−14.8	0.5244	1137	−55.1
0.1816	1090	−23.4	0.5919	1150	−55.2
0.2310	1095	−30.1	0.6598	1165	−52.5
0.2897	1112	−37.5	0.7481	1191	−45.0
0.3288	1107	−42.0	0.8624	1237	−28.6
0.3914	1115	−48.0	0.9319	1279	−15.2
$\kappa_S^0 = -218.115$; $\kappa_S^1 = -65.113$; $\kappa_S^2 = 46.095$; $\sigma(\kappa_S^E) = 0.4$					
1,3-Dioxolane (i) + n-heptane (j)					
0.0487	1140	−15.5	0.4973	1189	−62.7
0.1219	1152	−36.6	0.5637	1197	−60.7
0.1937	1159	−46.3	0.6253	1206	−57.5
0.2480	1165	−53.1	0.7184	1222	−49.9
0.2922	1169	−57.2	0.7701	1234	−44.2
0.3416	1174	−60.3	0.8616	1263	−30.7
0.4165	1181	−62.8	0.9419	1300	−14.6
$\kappa_S^0 = -250.630$; $\kappa_S^1 = 36.240$; $\kappa_S^2 = 63.897$; $\sigma(\kappa_S^E) = 0.4$					
1,3-Dioxolane (i) + cyclohexane (j)					
0.0419	1253	2.8	0.5749	1258	24.4
0.0978	1253	6.7	0.6424	1262	23.1
0.1530	1253	10.4	0.7816	1274	17.0
0.2217	1254	14.7	0.8294	1279	13.9
0.3744	1254	22.0	0.9110	1289	7.8
0.4910	1255	24.5	0.9426	1293	5.1
$\kappa_S^0 = 49.966$; $\kappa_S^1 = 11.159$; $\kappa_S^2 = -22.711$; $\sigma(\kappa_S^E) = 0.1$					

Table 2
Ultrasonic speed U_{ijk}, excess isentropic compressibilities $(\kappa_S^E)_{ijk}$ for various ($i + j + k$) ternary mixtures at 298.15 k with values evaluated from graph theory; also included are the various parameters $(\kappa_S^E)_{ijk}$ ($n = 0$–2) along with standard deviation $\sigma(\kappa_S^E)_{ijk}$, interaction parameters χ_{ij}, etc. and $({}^3\xi_i)$, etc.

x_i	x_j	U_{ijk}	$(\kappa_S^E)_{ijk}$ (TPa^{-1})	
			Experimental	Graph
1,3-Dioxolane(i) + benzene (j) + cyclohexane (k)				
0.0530	0.9123	1298	4.4	9.88
0.0625	0.0483	1252	11.9	11.9
0.0176	0.0753	1275	6.7	6.9
0.1817	0.8183	1243	1.6	1.6
0.1763	0.1374	1258	4.5	4.4
0.4069	0.3954	1241	33.4	33.4
0.6280	0.1816	1268	26.5	9.4
0.8296	0.758	1306	6.4	4.8
0.8751	0.0680	1317	3.7	3.9
0.9394	0.0331	1329	0.7	1.9
$(\kappa_S^0)_{ijk} = 1235.7$; $(\kappa_S^1)_{ijk} = 9482.9$; $(\kappa_S^2)_{ijk} = -50490$; $\sigma(\kappa_S^E) = 0.1$; $(\kappa_S^0)_{jk} = 98.5$; $(\kappa_S^1)_{jk} = 12.7$; $(\kappa_S^2)_{jk} = -18.8$; $({}^3\xi_i) = 0.531$; $({}^3\xi_j) = 0.666$; $({}^3\xi_k) = 1.5$; $\chi''_{ij} = 53.88$; $\chi'_{jk} = -40.88$, $\chi'_{jk} = 32.89$.				
1,3-Dioxolane (i) + benzene (j) + n-hexane (k)				
0.0733	0.0567	1090	−22.2	−30.0
0.2514	0.6293	1303	−80.8	−57.9
0.3041	0.2365	1181	−101.4	−100.1
0.3151	0.5716	1301	−77.8	−70.0
0.4208	0.4090	1343	−155.0	−100.3
0.5404	0.1681	1219	−95.2	−95.2
0.6012	0.2110	1328	−154.3	−102.1
0.6723	0.2240	1334	−101.1	−101.1
0.8427	0.0771	1297	−45.3	−52.3
0.8837	0.0687	1311	−29.1	−44.6
0.9439	0.0332	1319	−11.3	−23.8
$(\kappa_S^0)_{ijk} = -4649.1$; $(\kappa_S^1)_{ijk} = -23430.9$; $(\kappa_S^2)_{ijk} = 279727.8$; $\sigma(\kappa_S^E) = 0.2$; $(\kappa_S^0)_{jk} = -108.1$; $(\kappa_S^1)_{jk} = -32.8$; $(\kappa_S^2)_{jk} = -6.6$; $({}^3\xi_i) = 0.53$; $({}^3\xi_j) = 0.666$; $({}^3\xi_k) = 0.957$; $\chi''_{ij} = -878.57$; $\chi'_{jk} = 1006.53$; $\chi'_{ik} = -86.38$.				
1,3-Dioxolane (i) + benzene (j) + n-heptane (k)				
0.0814	0.0692	1153	−32.5	−18.8
0.1117	0.7815	1296	−45.8	−56.6
0.2149	0.1675	1172	−39.0	−53.2
0.3209	0.2496	1234	−95.1	−83.3
0.4291	0.4171	1321	−98.3	−131.6
0.5590	0.1739	1261	−85.9	−88.3
0.6214	0.2205	1326	−105.8	−110.4
0.7649	0.1046	1293	−55.9	−69.3
0.8505	0.0778	1308	−34.8	−57.3
0.9462	0.0332	1325	−9.8	−31.1
$(\kappa_S^0)_{ijk} = -2792.9$; $(\kappa_S^1)_{ijk} = -16719.7$; $(\kappa_S^2)_{ijk} = 187319.5$; $\sigma(\kappa_S^E) = 0.2$; $(\kappa_S^0)_{jk} = -143.0$; $(\kappa_S^1)_{jk} = -6.6$; $(\kappa_S^2)_{jk} = 20.4$; $({}^3\xi_i) = 0.531$; $({}^3\xi_j) = 0.666$; $({}^3\xi_k) = 1.10$; $\chi''_{ij} = -34.93$; $\chi'_{jk} = -6.72$; $\chi'_{ik} = -456.89$.				

χ''_{ij}, χ'_{ij}, etc., $(\kappa_S^n)_{ijk}$ ($n = 0$–2) and $\sigma(\kappa_S^E)$ are in TPa^{-1}.

is reported in Tables 1 and 2. The isentropic compressibilities $(\kappa_S)_{ij}$ and $(\kappa_S)_{ijk}$ values for binary and ternary mixtures were calculated from experimentally measured speed of sound U_{ij} and U_{ijk} of mixtures by employing Eqs. (1) and (2)

$$\kappa_S = (\rho_{ij}U_{ij}^2)^{-1} \tag{1}$$

$$\kappa_S = (\rho_{ijk}U_{ij}^2)^{-1} \tag{2}$$

The density, ρ_{ij} and ρ_{ijk} of binary and ternary mixtures were evaluated from their molar excess volumes V^E data [4,6,7] using relations:

$$V_{ij}^E = \sum_{i=i}^{j} x_i M_i (\rho_{ij})^{-1} - \sum_{i=i}^{j} (x_i M_i)(\rho_i)^{-1} \tag{3}$$

$$V_{ijk}^E = \sum_{i=i}^{k} (x_i M_i)(\rho_{ijk})^{-1} - \sum_{i=i}^{k} (x_i M_i)(\rho_i)^{-1} \tag{4}$$

where x_i, M_i, ρ_i, etc. are the mole fraction, molecular mass and density of component (i) of ($i+j$) or ($i+j+k$) mixtures.

Excess isentropic compressibilities $(\kappa_S^E)_{ij}$ and $(\kappa_S^E)_{ijk}$ for binary and ternary mixtures were determined using Eqs. (5) and (6).

$$(\kappa_S^E)_{ij} = \kappa_S - \sum_{i=i}^{j} \phi_i (\kappa_S)_i \tag{5}$$

$$(\kappa_S^E)_{ijk} = \kappa_S - \sum_{i=i}^{k} \phi_i (\kappa_S)_i \tag{6}$$

where ϕ_i and $(\kappa_S)_i$ are the volume fraction and isentropic compressibility of the ith component of binary and ternary mixtures. Such κ_S^E values for the studied mixtures are recorded in Tables 1 and 2 and shown graphically in Figs. 1–4. These κ_S^E values for binary mixtures were fitted to Eq. (7)

$$(\kappa_S^E)_{ij} = x_i x_j [\sum_{n=0}^{2} \kappa_S^{(n)} (x_i - x_j)^n] \tag{7}$$

where x_i is the mole fraction of component (i), κ_S^n ($n = 0$–2), etc. are the adjustable parameters. These parameters were evaluated using the least squares method and are recorded along with standard deviation $\sigma(\kappa_S^E)$ defined by

$$\sigma(\kappa_S^E) = \left[\frac{\sum (\kappa_{S(\text{experimental})}^E - \kappa_{S\,\text{calculated Eq. (4)}}^E)^2}{m - n} \right]^{0.5} \tag{8}$$

where m is the number of data points; n is the adjustable parameter of Eq. (7) in Table 1. Excess isentropic compressibility data, $(\kappa_S^E)_{ijk}$, for ternary mixtures were fitted to Redlich–Kister Eq. (9)

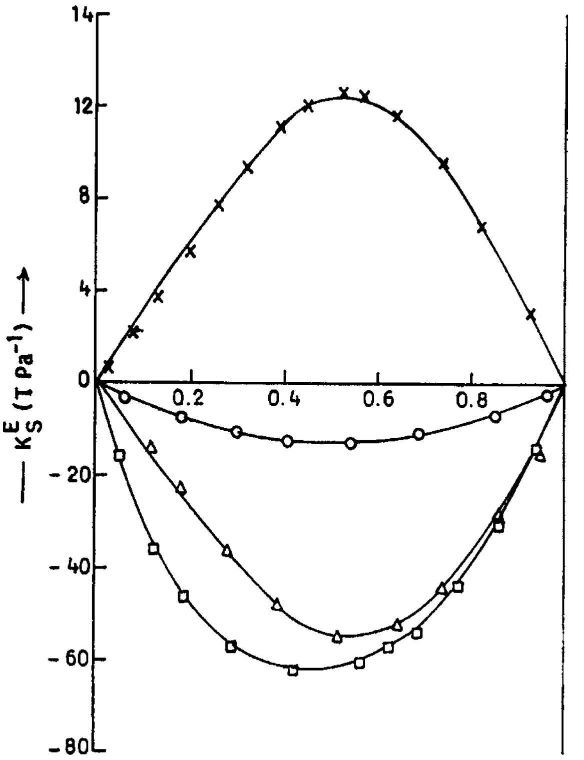

Fig. 1. Molar excess compressigilities, κ_S^E, for 1,3-dioxolane (i) + n-hexane (j) (△); 1,3-dioxolane (i) + cyclohexane (j) (×); 1,3-dioxolane (i) + n-heptane (j) (□); 1,3-dioxolane (i) + benzene (j) (○).

$$\begin{aligned}(\kappa_S^E)_{ijk} = {} & x_i x_j \left[\sum_{n=0}^{2} (\kappa_S^n)_{ij} (x_i - x_j)^n \right] \\ & + x_j x_k \left[\sum_{n=0}^{2} (\kappa_S^n)_{jk} (x_j - x_k)^n \right] \\ & + x_k x_i \left[\sum_{n=0}^{2} (\kappa_S^{(n)})_{ik} (x_k - x_i)^n \right] \\ & + x_i x_j x_k \left[\sum_{n=0}^{2} (\kappa_S^{(n)})_{ijk} (x_j - x_k) x_i{}^n \right]\end{aligned} \tag{9}$$

where κ_S^n ($n = 0$–2), etc. are the characteristic parameters of the ($i + j$), ($j + k$), ($i + k$) binary mixtures. $(\kappa_S^n)_{jk}$ parameters

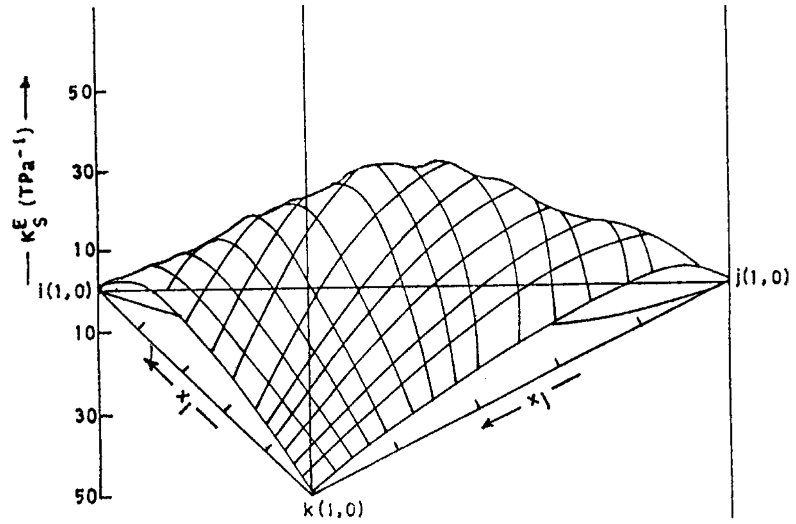

Fig. 2. Excess molar compressibilites (κ_S^E) ijk for 1,3-dioxolane (i) + benzene (j) + cyclohexane (k), at 298.15 K.

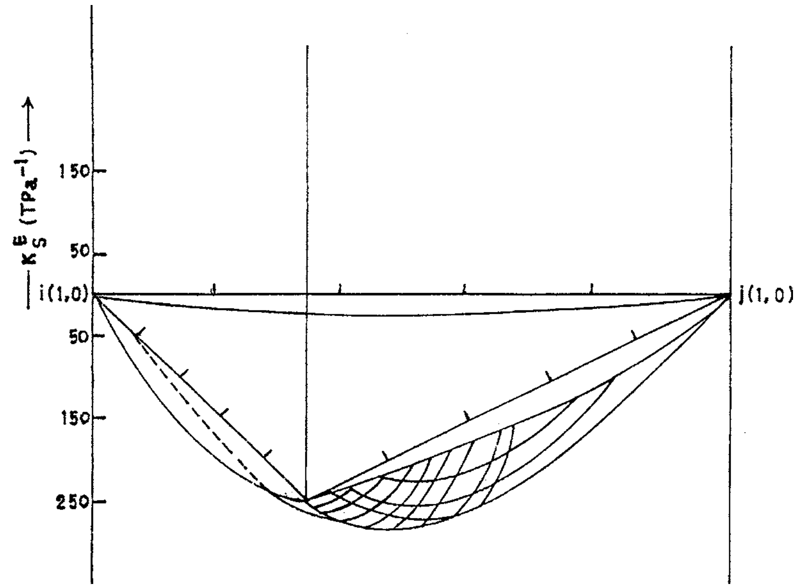

Fig. 3. Excess molar compressibilities (κ_S^E) *ijk* for 1,3-dioxolane (*i*) + benzene (*j*) + *n*-hexane (*k*), at 298.15 K.

for $(j + k)$ binary mixtures have been taken from literature [10] are recorded in Table 2. $(\kappa_S^n)_{ijk}$ $(n = 0$–$2)$, etc. are the parameters characteristics of $(i+j+k)$ ternary mixtures and were evaluated by fitting $(\kappa_S^E)_{ijk}$ to Eq. (10)

$$\left(\begin{aligned} &(\kappa_S^E)_{ijk} - \left[x_i x_j \left[\sum_{n=0}^{2}(\kappa_S^n)_{ij}(x_i - x_j)^n\right]\right] \\ &-(\kappa_S^E)_{ijk} - x_j x_k \left[\sum_{n=0}^{2}(\kappa_S^n)_{jk}(x_j - x_k)^n\right] \\ &-(\kappa_S^E)_{ijk} - x_{ijk} x_i \left[\sum(\kappa_S^n)_{ki}(x_k - x_i)^n\right] \end{aligned}\right) = \left(\sum_{n=0}^{2}(\kappa_S^n)_{ijk}(x_j - x_k)^n x_i^n\right) x_i x_j x_k \quad (10)$$

by the method of least squares. Such parameters along with standard deviation $\sigma(\kappa_S^E)_{ijk}$ are recorded in Table 2.

We are unaware of any existing κ_S^E data for studied mixtures with which to compare our results. However, good agreement is observed between the experimental and literature values of speed of sound for pure liquids benzene: 1299.1 ms^{-1} (1299.2) [11]; cyclohexane: 1252.9 ms^{-1} (1253.3 ms^{-1}) [12]; *n*-hexane: 1076.0 ms^{-1} (1076.5 ms^{-1}) [13]; *n*-heptane: 1131.2 ms^{-1} (1130.2 ms^{-1}) [14].

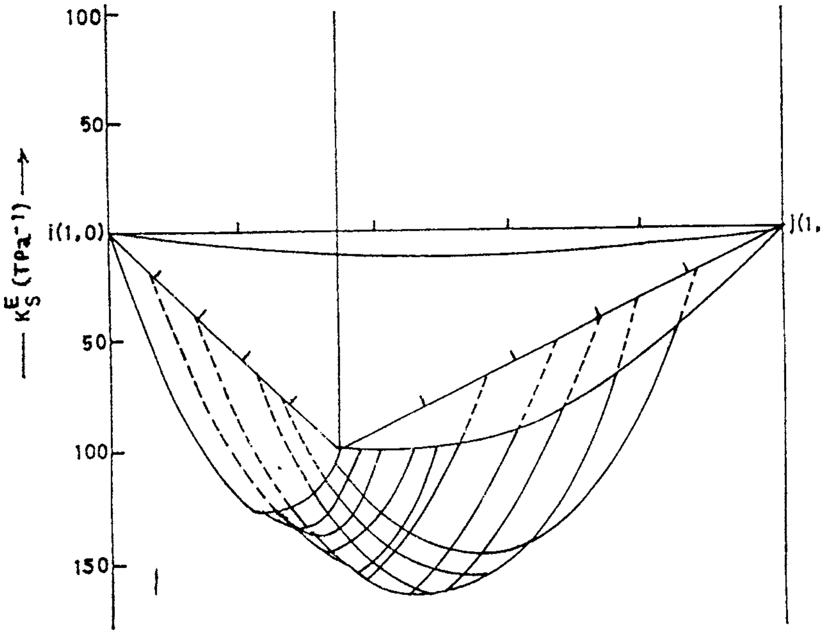

Fig. 4. Excess molar compressibilities, (κ_S^E) *ijk* for 1,3-dioxolane (*i*) + benzene (*j*) + *n*-hexane (*k*), at 298.15 K.

Values κ_S^E for D (i) + benzene or + n-hexane or + n-heptane (j) mixtures are negative over entire composition range. However for D (i) + cyclohexane (j) mixture κ_S^E values are positive over entire range of composition and an equimolar mixture vary in the order cyclohexane > benzene > n-hexane > n-heptane.

The negative values of κ_S^E for D (i) + benzene (j) mixture suggest the existence of specific interaction between delocalised π—electron cloud of aromatic hydrocarbon and lone electrons of oxygen atoms of D (i). Further negative values of κ_S^E for D (i) + n-hexane or + n-heptane (j) mixtures as compared to the positive κ_S^E values of D (i) + cyclohexane (j) mixture suggest that D (i) gives a more packed structure in n-hexane or n-heptane than in cyclohexane.

Values κ_S^E for 1,3-dioxolane (i) + benzene (j) + cyclohexane (k) mixtures are negative over the whole composition range, while those for 1,3-dioxolane (i) + benzene (j) + n-hexane or + n-heptane (k) mixtures are positive over the entire range of composition. The negative values of $(\kappa_S^E)_{ijk}$ for D (i) + benzene (j) + cyclohexane (k) than those for D (i) + benzene (j) or + n-heptane (k) mixtures suggest that addition of cyclohexane to D (i) + benzene (i) mixture favour compact structure as compared to the addition of n-hexane or n-heptane to D (i) + benzene (i) mixture.

The κ_S^E values for the studied ($i + j + k$) ternary mixture have also been calculated in terms of graph theory.

4. Conceptual aspects of graph–theoretical approach and results

According to mathematical discipline of graph theory, if atoms in a structural formula of a molecule are represented by coloured points and bonds joining them by lines then the resulting graph describes the total information contained in that molecule [15–19]. Consequently, if δ_m^v, δ_n^v, etc. represent the degree of m and n, etc. vertices of the graph of the the graph of a molecule, then connectivity parameter of third degree, ${}^3\xi$ is defined [20] by Eq. (11)

$$ {}^3\xi = \sum_{m<n<o<p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \tag{11} $$

where δ_m^v, etc. reflects explicitly the valency of mth vertex in the molecular graph and is related to maximum valence, Z_m and number of hydrogen atoms, h_m attached to mth vertex by Eq. (12).

$$ \delta_m^v = z_m - h_m \tag{12} $$

Thermodynamic studies of D (i) + benzene (j) mixtures [6] have revealed that D (i) in pure state exist as monomer and ($i + j$) mixtures are characterised by specific interactions between delocalised π-electrons of benzene and lone electrons of oxygen atoms of D (i). Further D (i) + benzene (j) mixture formation involves the process (1) establishment of unlike contact between i and j, (2) monomers of i and j then undergo specific interaction to form i:j molecular entity. Consequently, if χ_{ij}, χ_{12} are molar isentropic compressibility interactions and molar specific interaction parameters, then the change in molar isentropic compressibility due to process (i–ii) is given by [21–23]

$$ \Delta X_1(X = k_S) = \left[\frac{x_i x_j \chi_{ij} v_j}{\sum x_i v_i}\right] \tag{13} $$

$$ \Delta X_2(X = k_S) = \left[\frac{x_i x_j^2 \chi_{12} v_j}{\sum x_i v_i}\right] \tag{14} $$

where v_i is the molar volume of component i.

The overall changes in thermodynamic property, κ_S^E are given by

$$ (\kappa_S^E)_{ij} = \sum_{i=1}^{2} \Delta X_i = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right] [\chi_{ij} + x_j \chi_{12}] \tag{15} $$

Since $v_j/v_i = {}^3\xi_i/{}^3\xi_j$, [24] then Eq. (15) reduces to

$$ \kappa_S^E = \left[\frac{x_i x_j ({}^3\xi_i/{}^3\xi_j)}{x_i + x_j ({}^3\xi_i/{}^3\xi_j)}\right] [\chi_{ij} + x_j \chi_{12}] \tag{16} $$

For D (i) + cyclohexane or n-hexane or + n-heptane (k) mixtures only process (1) is involved, so, $\chi_{12=0}$ and κ_S^E for these ($i + j$) are defined by Eq. (17)

$$ (\kappa_S^E)_{ik} = \frac{[x_i x_k ({}^3\xi_i/{}^3\xi_k)] \chi_{ik}}{x_i + x_k ({}^3\xi_i/{}^3\xi_k)} \tag{17} $$

Eqs. (16) and (17) contains two and one unknown parameters χ_{ij}, χ_{12}. These parameters were evaluated from κ_S^E data of the studied mixtures at two or one arbitrary composition $x_i = 0.4$ and $x_i = 0.5$ and were subsequently utilised to predict κ_S^E at other values of x_i. Such κ_S^E values along with χ_{ij}, χ_{12}, etc. parameters are recorded in Table 3 and are also compared with corresponding experimental values.

Examination of Table 3 reveals that κ_S^E values compare reasonably well with their corresponding experimental values and thus basic arguments in deriving Eqs. (16) and (17) are justified.

If a hydrocarbon like cyclohexane or n-hexane or n-heptane (k) is added to D (i) + benzene (i) mixture, then ternary mixture ($i + j + k$) formation may be assumed to involve, (1) the establishment of (a) $i - j$, (b) $j - k$, (c) $i - k$; unlike contacts (2) monomers i and j then undergo specific interaction to yield i:j molecular entity. Consequently, if χ'_{ij}, $\chi'_{jk}$and χ'_{ik} are molar compressibility interaction parameters of $i - j$, $j - k$ and $i - k$ unlike contacts, then the change in thermoldynamic property due to process (1) (a), (b), (c) would be expressed [21–23] by Eq. (18)

$$ \Delta X_1(X = k_S) = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right] \chi'_{ij} + \left[\frac{x_j x_k v_k}{\sum x_j v_k}\right] \chi'_{jk} + \left[\frac{x_i x_k v_i}{\sum x_i x_k}\right] \chi'_{ik} \tag{18} $$

Table 3
Comparison of excess isentropic compressibility, κ_s^E values for the various $(i + j)$ mixtures as function of x_i, mole fraction of component i, at 298.15 K with values evaluated from graph theory, also included are the interaction energy parameters χ_{ij}, χ_{12}, etc.

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1,3-Dioxolane (i) + benzene (j)									
κ_s^E (experimental)	−4.6	−8.1	−10.8	−12.2	−12.7	−12.2	−10.6	−8.1	−4.5
κ_s^E (graph)	−4.6	−8.2	−10.7	–	–	−12.1	−10.6	−8.0	−4.6
$(^3\xi_i) = 0.531$, $(^3\xi_j) = 0.666$, $\chi_{ij} = -63.302$, $\chi_{12} = 12.089$									
1,3-Dioxolane (i) + cyclohexane (j)									
κ_s^E (experimental)	2.4	5.6	8.8	11.3	12.5	12.3	10.6	7.7	3.9
κ_s^E (graph)	7.3	11.2	13.0	13.3	–	10.9	8.8	6.2	3.2
$(^3\xi_i) = 0.531$, $(^3\xi_j) = 1.5$, $\chi_{ij} = 95.621$,									
1,3-Dioxolane (i) + n-hexane (j)									
κ_s^E (experimental)	−12.4	−26.1	−38.9	−48.8	−54.5	−55.0	−49.6	−38.3	−2.5
κ_s^E (graph)	−25.7	−42.3	−51.8	−55.6	–	−49.5	−41.0	−29.7	−15.8
$(^3\xi_i) = 0.531$, $(^3\xi_j) = 0.957$, $\chi_{ij} = -305.783$,									
1,3-Dioxolane (i) + n-heptane (j)									
κ_s^E (experimental)	−29.1	−47.1	−57.9	−62.5	−62.6	−59.9	−51.7	−40.2	−23.4
κ_s^E (graph)	−31.5	−50.8	−61.2	−64.6	–	−56.1	−46.0	−33.0	−17.4
$(^3\xi_i) = 0.531$, $(^3\xi_j) = 1.10$, $\chi_{ij} = -384.805$									

Further, if χ'_{12} is the molar interaction parameters due to specific interaction to form i:j molecular entity, then the change in molar property due to process (2) can be given [21–23] by

$$\Delta X_2(X = k_s) = \frac{x_i x_j^2 \chi'_{12} v_j}{\sum x_i v_i} \tag{19}$$

The overall change in themodynamic property $(\kappa_s^E)_{ijk}$ due to processes (1) (a), (b), (c) and (2) is given by

$$(\kappa_s^E)_{ijk} = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right][\chi'_{ij} + x_j \chi_{12}]\left[\frac{x_j x_k v_k}{\sum x_j v_j}\right]\chi'_{jk} + \left[\frac{x_i x_k v_i}{\sum x_k v_k}\right]\chi'_{ik} \tag{20}$$

since $v_j/v_i = {}^3\xi_i/{}^3\xi_j$ then Eq. (20) reduces to Eq. (21)

$$(\kappa_s^E)_{ijk} = \left[\frac{x_i x_j ({}^3\xi_i/{}^3\xi_j)}{x_i + x_j ({}^3\xi_i/{}^3\xi_j)}\right][\chi'_{ij} + x_j \chi_{12}] + \left[\frac{x_j x_k ({}^3\xi_i/{}^3\xi_k)}{x_j + x_k ({}^3\xi_l/{}^3\xi_k)}\right]\chi'_{jk} + \left[\frac{x_i x_k ({}^3\xi_i/{}^3\xi_k)}{x_i + x_k ({}^3\xi_i/{}^3\xi_k)}\right]\chi'_{ik} \tag{21}$$

Furthermore, if it be assumed that $\chi'_{ij} = \chi_{12} \cong \chi''_{ij}$ then Eq. (21) reduces to

$$(\kappa_s^E)_{ijk} = \left[\frac{x_i x_j ({}^3\xi_i/{}^3\xi_j)}{x_i + x_j ({}^3\xi_i/{}^3\xi_j)}\right][(1 + x_j)\chi''_{ij}] + \left[\frac{x_j x_k ({}^3\xi_j/{}^3\xi_k)}{x_j + x_k ({}^3\xi_j/{}^3\xi_k)}\right]\chi'_{jk} + \left[\frac{x_i x_k ({}^3\xi_i/{}^3\xi_k)}{x_i + x_k ({}^3\xi_i/{}^3\xi_k)}\right]\chi'_{ik} \tag{22}$$

Eq. (22) contains three unknown pararmeters χ''_{ij}, χ'_{ij} and χ'_{jk} and were determined by employing experimental $(\kappa_s^E)_{ijk}$ data of studied ternary mixtures at three compositions. These parameters were then subsequently utilised to determine $(\kappa_s^E)_{ijk}$ values at other values of x_i and x_j. Such predicted $(\kappa_s^E)_{ijk}$ values along with various interaction parameters are recorded in Table 3.

Examination of Table 2 reveals that predicted values are of the same sign and order, but the quantitative agreement is not so satisfactory. The failure of the theory to correctly predict the magnitude of $(\kappa_s^E)_{ijk}$ values may be due to the reason that ternary $i - j - k$ contacts have not been taken into consideration.

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