

# Molar Excess Volumes and Excess Isentropic Compressibilities of Ternary Mixtures Containing *o*-Toluidine

D. Sharma · J.S. Yadav · K.C. Singh · V.K. Sharma

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**Abstract** Molar excess volumes,  $V_{ijk}^E$ , and speeds of sound,  $U_{ijk}$ , of *o*-toluidine (*i*) + benzene (*j*) + cyclohexane or *n*-hexane or *n*-heptane (*k*) ternary mixtures have been measured as a function of composition at 308.15 K. The observed speed of sound data have been utilized to determine the excess isentropic compressibilities,  $(K_S^E)_{ijk}$ , of the ternary (*i* + *j* + *k*) mixtures. The Moelywn-Huggins concept (Huggins in Polymer 12: 389–399, 1971) of connectivity between the surfaces of the binary mixture constituents has been extended to ternary mixtures (using the concept of a connectivity parameter of third degree of molecules,  ${}^3\xi$ , which in turn depends on its topology) to obtain an expression that describes well the measured  $V_{ijk}^E$  and  $(K_S^E)_{ijk}$  data. The observed data have also been analyzed in terms of Flory's theory.

**Keywords** Molar excess volumes,  $V_{ijk}^E$  · Speeds of sound,  $U_{ijk}$  · Excess isentropic compressibilities,  $K_S^E$  · Connectivity parameter of third degree,  ${}^3\xi$  · Interaction energy parameter,  $\chi$

## 1 Introduction

Topological indices have found use in chemical and biological applications, and chemical graph theory has made important conceptual and quantitative contributions to chemistry. Topological indices are structural invariants based on modeling of chemical structures by molecular graphs. In a molecular graph, the atoms of a molecule are represented by dots and bonds joining them are represented by lines. The topology of the molecule then describes the total information contained in that molecule [1–3]. Topological indices have been designed [4] by transforming a molecular graph into numerical values, and a very good correlation has been observed between the topological index of a molecule [1, 2, 4–7] and its physico-chemical properties [8]. Recent studies [9–16] have shown that the thermodynamic

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**Table 1** Comparison of densities,  $\rho$ , and speeds of sound,  $U$ , of pure liquids with their literature values at 298.15 K

Liquid	$\rho/\text{kg}\cdot\text{m}^{-3}$		$U(\text{m}\cdot\text{s}^{-1})$	
	Experimental	Literature	Experimental	Literature
<i>o</i> -Toluidine	994.28	994.30 [19]	1603 <sup>a</sup>	–
Benzene	873.63	873.60 [19]	1298	1298.9 [21]
Cyclohexane	773.94	773.89 [19]	1255	1254.4 [2]
<i>n</i> -Hexane	654.82	654.84 [19]	1079	1078 [22]
<i>n</i> -Heptane	679.49	679.46 [19]	1088	1087.6 [23]

<sup>a</sup>Value at 308.15 K

properties (molar excess volumes, molar excess enthalpies, and excess isentropic compressibilities) of binary and ternary liquid mixtures can be predicted by the graph theoretical approach by taking the topology of the mixture constituents into consideration in terms of differences of shape, size and polarity.

In our earlier publications we reported [17, 18] molar excess volumes, molar excess enthalpies and excess isentropic compressibilities of *o*-toluidine + benzene or toluene or *o*- or *p*- or *m*-xylene binary mixtures, and the data have been successfully analyzed in terms of graph theory. It is of interest to see how well graph theory describes the molar excess volumes and excess isentropic compressibility data of ternary mixtures when an inert component like cyclohexane or *n*-hexane or *n*-heptane is added to the **OT** (*i*) + benzene (*j*) mixtures, where **OT** denotes *o*-toluidine. These considerations prompted us to measure the molar excess volumes,  $V_{ijk}^E$  and speeds of sound data,  $U_{ijk}$  for **OT** (*i*) + benzene(*j*) + cyclohexane or *n*-hexane or *n*-heptane (*k*) ternary mixtures.

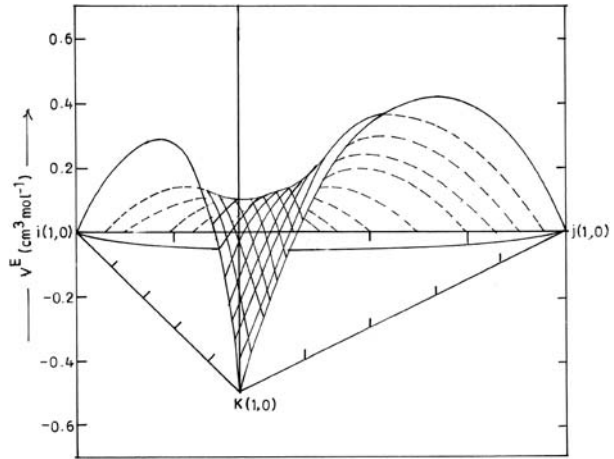
## 2 Experimental

*o*-Toluidine (**OT**) (Fluka), benzene (AR Grade, 99%), cyclohexane (AR Grade), *n*-hexane (AR Grade), and *n*-heptane (AR grade) were purified by standard methods. The purities of the purified samples were checked by measuring their densities (recorded in Table 1) at  $(298.15 \pm 0.01)$  K, and these results agreed to within  $\pm 5 \times 10^{-3}$   $\text{kg}\cdot\text{m}^{-3}$  of their corresponding literature values [19].

The molar excess volumes,  $V_{ijk}^E$ , of the studied mixtures were determined in a dilatometer by the procedure described elsewhere [20]. The dilatometer had three limbs for holding the three liquids. The temperature of the water bath was controlled within  $\pm 0.01$  K by means of a toluene regulator. The change in the level of liquid in the dilatometer was measured by a cathetometer with a precision of  $\pm 0.001$  cm. The uncertainty in measured  $V_{ijk}^E$  values is 0.5%.

Speeds of sound in various ternary mixtures were measured using a variable path interferometer (model M 84, Mittal Enterprises, India) and measuring cell. Water from the thermostat was circulated through the cell to maintain the desired temperature. The speeds of sound values for the purified liquids at  $(308.15 \pm 0.01)$  K (recorded in Table 1) compare well with their corresponding literature values [21–23]. The uncertainty in the measured speed of values is  $\pm 1$   $\text{ms}^{-1}$ .

**Fig. 1** Molar excess volume,  $V^E$  for *o*-toluidine (*i*) + benzene (*j*) + cyclohexane (*k*) at 308.15 K



### 3 Results and Discussion

Molar excess volumes,  $V_{ijk}^E$ , and speeds of sound,  $U_{ijk}$ , of ternary **OT** (*i*) + benzene (*j*) + cyclohexane or *n*-hexane or *n*-heptane (*k*) mixtures, measured over the entire composition range at 308.15 K, are recorded in Table 2 (and plotted in Figs. 1, 2 and 3) and Table 3, respectively. The isentropic compressibilities,  $(K_S)_{ijk}$  for ternary mixtures were determined from Eq. 1

$$(K_S)_{ijk} = (\rho_{ijk} U_{ijk}^2)^{-1} \tag{1}$$

The densities,  $\rho_{ijk}$  of ternary mixtures were calculated by employing their molar excess volume data using relation:

$$V_{ijk}^E = \sum_{i=i}^k x_i M_i (\rho_{ijk})^{-1} - \sum_{i=i}^k x_i M_i (\rho_i)^{-1} \tag{2}$$

where  $x_i$ ,  $M_i$  and  $\rho_i$  are the mole fraction, molar mass and density, respectively, of component (*i*) in the ternary mixtures. The excess isentropic compressibilities  $(K_S^E)_{ijk}$  for the ternary mixtures were calculated by employing Eq. 3

$$(K_S^E)_{ijk} = K_S - \sum_{i=i}^k \phi_i (K_S)_i \tag{3}$$

where  $\phi_i$  and  $(\kappa_S)_i$  are the volume fraction and isentropic compressibility of component (*i*). The resulting  $(K_S)_{ijk}$  and  $(K_S^E)_{ijk}$  values for the studied mixtures are recorded in Table 3 and the  $(K_S^E)_{ijk}$  values are plotted in Figs. 4, 5, and 6.

The  $V_{ijk}^E$  and  $(K_S^E)_{ijk}$  values for the ternary mixtures were fitted by the Redlich-Kister equation, Eq. 4

$$X_{ijk}^E (X = V \text{ or } K_S) = x_i x_j \left[ \sum_{n=0}^2 X_{ij}^{(n)} (x_i - x_j)^n \right] + x_j x_k \left[ \sum_{n=0}^2 X_{jk}^{(n)} (x_j - x_k)^n \right] + x_i x_k \left[ \sum_{n=0}^2 X_{ik}^{(n)} (x_k - x_i)^n \right] + x_i x_j x_k \left[ \sum_{n=0}^2 X_{ijk}^{(n)} (x_j - x_k)^n x_i^n \right] \tag{4}$$

**Table 2** Comparison of measured  $V_{ijk}^E$  values for the various  $(i + j + k)$  ternary mixtures, evaluated from the Graph and Flory theories, with their corresponding experimental values; also included are the various parameters  $V_{ijk}^{(n)}$  ( $n = 0$  to 2) along with their standard deviation,  $\sigma(V_{ijk}^E)$ , interaction parameters  $\chi_{ij}^*$ ,  $\chi'_{jk}$ ,  $\chi''_{ij}$  etc., and connectivity parameters of third degree,  ${}^3\xi_i$  ( $i = i$  to  $k$ )

$x_i$	$x_j$	$V_{ijk}^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )		
		Experimental	Graph	Flory
<i>o</i> -toluidine ( <i>i</i> ) + benzene ( <i>j</i> ) + cyclohexane ( <i>k</i> )				
0.0555	0.7182	0.384	0.371	0.381
0.0987	0.7643	0.225	0.199	0.549
0.1249	0.6589	0.316	0.304	0.690
0.1876	0.2278	0.383	0.410	0.932
0.2437	0.5311	0.260	0.262	1.155
0.2835	0.5975	0.107	0.127	1.268
0.3019	0.3345	0.285	0.360	1.345
0.3497	0.1897	0.205	0.239	1.454
0.4273	0.4018	0.143	0.160	1.659
0.4786	0.3132	0.167	0.174	1.747
0.5597	0.2185	0.146	0.150	1.820
0.5901	0.3187	0.035	0.072	1.839
0.6128	0.1121	0.118	0.074	1.807
0.7435	0.1897	0.038	0.048	1.667
0.7777	0.0991	0.089	0.056	1.552
$V_{ijk}^{(0)} = -6.636$ , $V_{ijk}^{(1)} = 41.617$ , $V_{ijk}^{(2)} = -244.290$ , $\sigma(V_{ijk}^E) = 0.004$ , $({}^3\xi_i) = 1.101$ , $({}^3\xi_j) = 0.666$ , $({}^3\xi_k) = 1.500$ , $\chi''_{ij} = -0.064$ , $\chi'_{jk} = 4.903$ , $\chi'_{ik} = -0.980$ , $\chi_{ij}^* = 6.5$ , $\chi_{jk}^* = 40.1$ , $\chi_{ik}^* = 16.2$				
<i>o</i> -toluidine ( <i>i</i> ) + benzene ( <i>j</i> ) + <i>n</i> -hexane ( <i>k</i> )				
0.0495	0.7017	-0.302	-0.315	-0.243
0.969	0.6345	-0.225	-0.228	-0.101
0.1317	0.6096	-0.146	-0.146	0.039
0.2963	0.5268	0.113	0.137	0.712
0.1339	0.5130	0.123	0.090	0.761
0.3684	0.3983	0.166	0.166	0.602
0.4227	0.4018	0.205	0.167	0.889
0.4876	0.3124	0.194	0.239	0.747
0.6365	0.2007	0.100	0.250	0.664
0.6978	0.2148	0.140	0.140	1.087
0.8189	0.0687	0.018	0.311	0.104
$V_{ijk}^{(0)} = -5.580$ , $V_{ijk}^{(1)} = 271.368$ , $V_{ijk}^{(2)} = -1374.194$ , $\sigma(V_{ijk}^E) = 0.003$ , $({}^3\xi_i) = 1.200$ , $({}^3\xi_j) = 0.666$ , $({}^3\xi_k) = 0.957$ , $\chi''_{ij} = -0.206$ , $\chi'_{jk} = -3.324$ , $\chi'_{ik} = 4.763$ , $\chi_{ij}^* = 6.5$ , $\chi_{jk}^* = 42.2$ , $\chi_{ik}^* = 14.8$				

**Table 2** (Continued)

$x_i$	$x_j$	$V_{ijk}^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )		
		Experimental	Graph	Flory
<i>o</i> -toluidine ( <i>i</i> ) + benzene ( <i>j</i> ) + <i>n</i> -heptane ( <i>k</i> )				
0.0982	0.7013	0.422	0.587	2.995
0.1277	0.5031	0.688	1.066	2.541
0.1565	0.6071	0.483	0.616	3.476
0.2004	0.2051	0.533	0.866	4.625
0.2597	0.4347	0.621	0.664	4.049
0.3009	0.3491	0.687	0.687	4.179
0.4798	0.2677	0.455	0.366	3.294
0.5091	0.1261	0.426	0.429	2.859
0.5789	0.1817	0.324	0.353	2.757
0.6201	0.2430	0.140	0.142	2.498
0.6992	0.1271	0.145	0.235	2.023
0.7109	0.0885	0.062	0.249	1.788
0.7462	0.1398	0.093	0.133	1.820

$$V_{ijk}^{(0)} = 14.319, V_{ijk}^{(1)} = -41.617, V_{ijk}^{(2)} = -645.112, \sigma(V_{ijk}^E) = 0.005,$$

$$({}^3\xi_i) = 1.201, ({}^3\xi_j) = 0.666, ({}^3\xi_k) = 1.100,$$

$$\chi_{ij}'' = -0.977, \chi_{jk}' = 7.050, \chi_{ik}' = 0.164,$$

$$\chi_{ij}^* = 6.5, \chi_{jk}^* = 41.8, \chi_{ik}^* = 9.4$$

Units:  $V_{ijk}^{(n)}$  ( $n = 0$  to 2) and  $\sigma(V_{ijk}^E)$  are in cm<sup>3</sup>·mol<sup>-1</sup>,  $\chi^*$  and  $\chi_{ij}'$  etc. are in cm<sup>3</sup>·mol<sup>-1</sup>, and  $\chi_{ij}^*$  etc. are in J·mol<sup>-1</sup>

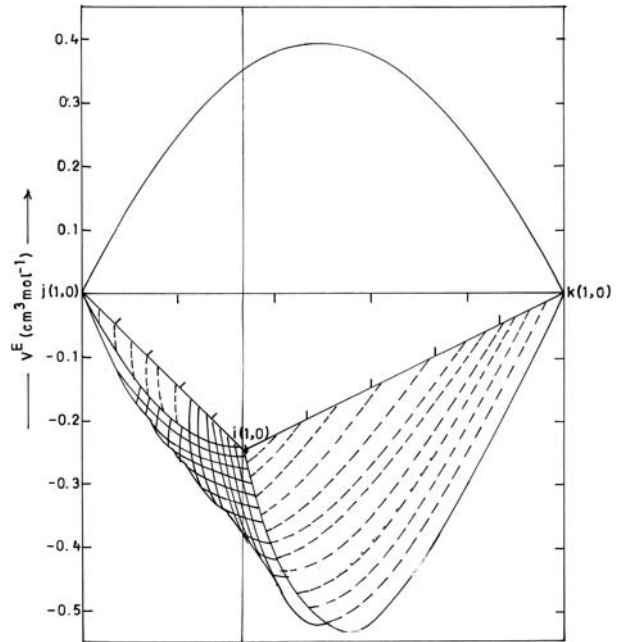
where the  $X_{ijk}^{(n)}$  ( $n = 0$  to 2) parameters characteristic of the ( $i + j$ ), ( $j + k$ ) and ( $i + k$ ) mixtures have been taken from the literature [24, 25]. The  $X_{ijk}^{(n)}$  ( $n = 0$  to 2) are parameters characteristics of ternary mixtures. These parameters were determined by fitting the parameters of Eq. 5 to the  $X_{ijk}^E$  ( $X = V$  or  $K_S$ ) data by the least-squares method:

$$\begin{bmatrix} X_{ijk}^E - x_i x_j \left[ \sum_{n=0}^2 X_{ij}^{(n)} (x_i - x_j)^n \right] \\ -x_j x_k \left[ \sum_{n=0}^2 X_{jk}^{(n)} (x_j - x_k)^n \right] \\ -x_k x_i \left[ \sum_{n=0}^2 X_{ik}^{(n)} (x_k - x_i)^n \right] \end{bmatrix} [x_i x_j x_k]^{-1} = \sum_{n=0}^2 X_{ijk}^n (x_j - x_k)^n x_i^n \quad (5)$$

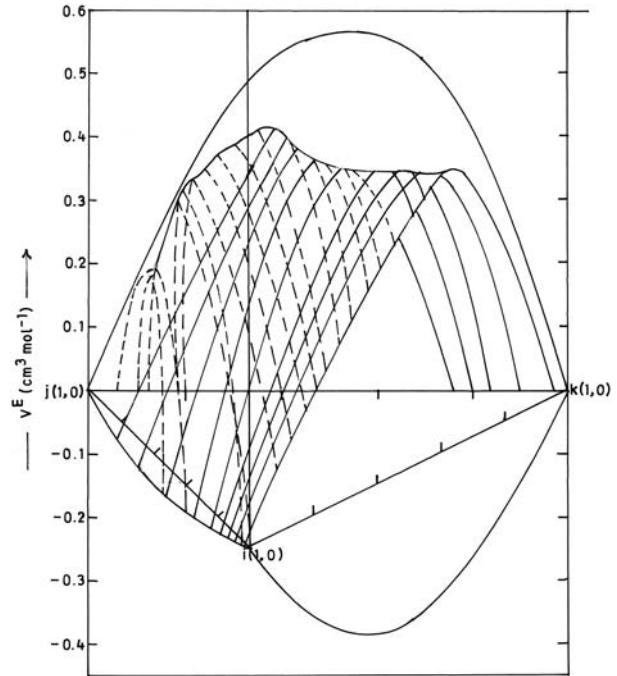
and their parameter values are reported along with their standard deviations in Tables 2 and 3, respectively. The standard deviations are given by equation

$$\sigma(X_{ijk}^E; X = V \text{ or } \kappa_S) = \left\{ \sum [X_{ijk}^E(\text{exptl}) - X_{ijk}^E(\text{calcd. Eq. 4})]^2 / (m - p) \right\}^{0.5} \quad (6)$$

**Fig. 2** Molar excess volume,  $V^E$  for *o*-toluidine (*i*) + benzene (*j*) + *n*-hexane (*k*) at 308.15 K



**Fig. 3** Molar excess volume,  $V^E$  for *o*-toluidine (*i*) + benzene (*j*) + *n*-heptane (*k*) at 308.15 K



where the  $X_{ijk}^{(n)}$  (calcd. Eq. 4) are values predicted from Eq. 4,  $m$  is the number of data points and  $n$  is the number of adjustable parameters of Eq. 4.

**Table 3** Speeds of sound,  $U_{ijk}$ , isentropic compressibilities,  $(K_S)_{ijk}$ , and excess isentropic compressibilities,  $(K_S^E)_{ijk}$ , for the various  $(i + j + k)$  ternary mixtures as a function of the mole-fraction composition,  $x_i$ , of component  $i$  at 308.15 K with  $(K_S^E)_{ijk}$  values evaluated from Graph theory and Flory's theory; also included are various parameters  $(K_S^{(n)})_{ijk}$  ( $n = 0$  to 2) along with their standard deviation,  $\sigma(K_S^E)_{ijk}$ , the interaction parameters  $\chi_{ij}$ ,  $\chi_{ij}^*$  etc. and  $({}^3\xi_i)$  ( $i = i$  to  $k$ )

$x_i$	$x_j$	$U_{ijk}$ (m·s <sup>-1</sup> )	$(K_S)_{ijk}$ (TPa <sup>-1</sup> )	$(K_S^E)_{ijk}$ (TPa <sup>-1</sup> )		
				Exptl	Graph	Flory
<i>o</i> -toluidine ( <i>i</i> ) + benzene ( <i>j</i> ) + cyclohexane ( <i>k</i> )						
0.1242	0.7165	1823	717.7	101.3	170.2	45.2
0.1673	0.6454	2135	706.8	173.6	173.7	29.8
0.2343	0.2012	754	748.3	-54.8	-36.8	-6.4
0.3212	0.3712	1123	824.7	-43.9	-39.9	-12.3
0.3951	0.3319	1046	652.7	-42.8	-44.8	-22.3
0.4013	0.3139	559	642.4	-88.9	-88.6	-23.6
0.4896	0.2270	1123	612.8	-156.3	-251.0	-31.6
0.5897	0.3325	3307	539.7	454.3	483.0	-22.7
0.6453	0.1891	1134	540.0	-53.1	-53.1	-27.0
0.6973	0.0887	1265	533.7	-44.1	-228.4	-27.9
$(K_S^{(0)})_{ijk} = 44.1$ , $(K_S^{(1)})_{ijk} = -364.3$ , $(K_S^{(2)})_{ijk} = 46.1$ , $\sigma(K_S^E)_{ijk} = 1.7$ TPa <sup>-1</sup> , $({}^3\xi_i) = 1.101$ , $({}^3\xi_j) = 0.666$ , $({}^3\xi_k) = 1.500$ , $\chi'_{ij} = 1973.1$ , $\chi'_{jk} = 3106.4$ , $\chi'_{ik} = -5100.1$						
<i>o</i> -toluidine ( <i>i</i> ) + benzene ( <i>j</i> ) + <i>n</i> -hexane ( <i>k</i> )						
0.1092	0.3145	923	1180.2	-171.4	-118.6	-0.8
0.1127	0.1241	987	1295.7	-160.2	-159.5	-7.4
0.1567	0.1476	1121	1238.9	-33.5	-209.1	-33.5
0.2273	0.2576	1157	1094.2	-298.8	-223.8	-56.7
0.3019	0.2179	1025	1042.1	-366.1	-279.7	-81.5
0.4019	0.4123	871	768.2	-49.4	-49.3	-55.9
0.4567	0.3019	923	798.4	-148.6	-159.9	-75.7
0.5395	0.0667	986	894.8	-395.0	-492.6	-120.4
0.5985	0.1271	1108	778.8	-302.5	-343.6	-96.9
0.6457	0.2124	1384	645.9	-90.0	-89.6	-61.9
0.6786	0.1211	1276	688.6	202.8	-266.9	-78.4
0.7027	0.1647	1164	619.0	-100.1	-185.2	-57.8
0.7619	0.1028	1090	603.0	-120.1	-42.0	-55.6
$(K_S^{(0)})_{ijk} = -917.9$ , $(K_S^{(1)})_{ijk} = 99.7$ , $(K_S^{(2)})_{ijk} = 235.3$ , $\sigma(K_S^E)_{ijk} = 3.9$ TPa <sup>-1</sup> , $({}^3\xi_i) = 1.201$ , $({}^3\xi_j) = 0.666$ , $({}^3\xi_k) = 0.957$ , $\chi'_{ij} = 751.8$ , $\chi'_{jk} = 7.8$ , $\chi'_{ik} = -2781.2$						

We are unaware of any previous  $V_{ijk}^E$  and  $(K_S^E)_{ijk}$  data for the studied ternary mixtures with which to compare our results. The  $V_{ijk}^E$  values of **OT** (*i*) + benzene (*j*) + cyclohexane (*k*) mixtures are positive and for **OT** (*i*) + benzene (*j*) + *n*-heptane (*k*) mixtures are negative over the whole composition range. However, for the **OT** (*i*) + benzene (*j*) + *n*-hexane

**Table 3** (Continued)

$x_i$	$x_j$	$U_{ijk}$ (m·s <sup>-1</sup> )	$(K_S)_{ijk}$ (TPa <sup>-1</sup> )	$(K_S^E)_{ijk}$ (TPa <sup>-1</sup> )		
				Exptl	Graph	Flory
<i>o</i> -toluidine ( <i>i</i> ) + benzene ( <i>j</i> ) + <i>n</i> -heptane ( <i>k</i> )						
0.1565	0.1263	1572	1111.2	135.4	242.5	-221.3
0.2255	0.2259	1736	1012.1	168.3	235.5	-232.5
0.3019	0.3597	1297	871.2	-108.3	-108.3	-186.9
0.4256	0.3576	896	750.0	-53.7	-53.7	-145.6
0.4567	0.1090	2786	877.3	562.0	408.6	-237.6
0.5675	0.1398	1997	756.0	185.7	185.7	-1825
0.6125	0.0928	2302	743.4	283.3	275.7	-131.3
0.6247	0.1854	739	666.7	-76.9	-33.1	-144.1
0.6842	0.0917	1803	673.1	108.2	196.6	-136.2
0.7342	0.0486	1816	653.0	106.9	284.5	-73.5
0.7565	0.1425	1033	557.7	-49.8	-141.1	-68.7
0.7982	0.1009	1119	545.3	-40.8	-40.8	-50.7
$(K_S^{(0)})_{ijk} = 380.9$ , $(K_S^{(1)})_{ijk} = -5.4$ , $(K_S^{(2)})_{ijk} = 153.0$ , $\sigma(K_S^E)_{ijk} = 2.8$ TPa <sup>-1</sup> , $({}^3\xi_i) = 1.201$ , $({}^3\xi_j) = 0.666$ , $({}^3\xi_k) = 1.100$ , $\chi''_{ij} = -1899.9$ , $\chi'_{jk} = 1695.6$ , $\chi'_{ik} = 2301.0$						

Units:  $(K_S^E)_{ijk}$  ( $n = 0$  to 2) and  $\sigma(K_S^E)_{ijk}$  are in TPa<sup>-1</sup>;  $\chi''_{ij}$ ,  $\chi'_{jk}$ , and  $\chi'_{ik}$  are in TPa<sup>-1</sup>

(*k*) ternary mixtures, the sign of  $V_{ijk}^E$  varies with the composition. Although the  $(K_S^E)_{ijk}$  values are negative for **OT** (*i*) + benzene (*j*) + *n*-hexane (*k*) ternary mixtures over the entire composition range, those for **OT** (*i*) + benzene (*j*) + cyclohexane or *n*-heptane (*k*) ternary mixtures are dictated by the relative proportions of various constituents. It appears that *n*-hexane forms a relatively more packed structure in the **OT**:benzene molecular entity as compared to *n*-heptane. This may be due to an increase in the C–C chain length of *n*-heptane, which in turn leads to an increase in steric repulsion between the terminal –CH<sub>3</sub> substituent of *n*-heptane as compared to *n*-hexane with the –CH<sub>3</sub> group in the **OT**:benzene molecular entity. Consequently, the approach of a *n*-heptane molecule will be hindered more for the **OT**:benzene molecular entity as compared to the *n*-heptane mixtures.

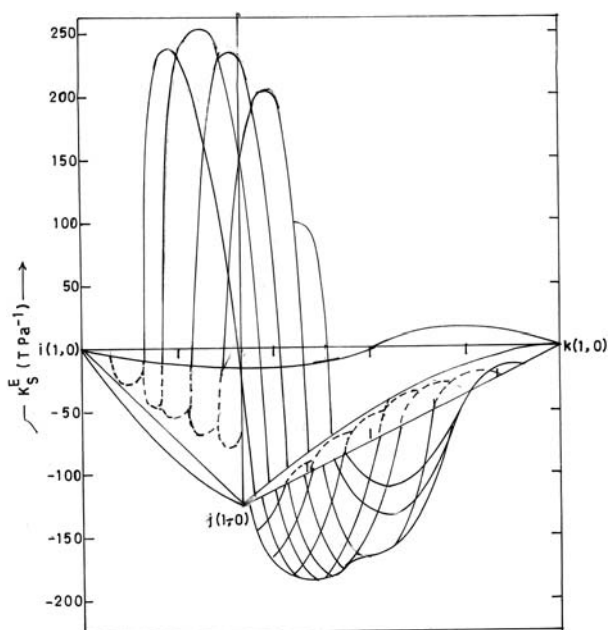
#### 4 Conceptual Aspects of the Graph Approach and Results

Our earlier studies on **OT** (*i*) + benzene or toluene or *o*- or *p*- or *m*-xylene (*j*) mixtures have suggested [17, 18] that (i) **OT** exists as an associated molecular entity, and (ii) the (*i* + *j*) mixture formation involves the following processes: (1) the establishment of *i*<sub>n</sub>-*j* contact between molecules *i*<sub>n</sub> and *j*; (2) unlike contact formation between molecules *i*<sub>n</sub> and *j* cause depolymerization of *i*<sub>n</sub> to yield monomers of *i*; and (3) monomers of *i* and *j* then undergo specific interactions to form an *i* : *j* molecular entity. Consequently, overall changes in thermodynamic properties,  $X^E$  ( $X = H$  or  $V$ ) due to these processes are expressed by Eq. 7

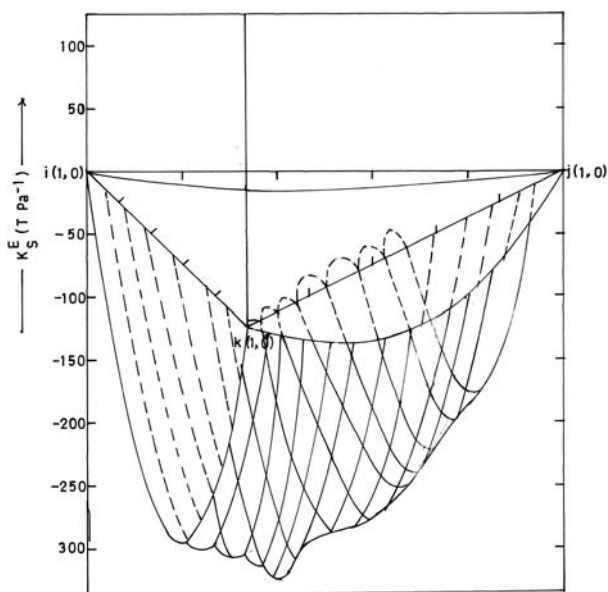
$$X^E (X = H \text{ or } V) = \sum_{i=1}^3 \Delta X_i = \frac{x_i x_j ({}^3\xi_i / {}^3\xi_j)}{x_i + x_j ({}^3\xi_i / {}^3\xi_j)} [(1 + x_j) \chi'_{ij} + 2x_i \chi^*] \quad (7)$$



**Fig. 4** Excess isentropic compressibility,  $K_S^E$  for *o*-toluidine (*i*) + benzene (*j*) + cyclohexane (*k*) at 308.15 K



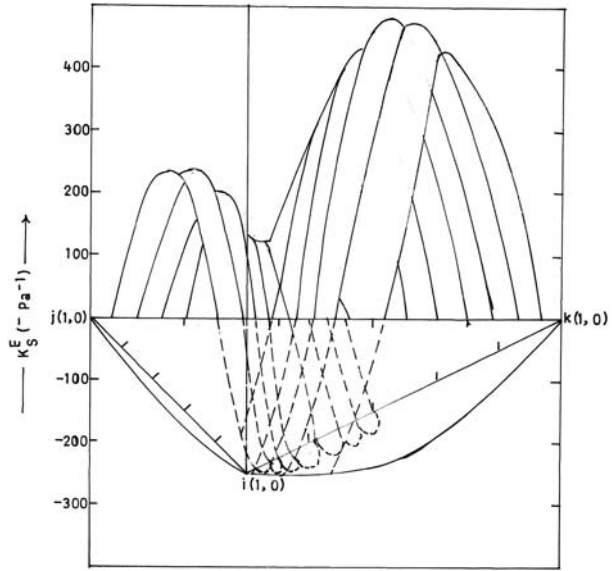
**Fig. 5** Excess isentropic compressibility,  $K_S^E$  for *o*-toluidine (*i*) + benzene (*j*) + *n*-hexane (*k*) at 308.15 K



where  $\chi'_{ij}$  and  $\chi^*$  are the molar enthalpy and molar compressibility interaction parameters due to *i*-*j* contacts and specific interactions, respectively. Because the  $H^E$  and  $K_S^E$  data of the (*i* + *j*) binary mixtures are reproduced by Eq. 7, these results lend support to the assumptions made in deriving this equation.

If a hydrocarbon such as cyclohexane or *n*-hexane or *n*-heptane (*k*) is added to **OT** (*i*) + benzene (*j*) binary mixture, then (*i* + *j* + *k*) ternary mixture formation is assumed

**Fig. 6** Excess isentropic compressibility,  $K_S^E$  for *o*-toluidine (*i*) + benzene (*j*) + *n*-heptane (*k*) at 308.15 K



to involve the following processes: (1) formation of (a)  $i_n$ - $j$ , (b)  $j$ - $k$  and (c)  $i_n$ - $k$  unlike contacts; (2) unlike contact formation then causes depolymerization of  $i_n$  to yield monomers of (*i*); and (3) monomers of *i* and *j* then undergo specific interactions to yield  $i : j$  molecular entities. Consequently, if  $\chi'_{ij}$ ,  $\chi'_{jk}$  and  $\chi'_{ik}$  are the molar volume and molar compressibility interaction parameters of unlike (*i*-*j*), (*j*-*k*) and (*i*-*k*) contacts, respectively, then changes in molar properties,  $X$  ( $X = V$  or  $K_S$ ), due to processes 1 (a)–(c) are given by Eq. 8 [26–28]

$$\Delta X_1 (X = V \text{ or } K_S) = x_i S_j \chi'_{ij} + x_j S_k \chi'_{jk} + x_k S_i \chi'_{ik} \tag{8}$$

where the  $S_i$ , etc. are defined [27] by

$$S_i = x_i v_i / \sum x_i v_i$$

where  $v_i$  is the molar volume of component (*i*). Consequently, Eq. 8 reduces to Eq. 9

$$\Delta X_1 (X = V \text{ or } K_S) = x_i x_j v_j \chi'_{ij} / \sum x_i v_i + x_j x_k v_k \chi'_{jk} / \sum x_j v_j + x_k x_i v_j \chi'_{ik} / \sum x_k v_k \tag{9}$$

Again, if  $\chi'_{ii}$  and  $\chi_{12}$  are the molar volume and molar compressibility interaction parameters for *i*-*i* contacts and specific interactions (leading to the formation of a  $i : j$  molecular entity, respectively), then changes in thermodynamic properties due to processes 2 and 3 are given by the following relations [26–28]:

$$\Delta X_2 (X = V \text{ or } K_S) = x_i^2 x_j v_j \chi'_{ii} / \sum x_i v_i \tag{10}$$

and

$$\Delta X_3 (X = V \text{ or } K_S) = x_i x_j^2 v_j \chi_{12} / \sum x_i v_i \tag{11}$$

The overall change in a thermodynamic property  $X^E$  ( $X = V$  or  $K_S$ ) due to processes 1 (a)–(c), 2 and 3, then can be expressed by Eq. 12

$$\begin{aligned}
 X_{ijk}^E &= \sum_{i=1}^3 \Delta X_i \\
 &= x_i x_j v_j / \sum x_i v_i [\chi'_{ij} + x_i \chi'_{ii} + x_j \chi_{12}] \\
 &\quad + x_j x_k v_j / \sum x_j v_j [\chi'_{jk}] \\
 &\quad + x_i x_k v_i / \sum x_i v_i [\chi'_{ik}]
 \end{aligned}
 \tag{12}$$

Because  $v_j/v_i = ({}^3\xi_i/{}^3\xi_j)$  [9], Eq. 12 reduces to Eq. 13

$$\begin{aligned}
 X_{ijk}^E &= [x_i x_j ({}^3\xi_i/{}^3\xi_j)/x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [\chi'_{ij} + x_i \chi'_{ii} + x_j \chi_{12}] \\
 &\quad + [x_j x_k ({}^3\xi_j/{}^3\xi_k)/x_j + x_k ({}^3\xi_j/{}^3\xi_k)] [\chi'_{jk}] \\
 &\quad + [x_i x_k ({}^3\xi_k/{}^3\xi_i)/x_k + x_i ({}^3\xi_k/{}^3\xi_i)] [\chi'_{ik}]
 \end{aligned}
 \tag{13}$$

Further, if it is assumed that  $\chi'_{ij} \cong \chi'_{ii} = \chi''_{ij} \gg \chi_{12}$ , then Eq. 13 can be expressed as Eq. 14:

$$\begin{aligned}
 X_{ijk}^E &= [x_i x_j ({}^3\xi_i/{}^3\xi_j)/x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [(1 + x_i) \chi''_{ij}] \\
 &\quad + [x_j x_k ({}^3\xi_j/{}^3\xi_k)/x_j + x_k ({}^3\xi_j/{}^3\xi_k)] [\chi'_{jk}] \\
 &\quad + [x_i x_k ({}^3\xi_k/{}^3\xi_i)/x_k + x_i ({}^3\xi_k/{}^3\xi_i)] [\chi'_{ik}]
 \end{aligned}
 \tag{14}$$

Equation 14 contains three unknown parameters,  $\chi''_{ij}$ ,  $\chi'_{jk}$  and  $\chi'_{ik}$ . These parameters were calculated by employing the experimental  $X_{ijk}^E$  ( $X = V$  or  $\kappa_s$ ) data of these ternary mixtures at three compositions and these parameters were then utilized to predict  $X_{ijk}^E$  values at other values of  $x_i$ . Such predicted  $X_{ijk}^E$  values, along with the  $\chi''_{ij}$ ,  $\chi'_{jk}$  and  $\chi'_{ik}$  parameters, are recorded in Table 3.

The  $V_{ijk}^E$  and  $(K_S)_{ijk}$  values for the studied ( $i + j + k$ ) ternary mixtures were next analyzed in terms of Flory’s theory. According to Flory’s theory [29, 30],  $V_{ijk}^E$  for a ternary mixture is given by:

$$V_{ijk}^E = \bar{V}_{cal}^E \left[ \sum_{i=1}^k x_i v_i^* \right]
 \tag{15}$$

where

$$\bar{v}_i = [1 + \alpha_i(T/3)/(1 + \alpha_i T)^3]^3
 \tag{16}$$

$$\bar{V}_{cal}^E = \bar{v}_0^{7/3} [(4/3) - (\bar{v}_0)^{1/3}]^{-1} [\bar{T} - \bar{T}_0]
 \tag{17}$$

$$\bar{T}_0 = (\bar{v}_0^{1/3} - 1)/\bar{v}_0^{4/3}
 \tag{18}$$

$$\bar{v}_i^* = v_i/\bar{v}_i
 \tag{19}$$

$$\bar{v}_0 = \sum \phi_i v_i^*
 \tag{20}$$

$$\bar{T} = \left[ \sum \left( \phi_i P_i^* \bar{T}_i / \sum \phi_i P_i^* \right) \right] \left[ 1 - (\phi_i \theta_j \chi_{ij}'') \left( \sum \phi_i P_i^* \right)^{-1} \right]^{-1} \quad (21)$$

$$\bar{T}_i = (\bar{v}_i^{1/3} - 1) / \bar{v}_i^{4/3} \quad (22)$$

$$P^* = \sum \phi_i P_i^* - \sum \phi_i^* \theta_j \chi_{ij}'' \quad (23)$$

$$P_i^* = \alpha_i T \bar{v}_i^2 [(K_T)_i]^{-1} \quad (24)$$

All of the terms have the same significance as described elsewhere [29, 30].

Evaluation of  $V_{ijk}^E$  by Flory's theory requires a knowledge of the reduced temperature,  $\bar{T}$ , which in turn depends upon the adjustable parameters  $\theta_j$ ,  $\chi_{ij}^*$ , etc., of the  $(i + j)$ ,  $(j + k)$  and  $(i + k)$  binary mixtures in the  $(i + j + k)$  ternary system. These parameters were determined by fitting using the  $H^E$  values [17, 24, 31], at  $x_i = 0.5$ , to Eq. 25

$$H^E = \sum x_i P_i^* (\bar{V}_i^{-1} - \bar{V}_{cal}^{-1}) + x_i V_i^* \theta_j \chi_{ij}^* V_{cal}^{-1} \quad (25)$$

Various parameters of the pure components were determined using isothermal compressibility ( $K_T$ ) values reported in literature [32]. The  $K_T$  values for **OT** were calculated by employing  $\Delta H_V$  in the manner suggested by Hilderbrand [33]. Such  $V_{ijk}^E$  values were evaluated via Eqs. 15–25 along with the  $\chi_{ij}^*$ , etc. parameters, and are recorded in Table 2 and compared with their corresponding experimental values.

According to Flory's theory,  $(K_S^E)_{ijk}$  is given by the relation:

$$K_S^E = K_S - K_S^{id} \quad (26)$$

The isentropic compressibility,  $K_S$ , of  $(i + j + k)$  ternary mixtures, at effectively zero pressure, is expressed by Eq. 27

$$K_S = K_T - T v_m^* \alpha_p^2 / C_{p,m} \quad (27)$$

The isothermal compressibility,  $K_T$ , of a mixture at effectively zero pressure is given by the relation

$$K_T = [(3\bar{v}_m^2 / p^*) (\bar{v}_m^{1/3} - 1) / (4 - 3(\bar{v}_m^{1/3}))] \quad (28)$$

where

$$v_m^* = \sum_{i=i}^k \phi_i v_i^* \quad (29)$$

$$\alpha_p = 3[(\bar{v}_m^{1/3} - 1) / T \{4 - 3(\bar{v}_m^{1/3})\}] \quad (30)$$

$$p^* = \sum_{i=i}^k \phi_i P_i^* - \sum_{i=i}^k \phi_i \theta_j \chi_{ij}^* \quad (31)$$

$$\bar{v} = v / v^* \quad (32)$$

$$\bar{v}_m = \sum_{i=i}^k \phi_i v_i^* \quad (33)$$

$$C_{p,m} = (\partial H_{ijk}^E / \partial T) + \sum_{i=i}^k x_i C_{p,i} \quad (34)$$

and where  $\bar{v}$ ,  $v^*$ ,  $c_{p,i}$  represent the reduced volume, characteristic volume, and molar heat capacities of component ( $i$ ) in the ternary mixtures. The  $(\partial H_{ijk}^E/\partial T)$  values at 308.15 K for **OT**( $i$ ) + benzene ( $j$ ) + toluene or *o*- or *p*-xylene ( $k$ ) ternary mixtures were evaluated by employing the available  $H^E$  values [16, 24, 31] for their binary subsystems ( $i + j$ ), ( $j + k$ ), ( $i + k$ ) mixtures. The  $H_{ijk}^E$  values were taken as being equal to  $H_{ij}^E + H_{jk}^E + H_{ik}^E$ . The  $H_{ij}^E$ , etc., values at 298.15 K were calculated as described elsewhere [34]. The  $\kappa_S^{\text{id}}$  values for the corresponding ideal mixtures were calculated using Eq. 27. Although  $\alpha_p^{\text{id}}$  and  $c_{p,m}^{\text{id}}$  were taken as their mole-fraction averages, the  $K^{\text{id}}$  values were taken as their volume-fraction averages. Such  $(K_S^E)_{ijk}$  values calculated for the present ternary mixtures are recorded in Table 3 where they are also compared with their corresponding experimental values.

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