Thermochimica Acta 503–504 (2010) 85–89

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Excess molar volumes and excess isentropic compressibilities of tetrahydropyran + benzene + cyclo or n-alkanes ternary mixtures at 308.15 K

Rajesh K. Siwach, Dimple Sharma, V.K. Sharma*

Department of Chemistry, Maharshi Dayanand University, Rohtak 124001, India

ARTICLE INFO

Article history:
Received 23 December 2009
Received in revised form 12 March 2010
Accepted 15 March 2010
Available online 23 March 2010

Keywords:
Connectivity parameter of third degree, 3ξ
Excess molar volumes, V^E_{ijk}
Excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$
Speeds of sound, u_{ijk}

ABSTRACT

Excess molar volumes, V^E_{ijk}, speeds of sound, u_{ijk}, of tetrahydropyran (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 and atmospheric pressure. The observed speeds of sound data of the investigated ternary mixtures have been utilized to calculate their excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$. The V^E_{ijk} and $(\kappa^E_S)_{ijk}$ have been fitted to the Redlich–Kister equation to calculate ternary adjustable parameters and standard deviations. Connectivity parameters of third degree of the constituents of mixtures (which in turn depends on the topology of a molecule) have been employed to determine excess molar volumes, V^E_{ijk}, and excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$. It has been observed that V^E_{ijk} and $(\kappa^E_S)_{ijk}$ values calculated by the Graph theory (which involves connectivity parameter of third degree of a molecule) compare well with their corresponding experimental values.

1. Introduction

Thermodynamic properties of liquid mixtures can be utilized to extract information about the existence of molecular interactions among the constituents of mixtures. Knowledge of thermodynamic properties is essential for the proper design of industrial processes, chemical engineering etc. and also for optimizing thermodynamic model/theories development. Compared to large numbers of data reported in the literature for binary mixtures, the experimental data for ternary mixtures remain scarce. Keeping both the industrial and scientific interest in mind, our laboratory has been actively engaged in the measurements of various thermodynamic properties of ternary mixtures [1–5]. Cyclic ethers represent a class of technically important compounds frequently used as solvents in the chemical industry [6–8]. Recent studies [9] of excess molar volumes, and excess isentropic compressibilities of THP (i) + aromatic hydrocarbons (j) binary mixtures have shown that topology of the components of the mixtures can be successfully employed to predict excess molar volumes, excess molar enthalpies and excess isentropic compressibilities. In the present paper continuing our study, we report here excess molar volumes and speeds of sound of THP (i) + benzene (j) + cyclohexane or n-hexane or n-heptane (k) ternary mixtures at 308.15 K.

2. Experimental

2.1. Materials

Tetrahydropyran (THP) (Fluka, 99 mol%), benzene (Fluka, 99 mol%), cyclohexane (Fluka, 99 mol%), n-hexane (Fluka, 99 mol%) and n-heptane (Fluka, 99 mol%) were purified by standard methods [11].The purities of the liquids were checked by measuring their densities with bicapillary pycnometer (with an accuracy of two parts in 10^5) at 298.15 ± 0.01 K and the resulting densities (reported in Table 1) agreed to within 0.05 kg m^{-3} with their corresponding literature values [10,11].

The excess molar volumes, V^E_{ijk}, for the ternary mixtures were measured in a three limbed dilatometer in the manner described elsewhere [12]. The change in liquid level of the dilatometer capillary was measured with a cathetometer that could be read to 0.001 cm. The uncertainty in the measured V^E_{ijk} values is 0.5%.

The speeds of sound were determined at 2 MHz using a quartz crystal interferometer (Model-M 84, 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 (308.15 ± 0.01) K. The speeds of sound values for the purified liquids at 298.15 ± 0.01 K (recorded in Table 1) compare well with their corresponding literature values [6,13–15]. The uncertainty in measured sound speeds is 1 m s^{-1}.

---

* Corresponding author. Tel.: +91 1262295012.
E-mail address: v_sharmachem58@rediffmail.com (V.K. Sharma).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.03.012

Table 1
Comparison of densities, ρ, and speeds of sound, u, of pure liquids with literature values at 298.15 K.

Liquids	u (m s^{-1})		ρ (kg m^{-3})	
	Exptl	Lit.	Exptl	Lit.
Tetrahydropyran	1272	1271.1 [6]	868.81[a]	868.82[a] [10]
n-hexane	1079	1078.0 [13]	654.82	654.84 [11]
n-heptane	1088[a]	1087.6 [14]	679.49	679.46 [11]
Cyclohexane	1255	1254.4 [13]	773.94	773.89 [11]
Benzene	1298	1298.9 [15]	873.64	873.60 [11]

[a] Value at 308.15 K.

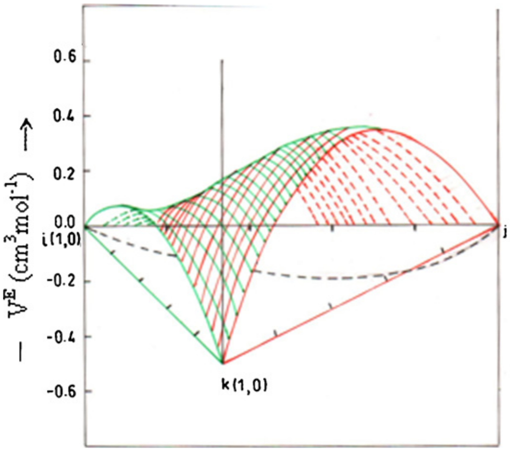

Fig. 1. Molar excess volumes, V^E for tetrahydropyran (i) + benzene (j) + cyclohexane (k) at 308.15 K.

3. Results

Excess molar volumes, V^E_{ijk}, and speeds of sound, u_{ijk}, data of THP (i) + benzene (j) + cyclohexane or n-hexane or n-heptane (k) ternary mixtures as a function of composition at 308.15 K are recorded in Tables 2 and 3 respectively. The isentropic compressibilities, $(\kappa_S)_{ijk}$, for ternary mixtures were determined by using Eq. (1)

$$(\kappa_S)_{ijk} = (\rho_{ijk}u^2_{ijk})^{-1} \tag{1}$$

The densities, ρ_{ijk}, of the ternary mixtures were calculated from their corresponding experimental excess molar volumes data via Eq. (2)

$$V^E_{ijk} = \sum_{i=i}^{k} x_iM_i(\rho_{ijk})^{-1} - \sum_{i=i}^{k} x_iM_i(\rho_i)^{-1} \tag{2}$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density, respectively, of component (i) of the ($i+j+k$) ternary mixture.

The excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$ for the various ternary mixtures were determined using

$$(\kappa^E_S)_{ijk} = (\kappa_S)_{ijk} - \kappa^{id}_S \tag{3}$$

κ^{id}_S values were obtained as suggested by Benson and Kiyohara [16]

$$\kappa^{id}_S = \sum_{i=i}^{k}\phi_i\left[\kappa_{S,i} + \frac{Tv_i\alpha_i^2}{C_{p,i}}\right] - T\left(\sum_{i=i}^{k}x_iv_i\right)\frac{\left(\sum_{i=i}^{k}\phi_i\alpha_i\right)^2}{\left(\sum_{i=i}^{k}x_iC_{p,i}\right)} \tag{4}$$

where ϕ_i is the volume fraction of component (i) in the mixed state; $\kappa_{S,i}$, v_i, α_i and $C_{p,i}$ are the isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity respectively of pure component (i). The values of α and $C_{p,i}$ were taken from the literature [17]. α for THP was evaluated in the same manner as described elsewhere [18]. The resulting $(\kappa_S)_{ijk}$ and $(\kappa^E_S)_{ijk}$ values for the studied ($i+j+k$) ternary mixtures are recorded in Table 3.

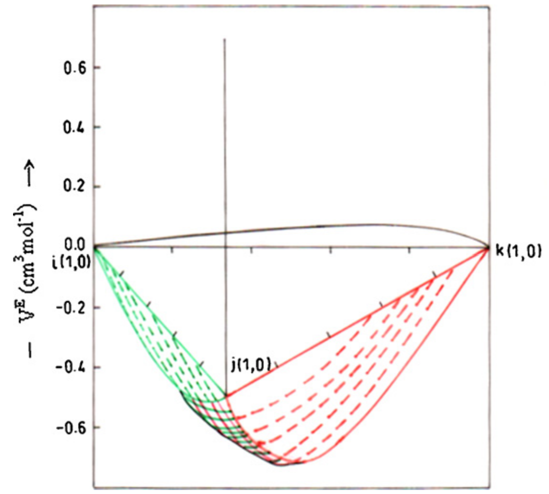

Fig. 2. Excess molar volume of tetrahydropyran (i) + benzene (j) + n-hexane (k) at 308.15 K.

The measured, V^E_{ijk}, and $(\kappa^E_S)_{ijk}$ for THP (i) + benzene (j) + cyclohexane or n-hexane or n-heptane (k) ternary mixtures were fitted to the Redlich–Kister equation [19]

$$X^E_{ijk}(X = V\text{or}\kappa_s) = x_ix_j\left[\sum_{n=0}^{2}(X^{(n)}_{ij})(x_i-x_j)^n\right] + x_jx_k\left[\sum_{n=0}^{2}(X^{(n)}_{jk})(x_j-x_k)^n\right] + x_ix_k\left[\sum_{n=0}^{2}(X^{(n)}_{ik})(x_k-x_j)^n\right] + x_ix_jx_k\left[\sum_{n=0}^{2}(X^{(n)}_{ijk})(x_j-x_k)^nx_i^n\right] \tag{5}$$

where x_i and x_j are the mole fractions of ith and jth components of ($i+j+k$) ternary mixtures. $X^{(n)}_{ij}$ (n = 0–) etc. are the adjustable parameters of ($i+j$), ($j+k$), and ($i+k$) binary mixtures and were taken from the literature [9,14,20], where as $X^{(n)}_{ijk}$ etc. (n = 0–2) are adjustable parameters of the ternary mixtures and were determined by fitting the X^E_{ijk} data to the Eq. (5) by least squares method. Such parameters along with standard deviations, $\sigma\, X^E_{ijk}(X = V\text{or}\kappa_s)$

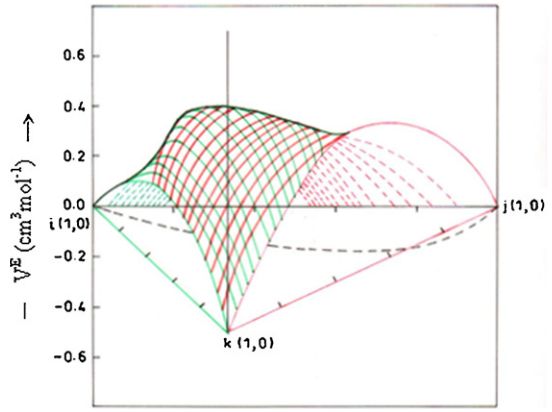

Fig. 3. Excess molar volumes, V^E for tetrahydropyran (i) + benzene (j) + n-heptane (k) at 308.15 K.

Table 2
Comparison of experimental, V^E_{ijk} results for the various $(i+j+k)$ ternary mixtures with values evaluated by the Graph theory; also included are the various parameters $V^{(n)}_{ijk}$ $(n=0–2)$ along with their, interaction parameters χ''_{ij}, χ'_{jk} and χ'_{ik} etc. and connectivity parameters of third degree, ${}^3\xi_i$ $(i=i-k)$.

x_i	x_j	V^E (cm^3 mol^{-1})	V^E (Graph)
Tetrahydropyran (i) + benzene (j) + cyclohexane (k)			
0.0791	0.6790	0.414	0.405
0.0881	0.6649	0.415	0.405
0.1490	0.5621	0.430	0.421
0.1979	0.5921	0.346	0.319
0.2871	0.4940	0.340	0.323
0.2719	0.4621	0.359	0.356
0.3479	0.3401	0.338	0.338
0.3840	0.3556	0.292	0.321
0.4131	0.2949	0.300	0.300
0.4490	0.2871	0.264	0.288
0.5391	0.2681	0.187	0.274
0.5629	0.1931	0.244	0.205
0.6381	0.1649	0.183	0.183
0.7970	0.0871	0.099	0.103
0.8371	0.0631	0.087	0.064
0.8730	0.0511	0.063	0.058
0.0621	0.7821	0.292	0.274
0.2021	0.5731	0.359	0.335
0.2541	0.5551	0.332	0.300
0.3033	0.4312	0.342	0.348
0.3234	0.3611	0.351	0.353
0.4682	0.2721	0.256	0.278
0.4816	0.2611	0.251	0.269
0.5018	0.2418	0.250	0.253
0.5813	0.1786	0.244	0.187
0.6014	0.1708	0.229	0.180
0.6588	0.1451	0.190	0.155
0.6857	0.1326	0.174	0.143
0.7013	0.1129	0.190	0.105

$V^{(0)}_{ijk} = -0.103$; $V^{(1)}_{ijk} = -9.239$; $V^{(2)}_{ijk} = 498.558$; $\sigma(V^E_{ijk}) = 0.003 \rightleftarrows \mathrm{cm}^3 \rightleftarrows \mathrm{mol}^{-1}$
$\chi^{//}_{ij} = 0.564$; $\chi^{/}_{jk} = 5.343$; $\chi^{/}_{ik} = -2.060$
$({}^3(_i) = ({}^3(_i)_m = 1.301$; $({}^3(_j) = ({}^3(_j)_m = 0.666$; $({}^3(_k) = ({}^3(_k)_m = 1.5$

x_i	x_j	V^E (cm^3 mol^{-1})	V^E (Graph)
Tetrahydropyran (i) + benzene (j) + n-hexane (k)			
0.0910	0.5443	–0.184	–0.255
0.0913	0.1421	–0.037	–0.046
0.1214	0.1671	–0.022	–0.014
0.1278	0.1812	–0.020	–0.020
0.1301	0.1876	–0.020	–0.024
0.1421	0.2001	–0.013	–0.014
0.1511	0.2042	–0.005	–0.002
0.1629	0.2215	–0.011	–0.001
0.1712	0.6421	–0.101	–0.103
0.3452	0.3312	0.072	0.072
0.3352	0.3112	0.074	0.094
0.3122	0.2913	0.072	0.109
0.2987	0.3013	0.067	0.091
0.2612	0.2670	0.055	0.097
0.3621	0.3422	0.072	0.057
0.3713	0.3489	0.071	0.046
0.3812	0.3621	0.067	0.024
0.3942	0.3202	0.076	0.073
0.3937	0.3498	0.070	0.032
0.1214	0.6123	–0.153	–0.149
0.1131	0.5002	–0.139	–0.212
0.0910	0.5443	–0.184	–0.246
0.0500	0.6111	–0.266	–0.316
0.0482	0.7121	–0.258	–0.237
0.6121	0.2131	0.034	0.029
0.6343	0.1998	0.026	0.026
0.6567	0.1821	0.019	0.042
0.6813	0.1712	0.010	0.024
0.7011	0.1541	0.003	0.005
0.7898	0.1223	–0.024	–0.059

$V^{(0)}_{ijk} = 8.990$; $V^{(1)}_{ijk} = 3.823$; $V^{(2)}_{ijk} = 47.461$; $\sigma(V^E_{ijk}) = 0.002 \rightleftarrows \mathrm{cm}^3 \rightleftarrows \mathrm{mol}^{-1}$
$\chi^{//}_{ij} = -1.066$; $\chi^{/}_{jk} = -2.549$; $\chi^{/}_{ik} = 5.177$
$({}^3(_i) = ({}^3(_i)_m = 1.301$; $({}^3(_j) = ({}^3(_j)_m = 0.666$; $({}^3(_k) = ({}^3(_k)_m = 0.957$

Table 2 (*Continued*)

x_i	x_j	V^E (cm^3 mol^{-1})	V^E (Graph)
Tetrahydropyran (i) + benzene (j) + n-heptane (k)			
0.0587	0.7349	0.330	0.328
0.0652	0.7032	0.362	0.361
0.0764	0.6542	0.404	0.402
0.0867	0.5891	0.455	0.453
0.1007	0.4925	0.502	0.504
0.1216	0.4731	0.492	0.492
0.1307	0.4625	0.489	0.488
0.1482	0.4827	0.467	0.461
0.1621	0.5113	0.442	0.430
0.1831	0.4931	0.435	0.408
0.2023	0.4711	0.430	0.416
0.2321	0.4454	0.418	0.403
0.2511	0.4221	0.410	0.399
0.2772	0.3679	0.398	0.397
0.3032	0.3452	0.380	0.383
0.3691	0.2191	0.319	0.319
0.3325	0.2381	0.343	0.346
0.3823	0.2001	0.309	0.300
0.4012	0.1982	0.299	0.292
0.3033	0.4312	0.371	0.349
0.3234	0.3611	0.368	0.366
0.4682	0.2721	0.271	0.289
0.4816	0.2611	0.262	0.282
0.5018	0.2418	0.248	0.272
0.5813	0.1786	0.202	0.221
0.6014	0.1708	0.191	0.211
0.6588	0.1451	0.161	0.180
0.6857	0.1326	0.148	0.165
0.7013	0.1129	0.147	0.147

$V^{(0)}_{ijk} = 1.400$; $V^{(1)}_{ijk} = 30.831$; $V^{(2)}_{ijk} = 85.071$; $\sigma(V^E_{ijk}) = 0.002 \rightleftarrows \mathrm{cm}^3 \rightleftarrows \mathrm{mol}^{-1}$
$\chi^{//}_{ij} = 0.147$; $\chi^{/}_{jk} = 3.208$; $\chi^{/}_{ik} = -0.535$
$({}^3(_i) = ({}^3(_i)_m = 1.301$; $({}^3(_j) = ({}^3(_j)_m = 0.666$; $({}^3(_k) = ({}^3(_k)_m = 1.1$
$\chi^{//}_{ij}$, $\chi^{/}_{jk}$ and $\chi^{/}_{ik}$ are in cm^3 mol^{-1}

expressed by the relation:

$$\sigma X^E_{ijk} = \left\{ \frac{\left[\Sigma X^E_{ijk} - X^E_{ijk}(\text{calc. Eq. (5)}) \right]^2}{(m-n)} \right\}^{0.5} \tag{6}$$

where m is the number of data points and n is the number of adjustable parameters of Eq. (6) are recorded in Tables 2 and 3 respectively. The surfaces for the various ternary mixtures generated by $(V^E)_{ijk}$ and $(\kappa^E_S)_{ijk}$ values (predicted via Eq. (5)) are shown in Figs. 1–3 and Figs. 4–6 respectively.

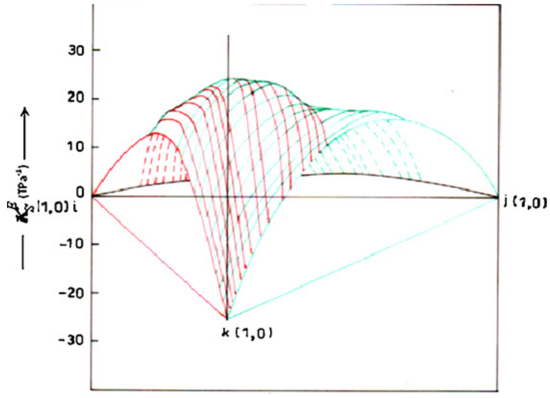

Fig. 4. Excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$ for tetrahydropyran (i) + benzene (j) + cyclohexane (k) at 308.15 K.

Table 3

Speeds of sound, u_{ijk}, isentropic compressibilities, κ_S, excess isentropic compressibilities, $(\kappa_S^E)_{ijk}$ for the various $(i+j+k)$ ternary mixtures at various compositions (in mole fractions) at 308.15 K with $(\kappa_S^E)_{ijk}$ evaluated from the Graph theory with their corresponding experimental values; also included are the various parameters $\kappa^{(n)}_{S(ijk)}$ $(n = 0–2)$ along with their, interaction parameters χ''_{ij}, χ'_{jk} and χ'_{ik} etc.

Tetrahydropyran (i) + benzene (j) + cyclohexane (k)

x_i	x_j	u_{ijk} (m s^{-1})	$(\kappa_S)_{ijk}$ (T Pa^{-1})	$(\kappa_S^E)_{ijk}$ (T Pa^{-1})	
				Exptl	Graph
0.1542	0.3013	1204	859.8	30.2	34.8
0.1882	0.3134	1204	854.3	30.8	27.5
0.1741	0.2321	1202	867.5	29.9	22.8
0.0876	0.1116	1204	884.1	18.8	18.9
0.1000	0.1303	1204	882.2	21.0	20.8
0.1249	0.1884	1203	876.1	26.1	28.0
0.1443	0.5764	1221	809.4	22.6	28.1
0.1843	0.6119	1227	792.7	17.5	17.5
0.2125	0.6411	1232	778.0	12.8	12.9
0.2384	0.6201	1233	770.2	12.0	12.7
0.3821	0.4413	1225	791.1	13.8	13.3
0.4110	0.4182	1224	790.7	13.4	13.4
0.4512	0.3810	1223	791.5	13.4	13.2
0.4883	0.3500	1222	791.5	13.1	13.2
0.5001	0.3401	1222	791.4	13.0	13.1
0.5429	0.3115	1222	789.5	12.0	13.8
0.5819	0.2744	1220	790.8	12.3	12.6
0.6263	0.2313	1219	792.3	12.6	10.2
0.6544	0.2160	1219	790.0	11.5	10.9
0.6813	0.1981	1219	788.6	10.7	10.7
0.7113	0.1768	1219	787.4	10.0	10.0
0.7384	0.1601	1220	785.6	9.0	9.9
0.7495	0.1506	1220	785.5	8.8	9.0

$(\kappa_S^{(0)})_{ij} = 82.3$; $(\kappa_S^{(1)})_{ij} = -1387.2$; $(\kappa_S^{(2)})_{ij} = -3903.6$; $\sigma\sigma(\kappa_S^E)_{ij} = 0.1$
$\chi^{//}_{ij} = 65.3$; $\chi^{/}_{jk} = 582.0$; $\chi^{/}_{ik} = -391.5$

Tetrahydropyran (i) + benzene (j) + n-hexane (k)

x_i	x_j	u_{ijk} (m s^{-1})	$(\kappa_S)_{ijk}$ (T Pa^{-1})	$(\kappa_S^E)_{ijk}$ (T Pa^{-1})	
				Exptl	Graph
0.1073	0.1998	1080	1228.2	−62.3	−56.8
0.1312	0.2417	1092	1181.2	−68.4	−65.3
0.1554	0.2713	1102	1142.2	−72.6	−72.6
0.1753	0.3089	1114	1099.2	−77.8	−77.0
0.1003	0.1100	1065	1294.0	−53.1	−51.2
0.0876	0.0645	1057	1333.4	−46.2	−44.2
0.2021	0.3500	1131	1046.8	−81.7	−80.7
0.2353	0.3821	1148	994.6	−85.9	−82.6
0.2568	0.4110	1163	955.0	−86.9	−80.7
0.3037	0.5076	1199	858.6	−64.8	−58.6
0.2887	0.4446	1181	907.4	−82.2	−74.6
0.3213	0.4813	1197	863.0	−68.3	−61.5
0.3394	0.5489	1210	821.1	−33.2	−33.4
0.3572	0.5619	1214	806.6	−19.0	−19.0
0.3823	0.5322	1212	810.3	−20.5	−20.2
0.4165	0.4812	1209	819.0	−28.6	−27.2
0.4432	0.4352	1207	826.9	−39.3	−35.6
0.4873	0.3812	1207	830.0	−46.4	−35.2
0.5225	0.3143	1203	843.9	−61.6	−54.9
0.5017	0.2812	1190	877.5	−74.0	−75.4
0.6332	0.2144	1201	842.4	−56.0	−55.5
0.6676	0.2021	1205	830.3	−49.3	−45.9
0.6894	0.1866	1205	827.7	−46.8	−44.1
0.7021	0.1721	1204	830.0	−46.4	−46.4
0.7313	0.1454	1203	831.0	−43.9	−48.2

$(\kappa_S^{(0)})_{ij} = -338.7$; $(\kappa_S^{(1)})_{ij} = -9396.8$; $(\kappa_S^{(2)})_{ij} = 71717.5$; $\sigma\sigma(\kappa_S^E)_{ij} = 0.2$
$\chi^{//}_{ij} = 83.9$; $\chi^{/}_{jk} = -93.2$; $\chi^{/}_{ik} = -726.1$

Tetrahydropyran (i) + benzene (j) + n-heptane (k)

x_i	x_j	u_{ijk} (m s^{-1})	$(\kappa_S)_{ijk}$ (T Pa^{-1})	$(\kappa_S^E)_{ijk}$ (T Pa^{-1})	
				Exptl	Graph
0.0567	0.8921	1230	777.8	2.3	1.4
0.0942	0.8657	1232	775.9	4.0	4.0
0.1217	0.8341	1229	781.9	5.5	4.8
0.1542	0.7091	1226	786.5	19.0	6.7
0.1828	0.1513	1092	1173.1	32.3	29.9
0.2125	0.7612	1234	770.8	9.4	7.2
0.2321	0.7511	1241	759.5	8.3	6.0
0.2617	0.7111	1232	773.6	17.5	12.5
0.2889	0.6888	1234	769.6	9.5	7.4
0.3012	0.6421	1214	805.5	7.9	5.6
0.3361	0.6132	1222	789.7	29.6	30.7
0.3721	0.5439	1229	777.1	12.4	10.4
0.4012	0.1871	1099	1089.1	56.8	64.7
0.4813	0.1885	1109	1046.5	54.7	65.0
0.5001	0.2110	1117	1021.3	55.6	57.9
0.6012	0.1998	1139	955.5	40.5	46.9
0.4112	0.1900	1100	1083.9	57.4	64.5
0.4321	0.1921	1102	1072.9	57.5	64.7
0.4613	0.2001	1106	1055.1	57.7	62.7
0.6990	0.2169	1185	850.4	16.3	14.9
0.7127	0.2010	1184	852.2	16.4	16.4
0.1915	0.1500	1090	1174.7	33.0	33.0
0.4131	0.5431	1219	794.7	4.7	3.2
0.5113	0.4002	1188	848.9	15.1	11.7
0.4221	0.5154	1208	814.9	7.7	5.3

$(\kappa_S^{(0)})_{ij} = 2103.9$; $(\kappa_S^{(1)})_{ij} = -3968.6$; $(\kappa_S^{(2)})_{ij} = -19809.2$; $\sigma(\kappa_S^E)_{ij} = 0.1$
$\chi^{//}_{ij} = -32.7$; $\chi^{/}_{jk} = -403.131$; $\chi^{/}_{ik} = 626.8$
$\chi^{//}_{ij}$, $\chi^{/}_{jk}$ and $\chi^{/}_{=}$ are in T Pa^{-1}

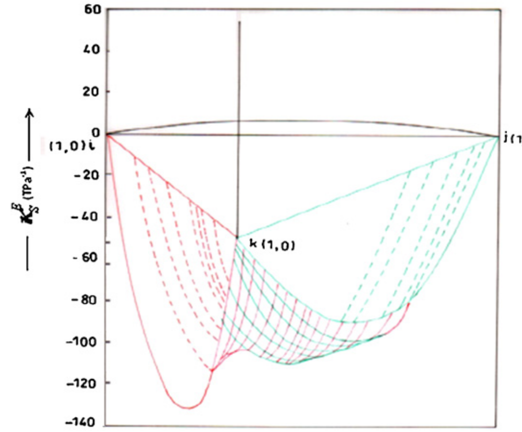

Fig. 5. Excess isentropic compressibilities, $(\kappa_S^E)_{ijk}$ for tetrahydropyran (i) + benzene (j) + n-hexane (k) at 308.15 K.

4. Discussion

We are unaware of any V^E_{ijk} and $(\kappa_S^E)_{ijk}$ of the studied $(i+j+k)$ ternary mixtures with to compare our results. V^E_{ijk} and $(\kappa_S^E)_{ijk}$ are positive for THP (i) + benzene (j) + cyclohexane or n-heptane (k) mixtures over entire composition range. However, V^E_{ijk} are negative for THP (i) + benzene (j) + cyclohexane or n-hexane (k) mixtures and $(\kappa_S^E)_{ijk}$ values are directed by the relative proportions of component (i).

Topological and thermodynamic studies [9] of binary mixtures of THP (i) with aromatic hydrocarbons (j) have revealed that while THP exists as an associated molecular entity; aromatic hydrocarbons (benzene or toluene or o- or m- or p-xylene) exist as monomers. Furthermore, excess molar volumes, excess molar enthalpies and excess isentropic compressibilities of various $(i+j)$ predicted by the Graph theory (which in turns depends upon the topology of constituents of mixtures) compare well with their corresponding experimental values. If an inert hydrocarbon like cyclohexane or n-hexane or n-heptane (k) is added to THP (i) + benzene (j) binary mixtures, then THP (i) + benzene (j) + cyclohexane or n-hexane or n-heptane (k) ternary mixtures formation may involve processes: (1) establishment of unlike (a) $i_n - j$, (b) $j - k$, (c) $i_n - k$ contacts; (2) unlike molecular contacts $i_n - j$ formation leads to depolymerization of i_n to yield monomer of (i); (3) the monomers of (i) and (j) then undergo specific interaction to

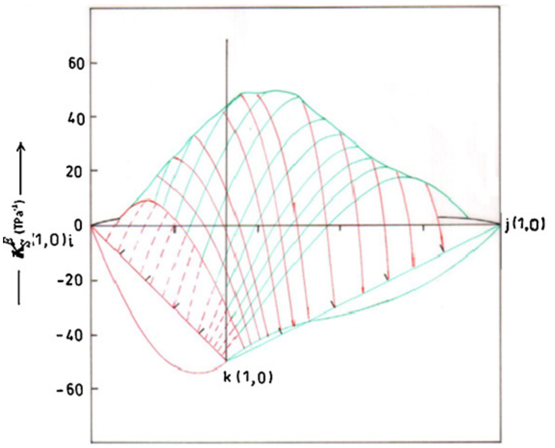

Fig. 6. Excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$ for tetrahydropyran (i) + benzene (j) + n-heptane (k) at 308.15 K.

yield *i*:*j* molecular entities. If χ'_{ij}, χ'_{jk} and χ'_{ik} are the molar volumes and molar compressibility interaction parameters of i–j, j–k and i–k unlike contact, and $\chi^{/}_{12}$ is the interaction energy parameter for specific interaction between *i* and *j* monomers, then change in thermodynamic properties X^E_{ijk} ($X = V$ or κ_S) due to processes 1 (a)–(c) and (2) would be expressed [21–23] by Eq (7)–(8)

$$X^E_{ijk} = \left[\frac{x_i x_j \upsilon_j}{\sum x_i \upsilon_i}\right][\chi'_{ij} + x_j \chi_{12}] + \left[\frac{x_j x_k \upsilon_k}{\sum x_j \upsilon_j}\right]\chi'_{jk} + \left[\frac{x_i x_k \upsilon_j}{\sum x_i \upsilon_i}\right]\chi'_{ik} \qquad (7)$$

where x_i and υ_i are the mole fraction and molar volume of component (i) in the ternary mixture.

Since [24] $\upsilon_j/\upsilon_i = ({}^3\xi_i/{}^3\xi_j)$, where ${}^3\xi_i$ ($i = i$ or j or k) etc. are the connectivity parameters of third degree of components *i*/*j*/*k* and are defined [25] by Eq.

$${}^3\xi = \sum_{\ell<m<n<o} (\delta^v_\ell \delta^v_m \delta^v_n \delta^v_o)^{-0.5} \qquad (8)$$

δ^v_ℓ etc. reflects explicitly the valency of *m*th vertex in the molecular graph of a molecule and is related to the maximum valency of atom Z_m and number of hydrogen atoms attached (h_m) by the relation[26] $\delta\delta^v_m = Z_m - h_m$ Eq. (7) therefore reduces to

$$X^E_{ijk}(X = \mathrm{Vor}\kappa_s) = \left[\frac{x_i x_j({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right][\chi'_{ij} + x_j \chi_{12}] + \left[\frac{x_j x_k({}^3\xi_j/{}^3\xi_k)}{x_j + x_k({}^3\xi_j/{}^3\xi_k)}\right]\chi'_{jk} + \left[\frac{x_i x_k({}^3\xi_i/{}^3\xi_{kk})}{x_i + x_k({}^3\xi_i/{}^3\xi_k)}\right]\chi'_{ik} \qquad (9)$$

If it is assumed that $\chi'_{ij} \cong \chi'_{12} = \chi''_{ij}$ then Eq. (9) can be expressed as

$$X^E_{ijk}(X = \mathrm{Vor}\kappa_s) = \left[\frac{x_i x_j({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right](1 + x_j)\chi''_{ij} + \left[\frac{x_j x_k({}^3\xi_j/{}^3\xi_{kk})}{x_j + x_k({}^3\xi_j/{}^3\xi_k)}\right]\chi'_{jk} + \left[\frac{x_i x_k({}^3\xi_i/{}^3\xi_{kk})}{x_i + x_k({}^3\xi_i/{}^3\xi_k)}\right]\chi'_{ik} \qquad (10)$$

Eq. (10) contains three unknown parameters (χ''_{ij}, χ'_{ik} and χ'_{ik}) and for present studies, we employed V^E_{ijk} and $(\kappa^E_S)_{ijk}$ at three arbitrary compositions to evaluate the parameters values. These parameters were then utilized to predict $X^E_{ijk}(X = \mathrm{Vor}\kappa_s)$ at various values of x_i and x_j. Such $X^E_{ijk}(X = \mathrm{Vor}\kappa_s)$ values along with χ''_{ij}, χ'_{jk} and χ'_{ik} parameters are recorded in Tables 2 and 3. Examination of Tables 2 and 3 reveals that V^E_{ijk} and $(\kappa^E_S)_{ijk}$ values predicted by the Graph theory compare well with their corresponding experimental values and thus lends support to the assumptions made in deriving Eq. (10). Even in those cases where agreement between the experimental and measured values is not impressive, the magnitudes are with same sign.

Acknowledgement

The authors are grateful to the Head, Chemistry Department and authorities of M.D. University, Rohtak, for providing research facilities.

References

[1] D. Sharma, J.S. Yadav, K.C. Singh, V.K. Sharma, J. Solut. Chem. 37 (8) (2008) 1099–1112.
[2] V.K. Sharma, S. Kumar, J. Solut. Chem. 34 (2005) 839–852.
[3] V.K. Sharma, R.S. Kumar, Thermochim. Acta 417 (2004) 91–97.
[4] V.K. Sharma, K.C. Kalra, R.A. Katoch, Indian J. Chem. 42A (2003) 292–294.
[5] V.K. Sharma, R. Kumar, Can. J. Chem. 79 (12) (2001) 1910–1914.
[6] C. Valles, E. Perez, M. Cardoso, M. Dominguez, A.M. Mainar, J. Chem. Eng. Data 49 (2004) 1460–1464.
[7] K. Tamura, J. Chem. Eng. Data 50 (2005) 66–71.
[8] S. Aoshima, T. Fujisawa, E. Kobayashi, J. Polym. Sci. Part A: Polym. Chem. 32 (1994) 1719–1728.
[9] V.K. Sharma, R.K. Siwach, D. Sharma, J. Chem. Thermodyn., in press.
[10] E. Calvo, P. Brocos, A. Pineiro, M. Pintos, A. Amigo, R. Bravo, A.H. Roux, G. Roux-Desgranges, J. Chem. Eng. Data 44 (1999) 948–954.
[11] J.A. Riddick, W.B. Bunger, T.K. Skano, Organic Solvents Physical Properties and Methods of Purification, fourth ed., Wiley, New York, 1986.
[12] P.P. Singh, S.P. Sharma, J. Chem. Eng. Data 30 (1985) 477–479.
[13] E. Junquera, G. Tardajos, E. Aicart, J. Chem. Thermodyn. 20 (1988) 1461–1467.
[14] T.M. Letcher, J. Chem. Thermodyn. 16 (1984) 805–810.
[15] K. Tamura, S. Murakami, S. Doi, J. Chem. Thermodyn. 17 (1985) 325–333.
[16] G.C. Benson, O. Kiyohara, J. Chem. Thermodyn. 11 (1999) 1061–1064.
[17] R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC, 1987.
[18] J.H. Hildebrand, J.M. Prusnitz, R.L. Scott, Regular and Related Solutions, Van-Nonstand Reinheld Compound, New York, 1971.
[19] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 343–348.
[20] R. Kumar, Ph.D. Thesis, Maharshi Dayanand University, Rohtak, Haryana, India, 2001.
[21] M.L. Huggins, J. Phys. Chem. 74 (2) (1970) 371–378.
[22] M.L. Huggins, Polymer 12 (1971) 387–399.
[23] P.P. Singh, M. Bhatia, J. Chem. Soc., Faraday Trans. 185 (1989) 3807–3812.
[24] P.P. Singh, R.K. Nigam, K.C. Singh, V.K. Sharma, Thermochim. Acta 46 (2) (1981) 175–190.
[25] P.P. Singh, Thermochim. Acta 66 (1993) 37–73.
[26] L.B. Kier, S.H. Yalkowasky, A.A. Sinkula, S.C. Valvani, Physico-chemical Properties of Drugs, Mercel Dekker, New York, 1980.