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Topological Investigations of Excess Molar Volumes and Excess Isentropic Compressibilities of Ternary Mixtures Containing Pyrrolidin-2-one at 308.15 K

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Abstract Excess molar volumes, V^{E}_{ijk}, and speeds of sound, u_{ijk}, of pyrrolidin-2-one (2-Py) (i) + benzene or methyl benzene (j) + propan-1-ol (k) ternary mixtures and speeds of sound, u_{ij}, of benzene or methyl benzene (i) + propan-1-ol (j) binary mixtures have been measured dilatometrically and interferrometrically over the complete mole fraction range at 308.15 K. Speed-of-sound data have been utilized to evaluate excess isentropic compressibilities for binary and ternary mixtures. V^{E}_{ijk} and $\left(\kappa^{\mathrm{E}}_{S}\right)_{ijk}$ values have been fitted to a Redlich–Kister equation to predict ternary adjustable parameters and standard deviations. Topological investigations employed for predicting excess molar volumes and excess isentropic compressibilities, $\left(\kappa^{\mathrm{E}}_{S}\right)_{ij}$, of 2-Py + benzene or methyl benzene or propan-1-ol binary mixtures have been extended to ternary mixtures (by employing the concept of a connectivity parameter of third degree, ${}^{3}\xi$, of a molecule) to obtain an expression that describes well the measured V^{E}_{ijk} and $\left(\kappa^{\mathrm{E}}_{S}\right)_{ijk}$ values.

Keywords Connectivity parameter of third degree $\left({}^{3}\xi\right)$ · Excess isentropic compressibility $\left(\left(\kappa^{\mathrm{E}}_{S}\right)_{ijk}\right)$ · Excess molar volume $\left(V^{\mathrm{E}}_{ijk}\right)$ · Interaction energy parameter (χ) · Speed of sound $\left(u_{ijk}\right)$

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1 Introduction

One of the current tendencies in chemical and biological investigations is the prediction of physicochemical and biological properties of chemical compounds and drugs from their structure [1–4]. The physicochemical properties of a solution depend upon the manner in which its constituents are associated with each other. A characterization of binary [5–8] or ternary [9–11] mixtures through topological investigations has provided an important tool to understand (i) the nature of the state of components of the mixtures in pure and mixed states and (ii) the nature and extent of interactions along with molecular entities in the mixtures. Topological and thermodynamic studies have also been employed [12–14] successfully to predict excess molar volumes, excess molar enthalpies, excess free energies of mixing, and excess isentropic compressibilities of various binary and ternary mixtures. Pyrrolidinones are of interest due to their structural similarity to cyclic peptides.

Ab initio [15,16] and topological investigations [17,18] on pyrrolidin-2-one (i) + water or benzene or methyl benzene or *p*- or *m*-xylene or ethanol or propanol or butanol (j) binary mixtures have revealed that 2-Py is an associated molecular entity (mixture of cyclic and open dimers), and thermodynamic properties such as excess molar volumes, excess molar enthalpies, and excess isentropic compressibilities for these binary mixtures predicted by employing graph theory compare well with their corresponding experimental values. As a part of our experimental program on thermodynamic properties of binary and ternary mixtures containing 2-Py as a common constituent, we report here excess molar volumes, V^{E}, speeds of sound, u_{ijk}, of 2-Py (i) + benzene or methyl benzene (j) + propan-1-ol (k) ternary mixtures, and speeds of sound, u_{ij}, of benzene or methyl benzene (i) + propan-1-ol (j) binary mixtures at 308.15 K. An attempt has also been made to extend topological investigations of binary mixtures to ternary mixtures (using topology of the constituents) to obtain an expression that describes well their excess molar volumes and excess isentropic compressibilities.

2 Experimental

2.1 Materials

2-Py (Fluka), benzene, methyl benzene, and propan-1-ol (AR Grade) were purified by standard methods [19].

2.2 Methods

The purities of the component liquids were checked by measuring their densities with a pycnometer at (298.15 ± 0.01) K and the resulting densities (reported in Table 1) agreed to within $\pm 0.05\ \mathrm{kg \cdot m^{-3}}$ of their corresponding literature values [19,20].

Excess molar values, V^{E}_{ijk} for ternary mixtures were measured by means of a dilatometer as has been described elsewhere [21]. The dilatometer had three limbs for three components. The change in the liquid level of the dilatometer capillary was

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

Liquid	$\rho\left(\mathrm{kg \cdot m^{-3}}\right)$		$u\left(\mathrm{m \cdot s^{-1}}\right)$	
	Experimental	Literature	Experimental	Literature
2-Py	1107.26	1107.63 [20]	1603[a]	1603.1[a] [22]
Benzene	873.62	873.60 [19]	1298	1298.9 [23]
Methyl benzene	862.23	862.19 [19]	1305	1304.0 [24]
Propan-1-ol	799.28	799.60 [19]	1188	1188.8 [25]

[a] Value at 308.15 K

measured with a cathetometer that could read to ±0.001 cm. The temperature of the water thermostat was controlled to be better than ±0.01 K by means of a methyl benzene regulator. The uncertainty in the measured V^{E}_{ijk} values is 0.5 %.

The speed of sound was determined at a frequency of 2 MHz using a quartz crystal interferometer (Model-M 80, 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 speed-of-sound values for the component liquids at (298.15 ± 0.01) K (recorded in Table 1) is compared with their corresponding experimental values [22–25]. The uncertainty in the measured speed-of-sound measurements is 1 $\mathrm{m \cdot s^{-1}}$.

3 Results

Excess molar volumes, V^{E}_{ijk}, and speeds of sound, u_{ijk}, of 2-Py (i) + benzene or methyl benzene (j) + propan-1-ol (k) ternary mixtures and speeds of sound, u_{ij}, of their two subbinary mixtures of benzene or methyl benzene (i) + propan-1-ol as a function of composition at 308.15 K are recorded in Tables 2, 3, and 4, respectively. The isentropic compressibilities for binary, $(\kappa_S)_{ij}$, and ternary, $(\kappa_S)_{ijk}$, mixtures were determined using

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

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

The densities, ρ_{ijk}, of ternary mixtures were calculated from their experimental excess molar-volume data by employing the relation,

$$V^{\mathrm{E}}_{ijk} = \sum_{i=i}^{k} x_i M_i (\rho_{ijk})^{-1} - \sum_{i=i}^{k} x_i M_i (\rho_i)^{-1} \tag{3}$$

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

Table 2 Comparison of measured V_{ijk}^{E} values for the various $(i + j + k)$ ternary mixtures at 308.15 K; also included are the various parameters $V_{ijk}^{(n)}$ $(n = 0$ to 2) along with their standard deviation, $\sigma\left(V_{ijk}^{E}\right)$, interaction parameters χ^{*}, χ_{ij}', etc., and connectivity parameters of third degree, ${}^{3}\xi_{i}$ $(i = i$ to $k)$

x_i	x_j	$V_{ijk}^{E}\left(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}\right)$	
		Exptl	Graph
Pyrrolidin-2-one (i) + benzene (j) + propan-1-ol (k)[a]			
0.0536	0.9131	−0.093	−0.114
0.0686	0.8037	−0.072	−0.085
0.0986	0.6178	−0.059	−0.035
0.1083	0.7697	−0.168	−0.176
0.1223	0.6538	−0.136	−0.129
0.1427	0.5689	−0.143	−0.120
0.1684	0.5603	−0.196	−0.178
0.1931	0.1522	−0.089	−0.089
0.2276	0.1931	−0.124	−0.127
0.2506	0.2352	−0.162	−0.162
0.2767	0.2006	−0.180	−0.190
0.2911	0.3889	−0.317	−0.300
0.3012	0.2136	−0.210	−0.221
0.3123	0.4704	−0.401	−0.395
0.3501	0.3866	−0.389	−0.376
0.3849	0.2968	−0.363	−0.356
0.3965	0.1899	−0.284	−0.299
0.4182	0.4093	−0.485	−0.487
0.4513	0.3116	−0.443	−0.431
0.4791	0.2238	−0.376	−0.374
0.5058	0.1949	−0.364	−0.364
0.5313	0.1642	−0.349	−0.348
0.5736	0.1956	−0.398	−0.389
0.6045	0.1573	−0.367	−0.356
0.6326	0.1317	−0.343	−0.332
0.6839	0.0676	−0.289	−0.266
0.7127	0.1395	−0.348	−0.338
0.7501	0.0335	−0.249	−0.214
0.8046	0.1128	−0.288	−0.286
0.8133	0.0789	−0.245	−0.232
0.9096	0.0535	−0.153	−0.151
Prrolidin-2-one (i) + methyl benzene (j) + propan-1-ol (k)[b]			
0.0538	0.9212	−0.081	−0.030
0.0892	0.0614	−0.078	−0.080
0.0964	0.0680	−0.081	−0.079

Table 2 continued

x_i	x_j	$V_{ijk}^{\mathrm{E}}\left(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}\right)$	
		Exptl	Graph
0.1026	0.0721	−0.088	−0.084
0.1399	0.7593	−0.159	−0.057
0.1736	0.1284	−0.171	−0.172
0.2186	0.1407	−0.182	−0.184
0.2472	0.1594	−0.206	−0.200
0.2853	0.2354	−0.279	−0.157
0.3067	0.5185	−0.216	−0.213
0.3198	0.5316	−0.209	−0.245
0.3750	0.4225	−0.285	−0.276
0.4271	0.4192	−0.282	−0.348
0.4698	0.3407	−0.361	−0.363
0.5146	0.3048	−0.392	−0.390
0.5491	0.2756	−0.405	−0.403
0.5740	0.1699	−0.423	−0.404
0.6047	0.1505	−0.414	−0.407
0.6410	0.1348	−0.402	−0.401
0.6488	0.2145	−0.412	−0.415
0.6507	0.1837	−0.408	−0.401
0.6942	0.1672	−0.395	−0.391
0.7659	0.1063	−0.336	−0.333
0.7801	0.1129	−0.327	−0.329
0.7917	0.0700	−0.289	−0.302
0.8192	0.0658	−0.265	−0.273
0.8508	0.0734	−0.247	−0.249
0.8701	0.0583	−0.215	−0.218
0.8852	0.0629	−0.205	−0.209
0.9411	0.0372	−0.120	−0.125

[a] $V_{ijk}^{(0)} = -0.773\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V_{ijk}^{(1)} = -18.308\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V_{ijk}^{(2)} = 60.091\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\sigma\left(V_{ijk}^{\mathrm{E}}\right) = 0.003\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $({}^3\xi_i) = 1.001$; $({}^3\xi_j) = 0.666$; $({}^3\xi_k) = 1.451$; $\chi^* = -0.583\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi'_{ij} = -1.258\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi'_{jk} = 1.593\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi'_{ik} = -0.500\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$

[b] $V_{ijk}^{(0)} = 1.116\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V_{ijk}^{(1)} = 27.272\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V_{ijk}^{(2)} = 335.094\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\sigma\left(V_{ijk}^{\mathrm{E}}\right) = 0.004\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $({}^3\xi_i) = 1.001$; $({}^3\xi_j) = 0.840$; $({}^3\xi_k) = 1.451$; $\chi^* = -2.325\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi'_{ij} = -0.458\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi'_{jk} = 2.808\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi'_{ik} = -0.931\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$

Table 3 Speed of sound, u_{ij}, isentropic compressibilities, $(\kappa_S)_{ij}$, and excess isentropic compressibilities, $\left(\kappa_S^{\mathrm{E}}\right)_{ij}$, for the various $(i + j)$ binary mixtures as a function of composition, x_i, mole fraction of component i at 308.15 K

x_i	u_{ij} (m · s^{-1})	$(\kappa_S)_{ij}$ (TPa^{-1})	$\left(\kappa_S^{\mathrm{E}}\right)_{ij}$ (TPa^{-1})
Benzene (i) + propan-1-ol (j)[a]			
0.0852	1192	882.9	4.5
0.1733	1196	870.3	8.3
0.2644	1200	857.4	11.8
0.3059	1201	851.9	13.6
0.3586	1203	844.9	15.7
0.3995	1204	840.2	17.9
0.4561	1206	833.6	20.8
0.5274	1208	825.4	24.2
0.5820	1210	819.5	27.0
0.6618	1213	809.7	29.7
0.7267	1216	800.8	30.7
0.7703	1219	793.6	30.0
0.8830	1233	769.5	22.2
0.9335	1242	755.0	14.9
Methyl benzene (i) + propan-1-ol (j)[b]			
0.0724	1193	880.9	2.0
0.1494	1199	867.2	4.1
0.2314	1204	853.5	6.3
0.3190	1209	839.8	8.4
0.3586	1211	833.8	9.3
0.4352	1216	822.6	10.8
0.5131	1220	811.6	12.0
0.5724	1224	803.2	12.4
0.6211	1227	796.5	12.7
0.6846	1231	787.2	12.2
0.7376	1235	779.5	11.6
0.7829	1239	772.5	10.5
0.8635	1247	759.7	7.7
0.9243	1253	749.6	4.8

Also included are various parameters, $\left(\kappa_S^{(n)}\right)_{ij}$ ($n = 0$ to 2), along with their standard deviation, $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ij}$

[a] $\left(\kappa_S^{(0)}\right)_{ij} = 91.8\,\mathrm{TPa}^{-1}$, $\left(\kappa_S^{(1)}\right)_{ij} = 102.9\,\mathrm{TPa}^{-1}$, $\left(\kappa_S^{(2)}\right)_{ij} = 76.9\,\mathrm{TPa}^{-1}$, $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ij} = 0.2\,\mathrm{TPa}^{-1}$

[b] $\left(\kappa_S^{(0)}\right)_{ij} = 47.6\,\mathrm{TPa}^{-1}$, $\left(\kappa_S^{(1)}\right)_{ij} = 24.4\,\mathrm{TPa}^{-1}$, $\left(\kappa_S^{(2)}\right)_{ij} = 1.9\,\mathrm{TPa}^{-1}$, $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ij} = 0.1\,\mathrm{TPa}^{-1}$

Table 4 Speed of sound, u_{ijk}, isentropic compressibilities, $(\kappa_S)_{ijk}$, and excess isentropic compressibilities, $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$, for the various $(i+j+k)$ ternary mixtures as a function of composition, x_i, mole fraction of component i at 308.15 K with $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values evaluated from graph theory

x_i	x_j	$u_{ijk}\left(\mathrm{m\cdot s^{-1}}\right)$	$(\kappa_S)_{ijk}\left(\mathrm{TPa^{-1}}\right)$	$\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ $(\mathrm{TPa^{-1}})$	
				Exptl.	Graph
Pyrrolidin-2-one (i) + benzene (j) + propan-1-ol (k)[a]					
0.0926	0.8862	1280	691.7	−11.0	−9.9
0.1138	0.8281	1279	690.8	−10.9	−16.7
0.1397	0.0549	1239	775.0	−33.2	−42.8
0.1585	0.4799	1278	698.5	−30.9	−54.5
0.1894	0.7325	1298	658.6	−20.0	−25.1
0.1984	0.0424	1260	734.7	−44.3	−46.3
0.2341	0.3279	1307	658.3	−55.4	−47.2
0.2778	0.6655	1326	616.6	−28.2	−28.0
0.2901	0.3084	1331	623.0	−65.0	−68.3
0.3006	0.0858	1304	658.4	−58.3	−62.8
0.3463	0.2581	1353	594.3	−71.8	−70.1
0.3827	0.5615	1356	573.8	−33.4	−33.5
0.3991	0.2243	1373	568.3	−75.2	−69.8
0.4017	0.0859	1346	596.9	−65.2	−65.1
0.4295	0.2319	1388	550.2	−76.5	−68.0
0.4515	0.3552	1394	537.6	−61.6	−55.3
0.4802	0.4109	1393	532.2	−45.5	−45.1
0.4990	0.0427	1383	549.7	−65.9	−57.4
0.5412	0.1933	1434	499.0	−74.8	−61.7
0.5730	0.2675	1443	486.0	−62.0	−52.2
0.5975	0.1851	1457	475.4	−70.0	−56.4
0.6050	0.0863	1442	487.3	−65.9	−56.8
0.6615	0.1340	1479	454.3	−64.0	−51.5
0.7193	0.1759	1500	433.2	−49.8	−40.9
0.7514	0.0584	1505	429.1	−50.6	−40.5
0.7737	0.0630	1516	420.1	−47.3	−37.8
0.8155	0.0746	1535	404.7	−39.4	−31.8
0.8615	0.0867	1553	390.2	−27.9	−23.5
0.8689	0.0755	1555	388.6	−27.4	−22.7
0.9073	0.0525	1568	378.4	−19.2	−16.8
Pyrrolidin-2-one (i) + methyl benzene (j) + propan-1-ol (k)[b]					
0.0923	0.8714	1291	690.3	−24.0	−31.0
0.1069	0.8485	1293	685.5	−25.7	−35.6
0.1126	0.0659	1232	789.8	−30.5	−34.8
0.1315	0.8014	1298	677.4	−28.6	−46.7

Table 4 continued

x_i	x_j	$u_{ijk}\left(\mathrm{m\cdot s^{-1}}\right)$	$(\kappa_S)_{ijk}\left(\mathrm{TPa^{-1}}\right)$	$\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ ($\mathrm{TPa^{-1}}$)	
				Exptl	Graph
0.1879	0.7701	1317	648.4	−37.5	−37.3
0.2153	0.7847	1353	607.8	−56.6	−53.5
0.2439	0.1012	1295	680.3	−64.2	−64.0
0.2857	0.6431	1332	619.6	−38.6	−45.1
0.3113	0.6251	1339	608.7	−39.9	−39.6
0.3436	0.1345	1348	606.4	−81.2	−88.6
0.3723	0.5529	1349	591.0	−37.4	−37.1
0.4074	0.0730	1364	581.1	−81.3	−74.6
0.4165	0.1011	1375	569.5	−85.4	−85.9
0.4211	0.5176	1363	571.2	−38.8	−24.3
0.4402	0.4583	1361	570.3	−37.0	−40.9
0.4681	0.1034	1399	541.3	−86.5	−91.0
0.4889	0.1056	1409	530.6	−86.2	−92.4
0.5025	0.0360	1396	538.2	−77.6	−75.2
0.5145	0.3689	1385	540.4	−39.7	−39.9
0.5378	0.0964	1427	508.9	−83.4	−92.4
0.5625	0.2935	1409	515.6	−47.7	−47.8
0.5816	0.0512	1436	496.5	−77.0	−88.2
0.6136	0.0733	1455	479.0	−75.5	−89.3
0.6214	0.2131	1443	484.4	−55.9	−55.6
0.6856	0.1235	1478	453.8	−60.5	−67.3
0.7404	0.1517	1486	441.9	−41.9	−30.1
0.7942	0.0834	1515	419.1	−41.3	−45.7
0.8738	0.0737	1542	395.8	−22.8	−10.5
0.8953	0.0564	1552	388.7	−19.5	−12.1
0.9382	0.0303	1572	374.4	−11.9	−9.8

Also included are various parameters, $\left(\kappa_S^{(n)}\right)_{ijk}$ ($n = 0$ to 2), along with their standard deviation, $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$, the interaction parameters χ'_{ij}, χ^*, etc., and $({}^3\xi_i)$ ($i = i$ to k)

[a] $\left(\kappa_S^{(0)}\right)_{ijk} = -735.8\,\mathrm{TPa^{-1}}$, $\left(\kappa_S^{(1)}\right)_{ijk} = 832.2\,\mathrm{TPa^{-1}}$, $\left(\kappa_S^{(2)}\right)_{ijk} = 24018.7\,\mathrm{TPa^{-1}}$, $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ijk} = 0.1\,\mathrm{TPa^{-1}}$; $\chi^* = -81.7\,\mathrm{TPa^{-1}}$; $\chi'_{ij} = -36.0\,\mathrm{TPa^{-1}}$; $\chi'_{jk} = -169.4\,\mathrm{TPa^{-1}}$; $\chi'_{ik} = -81.4\,\mathrm{TPa^{-1}}$

[b] $\left(\kappa_S^{(0)}\right)_{ijk} = -355.4\,\mathrm{TPa^{-1}}$, $\left(\kappa_S^{(1)}\right)_{ijk} = 6378.8\,\mathrm{TPa^{-1}}$, $\left(\kappa_S^{(2)}\right)_{ijk} = 12754.5\,\mathrm{TPa^{-1}}$, $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ijk} = 0.4\,\mathrm{TPa^{-1}}$; $\chi^* = 510.8\,\mathrm{TPa^{-1}}$; $\chi'_{ij} = -107.9\,\mathrm{TPa^{-1}}$; $\chi'_{jk} = -409.3\,\mathrm{TPa^{-1}}$; $\chi'_{ik} = -304.7\,\mathrm{TPa^{-1}}$

Excess isentropic compressibilities for binary and ternary mixtures were determined using

$$(\kappa_S^{\mathrm{E}})_{ij} = (\kappa_S)_{ij} - (\kappa_S^{\mathrm{id}})_{ij} \tag{4}$$

$$(\kappa_S^{\mathrm{E}})_{ijk} = (\kappa_S)_{ijk} - (\kappa_S^{\mathrm{id}})_{ijk} \tag{5}$$

κ_S^{id} for binary and ternary mixtures was obtained according to Benson and Kiyohara [26],

$$\kappa_S^{\mathrm{id}} = \sum_i^{j \text{ or } k} \phi_i \left[\kappa_{S,i} + \frac{T V_i \alpha_i^2}{C_{p,i}} \right] - T \left(\sum_i^{j \text{ or } k} x_i V_i \right) \frac{\left(\sum_i^{j \text{ or } k} \phi_i \alpha_i \right)^2}{\left(\sum_i^{j \text{ or } k} x_i C_{p,i} \right)} \tag{6}$$

where ϕ_i is the volume fraction of component i in the mixture referred to as the unmixed state, x_i is the corresponding mole fraction, T is the absolute temperature, and $\kappa_{S,i}$, V_i, α_i, and $C_{p,i}$ are the isentropic compressibility, molar volume, thermal expansion coefficient, and molar heat capacity of pure component i, respectively. The values of α_i and $C_{p,i}$ were taken from the literature [27]. The α value for 2-Py was evaluated in the same manner as suggested by Hildebrand et al. [28]. The resulting $\left(\kappa_S^{\mathrm{E}}\right)_{ij}$ and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values for the studied binary and ternary mixtures are recorded in Tables 3 and 4. V_{ijk}^{E} and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values for the investigated ternary mixtures are plotted in Figs. 1, 2, 3, and 4. $\left(\kappa_S^{\mathrm{E}}\right)_{ij}$ values for binary mixtures and V_{ijk}^{E} and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values for the investigated ternary mixtures were fitted, respectively, with

$$\left(\kappa_S^{\mathrm{E}}\right)_{ij} = x_i x_j \left[\sum_{n=0}^{2} \kappa_S^{(n)} (2x_i - 1)^n \right] \tag{7}$$

$$\begin{aligned} X_{ijk}^{\mathrm{E}}(X = V \text{ or } \kappa_S) = {} & x_i x_j \left[\sum_{n=0}^{2} X_{ij}^{(n)} (x_i - x_j)^n \right] + x_j x_k \left[\sum_{n=0}^{2} X_{jk}^{(n)} (x_j - x_k)^n \right] \\ & + x_i x_k \left[\sum_{n=0}^{2} X_{ik}^{(n)} (x_k - x_i)^n \right] \\ & + x_i x_j x_k \left[\sum_{n=0}^{2} X_{ijk}^{(n)} (x_j - x_k)^n x_i^n \right] \end{aligned} \tag{8}$$

where x_i and x_j are the mole fractions of the ith and jth components of $(i + j + k)$ ternary mixtures; $X_{ij}^{(n)}$ $(n = 0 - 2)$, etc. $(X = V \text{ or } \kappa_S)$ are the parameters characteristic of $(i + j)$, $(j + k)$, and $(i + k)$ binary mixtures and have been taken from the literature [17,18,29]. $\kappa_S^{(n)}$ and $X_{ij}^{(n)}$ $(X = V \text{ or } \kappa_S)$, parameters characteristic of binary and ternary mixtures, were determined by the least-squares method and are recorded along with their standard deviations, $\sigma\left(X^{\mathrm{E}}\right)_{ijk}$ $(X = V \text{ or } \kappa_S)$ in Tables 2 and 4, respectively.

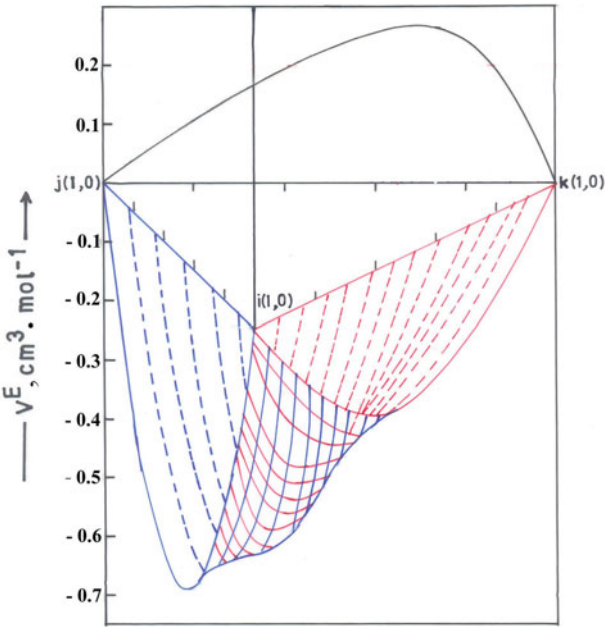

Fig. 1 Excess molar volumes, V^{E}, for 2-Py (i) + benzene (j) + propan-1-ol (k) ternary mixture at 308.15 K; —, the experimental data in front of the plane; − − −, the experimental data behind the plane

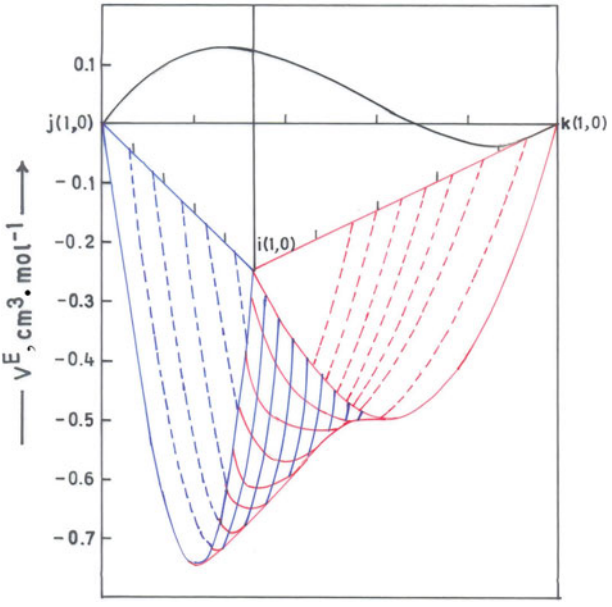

Fig. 2 Excess molar volumes, V^{E}, for 2-Py (i) + methyl benzene (j) + propan-1-ol (k) ternary mixture at 308.15 K; —, the experimental data in front of the plane; − − −, the experimental data behind the plane

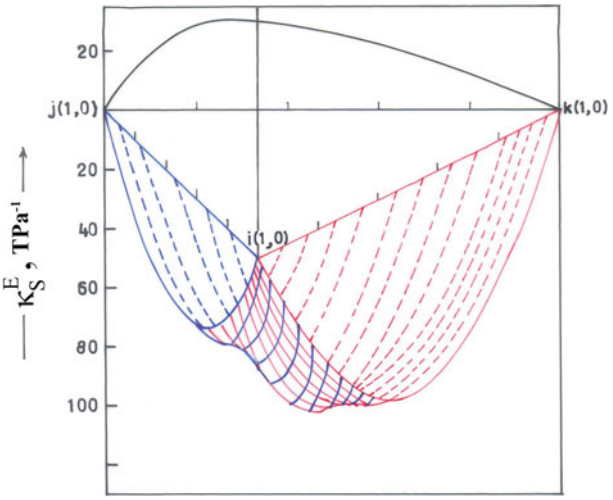

Fig. 3 Excess isentropic compressibilities, κ_S^E, for 2-Py (i) + benzene (j) + propan-1-ol (k) ternary mixture at 308.15 K; —, the experimental data in front of the plane; − − −, the experimental data behind the plane

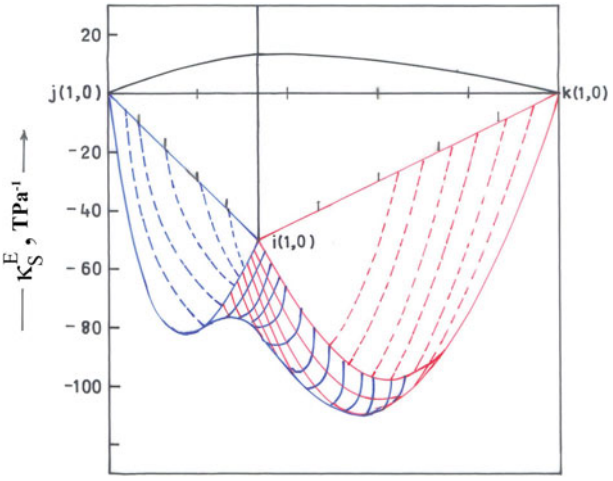

Fig. 4 Excess isentropic compressibilities, κ_S^E, for 2-Py (i) + methyl benzene (j) + propan-1-ol (k) ternary mixture at 308.15 K; —, the experimental data in front of the plane; − − −, the experimental data behind the plane

4 Discussion

We are unaware of any published V_{ijk}^E, $\left(\kappa_S^E\right)_{ij}$, and $\left(\kappa_S^E\right)_{ijk}$ data for the investigated mixtures with which to compare our results. V_{ijk}^E and $\left(\kappa_S^E\right)_{ijk}$ values for the studied mixtures are negative over the entire composition range and suggest that benzene gives a relatively more packed arrangement on the 2-Py:propan-1-ol molecular entity

as compared to methyl benzene. This may be due to the presence of the $-CH_3$ group in methyl benzene which restricts the approach of the methyl benzene molecule to the 2-Py:propan-1-ol molecular entity.

4.1 Graph Theory and Results

Our earlier studies on 2-Py $(i)+$ benzene or methyl benzene or propan-1-ol (j) binary mixtures have suggested [17,18] that while 2-Py and propan-1-ol exist as an associated molecular entity, benzene and methyl benzene exist as monomers, and 2-Py $(i)+$benzene or methyl benzene (j) mixture formation involves the processes: (i) establishment of $i_n - j$ unlike contact formation between i_n and j molecules; (ii) unlike contact formation $(i_n - j)$ cause depolymerization of i_n; and (iii) monomers of i and j then undergo specific interactions to form $i : j$ molecular entity. The overall change in thermodynamic properties, excess molar enthalpies $\left(H^{\mathrm{E}}\right)$, and excess isentropic compressibilities (X^{E}, $X = H$ or κ_S) due to these processes were expressed by

$$X^{\mathrm{E}}(X = H \text{ or } \kappa_S) = \sum_{i=i}^{k} \Delta X_i = \frac{x_i x_j \left({}^3\xi_i / {}^3\xi_j\right)}{x_i + x_j \left({}^3\xi_i / {}^3\xi_j\right)} \left[(1 + x_i)\chi'_{ij} + x_j \chi_{12}\right] \quad (9)$$

Furthermore, thermodynamic and topological investigations of 2-Py $(i)+$propan-1-ol (j) binary mixtures have revealed that processes involved in mixture formation are (1) establishment of unlike $i_n - j_n$ contacts; (2) unlike contact formation that weaken $i_n - j_n$ contacts, which leads to their depolymerization; and (3) monomers of i and j then undergo specific interactions to form $i : j$ molecular entity. Thermodynamic properties (X^{E}, $X = H$ or κ_S) for 2-Py $(i)+$propan-1-ol (j) mixtures were then expressed by the relation,

$$X^{\mathrm{E}}(X = V \text{ or } H) = \left[\left(1 + x_j\right) \chi'_{ij} + 2x_i \chi^*\right] \quad (10)$$

where χ'_{ij}, χ_{12}, etc. are the molar volume and enthalpy interaction parameters of unlike $i - j$ contacts and specific interactions, respectively between (i) and (j) components of $(i + j)$ binary mixtures. H^{E} and κ_S^{E} data predicted for these $(i + j)$ binary mixtures were in good agreement with their corresponding experimental values, which lends additional support to the assumptions made in deriving Eqs. 9 and 10.

If a third component such as propan-1-ol is added to 2-Py $(i)+$benzene or methyl benzene (j) binary mixtures, then 2-Py $(i)+$benzene or methyl benzene $(j)+$propan-1-ol (k) ternary mixtures would involve the following processes: (1) the establishment of (a) $i_n - j$, (b) $j - k_n$, and (c) $i_n - k_n$ unlike contacts; (2) formation of unlike contacts would then depolymerize i_n and k_n to form their respective monomers; and (3) specific interactions between monomers i, j, and k form $i : j$, $j : k$ molecular entities. If χ'_{ij}, χ'_{jk}, and χ'_{ik} are the molar volume and molar compressibility interaction parameters of unlike $(i - j)$, $(j - k)$, and $(i - k)$ contacts, then the change in molar properties (X^{E}, $X = V$ or κ_S) due to processes 1(a)–(c) can be expressed by the relation [30,31],

$$\Delta X_1 = x_i \chi'_{ij} S_j + x_j \chi'_{jk} S_k + x_k \chi'_{ik} S_i \tag{11}$$

where S_i, etc. are defined by $S_i = x_i v_i / \sum x_i v_i$, where v_i is the molar volume of component i. Therefore, Eq. 11 reduces to

$$\Delta X_1 = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right] \chi'_{ij} + \left[\frac{x_j x_k v_k}{\sum x_j v_j}\right] \chi'_{jk} + \left[\frac{x_k x_i v_i}{\sum x_k v_k}\right] \chi'_{ik} \tag{12}$$

Also, if χ'_{ii}, χ'_{kk}, χ_{12}, χ'_{12}, and χ''_{12} are the molar volume and compressibility interaction parameters for $i-i$, $k-k$ like contacts and specific interactions (leading to the formation of $i:j$, $j:k$, and $i:k$ molecular entities), then the change in molar properties, ΔX ($X = V$ or κ_S), due to processes (2) and (3) would be expressed [30–32] by

$$\Delta X_2 = x_i^2 x_j v_j \chi'_{ii} / \sum_{i=i}^{j} x_i v_i \tag{13}$$

$$\Delta X_3 = x_i x_k v_k \chi'_{kk} / \sum_{i=i}^{j} x_i v_i \tag{14}$$

$$\Delta X_4 = x_i x_j^2 v_j \chi_{12} / \sum x_i v_i \tag{15}$$

$$\Delta X_5 = x_j x_k^2 v_k \chi'_{12} / \sum x_j v_j \tag{16}$$

$$\Delta X_6 = x_k x_i^2 v_i \chi''_{12} / \sum x_k v_k \tag{17}$$

The overall changes in the thermodynamic property, X^{E} ($X = V$ or κ_S) due to processes 1(a)–(c), 2, and 3 then can be expressed by

$$X^{\mathrm{E}} = \sum_{i=1}^{6} \Delta X_i = \left[\frac{x_i x_j v_j}{\sum_{i=i}^{j} x_i v_i}\right] \left[\chi'_{ij} + x_i \chi'_{ii} + x_j \chi_{12}\right] + \left[\frac{x_j x_k v_k}{\sum_{j=j}^{k} x_j v_j}\right] \left[\chi'_{jk} + x_k \chi'_{12}\right] + \left[\frac{x_i x_k v_i}{\sum_{k=k}^{i} x_k v_k}\right] \left[x_k + x_i \chi''_{12} + x_k \chi'_{kk}\right] \tag{18}$$

The connectivity parameter of third degree, ${}^3\xi$, is defined [33,34] by

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

where δ_m^v, etc., values reflect the valency of the atoms forming the bond and are expressed [34] as $\delta^v = Z_m - h$, where Z_m is the maximum valency of the atom and h is the number of hydrogen atoms attached to it. Consequently, for carbon in $-CH_2$ (δ^v [C]) $= 4 - 2 = 2$.

Singh et al. [5] have postulated that the $({}^3\xi)^{-1}$ value of a molecule represents a measure of probability that the surface area of a molecule interacts effectively with the surface area of another molecule and is related to its molar volume by the relation, ${}^3\xi = (v)^{-1}$, where v is the molar volume.

Therefore, if $v_j/v_i = {}^3\xi_i/{}^3\xi_j$ [5], Eq. 18 thus reduces to

$$X^{\mathrm{E}} = \sum_{i=1}^{6} \Delta X_1 = \left[\frac{x_i x_j \left({}^3\xi_i/{}^3\xi_j\right)}{x_i + x_j \left({}^3\xi_i/{}^3\xi_j\right)}\right]\left[\chi'_{ij} + x_i \chi'_{ii} + x_j \chi_{12}\right] + \left[\frac{x_j x_k \left({}^3\xi_j/{}^3\xi_k\right)}{x_j + x_k \left({}^3\xi_j/{}^3\xi_k\right)}\right]\left[\chi'_{jk} + x_k \chi'_{12}\right] + \left[\frac{x_i x_k \left({}^3\xi_i/{}^3\xi_k\right)}{x_i + x_k \left({}^3\xi_i/{}^3\xi_k\right)}\right]\left[x_k + x_i \chi''_{12} + x_k \chi'_{kk}\right] \tag{19}$$

For the investigated mixtures, if it is assumed that $\chi'_{ij} \cong \chi_{12}$; $\chi'_{ik} \cong \chi''_{12}$; $\chi'_{jk} \cong \chi'_{12}$; $\chi'_{ii} \cong \chi'_{kk} \cong \chi^*$, then Eq. 19 can be written as

$$X^{\mathrm{E}} = \sum_{i=1}^{6} \Delta X_i = \left[\frac{x_i x_j \left({}^3\xi_i/{}^3\xi_j\right)}{x_i + x_j \left({}^3\xi_i/{}^3\xi_j\right)}\right]\left[\left(1 + x_j\right)\chi'_{ij} + x_i \chi^*\right] + \left[\frac{x_j x_k \left({}^3\xi_j/{}^3\xi_k\right)}{x_j + x_k \left({}^3\xi_j/{}^3\xi_k\right)}\right]\left[\left(1 + x_k\right)\chi'_{jk}\right] + \left[\frac{x_i x_k \left({}^3\xi_i/{}^3\xi_k\right)}{x_i + x_k \left({}^3\xi_i/{}^3\xi_k\right)}\right]\left[\left(1 + x_i\right)\chi'_{ik} + x_k \chi^*\right] \tag{20}$$

Equation 20 contains four unknown parameters, χ^*, χ'_{ij}, χ'_{jk}, and χ'_{ik}, and were predicted by employing experimental V^{E}_{ijk} and $\left(\kappa^{\mathrm{E}}_S\right)_{ijk}$ data of the investigated $(i+j+k)$ ternary mixtures at four compositions. These parameters were then subsequently utilized to predict X^{E} ($X = V$ or κ_S) values at other values of x_i and x_j. Such predicted V^{E}_{ijk} and $\left(\kappa^{\mathrm{E}}_S\right)_{ijk}$ values along with χ^*, χ'_{ij}, etc. parameters for the studied ternary mixtures are recorded in Tables 2 and 4, respectively.

Examination of Tables 2 and 3 data reveals that predicted V^{E}_{ijk} and $\left(\kappa^{\mathrm{E}}_S\right)_{ijk}$ compare well with their experimental values. This lends additional support to the assumptions made in deriving Eq. 19. Even in those cases where agreement between experimental and calculated values is not good, the predicted values are of the same sign as the experimental values. This may be due to the presence of ternary $i - j - k$ contacts which have not been presently considered.

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References

1. S.C. Basak, L.J. Monsrud, M.E. Rosen, C.M. Frane, V.R. Mangusen, Acta Pharm. Yagosl. **36**, 81 (1986)
2. Z. Mihalic, N. Trinajstic, J. Chem. Educ. **69**, 701 (1992)
3. N. Trinajstic, *Chemical Graph Theory* (CRC Press, Boca Raton, FL, 1992)
4. J. Deviller, A.T. Balaban, *Topological Indices and Related Described in QSAR and QSPR* (Gordon and Breach, The Netherlands, 1999)
5. P.P. Singh, R.K. Nigam, K.C. Singh, V.K. Sharma, Thermochim. Acta **46**, 175 (1981)
6. H.P. Dahiya, P.P. Singh, S. Dagar, Fluid Phase Equilib. **33**, 191 (1987)
7. V.K. Sharma, S.P. Sharma, S. Aggarwal, Indian J. Chem. **31A**, 398 (1992)
8. V.K. Sharma, R. Arora, R. Sharma, Indian J. Chem. **40A**, 1277 (2001)
9. P.P. Singh, V.K. Sharma, Z. Phys. Chemie (Leipzig) **5**, 915 (1984)
10. P.P. Singh, R. Malik, S. Maken, W.E. Acree Jr., S.A. Tucker, Thermochim. Acta **162**, 291 (1990)
11. V.K. Sharma, R. Sharma, Can. J. Chem. **79**, 1910 (2001)
12. V.K. Sharma, R. Sharma, S. Kumar, Indian J. Chem. **42A**, 1379 (2003)
13. V.K. Sharma, S. Kumar, Thermochim. Acta **428**, 83 (2005)
14. D. Sharma, J.S. Yadav, K.C. Singh, V.K. Sharma, J. Solution Chem. **37**, 1099 (2008)
15. H. Yekeler, A. Guven, R. Ozkan, J. Comput. Aided Mol. Des. **13**, 589 (1999)
16. H. Yekeler, J. Comput. Aided Mol. Des. **15**, 287 (2001)
17. J.S. Yadav, D. Sharma, V.K. Sharma, Thermochim. Acta **489**, 45 (2009)
18. J.S. Yadav, D. Sharma, V.K. Sharma, Thermochim. Acta **493**, 19 (2008)
19. J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvents Physical Properties and Methods of Purification*, 4th edn. (Wiley, New York, 1986)
20. P.L. Pirlia-Honkanen, P.A. Ruostesuo, J. Chem. Eng. Data **32**, 303 (1987)
21. P.P. Singh, S.P. Sharma, J. Chem. Eng. Data **30**, 477 (1985)
22. J. George, N.V. Sastry, J. Chem. Eng. Data **49**, 235 (2004)
23. K. Tamura, S. Murakami, S. Doi, J. Chem. Thermodyn. **17**, 325 (1985)
24. C.M. Sehgal, B.R. Porter, J.F. Greenleaf, J. Acoust. Soc. Am. **79**, 586 (1986)
25. T.S. Rao, N. Veeraiah, C. Rambabu, Indian J. Chem. **41A**, 2268 (2002)
26. G.C. Benson, O. Kiyohara, J. Chem. Thermodyn. **11**, 1061 (1979)
27. R.C. Weast (ed.), *CRC Handbook of Chemistry and Physics*, 68th edn. (CRC Press, Boca Raton, FL, 1987)
28. J.H. Hildebrand, J.M. Prusnitz, R.L. Scott, *Regular and Related Solutions* (Van-Nostrand Reinheld, New York, 1971)
29. V. Gupta, Ph.D. Thesis, Maharshi Dayanand University, Rohtak, India, 1996
30. M.L. Huggins, J. Phys. Chem. **74**, 371 (1970)
31. M.L. Huggins, Polymer **12**, 387 (1971)
32. P.P. Singh, M. Bhatia, J. Chem. Soc. Faraday Trans. 1 **85**, 3807 (1989)
33. P.P. Singh, Thermochim. Acta **66**, 37 (1983)
34. L.B. Kier, S.H. Yalkowasky, A.A. Sinkula, S.C. Valvani, *Physico-Chemical Properties of Drugs* (Mercel Dekker, New York, 1980)