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Excess molar volumes and excess isentropic compressibilities of 2-pyrrolidinone at 308.15 K

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ABSTRACT

Molar excess volumes V^E_{ijk} and speeds of sound, u_{ijk} of 2-pyrrolidinone (i) + benzene (j) + toluene or o- or p-xylene (k) ternary mixtures have been measured as a function of composition at 308.15 K. The observed speeds of sound data have been utilized to calculate their excess isentropic compressibilities. The observed data have been fitted to Redlich–Kister equation to calculate ternary adjustable parameters and standard deviations. Molar excess volumes, V^E_{ijk} and excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$ data for the investigated mixtures have been analyzed in terms of Graph theory and Flory theory. It has been observed that V^E_{ijk} and $(\kappa^E_S)_{ijk}$ values calculated by Graph theory compare well with their corresponding experimental values.

1. Introduction

A ternary (i + j + k) mixture is assumed to consist of its (i + j), (j + k) and (i + k) sub-binary mixtures. Thermodynamic properties of ternary mixtures can thus be calculated by employing thermodynamic properties of their sub-binary mixtures. Topological investigations [1] of 2-pyrrolidinone + benzene or toluene or o- or p-xylene binary mixtures and ab initio calculation [2] on the different associated structures of 2-pyrrolidinone with water reveal that 2-pyrrolidinone mainly exist as a mixture of open and cyclic dimer. Further, Graph theory (which involves the topology of the constituents of mixtures) describes well the molar excess volumes, molar excess enthalpies and excess isentropic compressibilities of 2-pyrrolidinone (i) + aromatic hydrocarbons (j) binary mixtures. It would, therefore, be of interest to see how well Graph theory calculate the molar excess volumes and excess isentropic compressibilities of ternary mixtures when a third component like toluene or o- or p-xylene (k) is added to 2-pyrrolidinone (i) + benzene (j) binary mixtures. These considerations prompted us to measure molar excess volumes and speeds of sound of 2-pyrrolidinone (i) + benzene (j) + toluene or o- or p-xylene (k) ternary mixtures.

2. Experimental

2.1. Materials

2-Pyrrolidinone (**2-Py**) (Fluka), benzene, toluene, o- and p-xylene (AR Grade) were purified by standard methods [3].

2.2. Methods

The purities of the purified liquids were checked by measuring their densities with a bicapillary pycknometer (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 $\pm 0.05\,\mathrm{kg\,m^{-3}}$ of their corresponding literature values [3,4].

Molar excess volumes, V^E_{ijk} for ternary mixture were measured in a dilatometer in the manner described elsewhere [5]. The dilatometer had three limbs for three components. The change in liquid level of dialatometer capillary was measured with a cathetometer that could read to ±0.001 cm. The uncertainty in the measured V^E_{ijk} values is ±0.5 percent.

The speed of sound at frequency 2 MHz was determined using a quartz crystal interferometer (Model-M 84, Mittal Enterprises, New Delhi, India). 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 [6–10]. The uncertainty in measured speeds of sound measurement is ±1 m/s.

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Table 1
Comparison of densities, ρ; speeds of sound, u; thermal expansion coefficients, α and molar heat capacities, C_p of pure liquids with their literature values at 298.15 K.

Liquid	ρ (kg m^{-3})		u (ms^{-1})		$\alpha \times 10^3$ (K^{-1})	C_p (Joule)
	Experimental	Literature	Experimental	Literature		
2-Pyrrolidinone	1107.3	1107.22[4]	1603[a]	1603.1[a6]	0.732	169.37
Benzene	873.62	873.60[3]	1298	1298.9[7]	1.252	135.76
Toluene	862.23	862.19[3]	1305	1304.0[8]	1.085	157.29
o-Xylene	875.91	875.94[3]	1344	1345.0[9]	0.995	188.07
p-Xylene	858.68	856.61[3]	1310	1309.6[10]	1.060	187.66

[a] Values at 308.15 K.

3. Results

Molar excess volumes, V^E_{ijk} and speeds of sound, u_{ijk} data of **2-Py** (i) + benzene (j) + toluene or o- or p-xylene (k) ternary mixtures over entire composition range at 308.15 K are recorded in Tables 2 and 3, respectively. The isentropic compressibilities $(\kappa_S)_{ijk}$

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

2-Pyrrolidinone (i) + benzene (j) + toluene (k)

x_i	x_j	V^E_{ijk} (cm^3 mol^{-1}) Exptl	Graph	Flory
0.0648	0.8352	−0.121	−0.138	−0.430
0.0759	0.0464	−0.095	−0.052	−0.412
0.1027	0.7635	−0.206	−0.225	−0.638
0.1198	0.0401	−0.164	−0.141	−0.613
0.1261	0.4663	−0.159	−0.103	−0.834
0.1315	0.0527	−0.178	−0.147	−0.659
0.1393	0.1982	−0.145	−0.026	−0.683
0.1691	0.5517	−0.295	−0.260	−0.881
0.1837	0.6653	−0.415	−0.425	−0.996
0.2089	0.3642	−0.249	−0.236	−0.967
0.2334	0.4632	−0.381	−0.382	−1.079
0.2463	0.2684	−0.280	−0.292	−1.050
0.2515	0.0476	−0.370	−0.342	−1.024
0.2997	0.1359	−0.396	−0.385	−1.129
0.3073	0.6133	−0.685	−0.688	−1.349
0.3605	0.5646	−0.763	−0.743	−1.408
0.3974	0.5675	−0.716	−0.772	−1.451
0.4032	0.1068	−0.528	−0.522	−1.223
0.4120	0.5136	−0.812	−0.769	−1.426
0.4753	0.3729	−0.745	−0.740	−1.354
0.5146	0.4395	−0.778	−0.780	−1.383
0.5279	0.3387	−0.737	−0.740	−1.312
0.5342	0.3824	−0.799	−0.761	−1.334
0.5794	0.0698	−0.594	−0.615	−1.123
0.6148	0.3145	−0.709	−0.710	−1.205
0.6470	0.2895	−0.665	−0.682	−1.140
0.6897	0.2128	−0.556	−0.614	−1.015
0.7086	0.2179	−0.551	−0.599	−0.979
0.8429	0.0567	−0.316	−0.372	−0.546
0.8972	0.0620	−0.218	−0.253	−0.383

$V^{(0)}_{ijk} = 1.270$; $V^{(1)}_{ijk} = -44.757$; $V^{(2)}_{ijk} = -333.435$; $\sigma(V^E_{ijk}) = 0.004$
$(^3\xi_i) = 1.001$; $(^3\xi_j) = 0.666$; $(^3\xi_k) = 0.840$;
$\chi^* = -1.723$; $\chi'_{ij} = -0.043$; $\chi'_{jk} = 1.542$; $\chi'_{ik} = -1.753$
$\chi^*_{ij} = -4.405$; $\chi^*_{jk} = 5.569$; $\chi^*_{ik} = 1.146$

2-Pyrrolidinone (i) + benzene (j) + o-xylene (k)

Table 2 (*Continued*)

x_i	x_j	V^E_{ijk} (cm^3 mol^{-1}) Exptl	Graph	Flory
0.1175	0.7450	−0.112	−0.170	−0.630
0.1716	0.5099	−0.040	−0.088	−0.696
0.2141	0.5513	−0.195	−0.243	−0.902
0.2456	0.5095	−0.228	−0.275	−0.970
0.2723	0.1280	−0.091	−0.078	−0.764
0.2943	0.4875	−0.327	−0.358	−1.089
0.3225	0.5288	−0.464	−0.461	−1.209
0.3384	0.5496	−0.519	−0.514	−1.274
0.3464	0.1667	−0.104	−0.159	−0.891
0.3751	0.4683	−0.494	−0.489	−1.238
0.4302	0.3636	−0.423	−0.447	−1.175
0.4421	0.4889	−0.620	−0.616	−1.362
0.4584	0.4307	−0.591	−0.568	−1.291
0.4891	0.1154	−0.241	−0.244	−0.919
0.5099	0.1169	−0.250	−0.255	−0.918
0.5394	0.3265	−0.530	−0.525	−1.175
0.5486	0.0928	−0.297	−0.253	−0.878
0.5702	0.1152	−0.288	−0.277	−0.891
0.6168	0.2570	−0.482	−0.486	−1.050
0.6540	0.1298	−0.333	−0.315	−0.841
0.6713	0.1137	−0.331	−0.297	−0.801
0.6966	0.1893	−0.414	−0.416	−0.878
0.7432	0.1824	−0.412	−0.417	−0.807
0.7739	0.1358	−0.349	−0.338	−0.690
0.7983	0.1292	−0.334	−0.327	−0.639
0.8246	0.0986	−0.291	−0.268	−0.545
0.8549	0.0872	−0.257	−0.241	−0.469
0.8865	0.0669	−0.210	−0.193	−0.372

$V^{(0)}_{ijk} = 5.521$; $V^{(1)}_{ijk} = -54.284$; $V^{(2)}_{ijk} = -74.059$; $\sigma(V^E_{ijk}) = 0.003$
$(^3\xi_i) = 1.001$; $(^3\xi_j) = 0.666$; $(^3\xi_k) = 1.426$
$\chi^* = -1.346$; $\chi'_{ij} = -0.628$; $\chi'_{jk} = 1.993$; $\chi'_{ik} = -0.559$
$\chi^*_{ij} = -4.405$; $\chi^*_{jk} = 13.816$; $\chi^*_{ik} = 7.857$

2-Pyrrolidinone (i) + benzene (j) + p-xylene (k)

x_i	x_j	V^E_{ijk} (cm^3 mol^{-1}) Exptl	Graph	Flory
0.0489	0.8862	−0.049	−0.056	−0.323
0.0585	0.8658	−0.058	−0.067	−0.380
0.0947	0.0625	−0.110	−0.101	−0.439
0.1103	0.7712	−0.110	−0.127	−0.656
0.1592	0.4564	−0.107	−0.119	−0.728
0.1951	0.1511	−0.232	−0.219	−0.792
0.2141	0.3554	−0.208	−0.209	−0.896
0.2593	0.6214	−0.266	−0.266	−1.202
0.2719	0.1251	−0.345	−0.367	−0.975
0.3065	0.2341	−0.362	−0.362	−1.072
0.3326	0.3945	−0.338	−0.360	−1.203
0.3849	0.5003	−0.347	−0.329	−1.362
0.4290	0.4008	−0.383	−0.383	−1.317
0.4387	0.2134	−0.475	−0.479	−1.187
0.4682	0.3692	−0.405	−0.392	−1.306
0.4948	0.2483	−0.478	−0.466	−1.211
0.5488	0.1675	−0.515	−0.515	−1.127
0.5941	0.2069	−0.483	−0.453	−1.115
0.6012	0.2110	−0.478	−0.443	−1.110
0.6519	0.1196	−0.495	−0.500	−0.972
0.7032	0.0876	−0.465	−0.487	−0.859
0.7685	0.1306	−0.371	−0.31 7	−0.759
0.8143	0.0495	−0.335	−0.363	−0.583
0.8471	0.0727	−0.278	−0.256	−0.517
0.8623	0.0518	−0.261	−0.263	−0.459
0.8878	0.0637	−0.212	−0.175	−0.398
0.8909	0.0475	−0.208	−0.201	−0.376
0.9432	0.0339	−0.113	−0.090	−0.209

$V^{(0)}_{ijk} = 1.461$; $V^{(1)}_{ijk} = 15.032$; $V^{(2)}_{ijk} = 110.257$; $\sigma(V^E_{ijk}) = 0.003$
$(^3\xi_i) = 1.001$; $(^3\xi_j) = 0.666$; $(^3\xi_k) = 1.250$
$\chi^* = -0.450$; $\chi'_{ij} = -0.063$; $\chi'_{jk} = 1.168$; $\chi'_{ik} = -1.729$
$\chi^*_{ij} = -4.405$; $\chi^*_{jk} = 8.941$; $\chi^*_{ik} = 6.866$

$V^{(n)}_{ijk}$ (n = 0–2) and ($\sigma(V^E_{ijk})$) are in cm^3 mol^{-1}; χ^* and χ'_{ij}, etc., are in cm^3 mol^{-1}; χ^*_{ij}, etc., are in J mol^{-1}.

Table 3

Speeds of sound, u_{ijk}, isentropic compressibilities $(\kappa_S)_{ijk}$, excess isentropic compressibilities $(\kappa_S^E)_{ijk}$ 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 $(\kappa_S^E)_{ijk}$ values evaluated from Graph theory and Flory theory; also included are various parameters $(\kappa_S^{(n)})_{ijk}$ (n = 0–2) along with their standard deviation, $\sigma(\kappa_S^E)_{ijk}$, the interaction parameters χ'_{ij}, χ^*_{ij}, etc.,, and $({}^3\xi_i)$ (i = i–k).

x_i	x_j	u_{ijk} (m s^{-1})	$(\kappa_S)_{ijk}$ (Tpa^{-1})	$(\kappa_S^E)_{ijk}$ (Tpa^{-1})		
				Exptl.	Graph	Flory
2-Pyrrolidinone (i) + benzene (j) + toluene (k)						
0.0594	0.8759	1271	707.6	−4.7	−4.4	−39.8
0.0975	0.8264	1272	698.9	−9.6	−8.6	−43.3
0.1181	0.6545	1275	694.8	−3.9	−6.0	−35.4
0.1307	0.5812	1277	690.8	−2.8	−5.5	−30.1
0.1657	0.2765	1290	675.2	−10.6	−5.9	−11.2
0.1894	0.2998	1286	675.7	−11.8	−9.8	−59.5
0.1905	0.6631	1302	652.3	−18.5	−18.3	−49.3
0.2193	0.3151	1290	665.6	−12.6	−14.8	−12.2
0.2615	0.4351	1311	636.1	−15.0	−23.5	−41.7
0.2756	0.2415	1300	647.2	−22.5	−22.4	−15.0
0.3074	0.2256	1330	614.4	−25.8	−26.0	−21.4
0.3159	0.5548	1310	624.2	−35.2	−34.9	−63.8
0.3261	0.5835	1352	583.8	−39.1	−35.5	−66.8
0.3493	0.2014	1315	621.9	−30.8	−31.3	−29.2
0.3596	0.5162	1359	573.5	−39.2	−39.1	−69.1
0.4152	0.1763	1330	598.5	−35.4	−37.5	−43.9
0.4532	0.5121	1398	528.3	−47.6	−47.9	−84.0
0.5153	0.1232	1355	562.1	−41.7	−42.5	−64.2
0.5844	0.0961	1376	535.9	−42.9	−42.6	−79.9
0.6276	0.0758	1391	519.3	−41.6	−41.9	−89.6
0.6608	0.1514	1446	474.6	−31.6	−48.3	−106.7
0.7065	0.542	1421	487.6	−36.4	−38.5	−109.3
0.7324	0.0417	1480	446.6	−35.0	−35.5	−115.3
0.7619	0.0498	1447	463.9	−30.7	−35.7	−124.3
0.7995	0.0728	1505	423.2	−25.6	−35.9	−136.3
0.8537	0.0515	1497	421.9	−20.6	−29.2	−149.3
$(\kappa_S^{(0)})_{ijk} = 465.6$; $(\kappa_S^{(1)})_{ijk} = -1258.3$; $(\kappa_S^{(2)})_{ijk} = -20508.1$; $\sigma(\kappa_S^E)_{ijk} = 0.1\ \text{TPa}^{-1}$ $\chi^* = -37.6$; $\chi'_{ij} = -233.4$; $\chi'_{jk} = 60.6$; $\chi'_{ik} = -91.9$						
2-Pyrrolidinone (i) + benzene (j) + o-xylene (k)						
0.0545	.8579	1274	704.9	−3.9	−2.3	−38.4
0.0917	0.7053	1288	683.8	−3.8	−3.7	−34.1
0.1542	0.3947	1315	648.0	−4.3	−6.4	−55.9
0.1572	0.6742	1305	654.8	−11.3	−9.4	−43.6
0.1669	0.5311	1307	653.1	−8.6	−8.9	−29.9
0.1823	0.5562	1316	641.1	−10.7	−10.8	−36.6
0.2195	0.4534	1318	634.8	−13.3	−13.4	−31.6
0.2456	0.6272	1325	621.7	−18.4	−18.5	−55.6
0.2861	0.2842	1338	608.4	−16.6	−16.9	−22.2
0.3252	0.5048	1348	589.3	−21.6	−26.2	−61.0
0.3586	.3054	1347	589.3	−24.8	−24.5	−44.8
0.3818	0.2522	1381	558.6	−24.4	−24.5	−42.8
0.4219	0.2137	1364	567.6	−25.5	−25.8	−47.7
0.4649	0.1796	1375	553.9	−26.1	−26.5	−54.2
0.4872	0.1153	1406	526.9	−20.9	−21.6	−50.0
0.5032	0.1427	1415	518.3	−25.5	−25.4	−59.1
0.5373	0.1578	1392	530.9	−29.2	−29.0	−71.0
0.5764	0.1526	1402	518.1	−30.6	−30.7	−81.0
0.6058	0.1294	1411	508.1	−29.7	−29.1	−78.5
0.6356	0.0432	1454	475.7	−23.3	−14.6	−82.3
0.6947	0.1081	1439	477.2	−29.4	−29.1	−108.3
0.7513	0.0904	1461	456.2	−27.3	−27.2	−122.1
0.7778	0.1215	1513	420.9	−27.7	−34.9	−132.1
0.8031	0.0727	1483	436.4	−23.9	−24.1	−135.0
0.8207	0.0438	1526	410.9	−21.0	−16.5	−137.4
0.8612	0.0500	1512	413.4	−18.2	−18.5	−149.5
0.9010	0.0472	1535	396.6	−14.8	−17.9	−160.6
$(k_S^{(0)})_{ijk} = -33.5$; $(k_S^{(1)})_{ijk} = 628.0$; $(k_S^{(2)})_{ijk} = 16843.5$, $\sigma(\kappa_S^E)_{ijk} = 0.1\ \text{TPa}^{-1}$ $\chi^* = -17.1$; $\chi'_{ij} = -269.3$; $\chi'_{jk} = 17.5$; $\chi'_{ik} = -10.9$						
2-Pyrrolidinone (i) + benzene (j) + p-xylene (k)						
0.0588	0.6391	1281	702.2	−8.9	−7.0	−17.4
0.0726	0.6394	1276	705.6	−16.2	−16.4	−20.7
0.0972	0.5615	1300	676.6	−23.2	−23.0	−15.2
0.1287	0.6145	1285	685.8	−44.4	−44.9	−31.0
0.1712	0.5655	1293	670.8	−65.5	−61.1	−33.7
0.1849	0.7168	1372	590.0	−81.4	−81.6	−50.8
0.2198	0.4865	1302	655.6	−72.3	−70.2	−34.2
0.2573	0.0423	1322	638.0	−21.2	−49.9	−41.2
0.2976	0.4119	1315	630.6	−80.2	−82.1	−42.7
0.3455	0.5746	1527	458.3	−158.2	−105.7	−69.0
0.3653	0.3691	1329	607.5	−87.9	−87.7	−53.6
0.3942	0.5493	1538	445.8	−152.8	−106.4	−75.7
0.4273	0.3299	1343	586.2	−88.9	−87.8	−63.9
0.4834	0.2916	1356	567.3	−83.1	−84.3	−73.1
0.5376	0.2603	1370	547.7	−79.2	−79.0	−83.1
0.5686	0.2414	1379	536.6	−75.2	−75.1	−88.8
0.5974	0.2243	1388	526.0	−71.2	−71.0	−94.3
0.6016	0.3845	1505	441.2	−78.3	−78.9	−105.6
0.6471	0.1839	1479	457.5	−57.0	−62.6	−102.9
0.6709	0.3187	1511	430.2	−62.1	−63.5	−117.0
0.7218	0.1477	1432	478.6	−50.1	−49.7	−119.1
0.7524	0.1270	1445	466.5	−44.3	−44.2	−125.5
0.7781	0.1098	1517	420.6	−39.9	−39.7	−130.9
0.8044	0.0915	1469	445.6	−35.1	−35.3	−136.6
0.8351	0.0691	1484	433.0	−30.1	−30.7	−143.4
0.8725	0.0494	1506	416.4	−24.8	−24.5	−152.5
0.9112	0.341	1564	381.8	−18.2	−17.3	−162.6
$(\kappa_S^{(0)})_{ijk} = -556.1$; $(\kappa_S^{(1)})_{ijk} = -22347.5$; $(\kappa_S^{(2)})_{ijk} = -116300$; $(\kappa_S^E)_{ijk} = 0.2\ \text{TPa}^{-1}$ $\chi^* = -317.7$; $\chi'_{ij} = 301.8$; $\chi'_{jk} = 191.1$; $\chi'_{ik} = -178.5$						

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

for ternary mixtures were determined by Eq. (1):

$$(\kappa_S)_{ijk} = (\pi_{ijk} u_{ijk}^2)^{-1} \tag{1}$$

The densities, ρ_{ijk} of ternary mixtures were calculated from their experimental molar excess volumes data using the 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 ρ_i are the mole fraction, molar mass and density, respectively, of component (i).

Excess isentropic compressibilities, $(\kappa_S^E)_{ijk}$ for ternary mixtures were calculated using Eq. (3):

$$(\kappa_S^E)_{ijk} = \kappa_S - \kappa_S^{id} \tag{3}$$

κ_S^{id} for binary and ternary mixtures were obtained according to Benson and Kiyohara [11]:

$$\kappa_S^{id} = \sum_{i}^{k} \phi_i \left[\kappa_{S,i} + \frac{T V_i \alpha_i^2}{C_{p,i}} \right] - T \left(\sum_{i}^{k} x_i V_i \right) \frac{\left(\sum_i^k \phi_i \alpha_i \right)^2}{\left(\sum_i^k x_i C_{p,i} \right)} \tag{4}$$

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 the pure component (i), respectively. The values of α and $C_{p,i}$ were taken from literature [12]. α value for **2-Py** was evaluated in the same manner as suggested by Hilderbrand et al. [13]. The resulting $(\kappa_S)_{ijk}$ and $(\kappa_S^E)_{ijk}$ values for the various (i + j + k) ternary mixtures are recorded in Table 3. V_{ijk}^E and $(\kappa_S^E)_{ijk}$ values for various ternary mixtures are plotted in Figs. 1–3 and 4–6 respectively.

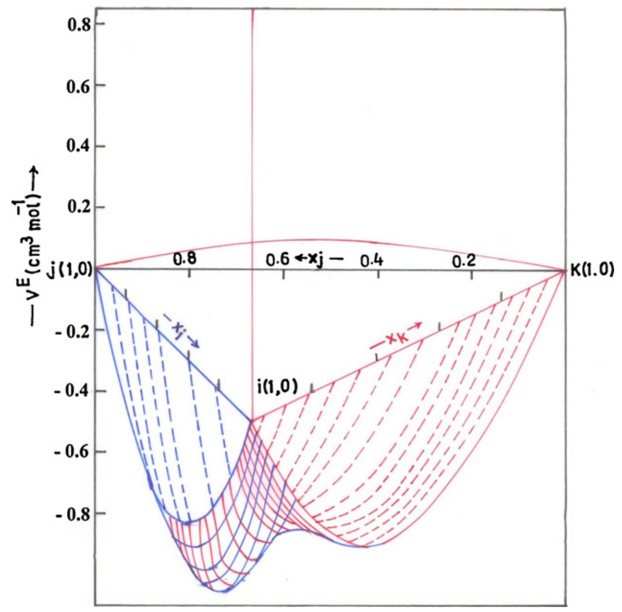

Fig. 1. Molar excess volumes, V^E, for 2-pyrrolidinone (i) + benzene (j) + toluene (k) ternary mixture at 308.15 K.

V^E_{ijk} and $(\kappa^E_S)_{ijk}$ values for ternary mixtures were fitted to Redlich–Kister equation, Eq. (5):

$$X^E_{ijk}(X = V \text{ or } \kappa_S) = x_i x_j \left[\sum_{n=0}^{2} X^{(n)}_{ij}(x_i - x_j)^n \right] + x_j x_k \left[\sum_{n=0}^{2} X^{(n)}_{jk}(x_j - x_k)^n \right] + x_i x_k \left[\sum_{n=0}^{2} X^{(n)}_{ik}(x_k - x_i)^n \right] + x_i x_j x_k \left[\sum_{n=0}^{2} X^{(n)}_{jk}(x_j - x_k)^n x_i^n \right] \quad (5)$$

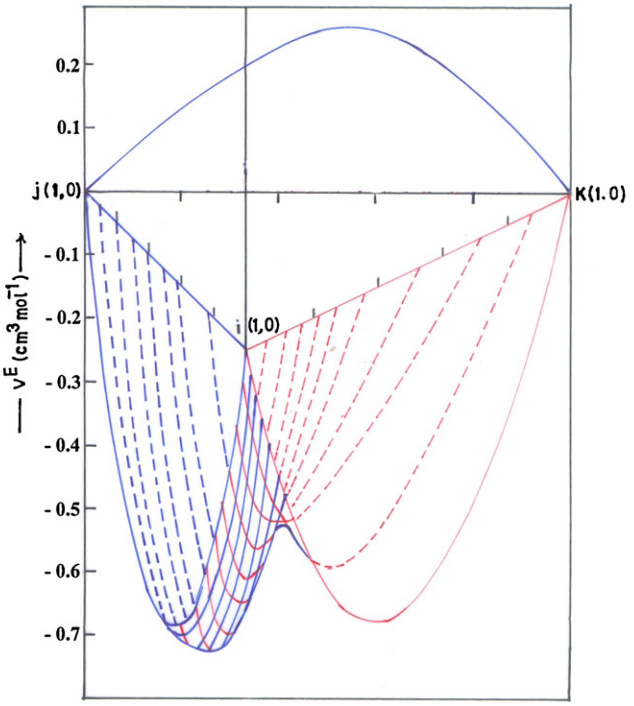

Fig. 2. Molar excess volumes, V^E, for 2-pyrrolidinone (i) + benzene (j) + o-xylene (k) ternary mixture at 308.15 K.

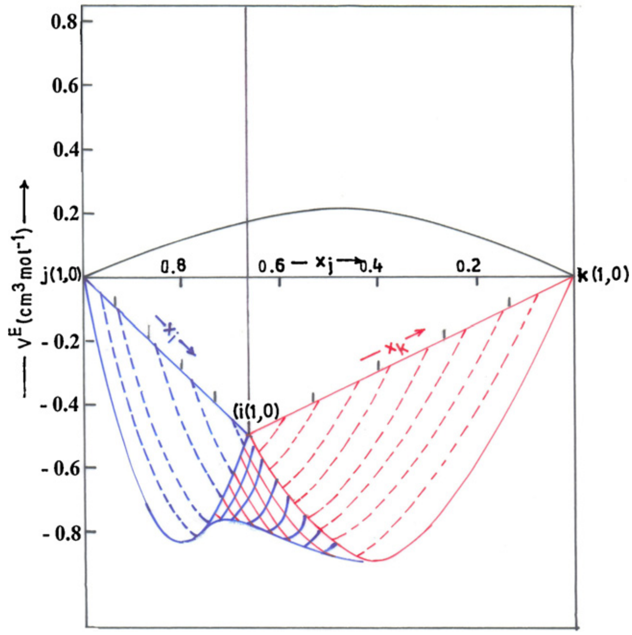

Fig. 3. Molar excess volumes, V^E, for 2-pyrrolidinone (i) + benzene (j) + p-xylene (k) ternary mixture at 308.15 K.

where x_i and x_j are the mole fractions of ith and jth components of (i + j + k) ternary mixture; $X^{(n)}_{ij}$ (n = 0–2), etc., ($X = V$ or κ_S) are the parameters characteristic of (i + j), (j + k) and (i + k) binary mixtures and have been taken from literature [1,14,15]. $X^{(n)}_{ijk}$ ($X = V$ or κ_S)

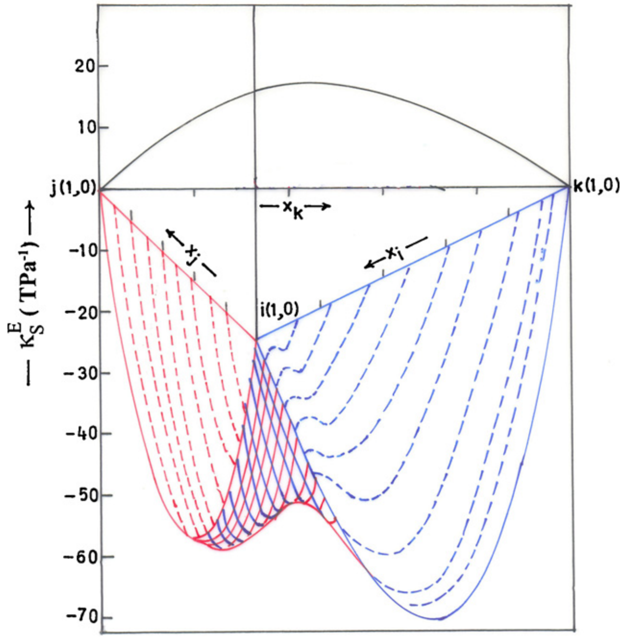

Fig. 4. Excess isentropic compressibilities, κ^E_S, for 2-pyrrolidinone (i) + benzene (j) + toluene (k) ternary mixture at 308.15 K.

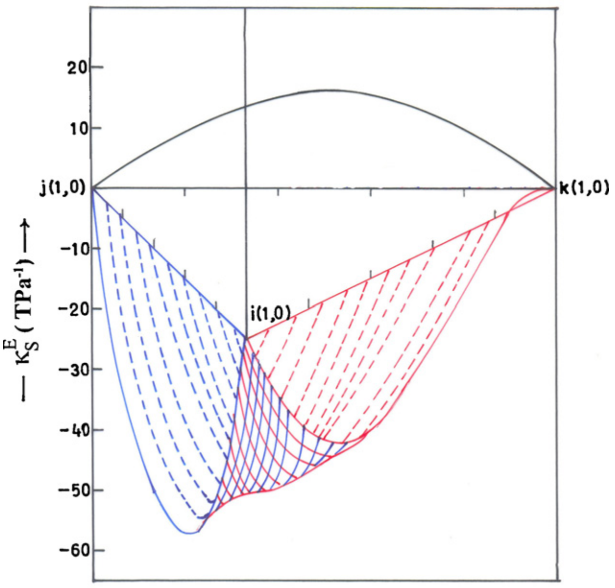

Fig. 5. Excess isentropic compressibilities, κ_S^E, for 2-pyrrolidinone (i) + benzene (j) + o-xylene (k) ternary mixture at 308.15 K.

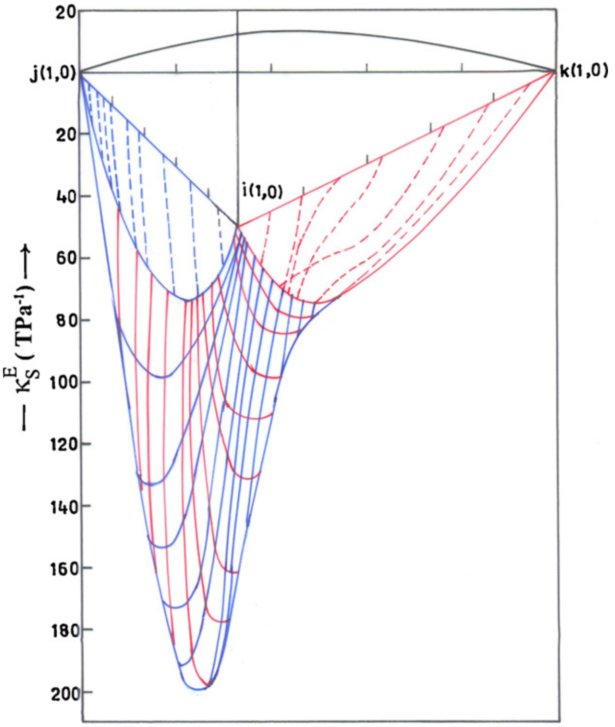

Fig. 6. Excess isentropic compressibilities, κ_S^E, for 2-pyrrolidinone (i) + benzene (j) + p-xylene (k) ternary mixture at 308.15 K.

parameters were determined by fitting X_{ijk}^E data to Eq. (5) by the least-squares method and are recorded along with their standard deviations, $\sigma(X^E)_{ijk}$ ($X = V$ or κ_S) in Tables 2 and 3, respectively. The surfaces of ternary mixtures for V_{ijk}^E and $(\kappa_S^E)_{ijk}$ values [calculated by employing Eq. (5)] are shown in Figs. 1–3 and 4–6, respectively.

4. Discussion

We are unaware of any published data for the investigated ternary mixtures with which to compare our results. V_{ijk}^E and $(\kappa_S^E)_{ijk}$ values for the studied mixtures are negative over the entire range of mole fractions. More negative V_{ijk}^E and $(\kappa_S^E)_{ijk}$ values for **2-Py** (i) + benzene (j) + toluene (k) mixtures than those for **2-Py** (i) + benzene (j) + o- or p-xylene (k) mixtures suggest that toluene gives relatively more packed structure as compared to o- or p-xylenes in **2-Py**:benzene molecular entity. This may be due to the presence of two bulky –CH_3 groups in xylenes which restrict the approach of xylene to **2-Py**:benzene molecular entity.

4.1. Graph theory and results

According to mathematical discipline of Graph theory, the atoms of a molecule are represented by dots and bonds joining them are represented by lines. The resulting molecular graph then describes the total information contained in that molecule. If δ_m^v, δ_n^v, etc., represent the degree of mth, nth, etc., vertices of the graph of a molecule, then connectivity parameter of third degree of a molecule, $^3\xi$, is defined [16] by

$$^3\xi = \sum_{m<n<o<p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \tag{6}$$

δ_m^v, etc., is related the maximum valency, Z_m and number of hydrogen atoms, h, attached to mth vertex by relation $\delta_m^v = Z_m - h$ [17].

Analysis of molar excess volumes, V^E, molar excess enthalpies, H^E and excess isentropic compressibilities data of **2-Py** (i) + benzene or toluene or o- or p- or m-xylene (j) binary mixtures by Graph theory [1] reveals that (i) **2-Py** in pure state exists mainly as a mixture of open dimer and cyclic dimer; (ii) (i + j) mixtures are characterized by interactions between π-electrons spilling over nitrogen and oxygen atom of **2-Py** and π-electron cloud of aromatic ring to form 1:1 molecular complex. The thermodynamic properties, X^E ($X = H$ or κ_S) for these mixtures were then expressed by Eq. (7):

$$X^E(X = H \,\text{or}\, \kappa_S) = \frac{x_i x_j(^3\xi_i/^3\xi_j)}{x_i + x_j(^3\xi_i 0 ^3\xi_j)}[(1 + x_i)\chi'_{ij} + x_j \chi_{12}] \tag{7}$$

where χ'_{ij} and χ_{12} are the molar enthalpy and molar compressibility interaction parameters due to i–j contacts and specific interactions, respectively. H^E and κ_S^E data of the studied binary mixtures were well described by Eq. (7) which lends support to the assumptions made in deriving Eq. (7).

If a compound like toluene or o- or p-xylene is added to **2-Py** (i) + benzene (j) binary mixtures, then **2-Py** (i) + benzene (j) + toluene or o- or p-xylene (k) ternary mixture formation may be assumed to involve processes: **(1)** (a) formation of i_n–j (b) j–k and (c) i_n–k unlike contacts; **(2)** unlike contact formation then cause depolymerisation of i_n; **(3)** monomers of i, j and k then undergo specific interactions to form i:j; j:k and i:k molecular entities. If χ'_{ij}, χ'_{jk} and χ'_{ik} are the molar volume and molar compressibility interaction parameter of unlike (i–j), (j–k) and (i–k) contacts, then change in molar properties, X^E ($X = V$ or κ_S) due to processes **(1)**(a)–(c) can be expressed [18–20] by the relation:

$$X^E(X = V \,\text{or}\, \kappa_S) = x_i S_j \chi'_{ij} + x_j S_k \chi'_{jk} + x_k S_i \chi'_{ik} \tag{8}$$

where S_j, etc., are defined [18] by

$$S_i = \frac{x_i v_i}{\sum x_i v_i}$$

where v_i is the molar volume of component (i). So Eq. (8) reduces to Eq. (9):

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

Further, if χ'_{ii}, χ_{12}, χ'_{12} and χ''_{12} are the molar volume and molar compressibility interaction parameters of i–i like contacts and specific interactions (leading to the formation of i:j, j:k and i:k molecular entities), then change in thermodynamic properties due to processes **(2)** and **(3)** are given by [18–20]:

$$\Delta X_2(X = V \text{ or } \kappa_S) = \frac{x_i^2 x_j \upsilon_j \chi'_{ii}}{\Sigma x_i \upsilon_i} \tag{10}$$

$$\Delta X_3(X = V \text{ or } \kappa_S) = \frac{x_i x_j^2 \upsilon_j \chi_{12}}{\Sigma x_i \upsilon_i} \tag{11}$$

$$\Delta X_4(X = V \text{ or } \kappa_S) = \frac{x_j x_k^2 \upsilon_k \chi'_{12}}{\Sigma x_j \upsilon_j} \tag{12}$$

$$\Delta X_5(X = V \text{ or } \kappa_S) = \frac{x_k x_i^2 \chi'_{12}}{\Sigma x_k \upsilon_k} \tag{13}$$

The overall change in thermodynamic property, $X^E(X = V \text{ or } \kappa_S)$ due to the processes **(1)**(a)–(c), **(2)** and **(3)** can then be expressed by Eq. (14):

$$\begin{aligned} X^E(X = V \text{ or } \kappa_S) &= \sum_{i=1}^{5} \Delta X_i \\ &= \left[\frac{x_i x_j \upsilon_j}{\Sigma x_i \upsilon_i}\right] [\chi'_{ij} + x_i \chi'_{ii} + x_j \chi_{12}] + \left[\frac{x_j x_k \upsilon_k}{\Sigma x_j \upsilon_j}\right] \\ &\quad \times [\chi'_{jk} + x_k \chi'_{12}] + \left[\frac{x_i x_k \upsilon_i}{\Sigma x_i \upsilon_k}\right] [\chi'_{ik} + x_i \chi''_{12}] \end{aligned} \tag{14}$$

since $\upsilon_j/\upsilon_i = ({}^3\xi_i/{}^3\xi_j)$ [21], So, Eq. (14) reduces to Eq. (15):

$$\begin{aligned} X^E_{ijk}(X = V \text{ or } \kappa_S) &= \left[\frac{x_i x_j ({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right] [\chi'_{ij} + x_i \chi'_{ii} + x_j \chi_{12}] \\ &\quad + \left[\frac{x_j x_k ({}^3\xi_j/{}^3\xi_k)}{x_j + x_k({}^3\xi_j/{}^3\xi_k)}\right] [\chi'_{jk} + x_k \chi'_{12}] \\ &\quad + \left[\frac{x_i x_k ({}^3\xi_k/{}^3\xi_i)}{x_k + x_i({}^3\xi_k/{}^3\xi_i)}\right] [\chi'_{ik} + x_i \chi''_{12}] \end{aligned} \tag{15}$$

Further, if it be assumed for the investigated (i + j + k) mixtures that $\chi'_{ij} \equiv \chi_{12} = \chi*$; $\chi'_{jk} \equiv \chi'_{12}$; $\chi'_{ik} \equiv \chi''_{12}$; then Eq. (15) can be expressed as

$$\begin{aligned} X^E_{ijk}(X = V \text{ or } \kappa_S) &= \left[\frac{x_i x_j ({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right] [(1 + x_j)\chi^* + x_i \chi'_{ii}] \\ &\quad + \left[\frac{x_j x_k ({}^3\xi_j/{}^3\xi_k)}{x_j + x_k({}^3\xi_j/{}^3\xi_k)}\right] [(1 + x_k)\chi'_{jk}] \\ &\quad + \left[\frac{x_i x_k ({}^3\xi_k/{}^3\xi_i)}{x_k + x_i({}^3\xi_k/{}^3\xi_i)}\right] [(1 + x_i)\chi'_{ik}] \end{aligned} \tag{16}$$

Eq. (16) contains four unknown parameters, and the values of these parameters were determined by employing X^E ($X = V$ or κ_S) data at four compositions. The resulting parameters were then utilized to predict V^E_{ijk} and $(\kappa^E_S)_{ijk}$ values over the entire composition range. The V^E_{ijk} and $(\kappa^E_S)_{ijk}$ values along with χ'_{ii}, χ'_{ij}, etc., parameters, are recorded in Tables 2 and 3.

4.2. Flory theory

V^E_{ijk} and $(\kappa^E_S)_{ijk}$ data for the studied (i + j + k) ternary mixtures were next analyzed in terms of Flory theory. According to Flory theory [22,23], V^E_{ijk} for a ternary mixture is given by:

$$V^E_{ijk} = \bar{V}^E_{cal} \left[\sum_{i=i}^{k} x_i \upsilon_i^*\right] \tag{17}$$

where

$$\bar{\upsilon}_i = \left[\frac{1 + \alpha_i(T/3)}{(1 + \alpha_i T)^3}\right]^3 \tag{18}$$

$$\bar{V}^E_{cal} = (\bar{\upsilon}_0)^{7/3} \left[\frac{4}{3} - (\bar{\upsilon}_0)^{1/3}\right]^{-1} [\bar{T} - \bar{T}_0] \tag{19}$$

$$\bar{T}_0 = \frac{(\bar{\upsilon}_0)^{1/3} - 1)}{(\bar{\upsilon}_0)^{4/3}} \tag{20}$$

$$\bar{\upsilon}_i^* = \frac{\upsilon_i}{\bar{\upsilon}_i} \tag{21}$$

$$\bar{\upsilon}_0 = \sum \phi_i \upsilon_i^* \tag{22}$$

$$\bar{T} = \left[\sum \frac{\phi_i P_i^* T_i}{\sum \phi_i P_i^*}\right] \left[1 - \phi_i \theta_j \chi''_{ij} \left(\sum \phi_i P_i^*\right)^{-1}\right]^{-1} \tag{23}$$

$$\bar{T}_i = \frac{\bar{\upsilon}_i^{1/3} - 1}{\bar{\upsilon}_i^{4/3}} \tag{24}$$

$$P^* = \sum \phi_i P_i^* - \sum \phi_i^* \theta_j \chi''_{ij} \tag{25}$$

$$P_i^* = \alpha_i T \bar{\upsilon}_i^2 [(\kappa_T)_i]^{-1} \tag{26}$$

all the terms have same significance as described elsewhere [22,23].

Evaluation of V^E_{ijk} by Flory theory requires a knowledge of reduced temperature, $\bar{T}$, which in turn depends upon adjustable parameters $\theta_j \chi^*_{ij}$, etc., of (i + j), (j + k) and (i + k) binary mixtures of (i + j + k) ternary mixtures. These parameters were determined by fitting H^E values [1,24] at $x_i = 0.5$ to Eq. (27).

$$H^E = \sum x_i P_i^* (\bar{V}_i^{-1} - \bar{V}_{cal}^{-1}) + x_i V_i^* \theta_j \chi^*_{ij} V_{cal}^{-1} \tag{27}$$

Various parameters of pure components were determined using isothermal compressibility (κ_T) reported in literature [12]. κ_T values for **2-Py** was calculated by employing ΔH_v values in the manner as suggested by Hilderbrand et al. [13]. Such V^E_{ijk} values evaluated via Eqs. (17)–(27) along with χ^*_{ij}, etc., parameters are recorded in Table 2.

$(\kappa^E_S)_{ijk}$ for a ternary mixture is expressed by Eq. (3) where the isentropic compressibility, κ_S, of (i + j + k) ternary mixture, at effectively zero pressure is expressed by Eq. (28):

$$\kappa_S = \frac{\kappa_T - T \upsilon_m^* \alpha_p^2}{C_{p,m}} \tag{28}$$

The isothermal compressibility, κ_T, of a mixture at effectively zero pressure is given by relation:

$$\kappa_T = \left[\frac{(3\bar{\upsilon}_m^2/p^*)(\bar{\upsilon}_m^{1/3} - 1)}{(4 - 3(\bar{\upsilon}_m^{1/3})}\right] \tag{29}$$

where

$$\upsilon_m^* = \sum_{i=i}^{k} \phi_i \upsilon_i^* \tag{30}$$

$$\alpha_p = \frac{3(\bar{\upsilon}_m^{1/3} - 1)}{T(4 - 3\bar{\upsilon}_m^{1/3})} \tag{31}$$

$$p* = \sum_{i=i}^{k} \phi_i p_i^* - \sum_{i=i}^{k} \phi_i \theta_j \chi_{ij}^* \tag{32}$$

$$\bar{v} = \frac{v}{v*} \tag{33}$$

$$\bar{v}_m = \sum_{i=i}^{k} \phi_i v_i^* \tag{34}$$

$$C_{p,m} = \left(\frac{\partial H_{ijk}^E}{\partial T} \right) + \sum_{i=i}^{k} x_i C_{p,i} \tag{35}$$

where $\bar{v}, v*, C_{p,i}$ represent the reduced volume, characteristics volume, and molar heat capacities of component (i) in ternary mixtures. $\partial H_{ijk}^E / \partial T$ values at 308.15 K for **2-Py** (i) + benzene (j) + toluene or o- or p-xylene (k) ternary mixtures were evaluated by employing H^E values [1,24] values for their sub-binary (i + j), (j + k), (i + k) mixtures. H_{ijk}^E were taken equal to $H_{ij}^E + H_{jk}^E + H_{jk}^E$. H_{ij}^E, etc., values at 298.15 K were calculated in the manner described elsewhere [25]. κ_S^{id} values for the corresponding ideal mixtures were calculated using Eq. (28). While α_p^{id} and $c_{p,m}^{id}$ were taken as mole fraction average; κ_S^{id} were taken as volume fraction averages. Such $(\kappa_S^E)_{ijk}$ values calculated for the present ternary mixtures are recorded in Table 2.

A pursual of data in Tables 2 and 3 reveals that V_{ijk}^E and $(\kappa_S^E)_{ijk}$ values predicted by Graph theory compare well with their experimental values. Even in those cases where the calculated and the experimental values are not in agreement, they are of same sign and magnitude. However, V_{ijk}^E and $(\kappa_S^E)_{ijk}$ values predicted by Flory theory are of same sign, but the qualitative agreement is poor. The failure of the Flory theory to correctly predict the magnitude of V_{ijk}^E values. $(\kappa_S^E)_{ijk}$ values may be due to the use of various parameters that were not available in the literature but have been estimated and also due to the nature of constituents of (i + j + k) mixtures.

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