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Thermodynamic Properties of Ternary Liquid Mixtures of 2-Pyrrolidinone with Aromatic Hydrocarbons

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Abstract Molar excess volumes, V_{ijk}^{E}, and speeds of sound, u_{ijk}, of 2-pyrrolidinone (2-Py) (i) + toluene (j) + o-xylene or p-xylene (k) ternary mixtures have been determined by using a dilatometer and interferometer as a function of composition at 308.15 K. The speeds of sound of ternary mixtures have been utilized to predict their excess isentropic compressibilities. The Redlich-Kister equation has been fitted to the molar excess volumes, V_{ijk}^{E}, and excess isentropic compressibilities, $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$, to predict ternary adjustable parameters and standard deviations. The observed data have been analyzed in terms of the Flory theory and the Sanchez and Lacombe theory.

Keywords Excess isentropic compressibilities · Molar excess volumes · 2-Pyrrolidinone · Speeds of sound

1 Introduction

The study of thermodynamic properties of ternary mixtures is significant for many reasons, one of which is to obtain information on molecular features of the studied mixtures [1–3]. In the chemical industry, a knowledge of molar excess volumes and excess isentropic compressibility data is important in the design of processes involving chemical separations, mass transfer, heat transfer, and process equipment. Thermodynamic properties of ($i + j + k$) ternary mixtures can be predicted from the thermodynamic properties of their ($i + j$), ($j + k$), and ($i + k$) sub-binary mixtures. In recent studies [4], we have reported molar excess volumes, molar excess enthalpies, and excess isentropic compressibilities of 2-pyrrolidinone (i) + benzene or toluene or

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o- or *p*- or *m*-xylene (*j*) binary mixtures. In the present paper continuing our study, we report here molar excess volumes and speeds of sound of 2-pyrrolidinone (*i*) + toluene (*j*) + *o*- or *p*-xylene (*k*) ternary mixtures.

2 Experimental

2-Pyrrolidinone (2-Py) (Fluka, 99 mass% USA), toluene (99.5 mass%) and, *o*- and *p*-xylene (99 mass%) (AR Grade) were purified by standard methods [5]. The purities of the 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 [5].

The molar excess volumes, V^{E}_{ijk}, for the ternary mixtures were measured dilatometrically as described elsewhere [6]. The dilatometer had three limbs for three components of ternary mixtures. The dilatometer was equilibrated in a constant temperature water bath at (308.15 ± 0.01) K. After attainment of thermal equilibrium, 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} values is 0.5 %.

The speeds of sound were determined at 2 MHz using a quartz crystal interferometer [7] (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 uncertainty in the measured speeds of sound is $1\ \mathrm{m \cdot s^{-1}}$.

3 Results

The measured molar excess volumes, V^{E}_{ijk},and speeds of sound, $u_{ijk,}$ of 2-Py (*i*) + toluene (*j*) + *o*- or *p*-xylene (*k*) ternary mixtures as a function of composition are reported in Tables 2 and 3, respectively.

Isentropic compressibilities, $(\kappa_S)_{ijk}$, for ternary mixtures were calculated by the relation,

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

The densities, ρ_{ijk} of the various ternary mixtures were predicted by employing their molar excess volumes data using

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

Liquids	$u(\mathrm{m \cdot s^{-1}})$		$\rho(\mathrm{kg \cdot m^{-3}})$	
	Exp	Lit	Exp	Lit
2-pyrrolidinone	1603[a]	1603.1[a] [13]	994.28	994.30 [5]
Toluene	1305	1304.0 [14]	862.21	862.19 [5]
o-xylene	1344	1345.0 [14]	875.99	875.94 [5]
p-xylene	1310	1309.6 [16]	856.58	856.61 [5]

[a] Speed-of-sound value 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 Flory and the Sanchez and Lacombe theories at 308.15 K at various mole fractions

x_i	x_j	$V^{\mathrm{E}}_{ijk}(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$		
		Exp	Flory	Sanchez and Lacombe
2-Pyrrolidinone (i) + toluene (j)+ o-xylene (k)[a]				
0.0584	0.9141	−0.076	−0.327	−0.081
0.0755	0.8229	−0.099	−0.387	−0.338
0.1046	0.7674	−0.155	−0.508	−0.161
0.1229	0.1967	−0.107	−0.443	−0.132
0.1453	0.5616	−0.219	−0.603	−0.193
0.1930	0.1994	−0.165	−0.637	−0.159
0.2588	0.3971	−0.354	−0.855	−0.309
0.2939	0.6361	−0.482	−1.057	−0.434
0.3756	0.4713	−0.593	−1.080	−0.520
0.4100	0.4082	−0.605	−1.069	−0.445
0.4689	0.3229	−0.596	−1.036	−0.336
0.5313	0.1633	−0.437	−0.911	−0.165
0.7963	0.0885	−0.388	−0.540	−0.275
0.9319	0.0471	−0.243	−0.307	−0.112
0.9418	0.0321	−0.143	−0.177	−0.092
2-Pyrrolidinone (i) + toluene (j)+ p-xylene (k)[b]				
0.0853	0.0784	0.040	0.292	0.153
0.1585	0.2149	0.261	0.366	0.254
0.1602	0.3766	0.083	0.239	0.170
0.1704	0.7382	−0.285	−0.793	−0.336
0.2149	0.1065	0.307	0.535	0.222
0.2620	0.6346	−0.439	−1.026	−0.379
0.2704	0.3899	−0.149	−1.004	−0.143
0.3002	0.2011	0.472	0.568	0.145
0.3494	0.3146	−0.096	−1.102	−0.139
0.3776	0.5291	−0.565	−1.168	−0.569
0.4268	0.2821	−0.192	−1.138	−0.194
0.5079	0.4063	−0.635	−1.153	−0.582
0.5561	0.2356	−0.394	−1.075	−0.328
0.6709	0.1137	−0.131	−0.888	−0.102
0.6152	0.3017	−0.621	−1.026	−0.363
0.7244	0.2083	−0.518	−0.815	−0.091
0.8364	0.0816	−0.280	−0.513	−0.317

[a] $V^{(0)}_{ijk} = 1.758\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V^{(1)}_{ijk} = -\,42.587\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V^{(2)}_{ijk} = 45.762\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\sigma\left(V^{\mathrm{E}}_{ijk}\right) = 0.003\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi_{ij} = 1.1\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi_{jk} = 4.0\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi_{ik} = 7.9\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi^*_{ij} = -\,132.729\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi^*_{jk} = 376.267\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi^*_{ik} = -\,77.517\ \mathrm{J} \cdot \mathrm{mol}^{-1}$

[b] $V^{(0)}_{ijk} = 10.337\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V^{(1)}_{ijk} = -178.123\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V^{(2)}_{ijk} = 636.590\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\sigma\left(V^{\mathrm{E}}_{ijk}\right) = 0.004\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $\chi_{ij} = 1.1\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi_{jk} = 1.0\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi_{ik} = 6.9\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi^*_{ij} = -\,132.729\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi^*_{jk} = 108.324\ \mathrm{J} \cdot \mathrm{mol}^{-1}$; $\chi^*_{ik} = -\,113.805\ \mathrm{J} \cdot \mathrm{mol}^{-1}$

Table 3 Speeds 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 at various compositions (in mole fraction) at 308.15 K with $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values evaluated from the Flory theory

$\mathbf{x}_i$	$\mathbf{x}_j$	$u_{ijk}(\mathrm{m \cdot s^{-1}})$	$(\kappa_S)_{ijk}\left(\mathrm{TPa^{-1}}\right)$	$\left(\kappa_S^{\mathrm{E}}\right)_{ijk}(\mathrm{TPa^{-1}})$	
				Exp	Flory
2-Pyrrolidinone (*i*) + toluene (*j*) + *o* - xylene (*k*)[a]					
0.0749	0.1086	1312	661.5	6.2	3.3
0.0987	0.8578	1296	682.2	−24.4	−46.9
0.1398	0.7924	1308	662.5	−29.9	−50.0
0.1813	0.7572	1323	641.9	−38.5	−53.9
0.1934	0.3082	1299	643.2	17.0	8.7
0.2086	0.4398	1302	655.7	7.9	35.0
0.2749	0.7013	1355	598.5	−55.7	−63.6
0.3014	0.2986	1366	571.1	13.2	7.5
0.3789	0.5120	1381	560.6	−51.9	−71.6
0.4392	0.0435	1400	538.3	−22.6	−23.3
0.5246	0.4479	1430	505.0	−61.5	−92.4
0.5748	0.2280	1396	523.8	−10.6	−89.2
0.5951	0.0856	1426	499.8	−18.1	−76.8
0.6312	0.2967	1448	479.4	−41.9	−106.6
0.7140	0.0394	1475	453.6	−21.2	−105.0
0.8452	0.0532	1519	412.4	−12.9	−144.5
2-Pyrrolidinone (*i*) + toluene (*j*) + *p*-xylene (*k*)[b]					
0.0391	0.5560	1268	725.4	−4.7	−7.5
0.0650	0.8395	1282	703.1	−13.5	−42.3
0.1032	0.1346	1288	697.6	−3.3	−18.1
0.1381	0.1938	1293	687.2	−4.9	−21.7
0.1858	0.6657	1310	655.9	−26.1	−49.8
0.2328	0.4669	1320	640.7	−26.3	−38.3
0.2335	0.2531	1314	651.7	−14.5	−19.0
0.2587	0.0438	1317	649.0	−9.6	−26.4
0.3078	0.6112	1338	611.3	−32.8	−65.3
0.3981	0.5615	1364	573.7	−39.8	−76.4
0.5149	0.4362	1390	537.0	−34.8	−90.6
0.6233	0.3108	1425	497.1	−33.4	−105.5
0.6885	0.0999	1456	473.2	−34.6	−103.8
0.7850	0.1065	1501	431.0	−32.4	−131.3

[a] $\left(\kappa_S^{(0)}\right)_{ijk} = 1159.9\ \mathrm{TPa^{-1}}$; $\left(\kappa_S^{(1)}\right)_{ijk} = -2075.9\ \mathrm{TPa^{-1}}$; $\left(\kappa_S^{(2)}\right)_{ijk} = -\ 37650.9\ \mathrm{TPa^{-1}}$; $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ijk} = 0.7\ \mathrm{T.Pa^{-1}}$

[b] $\left(\kappa_S{}^{(0)}\right)_{ijk} = 21.7\ \mathrm{TPa^{-1}}$; $\left(\kappa_S^{(1)}\right)_{ijk} = -167.2\ \mathrm{TPa^{-1}}$; $\left(\kappa_S^{(2)}\right)_{ijk} = 43329.4\ \mathrm{TPa^{-1}}$; $\sigma\left(\kappa_S^{\mathrm{E}}\right)_{ijk} = 0.5\ \mathrm{TPa^{-1}}$

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

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of component i of the ternary mixture.

Excess isentropic compressibilities, $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$, were evaluated using

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

κ_S^{id} was obtained according to Benson and Kiyohara [8];

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

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 pure component i, respectively. The values of $\alpha$and $C_{p,i}$ were taken from the literature [3,9]. α for 2-Py was evaluated in the same manner as suggested by Hildebrand [10]. The $(\kappa_S)_{ijk}$and $(\kappa_S^{\mathrm{E}})_{ijk}$ values predicted from Eqs. 1 and 3, respectively, for the various $(i + j + k)$ ternary mixtures are reported in Table 3.

Molar excess volumes, V_{ijk}^{E}, and excess isentropic compressibilities, $(\kappa_S^{\mathrm{E}})_{ijk}$, (plotted in Figs. 1, 2,3, and 4, respectively) for the investigated ternary mixtures were fitted to a Redlich-Kister equation,

$$\begin{aligned} X_{ijk}^{\mathrm{E}}(X = \mathrm{V or} \kappa_s) = {} & x_i x_j \left[\sum_{n=0}^{2} X_{ij}^{(n)}(x_i - x_j)^n\right] + x_j x_k \left[\sum_{n=0}^{2} X_{jk}^{(n)}(x_j - x_k)^n\right] \\ & + x_k x_i \left[\sum_{n=0}^{2} X_{ik}^{(n)}(x_k - x_i)^n\right] + x_i x_j x_k \left[\sum_{n=0}^{2} X_{ijk}^{(n)}(x_j - x_k)^n x_i^n\right] \end{aligned} \tag{5}$$

where $\left(X^{(n)}\right)_{ij}$ etc. are adjustable parameters of $(i + j)$, $(j + k)$, and $(i + k)$ binary mixtures and were taken from the literature [4,11,12]. $X_{ijk}^{(n)}(n = 0 - 2)$ adjustable parameters of the $(i + j + k)$ ternary mixtures were calculated by least-squares optimization and are recorded along with standard deviations, $\sigma\left(X_{ijk}^{\mathrm{E}}\right)$, in Tables 2 and 3.

4 Discussion

We are unaware of any existing $V_{ijk}^{\mathrm{E}}$and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ data for the studied mixtures with which to compare our results. The $V_{ijk}^{\mathrm{E}}$and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values for various $(i + j + k)$ ternary mixtures have been analyzed in terms of the Flory and the Sanchez and Lacombe theories.

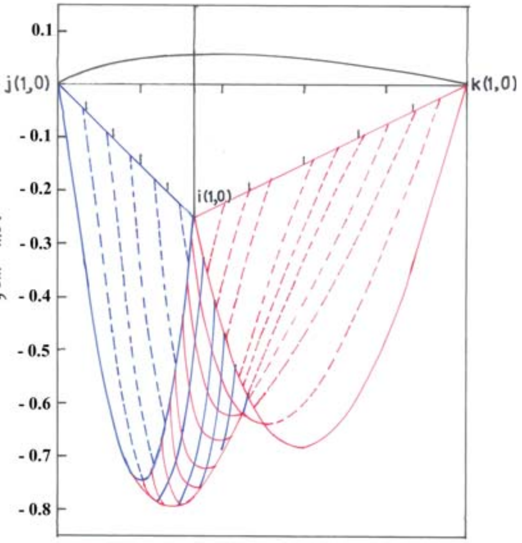

Fig. 1 Molar excess volume, V^{E}, for 2-pyrrolidinone (i) + toluene (j) + o-xylene (k), mixture at 308.15 K

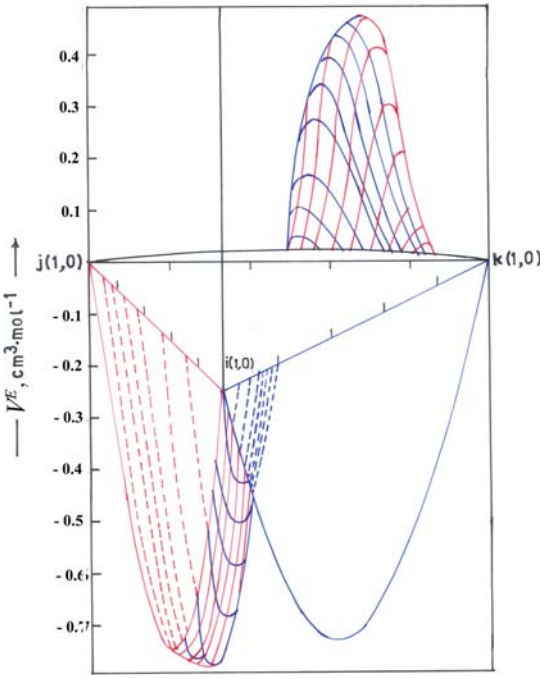

Fig. 2 Molar excess volume, V^{E}, for 2-pyrrolidinone (i) + toluene (j) + p-xylene (k), mixture at 308.15 K

4.1 Flory Theory

According to Flory's theory [17,18], V_{ijk}^{E} for a ternary mixture is given by

$$V^{\mathrm{E}} = \overline{V}_{\mathrm{cal}}^{\mathrm{E}} \left[\sum_{i=i}^{k} x_i v_i^* \right] \tag{6}$$

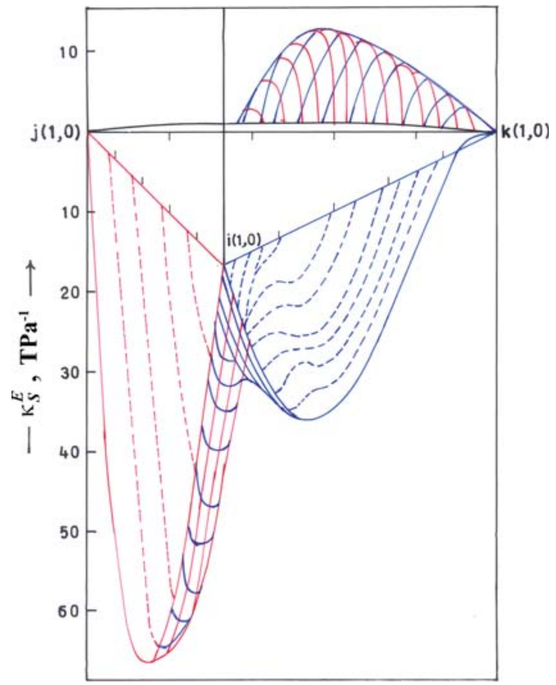

Fig. 3 Excess isentropic compressibilities, κ_S^{E} for 2-pyrrolidinone (i) + toluene (j) + o-xylene (k), mixture at 308.15 K

where

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

Furthermore, $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ is expressed as

$$\left(\kappa_S^{\mathrm{E}}\right)_{ijk} = \kappa_S - \kappa_S^{\mathrm{id}} \tag{8}$$

where

$$\kappa_S = \kappa_T - \mathrm{T} v_m^* \alpha_p^2 / C_{p,m} \tag{9}$$

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

$$\kappa_T = \left[(3\overline{V}_m^2/p^*)(\overline{V}_m^{1/3} - 1)/(4 - 3\overline{V}_m^{1/3})\right] \tag{10}$$

and

$$C_{p,m}/R = (\partial H_{ijk}^{\mathrm{E}}/\partial T) + \sum_{i=i}^{k} x_i C_{p,i} \tag{11}$$

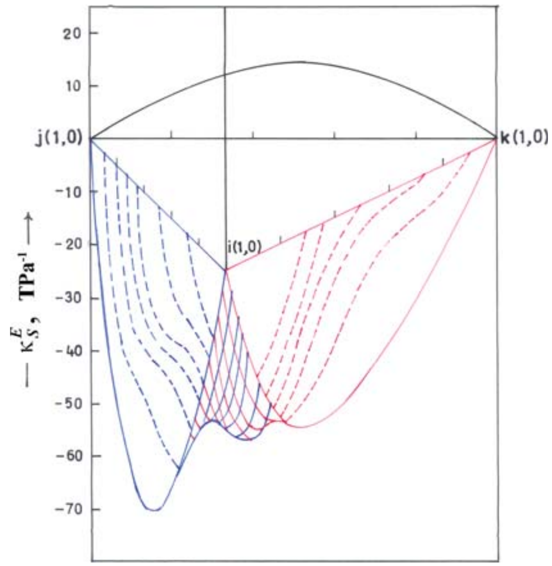

Fig. 4 Excess isentropic compressibilities, κ_S^{E} for 2-pyrrolidinone (i) + toluene (j) + p-xylene (k), mixture at 308.15 K

where all the terms have same significance as described elsewhere [17,18]. The values of $(\partial H_{ij}^{\mathrm{E}}/\partial T)$ for binary mixtures were calculated from experimental H^{E} values available in the literature [4,19]. $(\partial H_{ijk}^{\mathrm{E}}/\partial T)$ values for (i + j + k) ternary mixtures at 308.15 K were taken equal to $H_{ij}^{\mathrm{E}} + H_{jk}^{\mathrm{E}} + H_{ik}^{\mathrm{E}}$, and H_{ijk}^{E} values at 298.15 K were determined in the manner described elsewhere [20]. α_p^{id} and $C_{p,m}^{\mathrm{id}}$ were taken as mole fraction averages, and κ_S^{id} was taken as volume fraction averages.

Evaluation of $V_{ijk}^{\mathrm{E}}$and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ by the Flory theory requires a knowledge of the reduced temperature,$\overline{T}$, 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} value of sub-binary mixtures [4,19] at x_i= 0.5

$$H^{\mathrm{E}} = \sum x_i P_i^* (\overline{V}_i^{-1} - \overline{V}_{\mathrm{cal}}^{-1}) + x_i v_i^* \theta_j \chi_{ij} V_{\mathrm{cal}}^{-1} \tag{12}$$

Various parameters of pure components were determined using isothermal compressibilities (κ_T) reported in the literature [9]. V_{ijk}^{E} and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values for the investigated ternary mixtures were then evaluated in terms of the Flory theory in the manner described in detail elsewhere [17,18]. Such V_{ijk}^{E} and $\left(\kappa_S^{\mathrm{E}}\right)_{ijk}$ values for the various mixtures are recorded in Tables 2 and 3, respectively, together with the corresponding experimental values.

4.2 Sanchez and Lacombe Theory

According to this theory [21,22], V^{E}_{ijk} for a ternary mixture is given by

$$V^{\mathrm{E}}_{ijk} = r_{\mathrm{mix}} v_{\mathrm{mix}} \left[\overline{V}_{\mathrm{mix}} - \sum_{i=i}^{k} \phi_i \overline{V}_i \right] \tag{13}$$

$$\phi_i = m_i (\rho_i^*)^{-1} \left[\sum_{i=i}^{k} (m_i \rho_i^*)^{-1} \right] \tag{14}$$

$$r_{\mathrm{mix}} = \sum_{i=i}^{k} x_i r_i \tag{15}$$

$$\overline{V}_{\mathrm{mix}} = 1/\overline{\rho}_{\mathrm{mix}} \tag{16}$$

where all the terms have the same significance as described elsewhere [21,22].

Evaluation of V^{E}_{ijk} via Eqs. 13–16 requires a knowledge of the reduced density of their ternary mixture, $\overline{\rho}_{ijk}$, which in turn can be evaluated from the equation of state of a ternary mixture,

$$(\overline{\rho}_{ijk})^2 + \overline{P} + [\mathrm{RT}/ \in^*_{\mathrm{mix}}][\ln(1 - \overline{\rho}_{ijk}) + (1 - r^{-1}_{\mathrm{mix}})\overline{\rho}_{ijk}] = 0 \tag{17}$$

where

$$\in^*_{\mathrm{mix}} = \left[\sum_{i=i}^{k} \phi_i^2 \in_{ii} - \sum \phi_i \phi_j \chi^*_{ij} \right] \tag{18}$$

χ^*_{ij}, etc. are the interaction energy parameters for the various (*i* + *j*), (*j* + *k*), and (*i* + *k*) binary mixtures. These parameters have been evaluated by employing H^{E} values ($x_i = 0.5$) of the sub-binary mixtures (*i* + *j*), (*j* + *k*), and (*i* + *k*) available in the literature [4,18] using

$$H^{\mathrm{E}}_{ij} = 2\phi_i \phi_j \tilde{\rho}_{ij} \chi^*_{ij} + \mathrm{RT} r_{\mathrm{mix}} \left[\sum (\phi_i^0 \overline{\rho}_i - \overline{\rho}_{ij} \phi_i)(\overline{T}_i)^{-1} \right] \tag{19}$$

since (*i* + *j*), (*j* + *k*), and (*i* + *k*) binary mixtures of the investigated (*i* + *j* + *k*) ternary mixtures satisfy

$$(\overline{\rho}_{ij})^2 + \overline{P} + [\mathrm{RT}/ \in^*_{ij}][\ln(1 - \overline{\rho}_{ijk}) + (1 - r^{-1}_{\mathrm{mix}})\overline{\rho}_{ijk}] = (-0.002 - 0.001) \tag{20}$$

The present (*i* +*j* + *k*) ternary mixtures, therefore, would also not satisfy Eq.18. If the addition of the *k*th component to the (*i* + *j*) mixture does not drastically alter *i*–*j*, *j*–*k*, and *i*-*k* contacts, then ternary mixtures would also satisfy an equation of state like Eq.20. Since a ternary $(i + j + k)$ mixture is considered to be composed of $(i + j)$, $(j + k)$, and $(i + k)$ binary mixtures, then the extent to which the ternary mixture deviates from Eq. 21 would be nearly one third of the sum to which binary $(i + j)$, $(j + k)$, and $(i + k)$ mixtures deviate. Consequently, the equation of state for ternary mixtures can be expressed by

$$\begin{aligned}(\overline{\rho}_{ijk})^2 + \overline{P} + [\mathrm{RT}/\in^*_{\mathrm{mix}}][\ln(1-\overline{\rho}_{ijk}) + (1 - r^{-1}_{\mathrm{mix}})\overline{\rho}_{ijk}] \\ = 1/3\left[\sum \text{R.H.S of Eq. 20 for } (i+j), (j+k), \text{and } (i+k) \text{ binary mixtures}\right]\end{aligned} \tag{21}$$

V^{E}_{ijk} values calculated for various ternary mixtures using the established equation of state are recorded along with χ^*_{ij}, χ^*_{jk}, and χ^*_{ik} parameters in Table 2.

A pursual of data in Tables 2 and 3 reveals that the Flory theory correctly predicts the sign of V^{E}_{ijk} and $\left(\kappa^{\mathrm{E}}_S\right)_{ijk}$ for the studied mixtures. However, quantitative agreement is poor. The failure of the Flory theory to predict the magnitude of V^{E}_{ijk} and $\left(\kappa^{\mathrm{E}}_S\right)_{ijk}$ values may be due to the nature of components of the studied ternary mixtures. Furthermore, V^{E}_{ijk} values evaluated by the Sanchez and Lacombe theory are of the same sign but the quantitative agreement is not good. The failure of the Sanchez and Lacombe theory to correctly predict the magnitude of V^{E}_{ijk} values may be due to the assumption that the right-hand side of the equation of state for ternary mixtures is independent of composition.

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