Short Articles

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

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Molar excess volumes, V^E_{ijk}, and speeds of sound, U_{ijk}, of *o*-toluidine (i) + toluene (j) + *o*- or *p*-xylene (k) ternary mixtures and speeds of sound, U_{ij}, of *o*-toluidine (i) + toluene or *o*- or *p*-xylene (j) binary mixtures have been determined as a function of composition at 308.15 K. Speeds of sound data have been utilized to evaluate excess isentropic compressibilities for binary (i + j) and ternary (i + j + k) mixtures. Molar excess volumes, V^E_{ijk}, and excess isentropic compressiblities, $(\kappa^E_S)_{ijk}$ data have been fitted to the Redlich−Kister equation to calculate ternary adjustable parameters and standard deviations. Flory theory for binary mixtures has been extended to predict V^E_{ijk} and $(\kappa^E_S)_{ijk}$ for the studied ternary mixtures. It has been observed that theory correctly predicts the sign of V^E_{ijk} values for *o*-toluidine (i) + toluene (j) + *o*-xylene (k) and $(\kappa^E_S)_{ijk}$ values for *o*-toluidine (i) + toluene (j) + *p*-xylene (k) ternary mixtures.

1. Introduction

The characterization of the mixtures through their thermodynamic properties is considered to be one of the most extended and reliable ways to extract information about the structure and molecular interactions of the constituents of mixtures in the pure and mixed state.[1–5] A ternary mixture (i + j + k) is assumed to consist of (i + j), (j + k), and (i + k) sub-binary mixtures; consequently, thermodynamic properties of ternary mixtures can be determined from the thermodynamic properties of their sub-binary mixtures. From a practical point of view, molar excess volumes and isentropic compressibility data are useful for the design of mixing, storage, and process equipment. Also, the measured data reflect the interactions operating between the constituents of mixtures and can serve for testing the theories of the liquid state. In recent studies,[6] we have reported molar excess volumes, molar excess enthalpies of *o*-toluidine (i) + benzene or toluene, or *o*- or *p*- or *m*-xylene (j) binary mixtures at 308.15 K. As a continuation of our studies on the thermodynamic properties of binary and ternary mixtures, we report here molar excess volumes, V^E_{ijk}, speeds of sound, U_{ijk}, data for *o*- toluidine (i) + toluene (j) + *o*- or *p*-xylene (k) ternary mixtures, and speeds of sound, U_{ij}, data of *o*-toluidine (i) + toluene or *o*- or *p*-xylene (j) binary mixtures at 308.15 K.

2. Experimental

2.1. Materials. *o*-Toludine (OT) (Fluka), benzene, toluene, and *o*- and *p*-xylene (AR grade) were purified by standard methods.[7]

2.2. Methods. The purities of the purified liquids were checked by measuring their densities with a pycknometer at (298.15 ± 0.01) K, and the resulting densities (reported in Table 1) agreed to within ± 0.05 kg·m^{-3} of their corresponding literature values.[7]

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Table 1. Comparison of Densities, ρ, and Speeds of Sound, *U*, of Pure Liquids with Their Literature Values at 298.15 K

	ρ/kg·m^{-3}		U/m·s^{-1}	
liquid	exptl	lit.	exptl	lit.
o-toluidine	994.28	994.30[7]	1603[a]	–
toluene	862.21	862.19[7]	1304.6	1304.0[9]
o-xylene	875.99	875.94[7]	1344.0	1345.0[10]
p-xylene	856.58	856.61[7]	1310.1	1309.6[11]

[a] Value at 308.15 K.

Molar excess volumes, V^E_{ijk}, for ternary mixtures were measured dilatometerically as discussed by Singh and Sharma in the manner described elsewhere.[8] The dilatometer had three limbs for three components. The change in liquid level in the dilatometer was measured with a cathetometer that could read to within ± 0.001 cm. The uncertainty in the measured V^E_{ijk} values is ± 0.5 %.

The speed of sound at a frequency of 2 MHz was determined 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.[9–11] The uncertainty in the measured speed of values is ± 1 m·s^{-1}.

3. Results

Molar excess volumes, V^E_{ijk} speeds of sound, U_{ijk}, data of OT (i) + toluene (j) + *o*- or *p*-xylene (k) ternary mixtures and speeds of sound, U_{ij}, data of their sub-binary mixtures OT (i) + toluene or *o*- or *p*-xylene (j) as a function of composition are recorded in Tables 2, 4, and 3 (plotted in Figures 1 and 2), respectively.

The isentropic compressibilities for binary, $(\kappa^E_S)_{ij}$, and ternary, $(\kappa^E_S)_{ijk}$, mixtures were determined by using eqs 1 and 2

10.1021/je800100m CCC: $40.75
Published on Web 07/19/2008

$$(\kappa_s)_{ij} = (\rho_{ij}U_{ij}^2)^{-1} \quad (1)$$

$$(\kappa_s)_{ijk} = (\rho_{ijk}U_{ijk}^2)^{-1} \quad (2)$$

The densities, ρ_{ij} and ρ_{ijk}, of various binary and ternary mixtures were calculated by employing their molar excess volume data[6,12] using the relations

$$V_{ij}^E = \sum_{i=i}^{j} x_i M_i (\rho_{ij})^{-1} - \sum_{i=i}^{j} (x_i M_i)(\rho_i)^{-1} \quad (3)$$

$$V_{ijk}^E = \sum_{i=i}^{k} x_i M_i (\rho_{ijk})^{-1} - \sum_{i=i}^{k} x_i M_i (\rho_i)^{-1} \quad (4)$$

where x_i, M_i, ρ_i, etc. are the mole fraction, molecular mass, and density of component (i) in binary or ternary mixtures. Excess isentropic compressibility, $(\kappa_S^E)_{ij}$ and $(\kappa_S^E)_{ijk}$, values for the binary (i + j) and ternary (i + j + k) mixtures were determined using eqs 5 and 6.

$$(\kappa_s^E)_{ij} = \kappa_s - \sum_{i=i}^{j} \phi_i (\kappa_s)_i \quad (5)$$

$$(\kappa_s^E)_{ijk} = \kappa_s - \sum_{i=i}^{k} \phi_i (\kappa_s)_i \quad (6)$$

where ϕ_i and $(\kappa_S)_i$ are the volume fraction and isentropic compressibility of the component (i). Such $(\kappa_S^E)_{ij}$ and $(\kappa_S^E)_{ijk}$ values for binary and ternary mixtures are recorded in Tables 3 and 4, and $(\kappa_S^E)_{ijk}$ values are plotted in Figures 3 and 4. $(\kappa_S^E)_{ij}$ values for binary mixtures were fitted to eq 7

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

$\kappa_S^{(n)}$ (n = 0 to 2), etc. are parameters characteristic of (i + j) binary mixtures and were evaluated by the least-squares method. Such parameters along with standard deviation, $\sigma(\kappa_S^E)_{ij}$, defined by

$$\sigma(\kappa_s^E)_{ij} = \left[\sum \left(\kappa_{s(\text{exptl})}^E - \kappa_{s(\text{calcdeq7})}^E \right)^2 / (m - n) \right]^{0.5} \quad (8)$$

[m is the number of data points; n is the adjustable parameters] are recorded in Table 3.

Table 2. Comparison of Measured V_{ijk}^E Values for the Various (i + j + k) Ternary Mixtures Evaluated by the Flory Theory with Their Corresponding Experimental Values[a,b]

		V_{ijk}^E/cm^3·mol^{-1}	
x_i	x_j	exptl	Flory
o-Toluidine (i) + Toluene (j) + *o*-Xylene (k)			
0.0983	0.7278	0.030	0.269
0.1127	0.4341	0.060	0.267
0.1885	0.3439	0.068	0.424
0.2029	0.3989	0.066	0.468
0.3345	0.3131	0.067	0.708
0.4018	0.4461	0.053	0.900
0.4254	0.3597	0.043	0.893
0.4281	0.2241	0.054	0.820
0.5024	0.2567	0.049	0.942
0.6001	0.1021	0.035	0.910
0.6587	0.1094	0.035	0.935
0.7014	0.0897	0.034	0.912
0.7518	0.1464	0.013	0.956
o-Toluidine (i) + Toluene (j) + *p*-Xylene (k)			
0.0727	0.5295	0.019	0.211
0.1011	0.4132	0.024	0.287
0.3112	0.2125	0.064	0.773
0.3595	0.2284	0.047	0.868
0.3602	0.1868	0.074	0.864
0.4012	0.1783	0.069	0.933
0.4872	0.1265	0.075	1.046
0.5061	0.1129	0.073	1.064
0.5234	0.3041	−0.032	1.113
0.5783	0.2245	−0.030	1.141
0.6223	0.2312	−0.036	1.158
0.7665	0.1234	−0.031	1.045

[a] Also included are the various parameters $V_{ijk}^{(n)}$ (n = 0 to 2) along with their standard deviation, $\sigma(V_{ijk}^{(E)})$, interaction parameters, χ_{ij}, etc. [b] $V_{ijk}^{(0)} = 1.217$; $V_{ijk}^{(1)} = 7.103$; $V_{ijk}^{(2)} = -63.972$; $\sigma(V_{ijk}^{(E)}) = 0.001$; $\chi_{ij} = 5.2$; $\chi_{jk} = 1.0$; $\chi_{ik} = 4.6$; $V_{ijk}^{(0)} = 1.417$; $V_{ijk}^{(1)} = -12.926$; $V_{ijk}^{(2)} = 142.001$; $\sigma(V_{ijk}^{(E)}) = 0.001$; $\chi_{ij} = 5.2$; $\chi_{jk} = 0.3$; $\chi_{ik} = 4.9$.

Table 3. Speeds of Sound, U_{ij}, Isentropic Compressibilities, $(\kappa_S)_{ij}$, and Excess Isentropic Compressibilities, $(\kappa_S^E)_{ij}$, for the Various (i + j) Binary Mixtures as a Function of Composition, x_i, and Mole Fraction of Component (i) at 308.15 K[a]

	U_{ij}	$(\kappa_s)_{ij}$	$(\kappa_S^E)_{ij}$
x_i	m·s^{-1}	10^{-15} kPa^{-1}	10^{-15} kPa^{-1}
o-Toluidine (i) + Toluene (j)			
0.0457	1270	721.2	−1.9
0.0998	1283	700.9	−3.7
0.1516	1296	681.2	−4.8
0.2017	1308	663.7	−5.4
0.2773	1327	637.8	−5.6
0.3496	1346	613.3	−5.0
0.4070	1359	596.1	−2.6
0.4797	1381	571.1	−2.5
0.5882	1414	536.3	0.2
0.6667	1440	511.3	2.1
0.7464	1470	485.5	3.5
0.8033	1494	466.4	4.0
0.8647	1523	445.3	3.9
0.9223	1554	424.4	2.9
$(\kappa_S^{(0)})_{ij} = -8.0$, $(\kappa_S^{(1)})_{ij} = 49.0$, $(\kappa_S^{(2)})_{ij} = 9.6$, $\sigma\,(\kappa_S^E)_{ij} = 0.1 \cdot 10^{-15}$ kPa^{-1}			
o-Toluidine (i) + *o*-Xylene (j)			
0.0799	1325	650.4	10.4
0.1313	1328	644.0	16.1
0.1977	1333	633.9	22.2
0.2507	1338	624.5	26.0
0.3003	1345	614.1	28.0
0.3663	1355	600.7	31.2
0.4456	1370	581.4	32.2
0.5080	1385	564.5	31.7
0.5892	1408	540.5	29.3
0.6666	1434	515.5	25.5
0.7287	1459	494.5	21.6
0.7884	1485	473.6	17.3
0.8314	1505	458.0	13.9
0.9090	1547	429.1	7.4
$(\kappa_S^{(0)})_{ij} = 127.3$, $(\kappa_S^{(1)})_{ij} = -31.3$, $(\kappa_S^{(2)})_{ij} = -17.4$, $\sigma\,(\kappa_S^E)_{ij} = 0.3 \cdot 10^{-15}$ kPa^{-1}			
o-Toluidine (i) + *p*-Xylene (j)			
0.0534	1287	706.2	−0.5
0.1009	1295	693.2	−1.1
0.1707	1308	672.3	−2.0
0.2483	1325	647.9	−3.0
0.3200	1342	625.1	−3.8
0.3949	1361	600.6	−4.5
0.4559	1378	580.8	−4.9
0.5332	1402	554.9	−5.5
0.6007	1423	533.0	−5.0
0.6897	1455	502.9	−4.4
0.7417	1475	485.3	−3.9
0.8009	1500	465.3	−3.2
0.8668	1530	442.2	−2.2
0.9374	1567	417.3	−1.1
$(\kappa_S^{(0)})_{ij} = -20.1$, $(\kappa_S^{(1)})_{ij} = -4.1$, $(\kappa_S^{(2)})_{ij} = 7.5$, $\sigma\,(\kappa_S^E)_{ij} = 0.1 \cdot 10^{-15}$ kPa^{-1}			
$(\kappa_S^{(n)})_{ij}$ (n = 0−2) and $\sigma\,(\kappa_S^E)_{ij}$ are in kPa^{-1}			

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

Table 4. Speeds of Sound, U_{ijk}, Isentropic Compressibilities, $(\kappa_S)_{ijk}$, and Excess Isentropic Compressibilities $(\kappa_S^E)_{ijk}$ for the Various (i + j + k) Ternary Mixtures as a Function of Composition, x_i, and Mole Fraction of Component (i) at 308.15 K with $(\kappa_S^E)_{ijk}$ Values Evaluated from Flory's Theory[a]

		U_{ijk}	$(\kappa_S)_{ijk}$	$(\kappa_S^E)_{ijk}/10^{-15}$ kPa^{-1}	
x_i	x_j	ms^{-1}	10^{-15} kPa^{-1}	exptl	Flory
o-Toluidine (i) + Toluene (j) + *o*-Xylene (k)					
0.0485	0.7541	1304	709.8	4.5	17.9
0.1342	0.6948	1330	638.1	6.1	4.3
0.1879	0.6349	1378	664.5	12.3	−2.5
0.2567	0.5738	1459	641.9	23.3	−9.5
0.3045	0.5139	1492	624.9	26.9	−12.8
0.3412	0.4619	1493	611.5	24.7	−14.4
0.3817	0.3654	1509	594.1	24.2	−14.1
0.4361	0.2968	1627	575.0	42.3	−14.3
0.4673	0.3149	1535	567.8	23.9	−16.3
0.5140	0.2583	1631	551.6	37.7	−15.3
0.6208	0.1861	1711	518.0	43.3	−13.2
0.6693	0.1521	1750	502.6	46.2	−11.2
0.7513	0.1131	1708	477.4	32.1	−7.7
0.8341	0.0681	1677	451.4	20.8	−2.4
$(\kappa_S^{(0)})_{ijk} = 1143.8$; $(\kappa_S^{(1)})_{ijk} = -28604.8$; $(\kappa_S^{(2)})_{ijk} = 247431.1$; $\sigma(\kappa_S^E)_{ijk} = 0.3$					
o-Toluidine (i) + Toluene (j) + *p*-Xylene (k)					
0.1512	0.2576	1367	686.9	15.5	8.6
0.2267	0.6112	1127	664.6	−28.6	−5.6
0.2518	0.4216	1115	655.8	−31.9	−4.8
0.3026	0.4348	1054	639.1	−41.4	−9.8
0.3275	0.5216	1137	630.7	−29.7	−14.3
0.3480	0.3500	1132	624.2	−32.0	−11.2
0.3618	0.5814	1318	618.9	−3.6	−19.0
0.4326	0.3047	1155	519.1	−31.4	−14.8
0.5164	0.2596	1204	568.0	−27.4	−16.3
0.5710	0.3130	1241	548.4	−24.0	−19.3
0.6617	0.1750	1343	518.7	−14.0	−13.9
0.7023	0.1875	1339	504.0	−16.4	−14.1
0.7713	0.1345	1420	480.4	−8.9	−9.8
$(\kappa_S^{(0)})_{ijk} = -700.0$; $(\kappa_S^{(1)})_{ijk} = -16528.6$; $(\kappa_S^{(2)})_{ijk} = 104366.0$; $\sigma(\kappa_S^E)_{ijk} = 0.3$					
$(\kappa_S^{(n)})_{ijk}$ (n = 0 to 2) and $\sigma(\kappa_S^E)_{ijk}$ are in kPa^{-1}					

[a] Also included are various parameters $(\kappa_S^{(n)})_{ijk}$ (n = 0 to 2) along with their standard deviation, $\sigma(\kappa_S^E)_{ijk}$.

Molar excess volumes, V_{ijk}^E, and excess isentropic compressibilities, $(\kappa_S^E)_{ijk}$, for (i + j + k) ternary mixtures were fitted to Redlich−Kister eq 9

$$X_{ijk}^E(X = V or \kappa_s) = x_i x_j\left[\sum_{n=0}^{2} X_{ij}^{(n)}(x_i - x_j)^n\right] + x_j x_k\left[\sum_{n=0}^{2} X_{jk}^{(n)}(x_j - x_k)^n\right] + x_k x_i\left[\sum_{n=0}^{2} X_{ik}^{(n)}(x_k - x_i)^n\right] + x_i x_j x_k\left[\sum_{n=0}^{2} X_{ijk}^{(n)}(x_j - x_k)^n x_i^n\right] \quad (9)$$

where $X_{ijk}^{(n)}$ (n = 0 to 2) are the parameters characteristic of the (i + j + k) ternary mixtures. $X_{ijk}^{(n)}$, etc., are parameters characteristic of (i + j), (j + k), and (i + k) binary mixtures and were taken from the literature.[6,12] $X_{ijk}^{(n)}$ (n = 0 to 2) parameters were calculated by fitting V_{ijk}^E and $(\kappa_S^E)_{ijk}$ data to eq 10 by the least-squares method

$$\left(\begin{array}{l} X_{ijk}^E - x_i x_j\left[\sum_{n=0}^{2} (X_{ij}{}^{(n)}(x_i - x_j)^n\right] \\ -x_j x_k\left[\sum_{n=0}^{2} X_{jk}{}^{(n)}(x_j - x_k)^n\right] \\ -x_i x_k\left[\sum_{n=0}^{2} X_{ik}{}^{(n)}(x_k - x_i)^n\right] \end{array}\right)[x_i x_j x_k]^{-1} = \left(\sum_{n=0}^{2} X_{ijk}{}^{(n)}(x_j - x_k)^n x_i^n\right) \quad (10)$$

and are recorded along with standard deviation, $\sigma(X_{ijk}^E)$, defined by

$$\sigma\left(X_{ijk}^E(X = V or \kappa_s)\right) = \left[\sum X_{ijk(exptl)}^E - X_{ijk(calcd.eq.9)}^E\right]^{0.5} \quad (11)$$

[where $X_{ijk(calcdeq9)}^E$ are the values evaluated from eq 9; m is the number of data points; and n is the number of adjustable parameters in eq 9] in Tables 2 and 4.

4. Discussion

We are unaware of any existing V_{ijk}^E, $(\kappa_s^E)_{ij}$, and $(\kappa_s^E)_{ijk}$ for the studied mixtures with which to compare our results. V_{ijk}^E and $(\kappa_s^E)_{ijk}$ values for OT (i) + toluene (j) + *o*-xylene (k) ternary mixtures are positive over the entire composition range. However, for OT (i) + toluene (j) + *p*-xylene (k), ternary mixture V_{ijk}^E and $(\kappa_s^E)_{ijk}$ values change sign from positive to negative with an increase in mole fraction of OT. This may be due to the presence of two adjacent $-CH_3$ groups in *o*-xylene which restrict the approach of the *o*-xylene molecule to an OT:toluene molecular entity.

The V_{ijk}^E and $(\kappa_s^E)_{ijk}$ values for various (i + j + k) ternary mixtures have been analyzed in terms of Flory's theory. According to Flory's theory,[13,14] V_{ijk}^E for a ternary mixture is given by

$$V_{ijk}^E = \bar{V}_{calcd}^E\left[\sum_{i=i}^{k} x_i v_i^*\right] \quad (12)$$

where

$$\bar{v}_i = [1 + \alpha_i(T/3)/(1 + \alpha_i T)^3]^3 \quad (13)$$

$$\bar{V}_{calcd}^E = \bar{v}_0^{7/3}\left[(4/3) - (\bar{v}_0)^{1/3}\right]^{-1}[\bar{T} - \bar{T}_0] \quad (14)$$

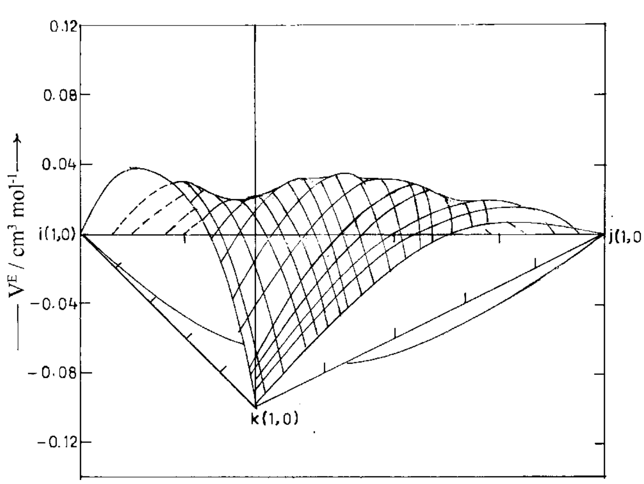

Figure 1. Molar excess volume, V^E, for *o*-toluidine (i) + toluene (j) + *o*-xylene (k) at 308.15 K.

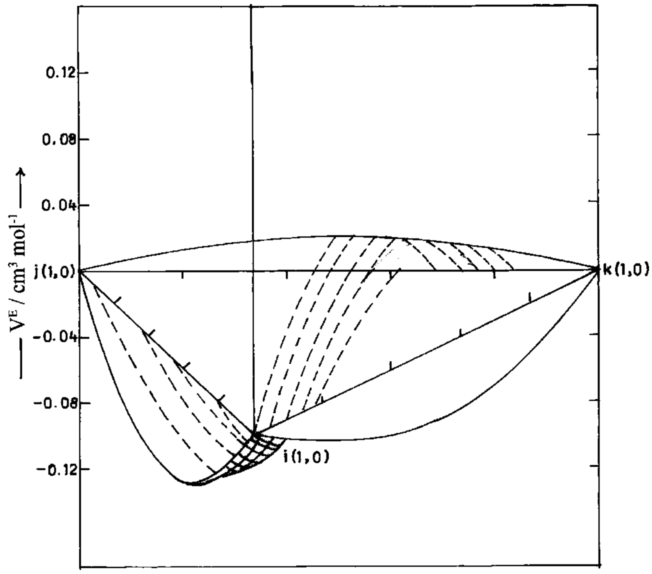

Figure 2. Molar excess volume, V^E, for *o*-toluidine (i) + toluene (j) + *p*-xylene (k) at 308.15 K.

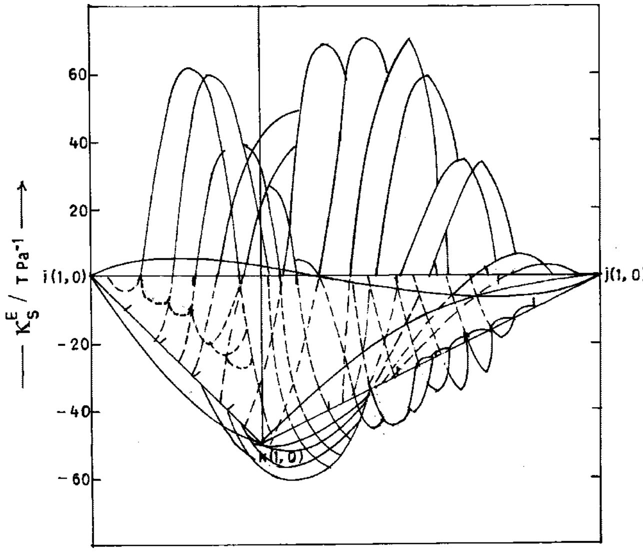

Figure 4. Excess isentropic compressibility, κ_S^E, for *o*-toluidine (i) + toluene (j) + *p*-xylene (k) at 308.15 K.

$$\bar{T}_0 = (\bar{v}_0^{1/3} - 1)/\bar{v}_0^{4/3} \quad (15)$$

$$\bar{v}_i^* = v_i/\bar{v}_i \quad (16)$$

$$\bar{v}_0 = \Sigma\phi_i v_i^* \quad (17)$$

$$\bar{T} = \left[\Sigma\left(\phi_i P_i^* \bar{T}_i/\Sigma\phi_i P_i^*\right)\right]\left[1 - (\phi_i\theta_j\chi_{ij})\left(\Sigma\phi_i P_i^*\right)^{-1}\right]^{-1} \quad (18)$$

$$\bar{T}_i = (\bar{v}_i^{1/3} - 1)/\bar{v}_i^{4/3} \quad (19)$$

$$P^* = \Sigma\phi_i P_i^* - \Sigma\phi_i^*\theta_j\chi_{ij} \quad (20)$$

$$P_i^* = \alpha_i T\bar{v}_i^2[(K_T)_i]^{-1} \quad (21)$$

where x_i, V_i^*, α_i, and $(\kappa_T)_i$ denote the mole fraction, characteristic volume, and cubic expansion coefficient of component (i) in the (i + j + k) mixture, respectively, while $\bar{T}_0$, $\bar{v}_0$, and $\bar{T}$ are ideal reduced temperature, ideal reduced volume, and the reduced temperature of the mixture and have the same significance as described elsewhere.[13,14]

Evaluation of V_{ijk}^E by the 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[6,15] at $x_i = 0.5$ to eq 22

$$H^E = \Sigma x_i P_i^*(\bar{V}_i^{-1} - \bar{V}_{calcd}^{-1}) + x_i V_i^*\theta_j\chi_{ij} V_{calcd}^{-1} \quad (22)$$

Various parameters of pure components were determined using isothermal compressibility (κ_T) reported in the literature.[16] κ_T values for OT were calculated by employing ΔH_V values in

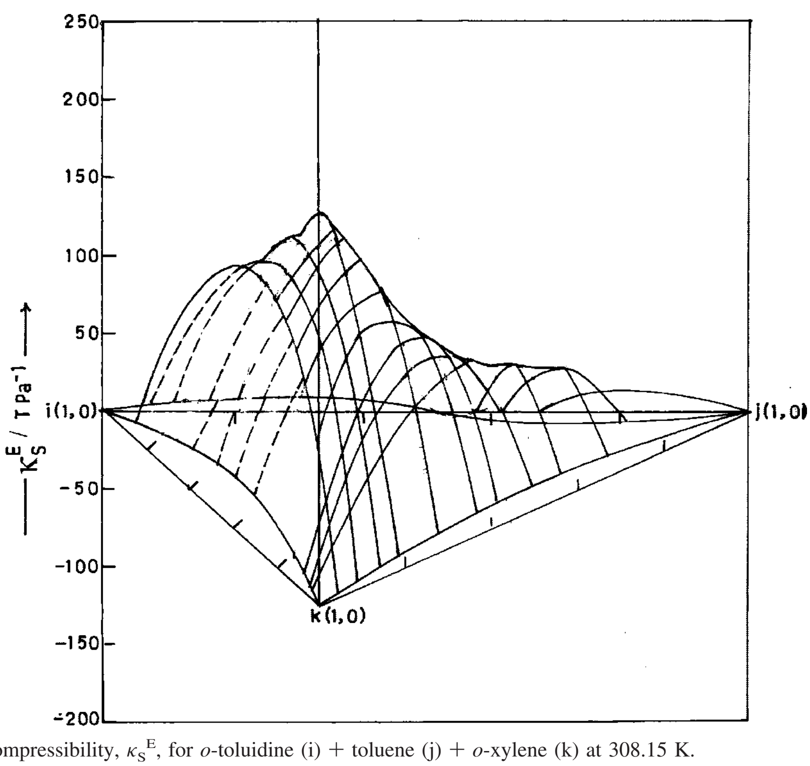

Figure 3. Excess isentropic compressibility, κ_S^E, for *o*-toluidine (i) + toluene (j) + *o*-xylene (k) at 308.15 K.

the manner as suggested by Hilderbrand.[17] Such V^E_{ijk} values evaluated via eqs 12 to 21 along with χ_{ij} etc. parameters are recorded in Table 2 and are also compared with their corresponding experimental values.

According to Flory's theory, $(\kappa^E_S)_{ijk}$ is expressed by the relation

$$\kappa_S^E = \kappa_s - \kappa_s^{id} \tag{23}$$

The isentropic compressibility, κ_S, of (i + j + k) ternary mixtures, at effectively zero pressure, is expressed by eq 24

$$\kappa_s = \kappa_T - T v^*_m \alpha_p^2 / C_{p,m} \tag{24}$$

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

$$\kappa_T = \left[\left(3\bar{v}_m^2/p^*\right)(\bar{v}_m^{1/3} - 1)/(4 - 3(\bar{v}_m^{1/3})\right] \tag{25}$$

where

$$v^*_m = \sum_{i=i}^{k} \phi_i v^*_i \tag{26}$$

$$\alpha_p = 3\left((\bar{v}_m^{1/3} - 1)/T(4 - 3(\bar{v}_m^{1/3}))\right) \tag{27}$$

$$p^* = \sum_{i=i}^{k} \phi_i p^*_i - \sum_{i=i}^{k} \phi_i \theta_j \chi_{ij} \tag{28}$$

$$\bar{v} = v/v^* \tag{29}$$

$$\bar{v}_m = \sum_{i=i}^{k} \phi_i v^*_i \tag{30}$$

$$C_{p,m} = (\partial H^E_{ijk}/\partial T) + \sum_{i=i}^{k} x_i C_{p,i} \tag{31}$$

where $C_{p,i}$ represents the molar heat capacities of component (i) in ternary mixtures. $(\partial H^E_{ijk}/\partial T)$ values at 308.15 K for OT (i) + toluene (j) + *o*- or *p*-xylene (k) ternary mixtures were evaluated by employing H^E values[6,15] for their sub-binary (i + j), (j + k), and (i + k) mixtures. H^E_{ijk} were taken equal to H^E_{ij} + H^E_{jk} + H^E_{ik}. H^E_{ij} etc. values at 298.15 K were calculated in the manner described elsewhere.[18] $\kappa_S{}^{id}$ values for the corresponding ideal mixtures were calculated using eq 24. While α_p^{id} and $C^{id}_{p,m}$ were taken as mole fraction average, $\kappa_S{}^{id}$ values were taken as volume fraction averages. Such $(\kappa^E_S)_{ijk}$ values calculated for the present ternary mixtures are recorded in Table 4, respectively, and are also compared with their corresponding experimental values.

A perusal of data in Tables 2 and 4 reveals that the Flory theory correctly predicts the sign of V^E_{ijk} for OT (i) + toluene (j) + *o*-xylene (k) and $(\kappa^E_S)_{ijk}$ for OT (i) + toluene (j) + *p*-xylene (k) ternary mixtures. However, Flory theory fails to predict sign of V^E_{ijk} values for OT (i) + toluene (j) + *p*-xylene (k) and $(\kappa^E_S)_{ijk}$ values for OT (i) + toluene (j) + *o*-xylene (k) mixtures. This may be due to the association of OT as Flory theory fails to predict molar excess volumes, molar excess enthalpies, and excess isentropic compressibilities of binary mixtures containing the associated molecular entity. The failure of theory to correctly predict the sign of V^E_{ijk} and $(\kappa^E_S)_{ijk}$ data may also be due to the parameters of pure components which have not been reported in the literature but have been determined theoretically.

Acknowledgment

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

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Received for review February 9, 2008. Accepted May 29, 2008.

JE800100M