Excess Properties for Binary Systems in the Temperature Range (298.15 to 323.15) K

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Abstract: *The measured densities, ρ, and speeds of sound, u, for pure ethyl propionate (EP) and m-xylene from (298.15 to 323.15) K and their binary mixtures have been reported. Excess internal pressure (π_i^E), excess free length (L_f^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) for binary mixtures were determined. The calculated excess values have been fitted to the Redlich-Kister polynomial equations and the results are analysed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules.*

Key words: **Excess properties; Internal Pressure; Excess Gibbs energy of activation; Molecular interactions; Ethyl propionate; xylene**

1. Introduction

Determination of density and speeds of sound is a valuable tool to know the liquid state [1,2], because there is a close connection between liquid structure and macroscopic properties. In recent years, measurements of optical, thermodynamic, acoustic and transport properties of binary mixtures have been used to investigate the nature of molecular interactions, molecular packing, molecular motion and physic-chemical behavior in liquid mixtures that influenced by size, shape and nature of chemical components and microscopic structure of liquids [3,4].

In this article we report the values of density, speed of sound, excess internal pressure (π_i^E), excess free length (L_f^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) for the binary mixtures of ethyl propionate + m-xylene at 298.15 K to 323.15 K over the entire mole fraction range. The excess values were fitted to Redlich-Kister polynomial equation to obtain their coefficients and have been interpreted in terms of molecular interactions.

2. Apparatus and Procedure

Speeds of sound and density of pure liquids and their blends have been measured by digital oscillating Density and Sound Analyzer (DSA 5000M, Anton Parr, Austria) with reproducibility of ± $1\cdot10^{-2}$ $m\cdot s^{-1}$ for speed of sound and ± $1\cdot10^{-3}$ $kg\cdot m^{-3}$ for density. It automatically performs the viscosity corrections for density during measurements up to 700 mPa. A propagation time technique is used to measure the speed of sound at frequency of 3 MHz. The densimeter was calibrated randomly with dry air [5] at atmospheric pressure and triply-distilled, freshly degassed and deionized water (ρ = 997.075 $kg\cdot m^{-3}$ at 298.15 K) supplied by Anton-Paar as described elsewhere [6]. After each measurement the distilled water and anhydrous ethanol were used to clean the vibrating tube. For temperature, density and speed of sound measurements, the standard uncertainties were estimated to be within ± 0.01 K, ± $5\cdot10^{-3}$ $kg\cdot m^{-3}$ and ± 0.5 $m\cdot s^{-1}$ respectively. Sartorius CPA 225D balance having precision of ± 0.01 mg is used for weighing. Uncertainties in calculation of the solution concentration were estimated at ± $1\cdot10^{-4}$. Based on the IUPAC relative atomic mass table, all molar quantities were expressed in this paper[7]. Detailed explanation of these equipment's can be found elsewhere [8,9].

3. Theory

The internal pressure of a fluid is related to the thermal pressure coefficient $(\partial P/\partial T)_V$ by the following well-known thermodynamic equation of state,

$$\pi_i = (\frac{\partial E}{\partial V})_T = T(\frac{\partial P}{\partial T})_V - P = T\left(\frac{\alpha_P}{k_T}\right) - P \quad --- \quad (1)$$

whereα_P is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. The external pressure (P) becomes negligible in comparison because, for most of the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e., $T(\alpha_P/k_T)$ is very high, therefore it may be neglected in Eq.(1). Thus, the internal pressure can be shown to be equal to the following relationship [10].

$$\pi_{i=\frac{\alpha_P}{k_T}}T \quad ---- \quad (2)$$

The free volume, V_f of the mixtures are calculated from the relation

$$V_f = \frac{RT}{(P+\pi_i)} \quad ---- \quad (3)$$

since P is very small as compared to π_i, it has been neglected in the Eq.(3) in the present calculations. k_T is calculated using the relationship [11,12],

$$k_T = k_s + \frac{TV\alpha_P^2}{C_P} \quad --- \quad (4)$$

where$k_s[=1/(\rho u^2)]$ is isentropic compressibility, V is the molar volume and C_p is the heat capacity of the mixture. The α_p values for the mixtures were evaluated from temperature dependence of density data. The C_p values of pure liquids have been taken from the literature [13,14] and the following relationship have been used for calculating the C_p values for the mixtures:

$$C_p = x_1C_{p,1} + x_2C_{p,2} \quad --- \quad (5)$$

Intermolecular free length,

$$L_f = K_T.\beta^{1/2} \quad --- \quad (6)$$

where, $\beta = 1/\rho u^2$ and K_T is temperature dependent constant.

The values of various parameters, C_p, α_p, k_s and k_T of pure liquids used in the calculations are taken from our earlier paper[4]. The π_i^E and V_f^E of binary mixtures have been calculated using the relationship,

$$Y^E = Y - (x_1Y_1 + x_2Y_2) \quad --- \quad (6)$$

where Y is π_i or V_f and subscripts 1 and 2 refers to pure DEC and xylenes respectively. The H^E and T_S^E are obtained from π_i and V_f by using the following relations based on regular solution theory [15,16,17].

$$-H^E = \pi_iV - [x_1\pi_{i,1}V_1 + x_2\pi_{i,2}V_2] \quad --- \quad (7)$$

$$T_S^E = R\,[x_1\ln V_{f,1} + x_2\ln V_{f,2} - \ln V_f] \quad --- \quad (8)$$

G^E of mixtures can be calculated by using,

$G^E = H^E - T_s^E$ --- (9)

The values of π_i^E, V_f^E, H^E, $T_S^E$and G^Ewere fitted to a Redlich-Kister [18] equation

$$Y^E = x_1 x_2 \sum_{i=0}^{j} A_i (1-2x_1)^i \quad --- \quad (10)$$

where Y^E is π_i^E or V_f^E or L_f^E or H^E or T_S^Eor G^E. The values of A_i are the coefficients of the polynomial equation and the corresponding standard deviations, $\sigma(Y^E)$ obtained by the method of least – squares with equal weights assigned to each point are calculated. The standard deviation $\sigma(Y^E)$ is defined as follows:

$\sigma(Y^E) = [\sum(Y^E_{obs} - Y^E_{cal})^2/(n-m)]^{1/2}$ --- (11)

where n is the total number of experimental points and m is the number of coefficients.

4. Results and Discussion

Densities and speeds of sound of blends consisting of EP and m-xylene were determined experimentally at six different temperatures in the range 298.15 K to 323.15 K at pressure 0.1Pa. The variation of density and speeds of sound with mole fraction of EP for the binary mixture at six different temperatures are shown in Table 1. The decrease in values of density and speed of sound are observed with increase in temperature. It is also observed from the same table that the increase in density values and decrease in speed of sound values with increase in mole fraction.

The excess internal pressure (π_i^E), excess free length (L_f^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) over the entire composition range for binary mixtures of EP + m-xylene were calculated from density and speed of sound data at the temperatures between 298.15 K and 323.15 K and atmospheric pressure.

The results are graphically present in figures 1-6. The experimental results were fitted by the method of least squares with all points weighted equally to the Redlich- Kister polynomial equation. The solid lines in figures 1 to 6 represents the values calculated from the smoothing equations. The parameters A_1, A_2,A_3 and standard deviations, σ are shown in Table 2.

Table 1. Density (ρ) and speed of sound (u) values of binary mixtures EP + m-xylene at different temperatures.

Mole fraction, x_1	Density, ρ / kg.m^{-3}					
	298.15	303.15	308.15	313.15	318.15	323.15
0.0000	859.9	855.6	851.2	846.9	842.6	838.2
0.0990	862.3	857.8	853.3	848.9	844.4	839.9
0.1937	864.6	860.0	855.4	850.7	846.1	841.4
0.2819	866.8	862.0	857.3	852.5	847.7	842.9
0.3799	869.2	864.3	859.4	854.4	849.5	844.6

0.4751	871.5	866.5	861.4	856.3	851.3	846.2
0.5868	874.2	869.0	863.8	858.5	853.3	848.0
0.6857	876.7	871.3	865.9	860.5	855.1	849.7
0.7892	879.2	873.7	868.1	862.6	857.0	851.4
0.8731	881.3	875.6	869.9	864.2	858.5	852.9
1.0000	884.4	878.5	872.6	866.7	860.9	855.0
	speed of sound, u / m.s^{-1}					
0.0000	1319.9	1299.2	1278.7	1258.3	1238.1	1218.0
0.0990	1303.7	1283.0	1262.4	1242.0	1221.7	1201.5
0.1937	1288.3	1267.5	1246.9	1226.4	1206.0	1185.7
0.2819	1273.9	1253.1	1232.4	1211.8	1191.3	1171.0
0.3799	1257.9	1237.0	1216.3	1195.6	1175.1	1154.6
0.4751	1242.4	1221.5	1200.6	1179.9	1159.3	1138.7
0.5868	1224.1	1203.2	1182.3	1161.5	1140.7	1120.0
0.6857	1208.0	1187.0	1166.1	1145.2	1124.3	1103.5
0.7892	1191.1	1170.1	1149.1	1128.1	1107.2	1086.2
0.8731	1177.4	1156.3	1135.3	1114.2	1093.2	1072.2
1.0000	1156.7	1135.6	1114.4	1093.3	1072.2	1051.0

Table 2.Least-squares parameters, A_i, of the equation 10 and the standard deviations, σ for binary mixtures at different temperatures

Property	T(K)	A_1	A_2	A_3	σ
π_i^E /10^8 Nm^{-2}	298.15	0.1254	-0.0097	0.0017	1.28E-05
	303.15	0.1287	-0.0100	0.0013	2.19E-05
	308.15	0.1326	-0.0102	0.0007	2.08E-05
	313.15	0.1363	-0.0107	0.0015	2.16E-05
	318.15	0.1417	-0.0110	0.0016	1.79E-05
	323.15	0.1466	-0.0115	0.0018	1.97E-05
L_f^E A^0	298.15	-0.0090	-0.0004	0.0003	3.24E-05
	303.15	-0.0097	-0.0008	0.0003	2.55E-05
	308.15	-0.0104	-0.0007	0.0000	2.86E-05
	313.15	-0.0113	-0.0008	-0.0003	2.47E-05
	318.15	-0.0122	-0.0009	0.0002	1.49E-05
	323.15	-0.0134	-0.0011	0.0000	2.16E-05
V_f^E/ 10^{-6} m^{3}mol^{-1}	298.15	-26.8713	2.1895	-0.5296	0.0013
	303.15	-27.7884	2.0510	-0.5090	0.0007
	308.15	-28.8358	1.9059	-0.5094	0.0006
	313.15	-29.8255	1.6798	-0.5137	0.0007
	318.15	-31.4298	1.5805	-0.5665	0.0015
	323.15	-32.9449	1.3193	-0.5415	0.0006
H^E / kJ mol^{-1}	298.15	-1.4649	0.1692	-0.0196	5.30E-05
	303.15	-1.4535	0.1658	-0.0193	4.51E-05
	308.15	-1.4429	0.1620	-0.0183	3.54E-05
	313.15	-1.4168	0.1557	-0.0179	3.04E-05
	318.15	-1.4219	0.1555	-0.0181	5.37E-05
	323.15	-1.4092	0.1518	-0.0173	3.24E-05
G^E / kJ mol^{-1}	298.15	-1.3724	0.1617	-0.0185	2.43E-05
	303.15	-1.3591	0.1590	-0.0179	3.64E-05
	308.15	-1.3462	0.1554	-0.0177	4.16E-05
	313.15	-1.3185	0.1495	-0.0165	3.13E-05
	318.15	-1.3201	0.1495	-0.0159	2.86E-05
	323.15	-1.3044	0.1461	-0.0157	4.84E-05

T_S^E / 10^{-2} J mol^{-1}	298.15	-0.0923	0.0074	-0.0015	2.88E-05
	303.15	-0.0944	0.0071	-0.0016	2.36E-05
	308.15	-0.0967	0.0068	-0.0009	2.11E-05
	313.15	-0.0983	0.0063	-0.0009	1.92E-05
	318.15	-0.1018	0.0062	-0.0015	2.91E-05
	323.15	-0.1046	0.0059	-0.0012	2.69E-05

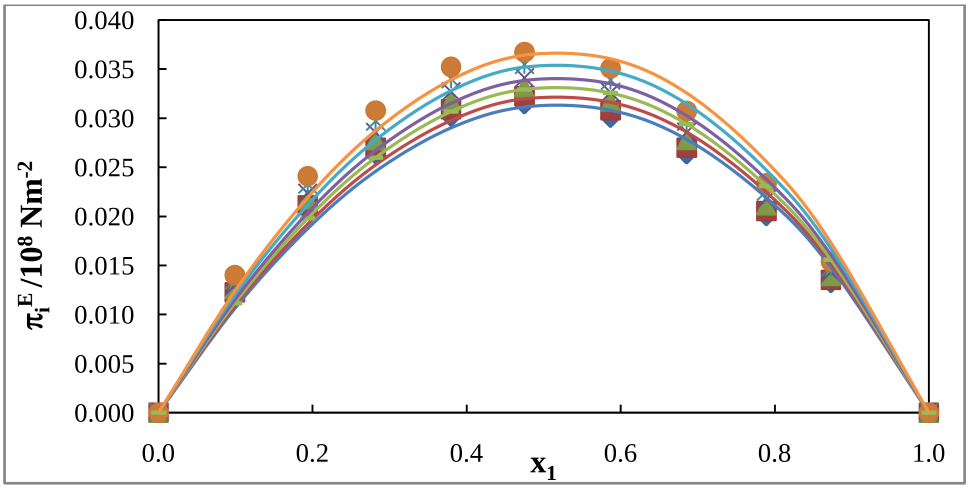

Figure 1: Plots of excess internal pressure, π_i^E*versus* mole fraction (x_1) of EP for binary systems at T = 298.15 K (◆), 303.15 K (■), 308.15 K (▲), 313.15 K (×), 318.15 K (∗) and 323.15 K (●). Points shown experimental values and curves show smoothed values using equation (10).

The internal pressure is the cohesive force, which is a result of force of attraction and force of repulsion between the molecules. The internal pressure is the single factor which varies due to all type of solvent-solute, solute-solute and solvent-solvent interactions. From Fig.1 it is observed that π_i^E values are first increases up to 0.5 mole fraction and then decreases. The increases in π_i^E values with increase in temperature are observed from the same figure. The EP is a polar molecule; m-xylene is a non-polar molecule. The mixtures formed by EP and m-xylene not only have dipolar-dipolar interaction between EP molecules, but also have the interaction of dipolar-induced dipolar between EP and m-xylene molecules.

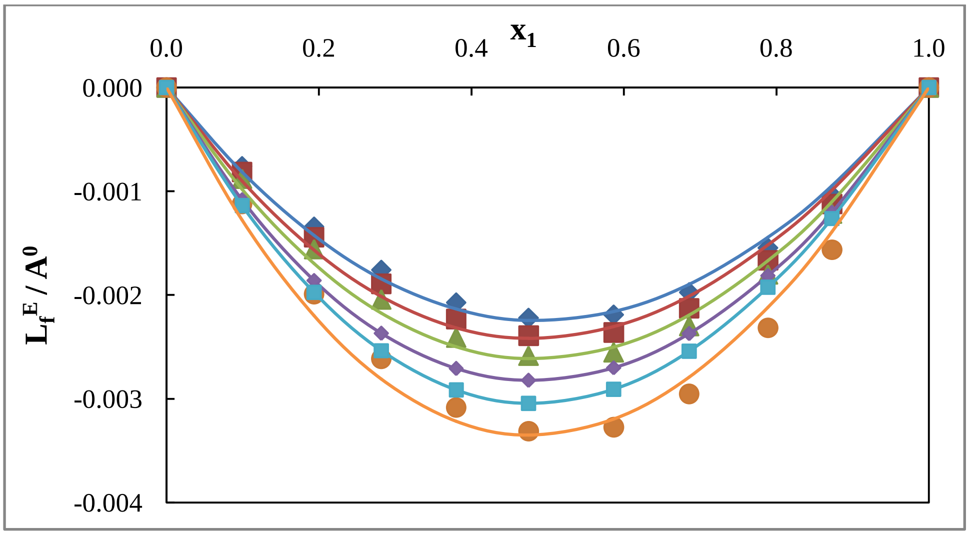

Figure 2: Plots of excess free length, L_f^E *versus* mole fraction (x_1) of EP for binary systems at T = 298.15 K (◆), 303.15 K (■), 308.15 K (▲), 313.15 K (×), 318.15 K (∗) and 323.15 K (●). Points shown experimental values and curves show smoothed values using equation (10).

The intermolecular free length is an important physical property of liquid mixtures which mainly affects the sound velocity. The intermolecular free length decreases with decreases the sound velocity. Variation of L_f^E with mole fraction is shown in Fig.2. At all the investigated temperatures, the L_f^E values are observed to be negative and these values are more negative at mole fraction 0.5. The negative trend is observed to be increased with increase of temperature. The negative L_f^E values shows, greater strength of interaction between the components and may be qualitatively interpreted in terms of closer approach of unlike molecules leading to reduction in volume.

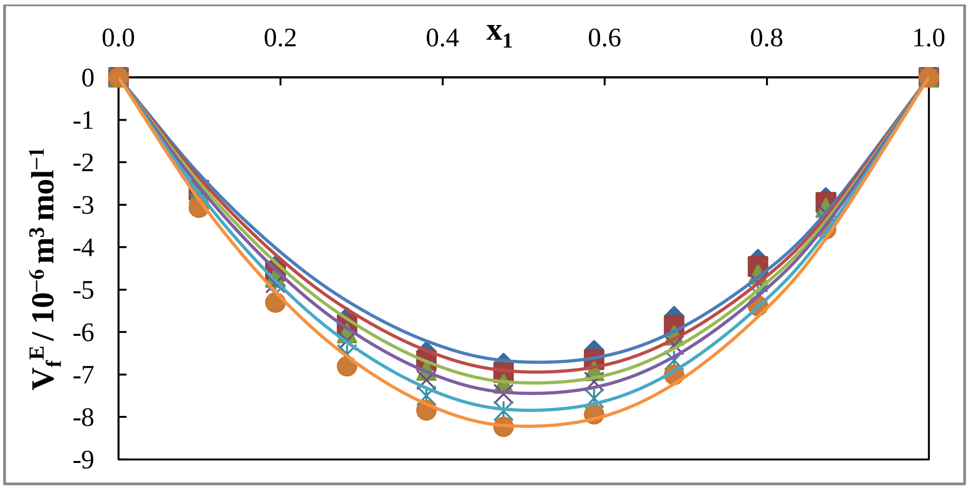

Figure 3: Plots of excess free volume, V_f^E *versus* mole fraction (x_1) of EP for binary systems at T = 298.15 K (◆), 303.15 K (■), 308.15 K (▲), 313.15 K (×), 318.15 K (∗) and 323.15 K (●). Points shown experimental values and curves show smoothed values using equation (10).

Rate process in liquids is determined by the free volume. So, free volume plays an important role in ultrasound wave propagation. The values of V_f^E (Fig. 3) are negative and increase with increase in temperature;it may be due to looser molecular packing. Which indicate the presence of strong molecular interaction and the magnitude of V_f^E indicates the formation of complex between the hetero molecules of the mixtures.

Variation of excess enthalpy with mole fraction for different temperatures is shown in Fig. 4. These values are observed to be negative over the entire mole fraction of EP. Excess enthalpy is defined as the change in enthalpy upon mixing of the two pure components. The process of mixing involves the disruption of interactions in the pure solvents and the establishment of new interactions in the mixture.

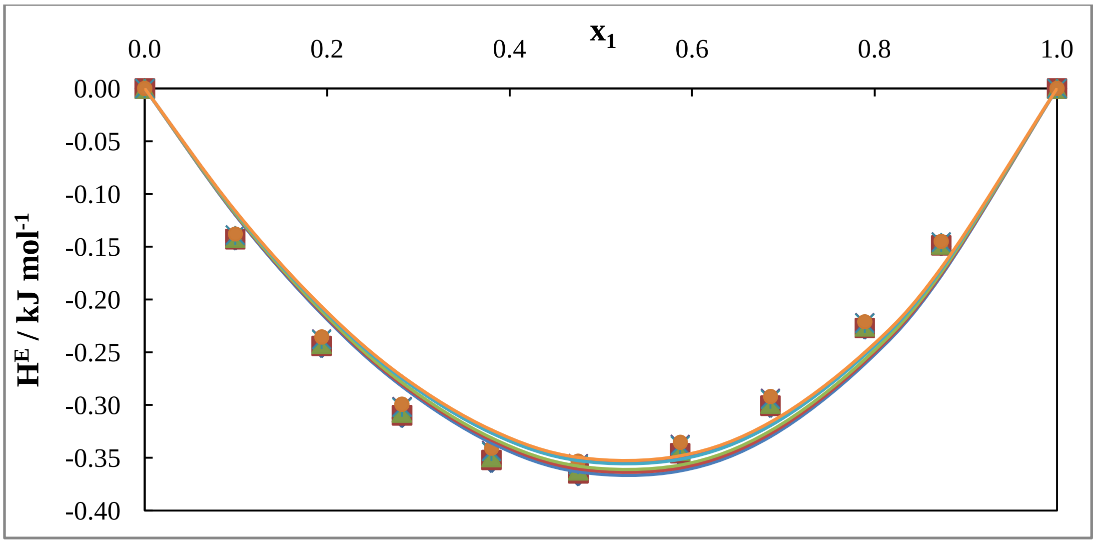

Figure 4: Plots of excess enthalpy, H^E*versus* mole fraction (x_1) of EP for binary systems at T = 298.15 K (◆), 303.15 K (■), 308.15 K (▲), 313.15 K (×), 318.15 K (✳) and 323.15 K (●). Points shown experimental values and curves show smoothed values using equation (10).

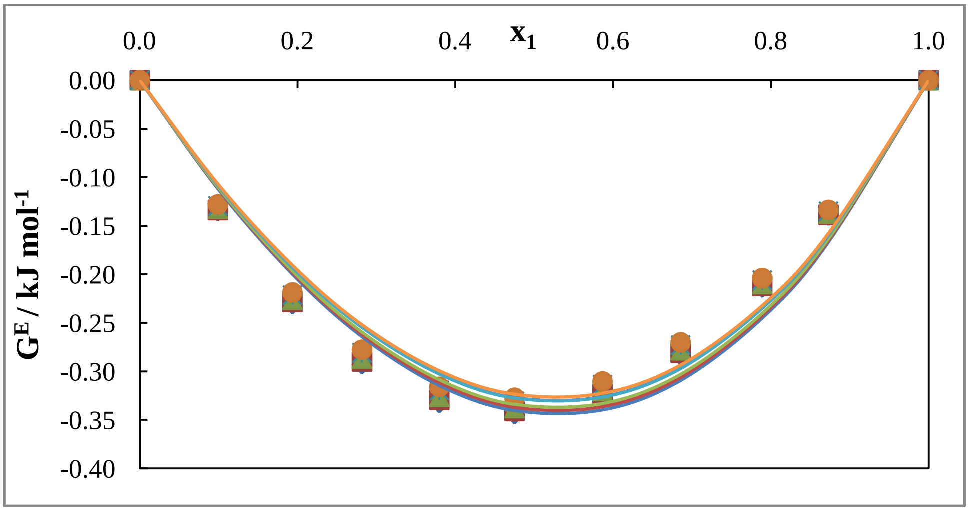

Figure 5: Plots of excess free energy, G^E*versus* mole fraction (x_1) of EP for binary systems at T = 298.15 K (◆), 303.15 K (■), 308.15 K (▲), 313.15 K (×), 318.15 K (✳) and 323.15 K (●). Points shown experimental values and curves show smoothed values using equation (10).

A negative excess free energy of mixing means that there is a thermodynamic driving force for mixing to occur, while a positive free energy of mixing means that the pure components will not mix. If the entropic energy contribution outweighs the enthalpy increase, the G^E values becomes negative and is more negative at higher temperature (as in Fig.5).

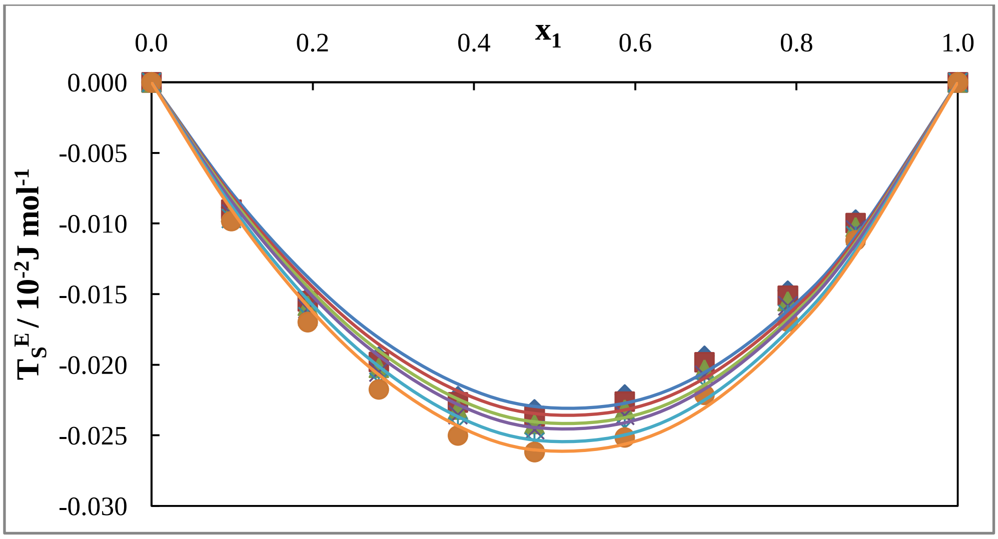

Figure 6: Plots of excess entropy, T_s^E*versus* mole fraction (x_1) of EP for binary systems at T = 298.15 K (◆), 303.15 K (■), 308.15 K (▲), 313.15 K (×), 318.15 K (✳) and 323.15 K (●). Points shown experimental values and curves show smoothed values using equation (10).

The three factors which may contribute to the excess entropy of mixing of binary solutions are the spatial distribution of the molecules about a given reference molecule, the relative volumes of the molecules and the lack of randomness of the orientation distribution of the molecules about a reference molecule. Of these, the smallest is the spatial distribution, which depends upon the energy of mixing. It yields a negative value for the excess entropy and becomes zero at infinite dilution (as shown in Fig.6).

Conclusions

Density and speed of sound values are measured at different temperatures for the blends EP + m-xylene at different temperatures and atmospheric pressure. By using the measured values various excess parameters are measured. All the excess parameters (except π_i^E) are observed to be negative. Whereas reverse trend is observed in excess internal pressure values at all investigated temperatures.

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