Excess Properties of Binary Mixtures of 2-Propanol and 3-Pentanone with *p*-Xylene at Different Temperatures

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The viscosities, densities and speeds of sound for binary mixtures of 2-propanol with *p*-xylene at 293.15 and 313.15 K and 3-pentanone with *p*-xylene at 293.15, 303.15 and 313.15 K have been measured over the whole compositional range. The excess thermodynamic properties such as excess volume (V^E), excess compressibility (K_S^E) and deviations in viscosity ($\Delta\eta$) were calculated.

Key Words: Excess volume, Excess compressibility, Deviations in viscosity, Binary mixtures.

INTRODUCTION

The studies of viscosity, density and speed of sound and other thermodynamic properties are used as tools for investigating properties of pure liquid mixtures and are also helpful in finding the nature of interactions between molecules. The knowledge of the dependence of these properties on composition is of great interest from the theoretical viewpoint since it may lead to better understanding of the fundamental behaviour of liquid systems. We have recently reported studies on 3-pentanone and *o*-xylene system[1] and also in our earlier studies we have reported the thermodynamic behaviour of several binary systems[2, 3].

In the present study the measurements of densities, viscosities and speeds of sound for binary liquid mixtures of 2-propanol with *p*-xylene at 293.15 and 313.15 K and 3-pentanone with *p*-xylene at 293.15, 303.15 and 313.15 K have been made. The excess volume and excess compressibility for the system 2-propanol with *p*-xylene at 303.15 K have already been reported earlier in the literature[4], so we have not studied this system at 303.15 K.

EXPERIMENTAL

3-Pentanone (Merck Schuchardt), 2-propanol (Qualigens Fine, India) and *p*-xylene (Pfizer, India) were purified using standard procedures[5] and stored over molecular sieves. The purity of the chemicals was checked by comparing the measured densities and viscosities with those reported in literature as shown in Table-1. The densities were measured using a calibrated bicapillary pycnometer having an uncertainty of $\pm 1 \times 10^{-4}$ g cm^{-3}. Viscosities were measured with the help of modified Ubbelohde viscometer as described earlier[6]. At each temperature

TABLE-1
PHYSICAL PROPERTIES OF THE PURE COMPONENTS
AT DIFFERENT TEMPERATURES

Component	ρ/g cm^{-3}			η/mPa s	
	T/K	expt.	lit.	expt.	lit.
2-Propanol	293.15	0.7856	0.7855[8]	2.371	2.3702[8]
	313.15	0.7684	0.7683[10]	1.342	1.3400[10]
p-Xylene	293.15	0.8610	0.86105[5]	0.647	0.6475[8]
	303.15	0.8524	0.85246[9]	0.578	0.5790[8]
	313.15	0.8435	0.84364[9]	0.511	0.5134[8]
3-Pentanone	293.15	0.8144	0.81430[5]	0.471	0.4705[8]
	303.15	0.8047	0.8047[1]	0.425	0.4240[5]
	313.15	0.7949	0.7949[1]	0380	0.3799[1]

the viscometer was calibrated so as to determine the two constants A and B in the equation:

$$\eta/\rho = At + B/t \quad (1)$$

The values of constants were obtained by measuring the flow time, t, with triply distilled water and double distilled benzene. The flow measurements were made with an electronic stop watch with precision of ±0.01 s. The uncertainty in the viscosity values is within ±0.003 mPa s. Speeds of sound were measured with the help of ultrasonic time intervalometer (UTI-101) with a reproducibility of ±0.1 m s^{-1}. All the measurements were made at constant temperature with the help of a circulating type cryostat where the temperature was controlled to ±0.02 K.

RESULTS AND DISCUSSION

The experimental values of density ρ, viscosity η and speed of sound u, measured at different temperatures for both the systems are given in Tables 2 and 3. The molar volume, V_m was calculated by using the relation

$$V_m = (x_1M_1 + x_2M_2)/\rho_m \quad (2)$$

where x_1 and x_2 are the mole fractions and M_1 and M_2 are the molecular weights of components 1 and 2 respectively and ρ_m is the mixture density.

The excess volume (V^E) for the binary mixtures was obtained from the following relation:

$$V^E = x_1M_1(1/\rho_m - 1/\rho_1) + x_2M_2(1/\rho_m - 1/\rho_2) \quad (3)$$

where ρ_1 and ρ_2 are the densities of pure components 1 and 2 respectively. The deviations in viscosity, Δη, were calculated by using the equation

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

where ρ_1 and ρ_2 are the viscosities of pure components 1 and 2 respectively and η_m is the mixture viscosity.

The values of mixture density, ρ_m, and speed of sound, u, are used to calculate the isentropic compressibility K_S by using the relation:

$$K_S = u^{-2} \cdot \rho_m^{-1} \tag{5}$$

The excess isentropic compressibility, K_S^E was obtained from the relation

$$K_s^E = K_S - (x_1 K_{S_1} + x_2 K_{S_2}) \tag{6}$$

where K_{S_1} and K_{S_2} are isentropic compressibility of pure components 1 and 2 respectively. The values of K_S are given in Tables 2 and 3.

TABLE-2
DENSITY ρ, SPEED OF SOUND u, VISCOSITY η, COMPRESSIBILITY K_S FOR 2-PROPANOL (1) + *p*-XYLENE (2) SYSTEM AT DIFFERENT TEMPERATURES

x_1	ρ ($g\ cm^{-3}$)	u ($m\ s^{-1}$)	η (mPa s)	10^{12} Ks (Pa^{-1})
		293.15 K		
1.0000	0.7856	1180.5	2.371	913.4
0.9457	0.7931	1189.2	2.108	891.5
0.8740	0.8031	1200.0	1.739	864.7
0.7975	0.8128	1212.7	1.453	836.6
0.7094	0.8232	1227.5	1.216	806.2
0.6159	0.8331	1243.2	1.029	776.7
0.5170	0.8419	1259.0	0.904	749.3
0.4016	0.8502	1276.7	0.821	721.6
0.2754	0.8566	1294.6	0.762	696.5
0.1321	0.8602	1312.3	0.706	675.0
0.0000	0.8610	1328.6	0.647	658.0
		313.15 K		
1.0000	0.7684	1102.6	1.342	1070.6
0.9457	0.7785	1111.4	1.278	1040.0
0.8740	0.7895	1121.7	1.160	1006.7
0.7975	0.7993	1134.6	1.039	971.8
0.7094	0.8091	1149.1	0.913	936.0
0.6159	0.8181	1164.0	0.790	902.3
0.5170	0.8261	1179.2	0.688	870.5
0.4016	0.8337	1196.4	0.617	837.9
0.2754	0.8399	1213.7	0.583	808.3
0.1321	0.8435	1231.7	0.545	781.5
0.0000	0.8435	1249.1	0.511	759.9

The excess compressibility, K_S^E, excess volume, V^E and deviations in viscosity, $\Delta\eta$, were fitted to a Redlich-Kister[7] type equation

$$A = x_1 x_2 \sum_{i=1}^{n} A_{j-1}(x_1 - x_2)^{(j-1)} \tag{7}$$

where A is the property under consideration, A_{j-1} is the polynomial coefficient and n is the polynomial degree.

TABLE-3
DENSITY ρ, SPEED OF SOUND u, VISCOSITY η, COMPRESSIBILITY K_S FOR 3-PENTANONE (1) + *p*-XYLENE (2) SYSTEM AT DIFFERENT TEMPERATURES

x_1	ρ ($g\ cm^{-3}$)	u ($m\ s^{-1}$)	η (mPa s)	$10^{12}\ K_S$ (Pa^{-1})
		293.15 K		
1.0000	0.8144	1230.7	0.471	810.8
0.9273	0.8218	1242.0	0.473	788.8
0.8330	0.8305	1254.1	0.480	765.6
0.7381	0.8382	1264.2	0.492	746.4
0.6382	0.8450	1275.3	0.508	727.6
0.5391	0.8504	1285.7	0.526	711.4
0.4375	0.8546	1295.2	0.547	697.5
0.3184	0.8580	1304.7	0.571	684.7
0.2052	0.8598	1314.6	0.596	673.0
0.0781	0.8603	1323.0	0.625	664.0
0.0000	0.8610	1328.6	0.647	658.0
		303.15 K		
1.0000	0.8047	1197.8	0.425	866.2
0.9273	0.8128	1208.3	0.429	842.6
0.8330	0.8218	1217.9	0.436	820.4
0.7381	0.8295	1227.5	0.446	800.2
0.6382	0.8363	1237.5	0.458	781.1
0.5391	0.8420	1247.0	0.473	764.1
0.4375	0.8460	1256.2	0.490	749.1
0.3184	0.8497	1264.8	0.512	735.5
0.2052	0.8516	1273.0	0.535	723.8
0.0781	0.8520	1279.6	0.561	716.0
0.0000	0.8524	1286.1	0.578	709.2
		313.15 K		
1.0000	0.7949	1159.1	0.380	936.4
0.9273	0.8035	1167.2	0.385	913.5
0.8330	0.8130	1180.1	0.393	883.2
0.7381	0.8209	1190.5	0.404	859.5
0.6382	0.8276	1199.0	0.416	840.5
0.5391	0.8330	1208.4	0.429	822.1
0.4375	0.8374	1217.6	0.443	805.4
0.3184	0.8409	1227.4	0.460	789.4
0.2052	0.8429	1236.0	0.477	776.5
0.0781	0.8430	1245.5	0.497	764.7
0.0000	0.8435	1249.1	0.511	759.9

The standard deviation in each case is calculated using the equation

$$\sigma(X) = \left[\frac{\Sigma(X_{expt} - X_{calc})^2}{N - n}\right]^{1/2} \quad (8)$$

where N is the number of data points and n is the number of coefficients.

The values of coefficients of the equation (7) as determined by the method of least squares along with the standard deviations at different temperatures for both the systems are reported in Table-4.

TABLE-4
VALUES OF COEFFICIENTS OF REDLICH-KISTER EQUATION (7) AND STANDARD DEVIATIONS EQUATION (8).

T/K	0	A_1	A_2	A_3	σ
		2-Propanol (1) + *p*-xylene (2)			
		VE/cm^3·mol^{-1}			
293.15	–5.3082	2.8167	0.7088	–0.3946	0.0094
313.15	–6,2206	1.5626	–2.0964	–1.1447	0.0075
		Δη/mPa s			
293.15	–2.4831	–1.7408	–0.1589	0.5402	0.0117
313.15	–0.9923	–0.1733	0.6249	0.2654	0.0047
		10^{12} K_S^E/Pa^{-1}			
293.15	–163.8292	0.8555	26.1365	–9.8721	0.2394
313.15	–200.0034	–25.9549	–0.8730	–30.2190	0.5480
		3-Pentanone (1) + *p*-xylene (2)			
		VE/cm^3·mol^{-1}			
293.15	–6.8468	–0.3808	1.1547	–0.8495	0.0140
303.15	–7.3022	–0.3954	0.3263	–1.2744	0.0164
313.15	–7.7908	–0.6316	–0.0999	–1.6536	0.0249
		Δη/mPa s			
293.15	–0.1007	–0.0434	–0.0477	0.0146	0.0002
303.15	–0.0894	–0.0246	0.0025	0.0004	0.0002
313.15	–0.0446	–0.0129	–0.0189	0.0002	0.0001
		10^{12} K_S^E/Pa^{-1}			
293.15	–112.9035	–22.0600	–9.0904	–29.3669	0.4624
303.15	–118.5893	–9.3030	0.9247	–69.1890	0.6073
313.15	–131.1171	–38.4817	–25.8145	17.0263	0.9596

The experimental data for both the systems show that there is a smooth nonlinear variation of viscosity, density and speed of sound over the entire composition range at given temperatures. The excess molar volumes (V^E) for both the systems are negative for the entire composition range, the values increase with the increase in temperature as shown in Figs. 1 and 4. The deviation in viscosity (Δη) are negative and decrease with the increase in temperature for both systems as shown in Fig. 2 and 5. The negative values of both (Δη) and (V^E) indicate the presence of dipolar forces and absence of specific interactions. The excess compressibility as shown in

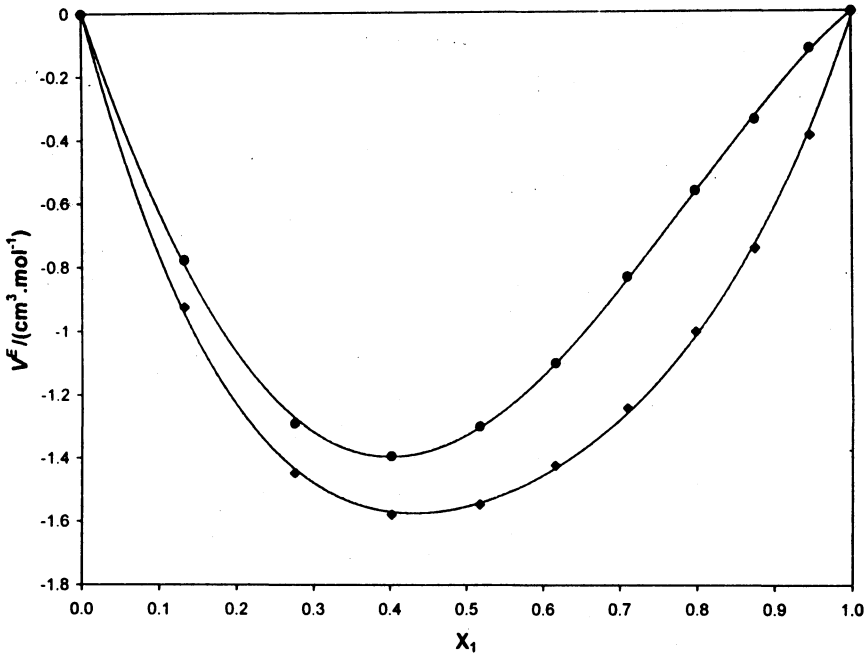

Fig. 1. Excess molar volume, V^E (cm^3 mol^{-1}) for the system 2-propanol (1) + *p*-xylene (2) at 293.15 K (•) and 313.15 K (♦).

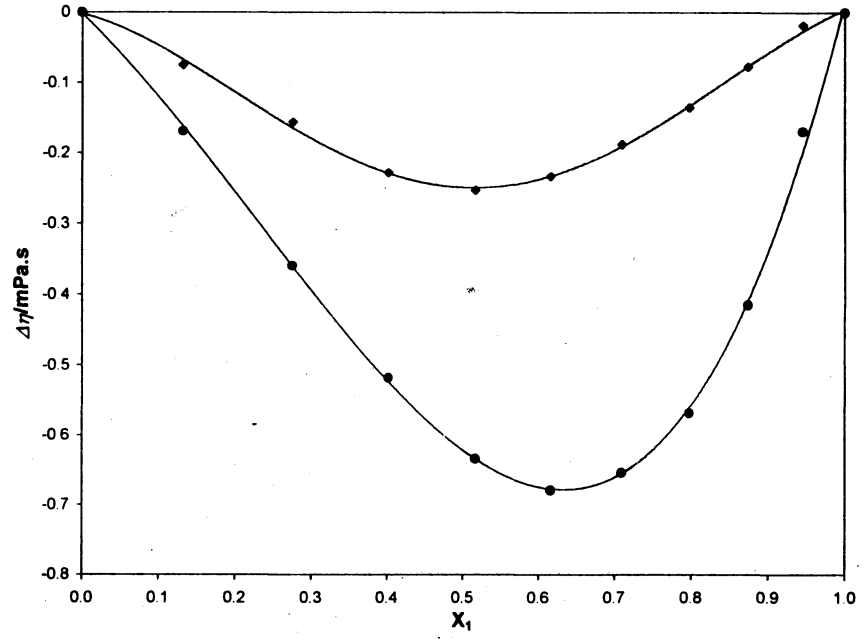

Fig. 2. Viscosity deviations, Δη/(mPa s) for the system 2-propanol (1) + *p*-xylene (2) at 293.15 K (•) and 313.15 K (♦).

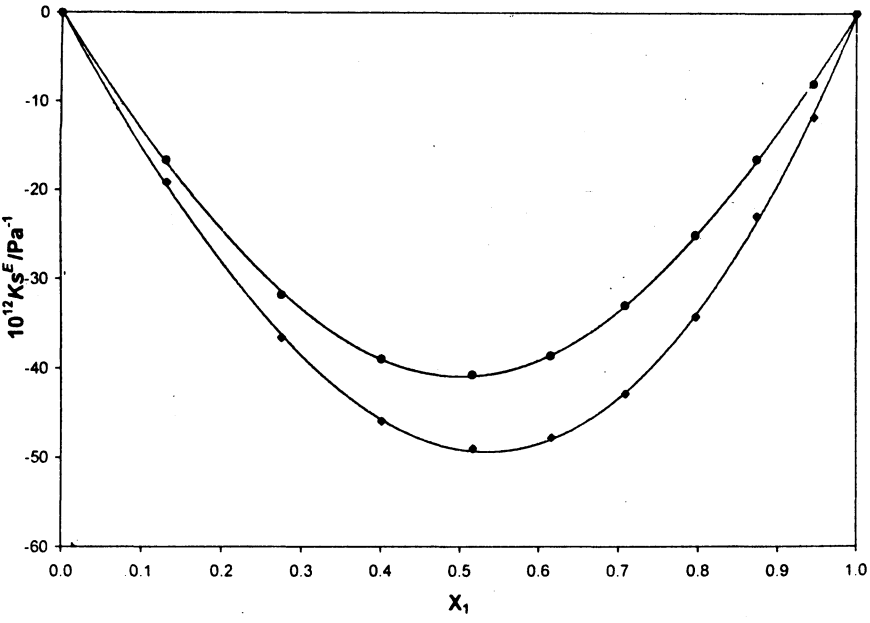

Fig. 3. Excess compressibility, 10^{12} K_S^E/Pa^{-1} for the system 2-propanol (1) + *p*-xylene (2) at 293.15 K (•) and 313.15 K (♦).

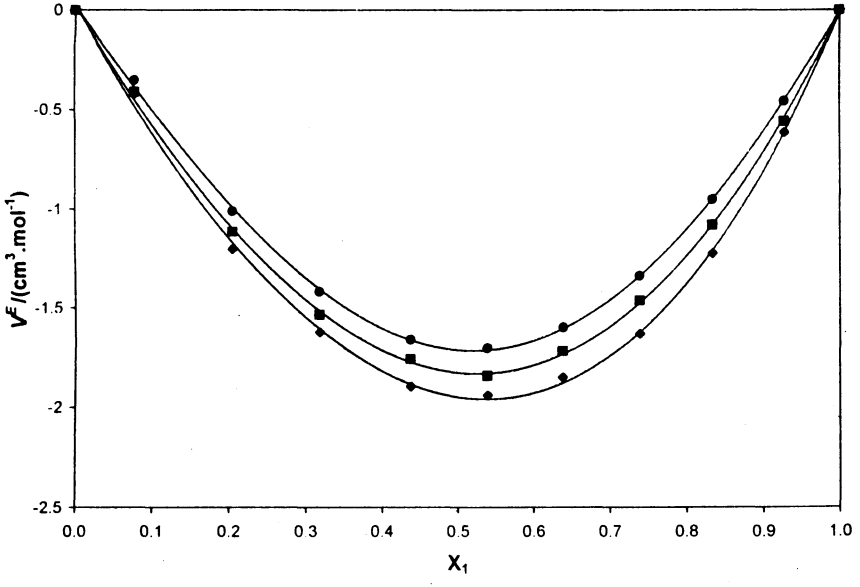

Fig. 4. Excess molar volume, V^E (cm^3 mol^{-1}) for the system 3-pentanone (1) + *p*-xylene (2) at 293.15 K (•), 303.15 K (■) and 313.15 K (♦).

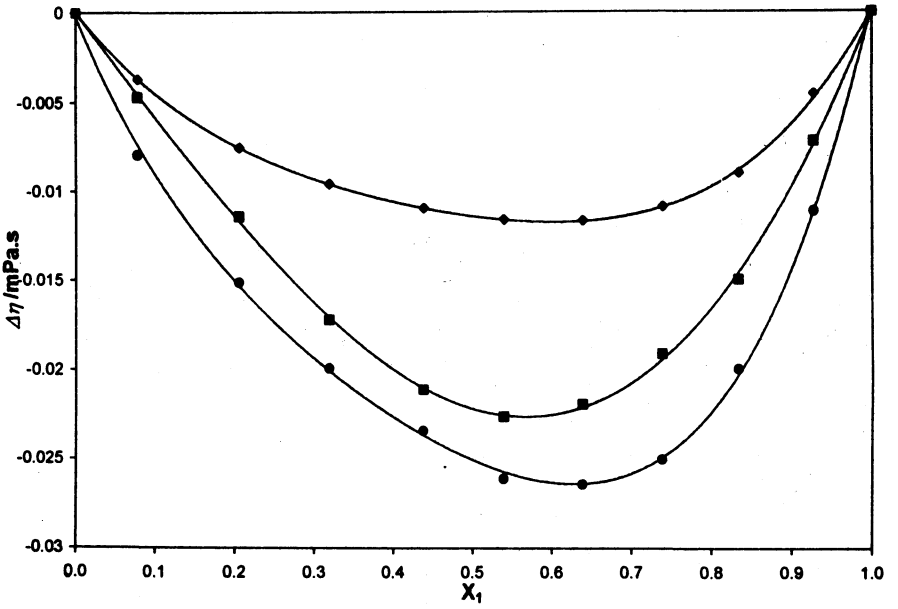

Fig. 5. Viscosity deviations, $\Delta\eta$/(mPa s) for the system 3-pentanone (1) + *p*-xylene (2) at 293.15 K (•), 303.15 K (■) and 313.15 K (♦).

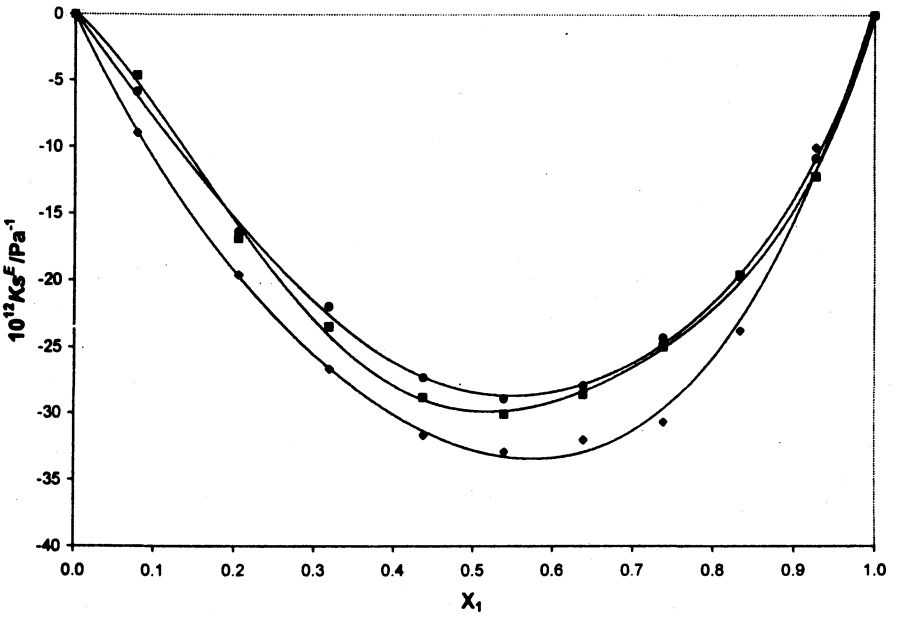

Fig. 6. Excess compressibility, 10^{12} K_S^E/Pa^{-1} for the system 3-pentanone (1) + *p*-xylene (2) at 293.15 K (•), 303.15 K (■) and 313.15 K (♦).

Figs. 3 and 6 is negative and decreases with the increase in temperature for both the systems. The negative K_S^E values indicate that the difference between the ideal and the observed behaviour may be attributed to the existence of an increased correlation of molecular sites in these mixtures[11].

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