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Excess Properties of Binary Mixture of 2-Nitropropane with *p*-Xylene at 303.15, 308.15, 313.15 and 318.15 K

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The viscosities, densities and speeds of sound for binary mixture of 2-nitropropane with *p*-xylene at 303.15, 308.15, 313.15, and 318.15 K have been measured over the whole compositional range. The excess thermodynamic properties such as excess volume (V^E), deviations in viscosity ($\Delta\eta$) and excess isentropic compressibility (K_S^E) were calculated.

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

INTRODUCTION

In recent years, there has been considerable interest in theoretical and experimental investigation of the excess thermodynamic properties of binary mixtures. In principle, the interaction between the molecules can be established from the study of the characteristic departure from ideal behaviour of some physical properties like volume, compressibility and viscosity. Viscosity data for liquid mixtures have also yielded information regarding the nature of interaction forces operating within and between the molecules and the existence of a complex[1], if any.

The knowledge of the dependence of these properties on composition is of great interest from the theoretical viewpoint since it may lead to a better understanding of the fundamental behaviour of liquid systems. The excess thermodynamic properties of the binary liquid mixtures are fundamental for the design of industrial equipments.

In the present study, the measurements of densities, viscosities and speeds of sound for binary liquid mixture of 2-nitropropane with *p*-xylene at 303.15, 308.15, 313.15 and 318.15 K have been made.

EXPERIMENTAL

2-Nitropropane (S.D. Fine Chem., Mumbai, India) and *p*-xylene (Riedel, Germany) were purified using standard procedures[2] 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.

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

Component	T (K)	ρ (g.cm^{-3})		η (mPa.s)	
		Expt.	Lit.	Expt.	Lit.
2-Nitropropane	303.15	0.9774	0.9774[2]	0.677	0.6771[2]
	308.15	0.9719	—	0.638	—
	313.15	0.9664	—	0.603	—
	318.15	0.9609	—	0.573	—
p-Xylene	303.15	0.8523	0.8523[5]	0.566	0.566[2]
	308.15	0.8478	0.8479[6]	0.539	0.539[6]
	313.15	0.8436	0.84364[7]	0.513	0.513[8]
	318.15	0.8394	—	0.480	—

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 a modified Ubbelohde viscometer as described earlier[3]. At each temperature, the viscometer was calibrated so as to determine the two constants A and B in the equation:

$$\eta/\rho = At + B/t \tag{1}$$

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 interferometer (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 the system are given in Table-2.

TABLE-2
DENSITY, ρ, SPEED OF SOUND, u, VISCOSITY,η, COMPRESSIBILITY, K_S, FOR 2-NITROPROPANE (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})
		303.15 K		
1.0000	0.9774	1200.8	0.677	709.6
0.9450	0.9698	1204.5	0.669	710.8
0.8561	0.9586	1209.8	0.656	712.8
0.7737	0.9483	1214.6	0.644	714.8
0.7259	0.9425	1217.4	0.637	715.9
0.5333	0.9186	1231.0	0.615	718.4
0.4777	0.9112	1235.9	0.608	718.5
0.3678	0.8962	1246.5	0.597	718.2
0.2417	0.8787	1259.8	0.585	717.1
0.1162	0.8632	1273.1	0.575	714.8
0.0500	0.8565	1279.7	0.570	713.0
0.0000	0.8523	1284.2	0.566	711.4
		308.15 K		
1.0000	0.9719	1182.5	0.638	735.8
0.9450	0.9640	1185.6	0.632	738.0
0.8561	0.9527	1190.9	0.619	740.1
0.7737	0.9425	1196.0	0.609	741.8
0.7259	0.9367	1199.1	0.603	742.6
0.5333	0.9126	1214.2	0.582	743.3
0.4777	0.9053	1219.4	0.576	742.9
0.3678	0.8903	1230.8	0.566	741.4
0.2417	0.8733	1244.8	0.555	739.0
0.1162	0.8583	1258.8	0.547	735.2
0.0500	0.8519	1266.3	0.543	732.1
0.0000	0.8478	1272.8	0.539	728.1

(Contd.)

x_1	ρ ($g.cm^{-3}$)	u ($m.s^{-1}$)	η (mPa.s)	10^{12} K_S (Pa^{-1})
		313.15 K		
1.0000	0.9664	1167.6	0.603	759.1
0.9450	0.9581	1170.5	0.598	761.8
0.8561	0.9465	1175.4	0.586	764.8
0.7737	0.9364	1180.2	0.577	766.7
0.7259	0.9307	1183.4	0.571	767.3
0.5333	0.9069	1199.0	0.552	767.0
0.4777	0.8995	1204.3	0.547	766.5
0.3678	0.8847	1215.8	0.538	764.6
0.2417	0.8679	1229.8	0.528	761.9
0.1162	0.8534	1243.8	0.520	757.4
0.0500	0.8473	1251.9	0.517	753.0
0.0000	0.8436	1259.1	0.513	747.7
		318.15 K		
1.0000	0.9609	1155.6	0.573	779.3
0.9450	0.9525	1157.7	0.567	783.3
0.8561	0.9403	1161.9	0.557	787.8
0.7737	0.9303	1165.4	0.547	791.5
0.7259	0.9245	1167.9	0.542	793.0
0.5333	0.9013	1180.9	0.522	795.6
0.4777	0.8941	1185.5	0.516	795.8
0.3678	0.8794	1195.8	0.507	795.3
0.2417	0.8630	1208.0	0.497	794.1
0.1162	0.8488	1220.9	0.488	790.4
0.0500	0.8429	1228.2	0.484	786.6
0.0000	0.8394	1235.2	0.480	780.8

The molar volume, V_m was calculated by using the relation:

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

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.

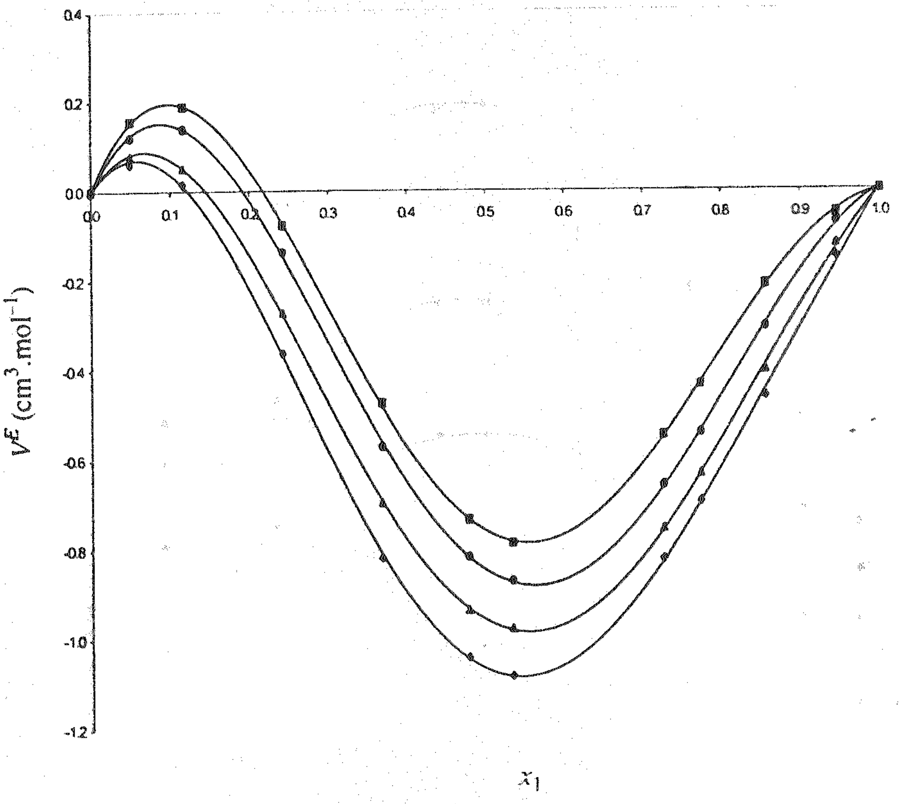

Fig. 1. Excess molar volume, V^E for the system 2-nitropropane (1) + *p*-xylene (2) at 303.15 K (◆), 308.15 K (▲), 313.15 (●) and 318.15 K (■)

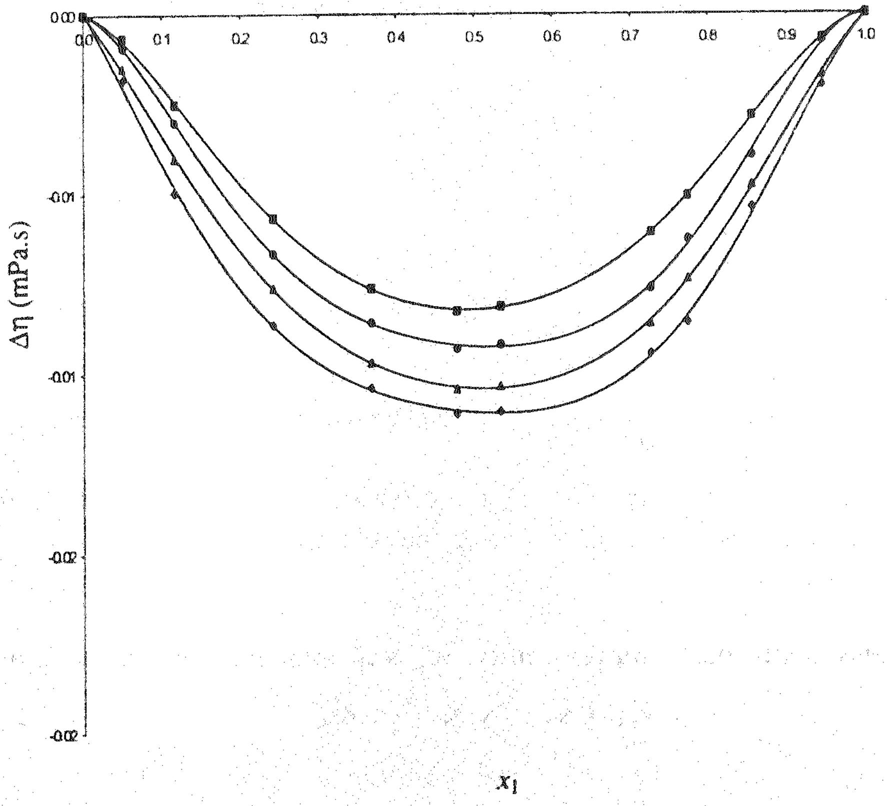

Fig. 2. Viscosity deviations, Δη, for the system 2-nitropropane (1) + *p*-xylene (2) at 303.15 K (◆), 308.15 K (▲), 313.15 (●) and 318.15 K (■)

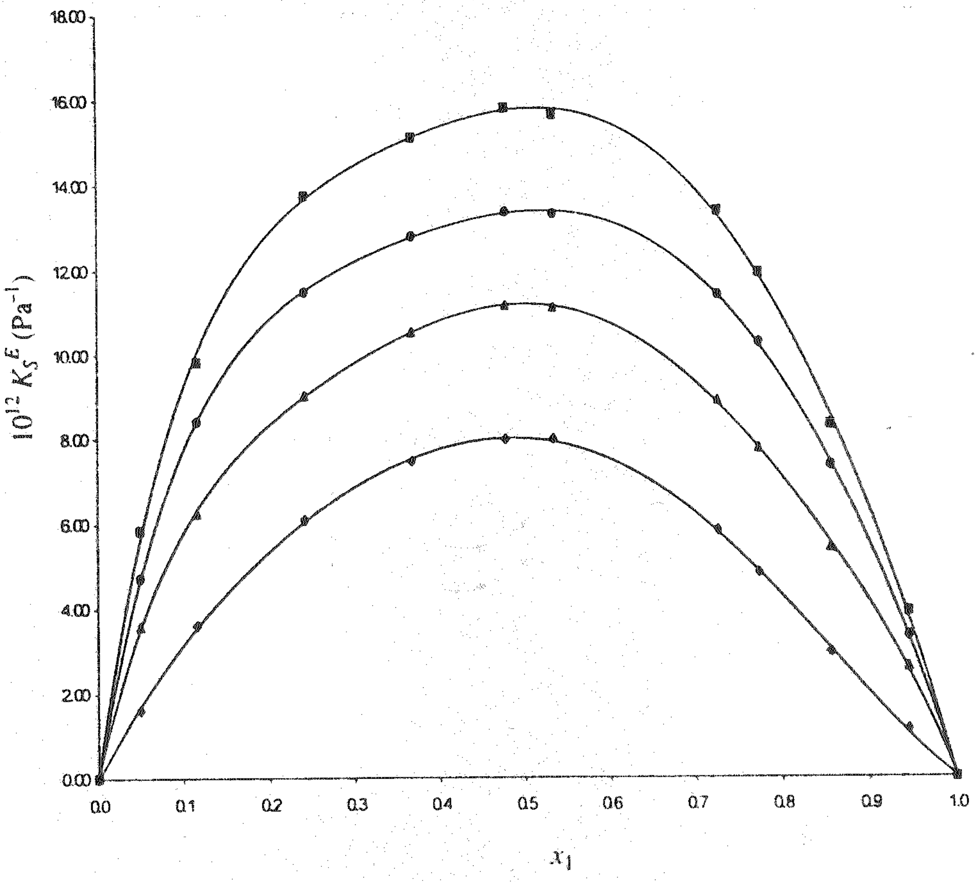

Fig. 3. Excess compressibility, K_S^E, for the system 2-nitropropane (1) + *p*-xylene (2) at 303.15 K (◆), 308.15 K (▲), 313.15 (●) and 318.15 K (■)

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

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

where ρ_1 and ρ_2 are the densities of pure components 1 and 2 respectively.

The deviations in viscosity, $\Delta\eta$ were calculated by using the equation:

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{4}$$

where η_1 and η_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:

$$K_S^E = K_S - (x_1K_{S_1} + x_2K_{S_2}) \tag{6}$$

where K_{S_1} and K_{S_2} are isentropic compressibilities of pure components 1 and 2 respectively. The values of K_S are given in Table-2.

The excess volume, V^E, excess isentropic compressibility, K_S^E and deviations in viscosity, $\Delta\eta$, were fitted to a Redlich-Kister[4] 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.

The standard deviation in each case is calculated using the equation:

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

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 the system are reported in Table-3.

TABLE-3
VALUES OF COEFFICIENTS OF REDLICH-KISTER EQUATION (7) AND STANDARD DEVIATION EQUATION (8).

T (K)	A_0	A_1	A_2	A_3	σ
			V^E (cm^3.mol^{-1})		
303.15	–4.2396	–1.6398	4.4081	–1.1496	0.01222
308.15	–3.8071	–1.9565	4.4229	–0.4925	0.00914
313.15	–3.3588	–2.2631	5.0575	–0.0116	0.00944
318.15	–2.9933	–1.9900	5.4760	–0.2769	0.01148
			$\Delta\eta$ (mPa.s)		
303.15	–0.0452	–0.0037	0.0023	0.0088	0.00033
308.15	–0.0423	–0.0023	0.0058	0.0040	0.00023
313.15	–0.0382	–0.0032	0.0136	0.0061	0.00038
318.15	–0.0335	0.0008	0.0173	0.0010	0.00022
			10^{12} K_S^E (Pa^{-1})		
303.15	31.8555	–2.4535	–5.2412	–8.4719	0.07623
308.15	43.8472	–0.5065	14.4662	–17.8296	0.21471
313.15	52.8011	2.2205	30.2633	–27.6108	0.14262
318.15	62.3142	1.7271	34.7993	–34.5761	0.23987

The negative values of V^E suggest the existence of specific interactions between the molecules. The curves at different temperatures are characterized by the presence of well defined minima occurring at around $x_1 = 0.533$. This minima indicates the presence of complex formation at this composition. With increase in temperature, the values of V^E become less negative.

The negative values of V^E and $\Delta\eta$ show that one type of molecules are interstitially accommodated into clusters of other molecules resulting in negative V^E and negative $\Delta\eta$.

The positive values of K_S^E show that the mixing is accompanied by increase in intermolecular free space between the molecules. This may be ascribed to the dominant nature of the structure breaking effect. The values of K_S^E become more positive with increase in temperature. It is difficult to assign any reason for the departure of K_S^E and V^E from the usual behaviour but large difference in relative sizes of the components may be one of the contributory factors.

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