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Excess Volume, Viscosity and Speed of Sound for *p*-Xylene with 2-Nitrotoluene System at 298.15, 303.15 and 313.15 K

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Excess volume (V^E), viscosity and speed of sound data at 298.15, 303.15 and 313.15 K were measured for binary system formed by *p*-xylene with 2-nitrotoluene. Excess volumes were measured directly using a dilatometer[1]. The excess properties such as excess volume (V^E), deviation in viscosity ($\Delta\eta$) and excess compressibility (K_S^E) are discussed in terms of molecular interactions between like and unlike molecules. All the excess properties have been fitted to the Redlich-Kister equation.

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

INTRODUCTION

Mixing properties, such as excess molar volume, deviation in viscosity and excess compressibility, have been used as a qualitative and quantitative guide to understand the molecular interactions between the components of the mixture, to develop new theoretical models and also to carry out engineering applications in the process industry. Data for these properties can be obtained experimentally or by using generalized methods that permit calculation of the properties of mixtures. The development of a calculation method requires that an adequate database is available. Although many tabulated values of the above properties are generally available for the pure solvents, literature data for the various binary mixtures are often scarce. The present work aims to contribute to the development of a database for the excess molar volume, viscosity and speed of sound for the binary mixture, *p*-xylene with 2-nitrotoluene, at 298.15, 303.15 and 313.15 K.

EXPERIMENTAL

p-Xylene (Riedel, Germany) and 2-nitrotoluene (S.D. Fine Chem., Mumbai), AR grade, were purified using standard procedures[2] and stored over molecular sieves. In Table-1, we compare the measured densities and viscosities of the chemicals with literature values. The densities of the binary mixture were obtained from excess volumes (V^E) data.

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.
p-Xylene	298.15	0.8566	0.85666[8]	0.605	0.605[2]
	303.15	0.8523	0.85230[8]	0.566	0.5662
	313.15	0.8436	0.84364[9]	0.513	0.51310
2-Nitrotoluene	298.15	1.1573	—	2.218	—
	303.15	1.1530	1.1531[8]	1.941	1.9408
	313.15	1.1431	1.1435[8]	1.632	1.6308

The excess volumes were determined directly to an accuracy of ±0.0003 cm^3.mol^{-1} using a continuous dilution dilatometer. 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:

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

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 a 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 excess volume, V^E, viscosity, η, and speed of sound, u, measured at different temperatures for the system are listed in Table-2. The density of the binary mixture was calculated from the excess molar volume data by the following relation:

$$\rho_m = (M_1x_1 + M_2x_2)/V_m \qquad (2)$$

where x_1 and x_2 are mole fractions and $M_1$and M_2 are molecular weights of components 1 and 2 respectively.

$$V_m = V^E + V^{id} \qquad (3)$$

where V^{id} is the ideal volume of the binary mixture and is given by:

$$V^{id} = V_1x_1 + V_2x_2 \qquad (4)$$

where

$$V_1 = M_1/\rho_1 \qquad (5)$$

$$V_2 = M_2/\rho_2 \qquad (6)$$

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

TABLE-2

EXCESS MOLAR VOLUME, V^E, VISCOSITY, η, SPEED OF SOUND, u, DENSITY, ρ, COMPRESSIBILITY, K_S, FOR *p*-XYLENE(1)+ 2-NITROTOLUENE(2) SYSTEM AT DIFFERENT TEMPERATURES

x_1	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	u ($m.sec^{-1}$)	ρ ($g.cm^{-3}$)	$K_S \times 10^{12}$ (Pa^{-1})
			298.15 K		
1.0000	0.0000	0.605	1291.0	0.8567	700.4
0.9563	–0.0936	0.621	1304.0	0.8699	676.0
0.8982	–0.2271	0.655	1316.4	0.8877	650.1
0.7882	–0.5084	0.732	1333.2	0.9219	610.3
0.6812	–0.8593	0.819	1347.6	0.9563	575.8
0.5732	–1.1705	0.922	1363.2	0.9912	542.9
0.4694	–1.3253	1.049	1378.9	1.0240	513.6
0.3683	–1.2675	1.201	1393.3	1.0545	488.5
0.2678	–0.9731	1.366	1408.1	1.0829	465.8
0.1722	–0.5412	1.547	1421.8	1.1086	446.2
0.0734	–0.1203	1.838	1436.2	1.1354	426.9
0.0000	0.0000	2.218	1443.4	1.1573	414.7
			303.15 K		
1.0000	0.0000	0.566	1283.7	0.8523	712.0
0.9563	–0.1197	0.602	1291.4	0.8657	692.6
0.8982	–0.2939	0.629	1300.4	0.8838	669.1
0.7882	–0.6271	0.684	1316.4	0.9183	628.4
0.6812	–0.9685	0.771	1331.5	0.9527	592.1
0.5732	–1.2803	0.890	1346.7	0.9876	558.3
0.4694	–1.4273	1.019	1361.4	1.0203	528.8
0.3683	–1.3254	1.156	1375.5	1.0505	503.1
0.2678	–1.0271	1.320	1390.1	1.0789	479.6
0.1722	–0.5841	1.510	1403.0	1.1046	459.9
0.0734	–0.1571	1.754	1416.8	1.1314	440.3
0.0000	0.0000	1.941	1426.3	1.1530	426.3

(Contd.)

x_1	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	u ($m.sec^{-1}$)	ρ ($g.cm^{-3}$)	$K_S \times 10^{12}$ (Pa^{-1})
			313.15 K		
1.0000	0.0000	0.513	1260.0	0.8436	746.6
0.9563	–0.2000	0.543	1262.3	0.8575	731.9
0.8982	–0.4402	0.572	1267.5	0.8759	710.6
0.7882	–0.9040	0.624	1280.8	0.9113	668.9
0.6812	–1.2959	0.693	1295.4	0.9459	630.0
0.5732	–1.5837	0.788	1310.3	0.9805	594.0
0.4694	–1.6834	0.902	1324.1	1.0128	563.2
0.3683	–1.5587	1.029	1337.7	1.0427	535.9
0.2678	–1.1922	1.178	1352.1	1.0706	510.9
0.1722	–0.7246	1.335	1365.7	1.0960	489.2
0.0734	–0.2443	1.509	1379.9	1.1224	467.9
0.0000	0.0000	1.632	1391.7	1.1431	451.7

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

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{7}$$

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:

$$K_S = u^{-2} \cdot \rho_m^{-1} \tag{8}$$

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

$$K_S^E = K_S - (x_1K_{S_1} + x_2K_{S_2}) \tag{9}$$

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:

$$A = x_1x_2 \sum_{i=1}^{n} A_{j-1}(x_1 - x_2)^{(j-1)} \tag{10}$$

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:

$$\sigma(X) = \left[\frac{\Sigma(X_{expt} - X_{calcd})^2}{N - n}\right]^{1/2} \tag{11}$$

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

The values of coefficients of eqn. (10) 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 EQN. (10)
AND STANDARD DEVIATION (EQN. 11).

T (K)	A_0	A_1	A_2	A_3	σ
		V^E (cm^3 mol^{-1})			
298.15	–5.1980	2.3477	4.3845	–3.7016	0.00431
303.15	–5.5767	1.8920	4.0905	–3.2837	0.00831
313.15	–6.6964	0.9713	3.5915	–2.3825	0.00748
		Δη (mPa.s)			
298.15	1.5598	0.6241	1.1151	1.1765	0.00109
303.15	1.1294	0.2077	0.0265	0.1918	0.00843
313.15	0.8407	0.0262	0.3029	0.1002	0.00291
		10^{12} K_S^E (Pa^{-1})			
298.15	–139.0920	–18.9892	–52.4576	–79.3599	0.80934
303.15	–127.2868	–14.0012	0.4214	–24.7070	0.20139
313.15	–109.6778	–5.50095	1.6944	29.2274	0.23317

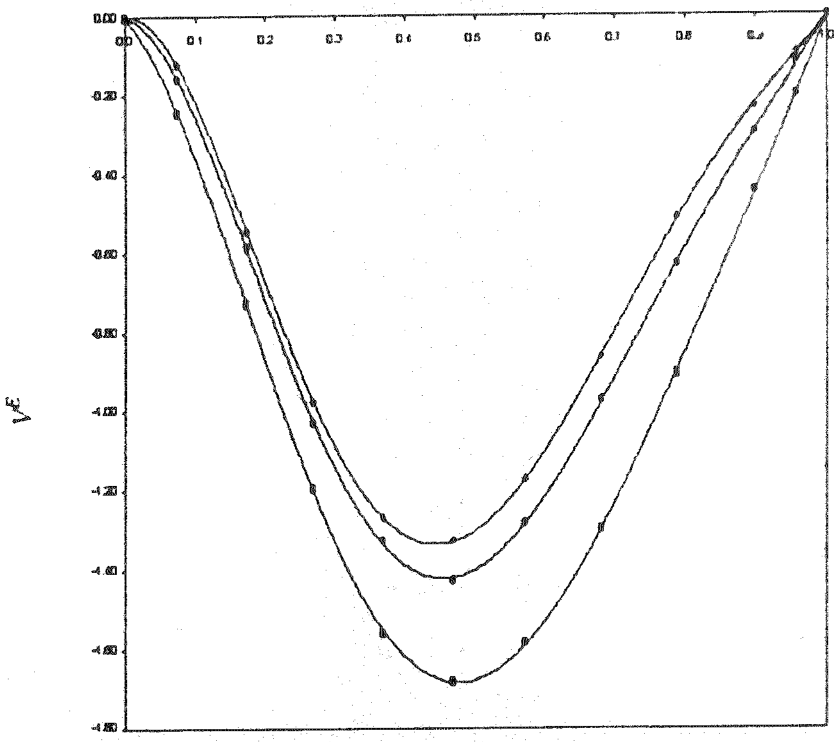

Fig. 1. Excess molar volume, V^E ($cm^3.mol^{-1}$) for the system *p*-xylene (1) + 2-nitrotoluene (2) at 298.15 K (◆), 303.15 K (●) and 313.15 K (■)

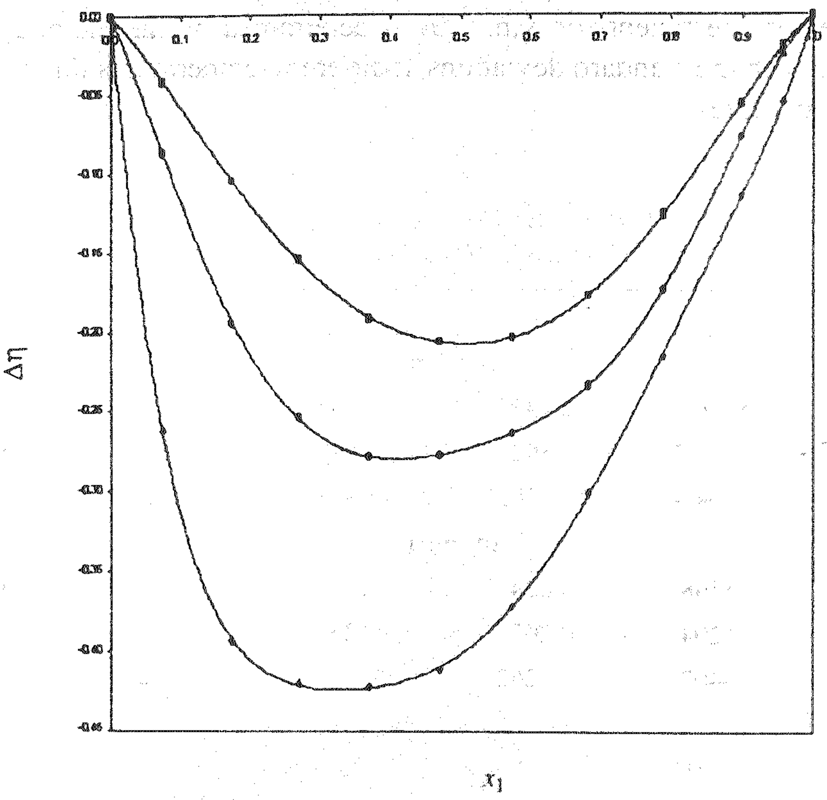

Fig. 2. Viscosity deviations, Δη (mPa.s) for the system *p*-xylene (1) + 2-nitrotoluene (2) at 298.15 K (◆), 303.15 K (●) and 313.15 K (■)

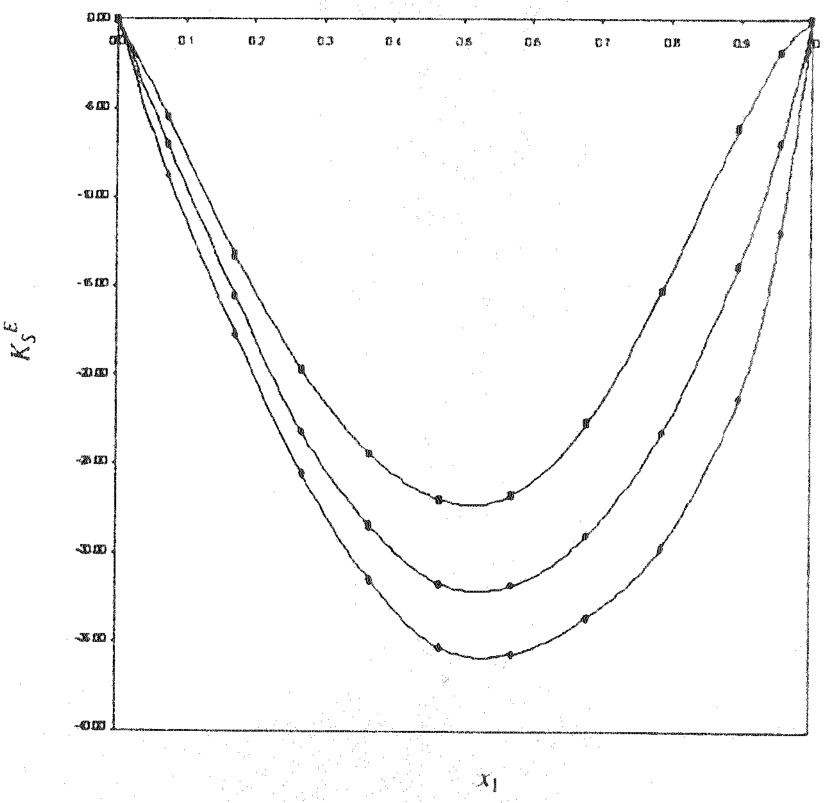

Fig. 3. Excess compressibility, 10^{12} K_S^E (Pa^{-1}) for the system *p*-xylene (1) + 2-nitrotoluene (2) at 298.15 K (◆), 303.15 K (●) and 313.15 K (■)

The negative values of V^E are attributed to the existence of specific interactions between the molecules such as formation of charge-transfer complexes between the electron donor *p*-xylene and the electron acceptor 2-nitrotoluene[5]. As the temperature is increased, the values of V^E become more negative. The maximum negative value of V^E occurs approximately at 0.47 mole fraction of *p*-xylene.

Negative values of V^E and $\Delta\eta$ indicate that one type of molecules are interstitially accommodated into clusters of other molecules resulting in negative V^E and negative $\Delta\eta$[6].

The values of K_S^E are also negative at all the temperatures and the values of K_S^E become less negative as temperature is increased. This may be attributed to the weakening of structure making interactions at elevated temperatures due to enhanced thermal motion[7].

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