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Excess Volumes and Viscosities of Isomeric Xylenes with *o*-Nitrotoluene or *m*-Nitrotoluene at 308.15 K

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Excess volume (V^E) and viscosity (η) data at 308.15 K were measured for binary systems formed by *o*-, *m*-, and *p*-xylenes with *o*-nitrotoluene or *m*-nitrotoluene. Excess volumes were measured directly using a dilatometer. Viscosities were measured with an Ostwald viscometer. The excess volumes and viscosities are discussed in terms of molecular interactions between like and unlike molecules.

Introduction

Thermodynamic properties of nonelectrolyte solutions have proven to be a very useful tool in elucidating the structural interactions among components. For example, excess volume, density, and viscosity can be used to study solvent−solvent specific interactions as a function of temperature, while the composition dependence provides valuable unsubstitutable information about the presence and the stoichiometry of complex adducts. Many workers (Francesconi and Comelli, 1994; Wagner and Sandler, 1995; Corradini et al., 1995; Hofman and Casanova, 1996; Moollan et al., 1997; Mollmann and Gmehling, 1997) both experimentalists and theoreticians, have shown the important and fundamental role of the molecular details of the solvent species to determine the specific interactions which are responsible for the thermodynamic and the transport properties in electrolytic and nonelectrolytic solutions. The knowledge of the structure of mixed solvent systems becomes an essential prerequisite to interpret and to understand the interaction patterns between solvent molecules. Our attention has been attracted by liquid mixtures, and the structures of various binary mixed solvent systems made up of pairwise combination of some selected solvents have been investigated in our laboratories with different techniques (Venkatesulu et al., 1997a, 1997b; Ramadevi et al., 1996a; Venkatesu et al., 1996; Venkatesu and Rao, 1997, 1998). In this work, experimental excess volumes and viscosities of the binary mixtures formed by *o*-, *m*-, and *p*-xylenes with *o*-nitrotoluene or *m*-nitrotoluene at 308.15 K are reported. We have undertaken this work to investigate the effect of aromatization and the influence of different substituents in the aromatic ring on V^E and η values.

Experimental Section

Chemicals. All chemicals were purified and maintained in special conditions before their use. *o*-, *m*-, *p*-xylenes were purified by the method described by Venkatesu and Rao (1994).

Nitrotoluenes were kept dried with 3 Å molecular sieves and distilled in a fractionating column under reduced pressure. The purities of the samples were checked by comparing the measured densities of the components determined with a bicapillary-type pycnometer of 12 cm^3

Table 1. Densities (ρ) of Pure Components at 303.15 K

component	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit.
o-xylene	0.871 81	0.871 84[a]
m-xylene	0.855 50	0.855 51[a]
p-xylene	0.852 28	0.852 30[a]
o-nitrotoluene	1.153 06	1.153 10[b]
m-nitrotoluene	1.147 63	1.147 66[b]

[a] Venkatesu and Rao, 1994. [b] Weast, 1980.

Table 2. Excess Volumes (V^E) for Isomeric Xylenes (1) with Nitrotoluenes (2) at 308.15 K

x_1	V^E/cm^3·mol^{-1}	x_1	V^E/cm^3·mol^{-1}
	o-Xylene (1) + *o*-Nitrotoluene (2)		
0.1218	−0.084	0.6324	−0.261
0.2344	−0.158	0.7304	−0.228
0.3304	−0.212	0.8412	−0.154
0.4173	−0.254	0.9212	−0.080
0.5025	−0.271		
	m-Xylene (1) + *o*-Nitrotoluene (2)		
0.1256	−0.146	0.6228	−0.333
0.2239	−0.235	0.7314	−0.296
0.3210	−0.289	0.8424	−0.216
0.4100	−0.322	0.9213	−0.129
0.4872	−0.336		
	p-Xylene (1) + *o*-Nitrotoluene (2)		
0.1153	−0.133	0.6341	−0.356
0.2143	−0.120	0.7194	−0.322
0.3111	−0.273	0.8559	−0.212
0.4002	−0.325	0.9208	−0.130
0.4913	−0.358		
	o-Xylene (1) + *m*-Nitrotoluene (2)		
0.1170	−0.076	0.5618	−0.258
0.2236	−0.133	0.6840	−0.250
0.3270	−0.186	0.7456	−0.233
0.4071	−0.215	0.8728	−0.156
0.4986	−0.246		
	m-Xylene (1) + *m*-Nitrotoluene (2)		
0.0804	−0.102	0.4949	−0.366
0.1668	−0.188	0.6335	−0.365
0.2671	−0.265	0.7433	−0.325
0.3122	−0.295	0.8550	−0.233
0.4032	−0.341	0.9214	−0.118
	p-Xylene (1) + *m*-Nitrotoluene (2)		
0.0956	−0.110	0.6766	−0.294
0.2284	−0.205	0.8019	−0.239
0.3132	−0.245	0.8630	−0.190
0.4175	−0.282	0.9142	−0.135
0.5539	−0.303		

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Table 3. Binary Parameters of Eq 2 and Standard Deviation $\sigma(V^E)$ at 308.15 K

	$cm^3 \cdot mol^{-1}$			
system	a_0	a_1	a_2	$\sigma(V^E)$
o-xylene (1) + *o*-nitrotoluene (2)	−1.0822	−0.2408	0.2305	0.002
m-xylene (1) + *o*-nitrotoluene (2)	−1.3518	−0.2105	−0.3267	0.002
p-xylene (1) + *o*-nitrotoluene (2)	−1.4267	−0.4125	−0.0027	0.002
o-xylene (1) + *m*-nitrotoluene (2)	−0.9768	−0.4495	−0.1605	0.002
m-xylene (1) + *m*-nitrotoluene (2)	−1.4637	−0.3600	−0.3068	0.002
p-xylene (1) + *m*-nitrotoluene (2)	−1.1844	−0.2645	−0.4548	0.002

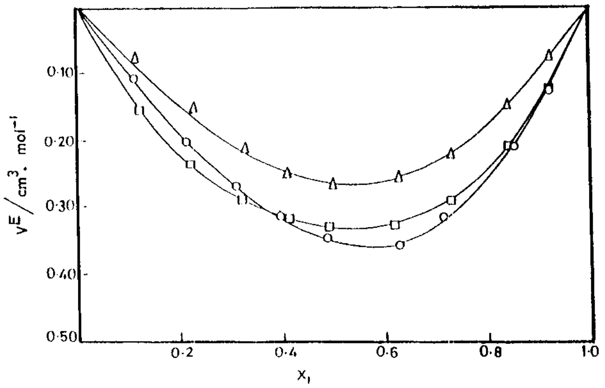

Figure 1. Excess volumes (V^E) for *o*-xylene (△), *m*-xylene (□), and *p*-xylene (○) + *o*-nitrotoluene at 308.15 K.

Table 4. Density (ρ) and Viscosity (η) for Isomeric Xylenes (1) with Nitrotoluenes (2) at 308.15 K

x_1	$\rho/g \cdot cm^{-3}$	$\eta/mPa \cdot s$	x_1	$\rho/g \cdot cm^{-3}$	$\eta/mPa \cdot s$
		o-Xylene (1) + *o*-Nitrotoluene (2)			
0.0000	1.14832	1.727	0.6102	0.97741	0.928
0.1023	1.11538	1.548	0.7028	0.95131	0.850
0.2014	1.09187	1.392	0.8056	0.92228	0.773
0.3006	1.06418	1.262	0.9008	0.89539	0.709
0.4018	1.03590	1.143	1.0000	0.86739	0.659
0.5041	1.00723	1.027			
		m-Xylene (1) + *o*-Nitrotoluene (2)			
0.0000	1.14832	1.727	0.6052	0.96824	0.792
0.1014	1.11821	1.358	0.6913	0.94276	0.735
0.2022	1.08799	1.154	0.8068	0.90850	0.654
0.3044	1.05764	1.027	0.8993	0.88114	0.596
0.4036	1.02809	0.938	1.0000	0.85140	0.542
0.4990	0.99972	0.870			
		p-Xylene (1) + *o*-Nitrotoluene (2)			
0.0000	1.14832	1.727	0.6032	0.96662	0.810
0.1044	1.11657	1.342	0.6951	0.93914	0.754
0.2016	1.08717	1.153	0.8009	0.90750	0.681
0.2968	1.05850	1.034	0.8955	0.87922	0.624
0.4024	1.02677	0.942	1.0000	0.84798	0.563
0.4938	0.99937	0.879			
		o-Xylene (1) + *m*-Nitrotoluene (2)			
0.0000	1.14243	1.692	0.6123	0.97482	0.867
0.1044	1.11384	1.384	0.7055	0.94929	0.810
0.2068	1.08580	1.211	0.8268	0.91571	0.742
0.2995	1.06044	1.102	0.9132	0.89169	0.698
0.4028	1.03219	1.010	1.0000	0.86739	0.659
0.5015	1.00519	0.944			
		m-Xylene (1) + *m*-Nitrotoluene (2)			
0.0000	1.14243	1.692	0.6028	0.96436	0.785
0.1017	1.11296	1.330	0.6999	0.93908	0.720
0.2062	1.08059	1.133	0.8043	0.90663	0.653
0.3032	1.05434	1.014	0.9007	0.88056	0.590
0.4055	1.02174	0.926	1.0000	0.85140	0.542
0.5001	0.99713	0.861			
		p-Xylene + *m*-Nitrotoluene (2)			
0.0000	1.14243	1.692	0.6076	0.96293	0.768
0.1004	1.11278	1.322	0.7023	0.93523	0.706
0.2046	1.08187	1.122	0.8036	0.90562	0.649
0.2963	1.05466	1.004	0.8975	0.87826	0.600
0.4016	1.02351	0.908	1.0000	0.84798	0.563
0.4954	0.99586	0.846			

capacity, which offers an accuracy of 2 parts in 10^5. Further the chemical purity was checked by gas chromatography and found to be >99.97 in all cases. In Table 1, we compare the measured densities of the chemicals with literature values. The densities of binary mixtures were obtained from excess volumes (V^E) using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V + V^E} \tag{1}$$

where x_1 and x_2 denote the mole fractions and M_1 and M_2 are the molar masses of components 1 and 2, respectively. V is the molar volume of the mixture.

Procedure. Excess volumes were determined directly to an accuracy of ±0.003 $cm^3 \cdot mol^{-1}$ using dilatometers described earlier (Rao and Naidu, 1974; Venkatesulu et al., 1996). An Ostwald viscometer was used to measure the viscosities of pure liquids and liquid mixtures, and the detailed procedure was described in our earlier papers (Rao and Naidu, 1977; Ramadevi et al., 1996b). The measured values of viscosities are accurate to ±0.3%. All the measurements were made at a constant temperature in a thermostat that could be maintained constant to 308.15 ± 0.01 K.

Results and Discussion

The excess volumes at 308.15 K for all the binary mixtures are listed in Table 2 and are graphically represented in Figures 1 and 2, respectively. The V^E data are fitted by the method of least squares using the polynomial form.

$$V^E = x_1 x_2 \sum_{i=0}^{2} a_1 (x_1 - x_2)^i \tag{2}$$

The parameters a_i, obtained by the least squares analysis, are given in Table 3 along with standard deviations. The viscosity data at 308.15 K for all these mixtures are reported in Table 4. The deviation in viscosity ($\Delta \ln \eta$) is determined from the relation

$$\Delta \ln \eta = \ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{3}$$

where η_{mix}, η_1, and η_2 are the viscosities of the mixture and the pure components, respectively, and x_1 and x_2 are the mole fractions of the components.

The dependence of $\Delta \ln \eta$ on mole fraction is shown in Figures 3 and 4, respectively. The curves in Figures 3 and 4 are fitted to a smoothing equation of the form

$$\Delta \ln \eta = x_1 x_2 [b_0 + b_1 + (x_1 - x_2) + b_2 (x_1 - x_2)^2] \tag{4}$$

The parameters b_0, b_1, and b_2 are obtained by the method of least squares and are reported in Table 5 along with standard deviations.

Table 5. Binary Parameters of Eq 3 and Standard Deviation $\sigma(\Delta \ln \eta)$ at 308.15 K

	mPa·s			
system	b_0	b_1	b_2	$\sigma(\Delta \ln \eta)$
o-xylene (1) + *o*-nitrotoluene (2)	−0.1210	−0.0609	−0.0922	0.003
m-xylene (1) + *o*-nitrotoluene (2)	−0.4346	0.6900	0.5699	0.002
p-xylene (1) + *o*-nitrotoluene (2)	−0.4688	0.7934	−0.5199	0.003
o-xylene (1) + *m*-nitrotoluene (2)	−0.4591	0.4799	−0.3794	0.004
m-xylene (1) + *m*-nitrotoluene (2)	−0.4315	0.6674	−0.6166	0.003
p-xylene (1) + *m*-nitrotoluene (2)	−0.5967	0.5948	−0.6565	0.004

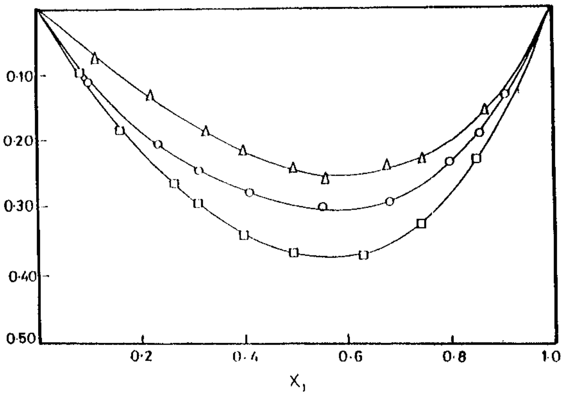

Figure 2. Excess volumes (V^E) for *o*-xylene (△), *m*-xylene (□), and *p*-xylene (○) + *m*-nitrotoluene at 308.15 K.

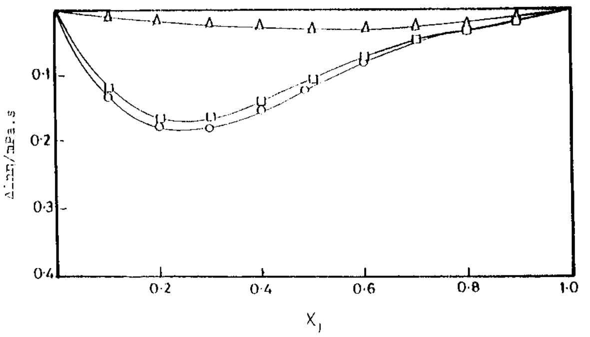

Figure 3. Δ ln η for *o*-xylene (△), *m*-xylene (□), and *p*-xylene (○) + *o*-nitrotoluene at 308.15 K.

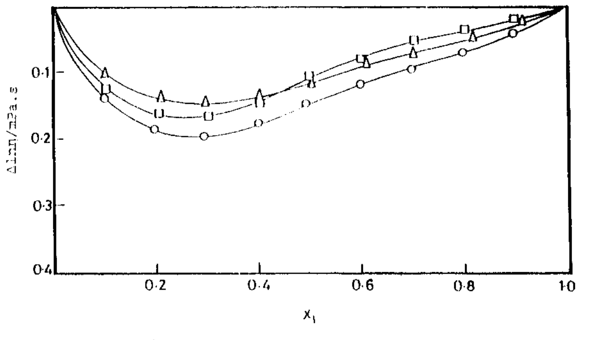

Figure 4. Δ ln η for *o*-xylene (△), *m*-xylene (□), and *p*-xylene (○) + *m*-nitrotoluene at 308.15 K.

The observed V^E values in all six binary systems are negative over the whole range of composition. The negative deviations in V^E values for all the systems may be attributed to the existence of specific interactions between the molecules such as formation of charge-transfer complexes between the electron donor xylenes and the electron acceptor nitrotoluenes. In the mixtures isomeric xylenes with *o*-nitrotoluene, the algebraic values of V^E fall in the order

o-xylene > *m*-xylene > *p*-xylene

The maximum values of V^E in all three binary systems occurred approximately at 0.55 mole fraction of isomeric xylene.

The algebraic values of V^E for the systems of xylenes with *m*-nitrotoluene fall in the order

o-xylene > *p*-xylene > *m*-xylene

The maximum value of V^E for these three systems occurred approximately at 0.57 mole fraction of isomeric xylene. Components with substituents in ortho positions have, in general, a smaller effect on V^E than similar compounds with the same substitutents in other positions. In the present study, we also reach the same conclusion. The maximum negative values of V^E were observed for *m*-xylene with *m*-nitrotoluene. This trend may be due to more interactions between the two meta substituent components.

The algebraic values of Δ ln η for the binary mixtures of xylenes with *o*-nitrotoluene or *m*-nitrotoluene fall in the order

o-xylene > *m*-xylene > *p*-xylene

The same order is observed in excess volumes for the mixtures of xylenes with *o*-nitrotoluene, whereas the order is different in the mixtures of xylenes with *m*-nitrotoluene.

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