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Density and Viscosity of Mixtures of Nitrobenzene with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at 298.15 and 303.15 K

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Densities and viscosities of mixtures of nitrobenzene with methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol were measured at 298.15 and 303.15 K. From these measurements, the excess volumes (V^E) and deviation in viscosity ($\Delta\eta$) were calculated. These results were fitted to the Redlich−Kister polynomial.

Introduction

Various excess properties (Marsh, 1985; Marsh et al., 1979; Alonso et al., 1994) like excess volume, excess enthalpy, and excess Gibbs free energy are quite useful in the study of molecular interactions in binary liquid mixtures. Nitrobenzene is a dipolar aprotic solvent having an electron-withdrawing tendency. Alkanols are protic, associated solvents. Strong interactions may exist between the hydroxyl group of an alkanol and the $-NO_2$ group of nitrobenzene. There are some reports (Reddy and Rao, 1985; Aminabhavi et al., 1989; Fried et al., 1977) of excess volumes of binary mixtures containing nitrobenzene as one of the components, but no report of excess molar volume and viscosity of nitrobenzene + alkanol mixtures appears in the literature. Therefore, our aim in the present study is to measure excess volumes and viscosities of these systems in order to analyze the influence of the hydrocarbon chain of the alkanol and chemical structure of the nitrobenzene upon the excess volumes and viscosities.

Experimental Section

Even though the purity of substances is not a crucial factor in V^E measurements (So-Jin-Park, 1994), it is very important for viscosity measurements. Therefore, all chemicals were used after purification. Nitrobenzene (S.D. Fine Chemicals, 99%, and Sarabhai Chemicals, 99.5%) was dried over anhydrous calcium chloride for 24 h. Dried nitrobenzene was distilled under reduced pressure using a fractionating column. Alkanols were of E. Merck grade (99.7 mol %). They were dried by refluxing the fused calcium oxide for 5 h and then distilled fractionally two to three times (Riddick et al., 1986). The purity of these solvents was checked by comparing their density (ϱ) and viscosity (η) values which compared well with the literature data (Table 1). Binary mixtures were prepared by known masses of each liquid in air-tight stoppered glass bottles. The mass measurements were made on a single pan Mettler balance (Switzerland, model AE-240) to an accuracy of ±0.01 mg. The more volatile component (alkanols) was filled directly into the bottle, and the closed bottle was weighed. The second component (nitrobenzene) was injected into the bottle through the stopper by means of a syringe. This method allowed negligible vapor loss and contamination. The possible error in mole fraction is calculated to be less than $\pm 1 \times 10^{-4}$.

The densities of pure liquids and their mixtures were determined in a 15 cm^3 double arm pycnometer as described earlier (Nikam and Mehdi, 1988; Nikam and Hiray, 1988). The pycnometer was calibrated by using conductivity water (conductivity less than $1.0 \times 10^{-6}\ \Omega^{-1}$) with 0.997 05 $g\cdot cm^{-3}$ as its density at 298.15 K. The pycnometer filled with air bubble free liquids was kept in a transparent-walled water bath with a stability of ±0.01 K for 10−15 min to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with a traveling microscope which read correct to ±0.01 mm. The density values were reproducible within $5 \times 10^{-5}\ g\cdot cm^{-3}$.

The viscosity of the binary liquid mixtures was measured using an Ostwald viscometer calibrated with conductivity water with 0.8937 mPa·s as its viscosity at 298.15 K. The thoroughly cleaned and dried viscometer, filled with the liquid, was placed vertically in a glass-sided water thermostat (stability ±0.01 K). After attaining thermal equilibrium, the flow times of the liquids were recorded with a digital stopwatch correct to ±0.01 s. Since all flow times were greater than 300 s, the kinetic energy corrections were found to be negligible. The viscosity, η, of the liquids was calculated by

$$\frac{\eta}{\eta_w} = \frac{\varrho t}{\varrho_w t_w} \tag{1}$$

where ϱ, ϱ_w and t, t_w refer to the density and flow time of the experimental liquids and water, respectively. The accuracy in the measurement of viscosity was ±0.1%. The other experimental details of the measurements of viscosity are the same as described previously (Nikam and Hiray, 1989, 1992).

Results and Discussion

The experimental density (ϱ) and viscosity (η) values given in Table 2 have been used to calculate the excess volume, V^E, using the following equation:

$$V^E/(cm^3\cdot mol^{-1}) = \frac{M_1X_1 + M_2X_2}{\varrho_{12}} - \frac{M_1X_1}{\varrho_1} - \frac{M_2X_2}{\varrho_2} \tag{2}$$

where ϱ_{12} is the density of the mixture and M_1, X_1, ϱ_1 and M_2, X_2, ϱ_2 are the molecular weight, mole fraction, and density of pure components 1 and 2, respectively. Excess volumes calculated from eq 2 are listed in Table 2.

The results of V^E were fitted to a polynomial of the type

$$V^E/(cm^3\cdot mol^{-1}) = X_1X_2\sum_{i=0}^{m} a_i(X_1 - X_2)^i \tag{3}$$

where m is the number of coefficients a_i. In each case, the

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Table 1. Densities, ϱ, and Viscosities, η, of Pure Components and Comparison with Literature Data at 298.15 K

	ϱ/(g·cm^{-3})		η/(mPa·s)	
component	exptl	lit. (Riddick et al., 1986)	exptl	lit. (Riddick et al., 1986)
methanol	0.7868	0.786 37	0.5570	0.5513
ethanol	0.7854	0.784 93	1.0789	1.0826
propan-1-ol	0.7992	0.799 60	1.9341	1.9430
propan-2-ol	0.7818	0.781 26	2.0498	2.0436
butan-1-ol	0.8064	0.805 75	2.5457	2.5710
2-methylpropan-1-ol	0.7978	0.799 80	3.4098	3.3330
2-methylpropan-2-ol	0.7809	0.781 2	4.4453	4.438
nitrobenzene	1.1984	1.198 3	1.6190[a]	1.619[a]

[a] At 303.15 K.

Table 2. Density, ϱ, Viscosity, η, and Excess Molar Volumes, V^E for Nitrobenzene (1) + Alkanols (2) at 298.15 and 303.15 K

	298.15 K			303.15 K				298.15 K			303.15 K		
x_1	ϱ/ (g·cm^{-3})	η/ (mPa·s)	V^E/ (cm^3·mol^{-1})	ϱ/ (g·cm^{-3})	η/ (mPa·s)	V^E/ (cm^3·mol^{-1})	x_1	ϱ/ (g·cm^{-3})	η/ (mPa·s)	V^E/ (cm^3·mol^{-1})	ϱ/ (g·cm^{-3})	η/ (mPa·s)	V^E/ (cm^3·mol^{-1})
Nitrobenzene + Methanol													
0.0000	0.7968	0.5570		0.7818	0.5232		0.3909	1.0593	1.0063	−1.137	1.0539	0.9279	−1.117
0.0281	0.8167	0.5789	−0.101	0.8134	0.5410	−0.194	0.5102	1.0937	1.1556	−0.621	1.0919	1.0932	−0.821
0.0612	0.8483	0.6110	−0.182	0.8451	0.5673	−0.278	0.5937	1.1164	1.3722	−0.444	1.1128	1.2976	−0.534
0.1003	0.8835	0.6507	−0.344	0.8783	0.6070	−0.340	0.8005	1.1687	1.5592	−0.622	1.1620	1.4846	−0.472
0.1478	0.9197	0.7156	−0.421	0.9147	0.6653	−0.431	0.8978	1.1837	1.6932	−0.317	1.1797	1.5342	−0.370
0.2065	0.9606	0.8044	−0.612	0.9537	0.7342	−0.511	1.0000	1.1975	1.8215		1.1930	1.6655	
0.2806	1.0059	0.8769	−0.886	0.9996	0.8100	−0.623							
Nitrobenzene + Ethanol													
0.0000	0.7854	1.0789		0.7811	0.9865		0.3595	0.9998	1.1661	−0.704	0.9947	1.0682	−0.791
0.0399	0.8144	1.0599	−0.073	0.8100	0.9662	−0.070	0.4661	1.0456	1.2008	−0.740	1.0399	1.0853	−0.709
0.0856	0.8460	1.0483	−0.182	0.8406	0.9579	−0.115	0.5995	1.0904	1.3173	−0.462	1.0852	1.2069	−0.413
0.1382	0.8842	1.0612	−0.603	0.8793	0.9691	−0.583	0.7711	1.1389	1.4400	0.000	1.1339	1.3121	−0.014
0.1997	0.9386	1.0726	−0.444	0.9336	0.9809	−0.431	1.0000	1.1984	1.7632		1.1933	1.6190	
0.2723	0.9588	1.1163	−0.731	0.9535	1.0102	−0.696							
Nitrobenzene + Propan-1-ol													
0.0000	0.7992	1.9341		0.7963	1.7309		0.4224	1.0039	1.4901	−0.480	0.9987	1.3632	−0.356
0.0517	0.8283	1.8151	−0.133	0.8238	1.6126	−0.001	0.5322	1.0464	1.4785	−0.409	1.0412	1.3412	−0.294
0.1088	0.8584	1.7249	−0.203	0.8546	1.5576	−0.139	0.6613	1.0929	1.4940	−0.336	1.0876	1.3518	−0.227
0.1730	0.8906	1.6057	−0.254	0.8859	1.4554	−0.121	0.8145	1.1432	1.5496	−0.220	1.1378	1.4314	−0.126
0.2456	0.9179	1.5596	−0.354	0.9210	1.3937	−0.220	1.0000	1.1975	1.8273		1.1930	1.6655	
0.3276	0.9628	1.5109	−0.389	0.9578	1.4017	−0.256							
Nitrobenzene + Propan-2-ol													
0.0000	0.7818	2.0498		0.7773	1.7764		0.4228	0.9945	1.4502	−0.558	0.9892	1.2916	−0.549
0.0512	0.8108	1.0810	−0.074	0.8062	1.5671	−0.073	0.5325	1.0400	1.4386	−0.564	1.0348	1.3227	−0.557
0.1088	0.8626	1.6698	−0.220	0.8378	1.4764	−0.208	0.6610	1.0800	1.5227	−0.478	1.0835	1.3976	−0.460
0.1732	0.8765	1.5287	−0.320	0.8716	1.3436	−0.319	0.8145	1.1403	1.6026	−0.173	1.1350	1.4344	−0.178
0.2456	0.9122	1.4618	−0.357	0.9071	1.2966	−0.346	1.0000	1.1990	1.8273		1.1937	1.6655	
0.3281	0.9518	1.4588	−0.477	0.9467	1.2772	−0.467							
Nitrobenzene + Butan-1-ol													
0.0000	0.8064	2.5457		0.8023	2.2225		0.4747	1.0054	1.6499	−0.345	1.005	1.4232	−0.340
0.0625	0.8328	2.3109	0.092	0.8296	2.0751	−0.016	0.5846	1.0478	1.5893	−0.136	1.0428	1.4463	−0.130
0.1311	0.8636	2.1425	−0.058	0.8591	1.8784	−0.050	0.7007	1.0940	1.6250	−0.124	1.0888	1.4755	−0.112
0.2051	0.8954	1.9535	−0.122	0.8909	1.7387	−0.110	0.8442	1.1435	1.6580	−0.011	1.1382	1.5088	−0.001
0.2885	0.9293	1.8138	−0.132	0.9245	1.6112	−0.111	1.0000	1.1990	1.8215		1.1937	1.6655	
0.3760	0.9672	1.7105	−0.280	0.9635	1.5595	−0.378							
Nitrobenzene + 2-Methylpropan-1-ol													
0.0000	0.7978	3.4098		0.7931	2.8812		0.4746	1.0012	1.8114	−0.290	0.9963	1.5956	−0.307
0.0630	0.8268	2.8041	−0.030	0.8225	2.4232	−0.199	0.6038	1.0518	1.7549	−0.250	1.0465	1.5378	−0.232
0.1521	0.8658	2.4161	−0.201	0.8615	2.0725	−0.254	0.7066	1.0906	1.7012	−0.147	1.0855	1.4946	−0.150
0.2051	0.8922	2.2278	−0.230	0.8843	1.9560	−0.274	0.8442	1.1411	1.6786	−0.005	1.1360	1.5174	−0.006
0.2864	0.9238	2.0538	−0.299	0.9190	1.8190	−0.326	1.0000	1.1984	1.8273		1.1932	1.6655	
0.3760	0.9614	1.8844	−0.350	0.9567	1.6766	−0.384							
Nitrobenzene + 2-Methylpropan-2-ol													
0.0000	0.7809	4.4453		0.7750	3.3775		0.4746	0.9891	1.7112	−0.185	0.9838	1.5062	−0.241
0.0627	0.8087	3.2047	0.050	0.8034	2.3754	−0.029	0.5843	1.0346	1.6550	−0.172	1.0292	1.4682	−0.220
0.1307	0.8399	2.5764	−0.070	0.8354	2.1522	−0.025	0.7067	1.0841	1.6966	−0.130	1.0790	1.4774	−0.184
0.2059	0.8738	2.2556	−0.160	0.8699	1.8962	−0.396	0.8442	1.1387	1.6815	−0.102	1.1326	1.5380	−0.140
0.2864	0.9095	2.0008	−0.231	0.9058	1.7316	−0.482	1.0000	1.1984	1.8215		1.1932	1.6655	
0.3758	0.9476	1.8378	−0.202	0.9422	1.6219	−0.267							

Table 3. Parameters and Standard Deviations, σ, of Eqs 3 and 4 for Nitrobenzene + Alkanols

system		temp/K	a_0	a_1	a_2	a_3	σ
nitrobenzene + methanol	$V^E/(cm^3 \cdot mol^{-1})$	298.15	−3.378	6.789	14.837	8.223	0.083
		303.15	4.068	5.226	27.855	26.730	0.076
	$\Delta\eta/(mPa \cdot s)$	298.15	−0.220	−0.256	0.284	0.950	0.007
		303.15	−0.174	−0.650	−1.252	−0.201	0.015
nitrobenzene + ethanol	$V^E/(cm^3 \cdot mol^{-1})$	298.15	−2.685	4.098	2.644	−2.598	0.095
		303.15	−2.594	3.966	2.718	−2.728	0.095
	$\Delta\eta/(mPa \cdot s)$	298.15	−0.716	−0.164	−0.553	0.242	0.009
		303.15	−0.687	−0.190	−0.511	0.284	0.012
nitrobenzene + propan-1-ol	$V^E/(cm^3 \cdot mol^{-1})$	298.15	−1.707	−0.030	0.067	1.253	0.029
		303.15	−1.234	0.732	0.653	−1.365	0.031
	$\Delta\eta/(mPa \cdot s)$	298.15	−1.598	0.212	−1.001	−0.444	0.008
		303.15	−1.369	−0.108	−1.124	0.032	0.015
nitrobenzene + propan-2-ol	$V^E/(cm^3 \cdot mol^{-1})$	298.15	−2.310	0.363	1.728	0.773	0.025
		303.15	−2.254	0.368	1.610	0.628	0.024
	$\Delta\eta/(mPa \cdot s)$	298.15	−1.903	0.600	−1.390	1.514	0.017
		303.15	−1.589	0.649	−1.524	0.708	0.020
nitrobenzene + butan-1-ol	$V^E/(cm^3 \cdot mol^{-1})$	298.15	−1.072	1.462	1.913	−3.099	0.053
		303.15	−1.056	0.562	1.654	−0.204	0.064
	$\Delta\eta/(mPa \cdot s)$	298.15	−2.234	0.479	−0.439	0.185	0.013
		303.15	−1.978	0.779	−0.111	−1.065	0.026
nitrobenzene + 2-methylpropan-1-ol	$V^E/(cm^3 \cdot mol^{-1})$	298.15	−1.285	1.396	1.297	−1.232	0.026
		303.15	−1.194	0.337	0.202	2.739	0.034
	$\Delta\eta/(mPa \cdot s)$	298.15	−3.163	0.829	−3.004	3.518	0.046
		303.15	−2.687	0.519	−2.169	2.634	0.024
nitrobenzene + 2-methylpropan-2-ol	$V^E/(cm^3 \cdot mol^{-1})$	298.15	−0.834	1.467	0.302	−3.684	0.034
		303.15	−1.172	2.309	−0.215	−4.639	0.086
	$\Delta\eta/(mPa \cdot s)$	298.15	−3.160	−24.345	0.443	54.761	0.111
		303.15	−3.822	−0.502	−4.422	11.057	0.105

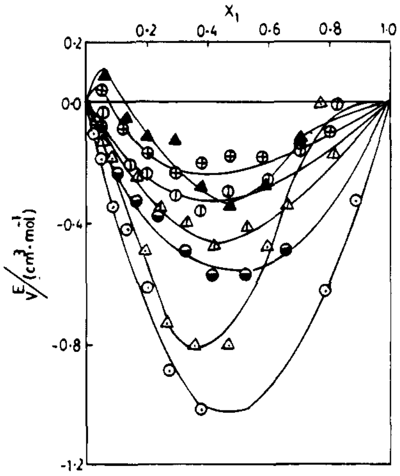

Figure 1. Excess molar volumes, V^E, at 298.15 K for x_1 nitrobenzene + $(1 - x_1)$ alkanols: (⊙) methanol, (△) ethanol, (triangle with vertical bar) propan-1-ol, (◒) propan-2-ol, (▲) butan-1-ol, (circle with vertical bar) 2-methylpropan-1-ol, (⊕) 2-methylpropan-2-ol.

optimum number of coefficients is ascertained from an examination of the variation in standard deviation, σ, as given by

$$\sigma = [\Sigma(X_{\text{obsd}} - X_{\text{calcd}})^2/n - m]^{1/2} \qquad (4)$$

where n is the total number of data points and m is the number of coefficients considered. The coefficients and standard deviations for V^E as computed from eqs 3 and 4, respectively, are presented in Table 2.

The viscosity deviations, $\Delta\eta$, are obtained by

$$\Delta\eta = \eta_m - X_1\eta_1 - X_2\eta_2 \qquad (5)$$

where η_m is viscosity of the mixture and X_1, η_1 and X_2, η_2 are the mole fraction and viscosity of pure components 1 and 2, respectively.

The coefficients, a_i, and standard deviation, σ, for $\Delta\eta$ as obtained from equations similar to eqs 3 and 4 are listed in Table 3.

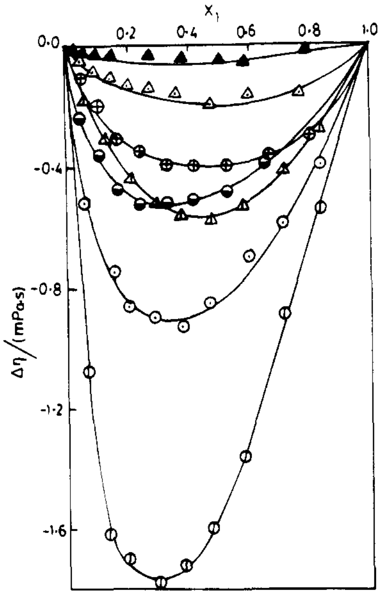

Figure 2. $\Delta\eta$ values at 298.15 K for x_1 nitrobenzene + $(1 - x_1)$ alkanols: (▲) methanol, (△) ethanol, (⊕) propan-1-ol, (◒) propan-2-ol, (triangle with vertical bar) butan-1-ol, (⊙) 2-methylpropan-1-ol, (circle with vertical bar) 2-methylpropan-2-ol.

Excess molar volumes are negative for mixtures of nitrobenzene with all the alkanols studied here (Figure 1). The V^E values at equimolar concentrations of nitrobenzene and normal alkanols follow the order methanol < ethanol < propan-1-ol < butan-1-ol.

The observed excess molar volume values in the present investigation may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical, and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution to V^E (Aminabhavi et al., 1993). The chemical or specific interactions between constituent molecules of the mixture result in a volume decrease. In the present investigation, specific interaction between alkanol and nitrobenzene molecules takes place through dipole−dipole interactions, forming the complex through hydrogen bond formation. The structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volumes and free volumes between components, lead to negative contributions to V^E. With higher alkanols, the geometrical contribution is negligible and clustering decreases with an increase in chain length of the alkanols. Therefore, the mixtures containing higher alkanols give less negative V^E values as compared to those containing lower chain alkanols. The higher alkanols possess less proton-donating ability than the lower ones, and hence heteroassociation effects are smaller in their mixtures which are not sufficient to outweigh the positive contribution to V^E. Thus, positive V^E values are observed in the mixture of nitrobenzene with higher alkanols. Figure 2 indicates that the deviations in viscosity are negative in all the systems and become more negative with an increase in the chain length of the 1-alkanols.

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