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Densities and Viscosities of Binary Liquid Mixtures of Nitrobenzene with Cyclohexane and *N,N*-Dimethylformamide[†]

Shrikant S. Joshi, Tejraj M. Aminabhavi,[*] and Ramachandra H. Balundgi

Department of Chemistry, Karnatak University, Dharwad 580 003, India

Shyam S. Shukla

Department of Chemistry, Lamar University, P.O. Box 10022, Beaumont, Texas 77710

Excess volume, excess viscosity, excess free energy of activation of flow, and contact interaction parameter have been computed for binary liquid mixtures of nitrobenzene with cyclohexane or *N,N*-dimethylformamide from density and viscosity measurements in the temperature interval of 298.15-313.15 K. The calculated quantities are discussed in terms of the nature of the molecular interactions between the components. Attempts were also made to test the validity of the viscosity models of Heric, Auslaender, and McAllister in predicting the binary viscosity data.

Introduction

Nitrobenzene is a versatile solvent used in synthetic and electrochemical research. It is a weak electron acceptor and forms weak charge-transfer complexes when mixed with a nonpolar liquid such as cyclohexane. However, when mixed with a strong dipolar aprotic solvent such as *N,N*-dimethylformamide (DMF), there is a considerable interaction. Mixtures of nitrobenzene with cyclohexane and *N,N*-dimethylformamide (DMF) have been studied earlier (*1-4*). However, to the best of our knowledge, extensive data in the temperature interval of 298.15-313.15 K have not been reported on mixtures of nitrobenzene with cyclohexane or DMF.

In this paper, we present density, ρ, and viscosity, η, data of mixtures of nitrobenzene with cyclohexane and DMF at 298.15, 303.15, 308.15, and 313.15 K over the entire mole fraction range. These properties are used to calculate molar excess volume, V^E, excess viscosity, η^E, and excess free energy of flow, ΔG^E, in addition to the binary contact interaction parameter A_{12}. Furthermore, we have tested the validity of viscosity models proposed by Heric (*5*, *6*), McAllister (*7*), and Auslaender (*8*).

Experimental Section

The solvents nitrobenzene (BDH; 99 mol %), cyclohexane (E. Merck; 98 mol %) and DMF (Fluka; 99 mol %) were purified by fractional distillation before use. The purity of the samples after distillation exceeded 99.5 mol % by gas chromatography. Some of the physical properties of the purified solvents are compared with the literature values (*9*) in Table I. Binary mixtures were prepared by mass with a possible error in the mole fraction estimated to be less than 10^{-4}.

Densities of pure liquids and their mixtures were determined by using a 10-cm^3 double-arm pycnometer. The pycnometer was calibrated by using double-distilled water with 0.997 07 g cm^{-3} as its density at 298.15 K. All weighings were done on a Mettler balance to within 0.05 mg. The necessary buoyancy correction was applied. The density values were reproducible within 0.0002 g cm^{-3}.

Viscosities were determined with a Cannon-Fenske viscometer, size 100, with a flow range of 3-15 cS, calibrated with double-distilled water and benzene. Kinetic energy corrections were applied to the viscosity data, and the estimated error in viscosity was 0.0007 cP. The other experimental details of measuring ρ and η are the same as described previously (*10*).

For each measurement, the same stock solutions were employed. A Toshniwal (Model GL-15) precision thermostat (±0.05 K) was used throughout. Sufficient time was allowed (usually 10-15 min) for attainment of thermal equilibrium.

Results and Discussion

Measured data of ρ and η are given in Table II. These data are further used to calculate V^E, A_{12}, η^E, and ΔG^E by using the following relations:

$$V^E = V_m - V_1 x_1 - V_2 x_2 \tag{1}$$

$$A_{12} = (\phi_1 \rho_1 + \phi_2 \rho_2 - \rho_m)/\phi_1 \phi_2 \rho_m \tag{2}$$

$$\eta^E = \eta_m - \eta_1 x_1 - \eta_2 x_2 \tag{3}$$

$$\Delta G^E = RT[\ln \eta_m V_m - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2] \tag{4}$$

Here, V_i, ρ_i, η_i, x_i, and ϕ_i are the molar volume, density, viscosity, mole fraction, and volume fraction, respectively, of the ith component of the mixture; T is the temperature and R the molar gas constant. The subscript m refers to mixtures. The results of eqs 1, 3, and 4 have been fitted to a polynomial equation of the type

$$X^E/\text{unit} = x_1 x_2 \sum_{i=0}^{m} a_i (x_2 - x_1)^i \tag{5}$$

where m is the number of coefficients a_i. The values of A_{12}, calculated by eq 2, are fitted to the relation

$$A_{12} = a_0 + a_1(\phi_2 - \phi_1) + a_2(\phi_2 - \phi_1)^2 \tag{6}$$

The coefficients a_i of eqs 5 and 6, together with the standard deviations, σ, between the calculated quantities and experimental data

$$\sigma = [\sum (X^E_{\text{expt}} - X^E_{\text{calc}})^2/(n - m)]^{1/2} \tag{7}$$

are included in Table III. Here, n is the total number of data points.

The V^E results for mixtures of nitrobenzene + cyclohexane are positive, suggesting the existence of weak dispersion forces between the mixing components. This is further confirmed by the negative values of η^E and ΔG^E. The same mixture has also been studied earlier by other researchers (*2-4*). For instance, the V^E data at equimolar compositions as observed by Suri and Ramakrishna (*3*) and Raman and Naidu (*4*) at 303.15 K are,

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[†] Based on the Ph.D. thesis of S.S.J. submitted to Karnatak University.

[*] Author to whom correspondence should be addressed.

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Table I. Normal Boiling Points, T_b, Densities, ρ, and Viscosities, η, of the Pure Liquid Components at 298.15 K

component	T_b/K this work	T_b/K ref 9	ρ/(g cm^{-3}) this work	ρ/(g cm^{-3}) ref 9	η/cP this work	η/cP ref 9
cyclohexane	354	353.88	0.773 89	0.773 89	0.8862	0.898
N,*N*-dimethylformamide	426	426.2	0.944 22	0.943 8	0.7987	0.802
nitrobenzene	484	483.95	1.193 41[a]	1.193 41[a]	1.6262[a]	1.619[a]

[a] At 303.15 K.

Table II. Densities, ρ, and Viscosities, η, of Binary Mixtures as a Function of Mole Fraction, x_i, and Temperature, T

x_1	$\rho(T)$/(g cm^{-3}) 298.15 K	303.15 K	308.15 K	313.15 K	$\eta(T)$/cP 298.15 K	303.15 K	308.15 K	313.15 K
				Nitrobenzene (1) + Cyclohexane (2)				
0.0000	0.7739	0.7687	0.7639	0.7592	0.8862	0.8130	0.7483	0.6886
0.0990	0.8117	0.8063	0.8016	0.7962	0.9069	0.8365	0.7722	0.7123
0.2037	0.8530	0.8480	0.8427	0.8379	0.9519	0.8775	0.8109	0.7485
0.2970	0.8924	0.8870	0.8820	0.8769	1.0172	0.9369	0.8638	0.7984
0.3968	0.9341	0.9271	0.9240	0.9193	1.0889	1.0000	0.9250	0.8553
0.4968	0.9749	0.9696	0.9647	0.9600	1.1598	1.0668	0.9868	0.9115
0.5973	1.0191	1.0144	1.0092	1.0044	1.2469	1.1527	1.0650	0.9854
0.6959	1.0611	1.0559	1.0507	1.0460	1.3456	1.2415	1.1466	1.0605
0.8011	1.1090	1.1038	1.0987	1.0937	1.4839	1.3666	1.2638	1.1670
0.8930	1.1495	1.1440	1.1390	1.1343	1.6032	1.4806	1.3576	1.2538
1.0000	1.1986	1.1934	1.1883	1.1832	1.7729	1.6262	1.4975	1.3729
				Nitrobenzene (1) + *N*,*N*-Dimethylformamide (2)				
0.0000	0.9442	0.9391	0.9344	0.9292	0.7987	0.7524	0.7077	0.6644
0.0953	0.9763	0.9709	0.9661	0.9613	0.9260	0.8671	0.8133	0.7628
0.1999	1.0085	1.0034	0.9982	0.9935	1.0261	0.9585	0.8949	0.8362
0.3027	1.0380	1.0329	1.0279	1.0228	1.1286	1.0528	0.9803	0.9134
0.4044	1.0652	1.0600	1.0551	1.0500	1.2310	1.1458	1.0750	0.9878
0.5040	1.0903	1.0851	1.0801	1.0749	1.3377	1.2461	1.1544	1.0704
0.6035	1.1148	1.1097	1.1043	1.0994	1.4409	1.3321	1.2318	1.1395
0.7034	1.1376	1.1321	1.1271	1.1222	1.5433	1.4230	1.3125	1.2140
0.8011	1.1579	1.1527	1.1478	1.1426	1.6378	1.5047	1.3887	1.2799
0.8937	1.1785	1.1730	1.1681	1.1632	1.7403	1.5946	1.4687	1.3508
1.0000	1.1986	1.1934	1.1883	1.1832	1.7729	1.6262	1.4975	1.3729

respectively, 0.85 and 0.26 cm^3/mol. However, our value at this temperature is 0.35 cm^3/mol. Similarly, the V^E results of Letcher (*2*) at 298.15 K are positive and are fairly comparable to our results.

In the case of the nitrobenzene + DMF system, we find that V^E data are negative over the entire composition scale of the mixture. However, the V^E results of Gopal and co-workers (*1*) for this system are much higher than our data. The negative V^E is attributed to dipole–dipole interactions between the components. The positive values of η^E and ΔG^E further confirm that specific interactions are operative in this mixture.

The parameter A_{12} is positive for nitrobenzene + cyclohexane, whereas it is negative for nitrobenzene + DMF mixture. This further confirms our earlier conclusions.

Among the viscosity models tested, the Heric and Auslaender models fit the experimental data with a better accuracy, σ/cP = 0.003–0.007, than the McAllister model, for which σ/cP varies from 0.06 to 0.09.

Glossary

V^E	molar excess volume, cm^3 mol^{-1}
η^E	molar excess viscosity, cP
ΔG^E	molar excess free energy of flow, kJ mol^{-1}
ρ	density, g cm^{-3}
η	viscosity, cP
x_i	mole fraction of component *i*
ϕ_i	volume fraction of component *i*
A_{12}	contact parameter
a_i	coefficients in eqs 5 and 6
σ	standard deviation, eq 7

Table III. Coefficients of Equations 5 and 6 for Excess Quantities, X^E

X^E/unit	T/K	a_0	a_1	a_2	a_3	σ/unit
			Nitrobenzene + Cyclohexane			
V^E/(cm^3 mol^{-1})	298.15	1.308	0.198	1.187	2.318	0.065
	303.15	1.399	1.161	0.907	0.115	0.076
	308.15	1.141	0.337	1.627	2.088	0.076
	313.15	0.308	−5.065	1.430	12.777	0.076
η^E/cP	298.15	−0.663	0.160	−0.138	−0.307	0.489
	303.15	−0.593	0.118	−0.063	−0.251	0.296
	308.15	−0.528	0.079	−0.082	−0.128	0.407
	313.15	−0.459	0.056	−0.034	−0.156	0.340
ΔG^E/(kJ mol^{-1})	298.15	−0.694	−0.011	−0.307	−0.705	0.843
	303.15	−0.670	−0.030	−0.178	−0.623	0.636
	308.15	−0.640	−0.101	−0.205	−0.361	0.783
	313.15	−0.604	−0.257	−0.129	−0.169	1.032
A_{12}	298.15	0.012	0.007	0.010		0.356
	303.15	0.012	0.007	0.011		0.378
	308.15	0.010	0.007	0.014		0.391
	313.15	0.000	0.002	0.027		1.978
			Nitrobenzene + DMF			
V^E/(cm^3 mol^{-1})	298.15	−0.082	−0.331	−0.627	0.048	3.617
	303.15	−0.099	−0.449	−0.424	0.213	2.998
	308.15	−0.064	−0.529	−0.485	0.664	2.445
	313.15	−0.091	−0.459	−0.838	0.210	3.566
η^E/cP	298.15	0.166	−0.118	0.473	−0.138	0.795
	303.15	0.176	−0.098	0.355	−0.114	0.754
	308.15	0.173	−0.040	0.307	−0.182	0.740
	313.15	0.164	−0.089	0.331	−0.055	0.640
ΔG^E/(kJ mol^{-1})	298.15	1.177	0.046	0.922	0.235	1.422
	303.15	1.190	0.061	0.771	0.196	1.514
	308.15	1.195	0.159	0.736	0.034	1.742
	313.15	1.177	0.025	0.859	0.313	1.598
A_{12}	298.15	−0.001	−0.003	−0.010		0.414
	303.15	−0.001	−0.003	−0.006		0.335
	308.15	−0.001	−0.002	−0.008		0.333
	313.15	−0.001	−0.004	−0.012		0.422

Registry No. DMF, 68-12-2; cyclohexane, 110-82-7.

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Densities and Viscosities of Binary Liquid Mixtures of Anisole with Methanol and Benzene[†]

Shrikant S. Joshi and Tejraj M. Aminabhavi*

Department of Chemistry, Karnatak University, Dharwad 580 003, India

Shyam S. Shukla

Department of Chemistry, Lamar University, P.O. Box 10022, Beaumont, Texas 77710

Excess volume, excess viscosity, excess free energy of activation of flow, and contact interaction parameter have been computed for binary liquid mixtures of anisole with methanol or benzene from densities and viscosities measured at 298.15, 303.15, 308.15, and 313.15 K over the entire mole fraction scale. The results are discussed in terms of specific type interactions between anisole and methanol. The interactions between anisole and benzene are somewhat less specific. Auslaender and Heric viscosity models reproduce the experimental viscosities better than the equation of McAllister.

Introduction

Binary mixtures of anisole with benzene or methanol are interesting examples of systems with specific interactions between the components. At 298.15 K, anisole possesses a rather low dielectric constant (4.33) and a large molar volume (109.22 cm^3 mol^{-1}) whereas methanol and benzene have dielectric constants and molar volumes of, respectively, 32.7 and 40.7 cm^3 mol^{-1} and 2.28 and 89 cm^3 mol^{-1}. Moreover, the strength of interaction in the anisole + methanol mixture is greater than that in the anisole + benzene mixture because of H bonding between the hydroxy group of methanol and the methoxy group of anisole. One other factor is that benzene exhibits zero dipole moment whereas anisole is a polar compound. Extensive thermodynamic studies on such mixtures have not been made earlier.

In order to gain a deeper understanding of the structure and interactions in these mixtures, we have calculated the molar excess volume, V^E, excess viscosity, η^E, and excess free energy of activation of flow, ΔG^E, from viscosity, η, and density, ρ, data, taken over the entire composition scale in the temperature interval of 298.15-313.15 K. From the temperature dependence of η^E, the enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, of activation for the flow process and the binary contact parameter, A_{12}, were calculated. Furthermore, we have tested the validity of the viscosity models proposed by McAllister (*1*), Heric (*2*), and Auslaender (*3*).

Table I. Densities, ρ, and Viscosities, η, of the Pure Liquid Components at 298.15 K

	ρ/(g cm^{-3})		η/cP	
component	ref 6	this work	ref 6	this work
anisole	0.989 32	0.989 32	0.789^a	0.920^a
benzene	0.868 50	0.868 25	0.562	0.562
methanol	0.786 64	0.787 02	0.545	0.526

^{a} At 303.15 K.

Experimental Section

The methods used earlier have been described elsewhere (*4*, *5*). The reagent-grade chemicals obtained were further double-distilled before use. Densities of pure liquids and their mixtures were measured with a 10-cm^3 double-arm pycnometer; calibration was done with distilled water with an accuracy of ±0.0001 g cm^{-3} in densities. All weighings were made on a Mettler balance (Switzerland). A thermostatically controlled bath, Toshniwal Model GL-15, with a precision of ±0.05 K was used, and the temperatures were recorded from a calibrated thermometer.

Viscosities were determined with a Cannon-Fenske viscometer, size 100, with a flow range of 3-15 cS, calibrated with distilled water and benzene. Kinetic energy corrections were applied to the viscosity data, and the estimated error in viscosity was within 0.0007 cP. During the measurements, the pycnometer and the viscometer were maintained in a constant-temperature bath until at least two consecutive readings of the liquid height in the capillaries of the flow time indicated that the sample had reached the temperature of the bath. An average of three independent readings were used to calculate the basic properties. Our results for pure liquids are compared with the literature (*6*) in Table I. The experimental data for mixtures are given in Table II.

[†] Based on the Ph.D. thesis of S.S.J. submitted to Karnatak University.

[*] Author to whom correspondence should be addressed.

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