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Literature Cited

(1) Gopal, R.; Agarwal, S.; Agarwal, D. K. *J. Chem. Thermodyn.* **1976**, *8*, 1205.
(2) Letcher, T. M. *J. Chem. Thermodyn.* **1972**, *4*, 159.
(3) Suri, S. K.; Ramakrishna, V. *Indian J. Chem.* **1969**, *7*, 490.
(4) Raman, G. K.; Naidu, P. R. *Proc. Indian Acad. Sci., Sect. A* **1973**, *77*, 263.
(5) Heric, E. L. *J. Chem. Eng. Data* **1966**, *11*, 66.
(6) Heric, E. L.; Brewer, J. G. *J. Chem. Eng. Data* **1967**, *12*, 574.
(7) McAllister, R. A. *AIChE J.* **1960**, *6*, 427.
(8) Auslaender, G. *Br. Chem. Eng.* **1964**, *9*, 610.
(9) Riddick, J. A.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Techniques in Chemistry, Vol. II; Wiley-Interscience: New York, 1970.
(10) Gokavi, G. S.; Raju, J. R.; Aminabhavi, T. M.; Balundgi, R. H.; Muddapur, M. V. *J. Chem. Eng. Data* **1986**, *31*, 15.

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

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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.

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Table II. Density, ρ, and Viscosity, η, Data of Binary Mixtures as a Function of Mole Fraction, x_1, and Temperatures, T

	$\rho(T)/(\mathrm{g\ cm^{-3}})$				$\eta(T)/\mathrm{cP}$			
x_1	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
				Anisole (1) + Benzene (2)				
0.0	0.8746	0.8683	0.8642	0.8584	0.5997	0.5620	0.5413	0.4863
0.1025	0.8890	0.8830	0.8787	0.8730	0.6396	0.6033	0.5736	0.5191
0.2004	0.9017	0.8953	0.8918	0.8862	0.6806	0.6433	0.6196	0.5555
0.3003	0.9146	0.9086	0.9048	0.8991	0.7121	0.6712	0.6447	0.5884
0.4020	0.9271	0.9209	0.9173	0.9120	0.7553	0.7045	0.6750	0.6099
0.4985	0.9383	0.9321	0.9289	0.9228	0.7849	0.7380	0.7086	0.6337
0.5991	0.9494	0.9439	0.9403	0.9345	0.8308	0.7765	0.7422	0.6690
0.6990	0.9602	0.9548	0.9510	0.9456	0.8709	0.8121	0.7763	0.7007
0.8050	0.9712	0.9658	0.9619	0.9566	0.9112	0.8545	0.8167	0.7318
0.9013	0.9810	0.9751	0.9720	0.9666	0.9506	0.8883	0.8509	0.7626
1.0	0.9901	0.9846	0.9814	0.9757	1.0023	0.9315	0.8896	0.7977
				Anisole (1) + Methanol (2)				
0.0	0.7873	0.7820	0.7786	0.7729	0.5394	0.5090	0.4879	0.4391
0.1024	0.8372	0.8318	0.8278	0.8226	0.6111	0.5740	0.5506	0.4934
0.2039	0.8734	0.8675	0.8641	0.8589	0.6700	0.6257	0.5983	0.5372
0.2982	0.8988	0.8930	0.8896	0.8842	0.7131	0.6672	0.6380	0.5706
0.4027	0.9210	0.9156	0.9123	0.9066	0.7591	0.7035	0.6731	0.6023
0.4998	0.9381	0.9321	0.9287	0.9229	0.8009	0.7455	0.7065	0.6345
0.5991	0.9522	0.9426	0.9429	0.9377	0.8271	0.7718	0.7350	0.6601
0.7068	0.9652	0.9592	0.9560	0.9501	0.8651	0.8059	0.7683	0.6865
0.8061	0.9746	0.9691	0.9658	0.9600	0.8975	0.8374	0.7978	0.7174
0.9023	0.9831	0.9777	0.9739	0.9685	0.9373	0.8779	0.8373	0.7510
1.0	0.9901	0.9846	0.9814	0.9757	1.0023	0.9315	0.8896	0.7977

Table III. Coefficients of Equations 4 and 7 for Excess Quantities X^E

X^E/unit	T/K	a_0	a_1	a_2	a_3	σ/unit
			Anisole (1) + Benzene (2)			
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	–0.100	–0.168	–0.064	0.582	0.014
	303.15	–0.106	0.433	–0.238	–0.847	0.025
	308.15	–0.173	–0.035	0.157	0.041	0.015
	313.15	–0.190	–0.137	–0.351	0.467	0.019
η^E/cP	298.15	–0.043	0.013	–0.016	0.109	0.029
	303.15	–0.030	0.024	0.056	0.087	0.020
	308.15	–0.026	0.055	0.035	–0.037	0.035
	313.15	–0.012	0.065	0.036	–0.027	0.035
A_{12}	298.15	–0.001	0.001	–0.003		0.001
	303.15	–0.001	0.000	–0.003		0.002
	308.15	–0.001	0.000	–0.001		0.001
	313.15	–0.002	0.001	–0.004		0.001
			Anisole (1) + Methanol (2)			
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	–0.947	–0.225	–0.390	–0.318	0.016
	303.15	–0.468	–1.557	–1.427	2.660	0.093
	308.15	–0.855	–0.380	–0.147	0.014	0.013
	313.15	–0.904	–0.455	–0.344	–0.192	0.017
η^E/cP	298.15	0.105	0.205	–0.122	0.152	0.002
	303.15	0.084	0.178	–0.065	0.101	0.002
	308.15	0.068	0.182	–0.044	0.094	0.001
	313.15	0.056	0.156	–0.043	0.077	0.001
A_{12}	298.15	–0.013	0.002	–0.006		0.002
	303.15	–0.009	–0.006	–0.017		0.010
	308.15	–0.013	0.003	0.003		0.002
	313.15	–0.014	0.001	–0.001		0.002

Treatment of Data

In the theoretical analysis of the experimental data of ρ and η, the following relations were used to calculate V^E, η^E, and ΔG^E:

$$V^E = V - (x_1V_1 + x_2V_2) \tag{1}$$

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

$$\Delta G^E = RT[\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2] \tag{3}$$

where V, V_1, and V_2 are the molar volumes and η, η_1, and η_2 are the viscosities of the mixture and of pure components 1 and 2, respectively. T is the temperature and R the molar gas constant; x_1 and x_2 are mole fractions. The definitions of η^E and ΔG^E are not universally accepted; nevertheless, such quantities have been studied in the literature (*7*). Results of V^E, η^E, and ΔG^E as computed from eqs 1–3 were fitted to a polynomial of the type

$$X^E/\text{unit} = x_1x_2\sum_{i=0}^{m} a_i(x_2 - x_1)^i \tag{4}$$

where X^E refers to V^E, η^E, or ΔG^E, and m is the number of coefficients. In each case, the optimum number of coefficients was ascertained from an examination of the variation in standard deviation, σ, as given by

$$\sigma = [\sum(X_{\text{obs}} - X_{\text{cal}})^2/(n - m)]^{1/2} \tag{5}$$

where n is the number of data points.

Following our earlier suggestions (*8*, *9*), the Flory–Scatchard-type contact interaction parameter, A_{12}, was computed as

$$A_{12} = (\phi_1\rho_1 + \phi_2\rho_2 - \rho)/\phi_1\phi_2\rho \tag{6}$$

where ϕ_i represents the volume fraction of component i of the mixture, and was fitted to the polynomial

$$A_{12} = a_0 + a_1(\phi_2 - \phi_1) + a_2(\phi_2 - \phi_1)^2 \tag{7}$$

The coefficients and standard deviations, σ, for V^E, η^E, and A_{12} are given in Table III.

The enthalpy, ΔH^*, and entropy, ΔS^*, of activation of flow have been calculated from a least-squares analysis of the temperature dependence of η (*10*) by using the relation

$$\ln \lambda V = (\ln hN - \Delta S^*/R) + \Delta H^*/RT \tag{8}$$

where $\lambda = \eta/\rho$ is the kinematic viscosity, h is Planck's constant, and N is the Avogadro number.

Discussion of Results

Viscosity and density profiles of mixtures of anisole with benzene or methanol at 298.15 K are given in Figure 1. The general trend in the variation of ρ and η of both the mixtures is somewhat identical. For both the mixtures, slight sigmoidal shapes are observed, and the sigmoidal shape is more pronounced with the anisole + methanol mixture than the other mixture. This may be due to the wide difference in the molar volumes of anisole and methanol. The specific type interactions in anisole + methanol appear to be stronger than in anisole + benzene. Also, for anisole + methanol, V^E is more negative than for anisole + benzene. The temperature dependence of

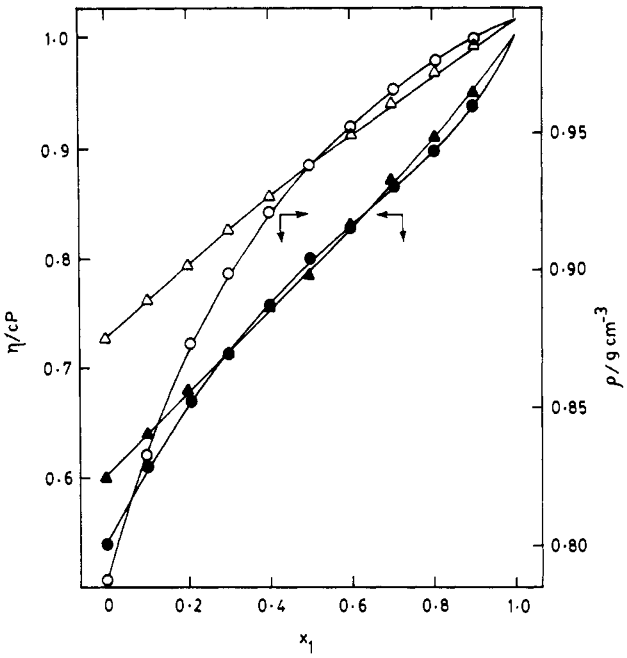

Figure 1. Viscosity, η, and density, ρ, of binaries versus mole fraction, x_1, at 298.15 K: ●, η of anisole + methanol; ▲, η of anisole + benzene; ○, ρ of anisole + methanol; △, ρ of anisole + benzene.

V^E shows a systematic increase with temperature. Interactions appear to be stronger for the anisole + methanol mixture, than for anisole + benzene. This implies that specific interactions become less significant as we raise the temperature of the system. The values of A_{12}, though negative for both the binaries, are more negative for anisole + methanol than for anisole + benzene.

The results of η^E for the anisole + benzene mixture are negative, whereas, for the anisole + methanol mixture, η^E is positive and decreases progressively with the rise in temperature. This further confirms that specific interactions are operative in mixtures of anisole with methanol.

The computed ΔG^E values for anisole + methanol are higher (cf. 485 J mol^{-1}) than that for the anisole + benzene mixture, for which it is only 63 J mol^{-1}. Such high ΔG^E values also support the conjecture that molecular complexes are formed in the mixture consisting of anisole and methanol.

For both the systems, $\Delta S^{\ddagger}$ values are negative but small and vary in the range of 38–50 J mol^{-1} K^{-1} while $\Delta H^{\ddagger}$ values are in the range of 8–10 kJ mol^{-1}. Such small and positive $\Delta H^{\ddagger}$ values have also been observed earlier in the literature for other systems (*11*). Negative $\Delta S^{\ddagger}$ values suggest that the availability of either methanol or benzene in the presence of anisole is sufficient for the formation of activated molecular complexes that lead to increased order as a result of viscous flow.

When the viscosity data were used to test the validity of viscosity models, it was found that the equations of Auslaender and Heric reproduced the experimental viscosities better than that of McAllister.

Glossary

ρ	density, g cm^{-3}
η	viscosity, cP
V	molar volume, cm^3 mol^{-1}
V^E	molar excess volume, cm^3 mol^{-1}
η^E	molar excess viscosity, cP
ΔG^E	molar excess free energy of activation of flow, J mol^{-1}
A_{12}	contact interaction parameter
x_i	mole fraction of component *i*
ϕ_i	volume fraction of component *i*
a_i	coefficients in eqs 4 and 7
σ	standard deviation, eq 5
$\Delta H^{\ddagger}$	enthalpy of activation of flow, kJ mol^{-1}
$\Delta S^{\ddagger}$	entropy of activation of flow, J mol^{-1} K^{-1}

Literature Cited

(1) McAllister, R. A. *AIChE J.* **1960**, *6*, 427.
(2) Heric, E. L. *J. Chem. Eng. Data* **1966**, *11*, 66.
(3) Auslaender, G. *Br. Chem. Eng.* **1964**, *9*, 610.
(4) Aminabhavi, T. M.; Manjeshwar, L. S.; Balundgi, R. H. *J. Chem. Eng. Data* **1987**, *32*, 50.
(5) Gokavi, G. S.; Raju, J. R.; Aminabhavi, T. M.; Balundgi, R. H.; Muddapur, M. V. *J. Chem. Eng. Data* **1986**, *31*, 15.
(6) Riddick, J. A.; Bunger, W. J.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques in Chemistry, Vol. II; Wiley-Interscience: New York, 1986.
(7) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1966**, *62*, 112.
(8) Aminabhavi, T. M.; Munk, P. *Macromolecules* **1979**, *12*, 1186.
(9) Aminabhavi, T. M. *J. Chem. Eng. Data* **1987**, *32*, 406.
(10) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.
(11) Singh, P. P.; Sinha, C. P. *Indian J. Chem.* **1983**, *22A*, 282.

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