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Densities, Viscosities, and Dielectric Constants of Acetonitrile + Toluene at 15, 25, and 35 °C

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The densities, viscosities, and dielectric constants of the acetonitrile–toluene system were measured as a function of mole fraction at 15, 25, and 35 °C. The results are given as a power series equation, and the values of computed constants are given. Excess dielectric constant, molar polarization, excess molar polarization, and excess viscosity were calculated.

Introduction

The binary solvent system acetonitrile–toluene is used in our laboratory as a solvent for various electrochemical researches. Because the physicochemical parameters of abovementioned system do not exist in the literature, we carried out this work in order to give information about the properties of this system.

Densities, viscosities, and dielectric constants for the acetonitrile–toluene system at the whole molar fraction range at temperatures 15, 25 and 35 °C are reported.

Smoothing values for the above properties are given by the following equation (*1*)

$$Y = \sum_{i=0}^{6} a_i x^i$$

in which the a_i coefficient was obtained by a curve-fitting method. The Y represents the corresponding property and x denotes the toluene mole fraction.

Experimental Section

Dielectric constants were measured with a dipolmeter employing the heterodyne beat method (Model WTW DM 01, Wissenschaftlich-Technische Werkstatten GmbH). The measurements were made at 2 MHz using two measuring cells. Cell MFL 2 was used with a range in dielectric constant from 7 to 21 and cell MFL 3 with a range of dielectric constant from 20 to 50. Reproducibility of measurements was approximately 0.2 units of dielectric constant (*2*). The temperature of the cell was maintained constant (0.02 °C) by circulating the water of a constant temperature bath. The cells were previously standardized with water, acetone, ethylene chloride, and nitrobenzene.

Densities were measured with a Sprengel-Ostwald pycnometer having a volume of about 25 mL. Temperature control was 0.01 °C.

Viscosities of the mixtures were measured at 15, 25, and 35 °C with an Ubbelohde-type suspended-level viscometer with a flow time of 180 s for water at 25 °C. Flow times were measured to 0.01 s with an electronic stopwatch (*3*). The average deviation for more than five measurements did not exceed 0.05 s. The viscometer was standardized with conductivity water η (H_2O, 25 °C) = 0.008 903 P and η (H_2O, 20 °C) = 0.010 02 P.

All solvent mixtures were made up by weight.

Acetonitrile (Merck 99.5%) was passed through molecular sieves 3A and followed by fractional distillation. The middle fraction was collected. The final product had a specific conductance of about 5×10^{-8} mho·cm^{-1}.

Table I. Experimental Density, Viscosity, and Dielectric Constant Data for the Acetonitrile–Toluene Mixture at 15, 25, and 35 °C

x	15 °C	25 °C	35 °C
	Density		
0	0.7871	0.7760	0.7669
0.1996	0.7954	0.7846	0.7750
0.3590	0.8040	0.7930	0.7831
0.4903	0.8123	0.8025	0.7920
0.5994	0.8198	0.8097	0.7991
0.6918	0.8285	0.8180	0.8082
0.7710	0.8368	0.8271	0.8170
0.8397	0.8460	0.8362	0.8268
0.8998	0.8541	0.8450	0.8351
0.9530	0.8630	0.8520	0.8443
1	0.8716	0.8623	0.8527
	Viscosity		
0	0.388	0.346	0.308
0.1996	0.392	0.348	0.309
0.3590	0.400	0.350	0.309
0.4903	0.405	0.365	0.330
0.5994	0.430	0.380	0.350
0.6918	0.445	0.403	0.375
0.7710	0.458	0.427	0.389
0.8397	0.506	0.457	0.421
0.8998	0.555	0.487	0.434
0.9530	0.590	0.527	0.450
1	0.623	0.556	0.492
	Dielectric Constant		
0	37.56	35.94	34.30
0.1996	33.98	32.31	31.00
0.3590	30.22	28.91	27.64
0.4903	26.67	25.20	24.20
0.5994	22.88	21.89	20.99
0.6918	19.20	18.40	17.60
0.7710	15.60	14.92	14.33
0.8397	12.10	11.61	11.22
0.8998	8.67	8.36	8.05
0.9530	5.70	5.03	5.00
1	2.405	2.380	2.355

Toluene (Merck, extra pure) was shaken with concentrated H_2SO_4, water, 5% $NaHCO_3$, and again with water. Then was dried with $CaSO_4$ and P_2O_5 and finally distilled from P_2O_5.

Results and Discussion

The data for acetonitrile–toluene mixtures are given in Table I at various mole fractions of toluene and at 15, 25, and 35 °C.

Dielectric Constants. The experimental results of dielectric constants for the acetonitrile–toluene mixture are given by the following equation

$$\epsilon = \sum_{i=0}^{6} a_i x^i \tag{2}$$

whose coefficients a_i obtained by a curve-fitting method are summarized in Table II.

The excess dielectric constant is also calculated because it gives a means of estimating the interactions between the molecules of the components.

The excess dielectric constant is determined by (*4*, *5*)

$$\epsilon^E = \epsilon - (\epsilon_1 x_1 + \epsilon_2 x_2) \tag{3}$$

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Table II

°C	a_0	a_1	a_2	a_3	a_4	a_5	a_6	σ_{n-1}
				Coefficients of Eq 10[a]				
15	0.7870	-0.7904	6.618	-20.1186	29.635	-21.1638	5.9047	9.5×10^{-5}
25	0.7760	0.1996	-1.1717	3.3844	-4.664	3.1969	-0.8589	1.7×10^{-5}
35	0.7669	-0.5780	4.9627	-15.2669	22.7800	-16.4356	4.6238	1.4×10^{-5}
				Coefficients of Eq 7[b]				
15	0.003880	0.07775	-0.64885	2.09511	-3.26995	2.4767	-0.72841	1.6×10^{-5}
25	0.00316	0.002964	-0.02423	0.073997	-0.10249	0.06965	-0.01779	6.7×10^{-6}
35	0.00308	-0.024746	0.19346	-0.588691	0.88357	-0.64876	0.187006	1.9×10^{-5}
				Coefficients of Eq 2[c]				
15	37.56	-57.086	312.507	-981.942	1438.597	-1042.703	295.470	1.7×10^{-3}
25	35.94	-16.43	-5.4637	-7.8626	-2.466	5.244	3.906	8.6×10^{-3}
35	34.3	-116.431	788.042	-2398.014	3478.835	-2469.06	684.6814	9.9×10^{-3}

[a] Applicable to the density of the system. [b] Applicable to the viscosity of the system. [c] Applicable to the dielectric constant of the system.

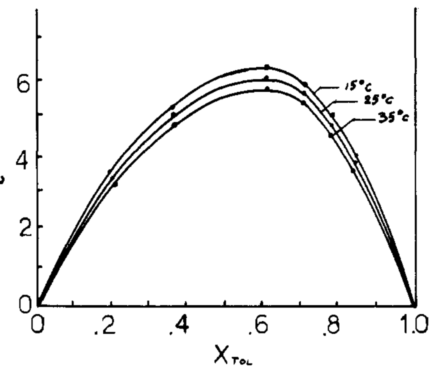

Figure 1. Variation of the excess dielectric constant with the mole fraction of toluene.

Figure 1 gives the variation of the calculated values with the mole fraction of toluene at 15, 25, and 35 °C. As is shown the excess dielectric constant has only positive values for all the temperatures considered here. The magnitude of the extrema decreases as the temperature increases. It means that the strength of interactions between the acetonitrile and toluene molecules decreases when the temperture increases (*6*).

Molar Polarization. The molar polarization of the acetonitrile–toluene mixture was calculated. This was not linear against mole fraction. This fact implies some interaction, between the acetonitrile and toluene molecules (*7*).

The excess molar polarization is given by the formula

$$P^{E} = P - (x_1P_1 + x_2P_2) \tag{4}$$

The excess molar polarization in Figure 2 is always positive. This also means that there are interactions between the molecules of the two substances (*8*, *9*).

Viscosity. Smoothing values for the viscosity are given by the following equation:

$$\eta = \sum_{i=0}^{6} a_i x^i \tag{5}$$

The coefficients a_i were obtained by a curve-fitting method and are listed in Table II.

Deviations from ideality are determined by the excess viscosity (*10*)

$$\eta^{E} = \eta - (x_1\eta_1 + x_2\eta_2) \tag{6}$$

Figure 3 shows negative excess viscosity for this system over the whole concentration range. However, since there is a minimum of the curve η^E vs. x according to Fialkov (*11*), this gives evidence of interactions between acetonitrile and toluene molecules.

As shown in Figure 3, the curve maximum decreases as the temperature increases. This is due to the weakenng of the interactions between the different kind of ions when the temperature increases.

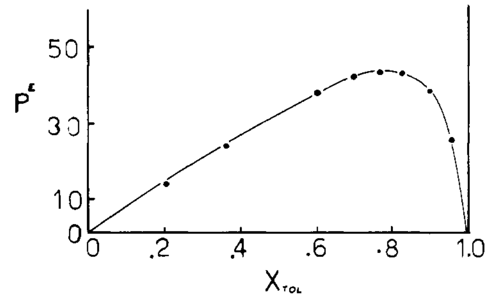

Figure 2. Variation of the excess molar polarization vs. mole fraction of toluene at 15 °C.

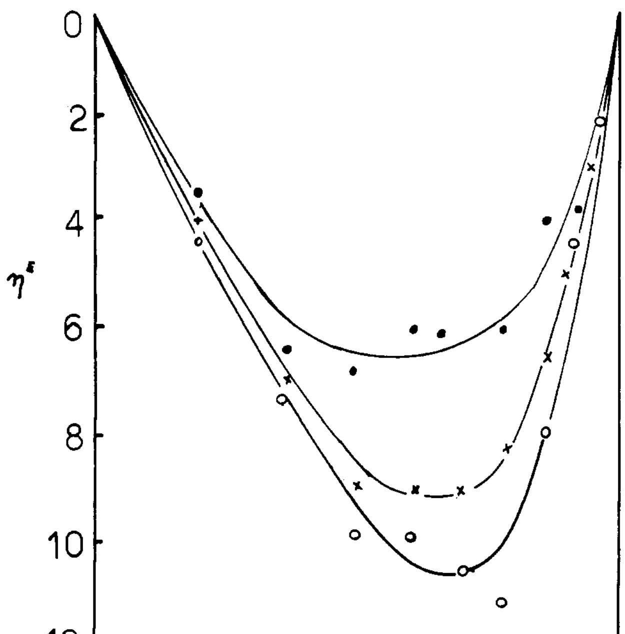

Figure 3. Variation of the excess viscosity vs. mole fraction of toluene (O, 15 °C; ×, 25 °C; ●, 35 °C).

Densities. The densities d of the system were also reported as a power series given by the following relation:

$$d = \sum_{i=0}^{6} a_i x^i \tag{7}$$

The coefficients obtained by the curve-fitting method are summarized in Table II.

Glossary

ϵ^E	excess dielectric constant
η^E	excess viscosity
P^E	excess molar polarization
x	mole fraction of the toluene
d	density

Registry No. Acetonitrile, 75-05-8; toluene, 108-88-3.

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Infinite-Dilution Activity Coefficients from Ebulliometric Isobaric Bubble Point–Composition Data of Hydrocarbon–Sulfolane Systems

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Isobaric bubble point temperature vs. composition data have been measured for three partially miscible binaries of hydrocarbon and sulfolane in their respective miscible regions at three different pressures. The limiting slopes, $(\partial T/\partial x)_P^\infty$ values, have been obtained in the sulfolane-dilute and hydrocarbon-dilute regions from the regression analysis of the experimental data for straight line relations. The activity coefficients at infinite dilution have been calculated at varied temperatures at two widely different temperature levels. These values can be used as a data source for evaluation of the group-interaction parameters for CH_2–sulfolane pair of groups and their temperature dependency in the modified UNIFAC/SUPERFAC model.

Introduction

Liquid–liquid extraction (LLE) of aromatic hydrocarbons from petroleum fractions is of great commercial importance and is carried out by using a selective polar solvent such as sulfolane. The liquid–liquid equilibrium data needed for the process engineering calculations are conveniently predicted by using the modified UNIFAC group-interaction model (*1*, *2*) as only five groups are involved such as (1) ACH, (2) $ACCH_3$, (3) CH_2, (4) CH_3, and (5) sulfolane. Since CH_3 and CH_2 are classified under the same main group, there are in all six possible pairs of groups and only six group-interaction parameters are needed for the prediction of LLE data (*3*, *4*). The activity coefficients at infinite dilution are considered an excellent data source for evaluation of the group-interaction parameters, especially for the CH_2–sulfolane pair of groups, as they are obtained from the binaries which are miscible only in the very dilute regions. Besides they can be determined by a relatively simple differential ebulliometric technique with reliable accuracy. This technique requires less experimental time and is well suited for the binaries whose boiling points differ widely. In the present work the activity coefficients at infinite dilution have been determined from the isobaric bubble point temperature vs. composition data in the respective miscible regions of three partially miscible binaries: (i) *n*-hexane–sulfolane, (ii) *n*-heptane–sulfolane, and (iii) cyclohexane–sulfolane. The physical properties of the pure components (*5*, *6*) are presented in Table I and the solubility limits of the three partially miscible binaries (*7*, *8*) in Table II.

Thermodynamic Relations

Gautreaux and Coates (*9*) developed an expression for activity coefficients at infinite dilution in terms of pure component properties and the limiting slope of the temperature with respect to the liquid phase mole fraction, which was further improved by Null (*10*) by including vapor–phase nonidealities as

$$\gamma_{1,\mathrm{exptl}}^\infty = [P_2^S - [1 - (P_2^S v_2^L/RT) + (P_2^S/\phi_2^S) \times (\partial\phi_2^S/\partial P)_T](\mathrm{d}P_2^S/\mathrm{d}T)(\partial T/\partial X_1)_P^\infty]/[(P_1^S\phi_1^S/\phi_{1,P_2^S}) \times \exp[(P_2^S - P_1^S)v_1^L/RT]] \quad (1)$$

where the pure component vapor pressures, P_i^S, and liquid molar volumes, v_i^L, are readily available in the literature (*5*, *6*) as a function of temperature. The fugacity coefficients of the pure components at the saturated vapor pressures, ϕ_i^S, their derivatives with respect to pressure $(\partial\phi_i^S/\partial P)_T$, and the fugacity coefficient of component i evaluated at P_j^S, ϕ_{i,P_j^S}, have been determined by using the virial equation of state with the second virial coefficients estimated by the method of Tsonopoulos (*11*, *12*). The limiting slope of temperature with respect to liquid-phase composition, $(\partial T/\partial X)_P^\infty$, is only required to be obtained experimentally by the differential ebulliometric technique. However, due to experimental difficulties in directly measuring the liquid-phase compositions, x, in equilibrium with the vapor phase in the ebulliometer, this limiting slope has been calculated in terms of $(\partial T/\partial X_F)_P^\infty$, where x_F is the composition of the dilute mixture feed charged to the ebulliometer. It can be seen (*13*) that the two limiting slopes are related as

$$(\partial X_1/\partial T)_P^\infty = (\partial X_F/\partial T)_P^\infty + L_2\theta/RT^2 \quad (2)$$

where L_2 is the latent heat of vaporization of component 2 and θ the fraction of the feed that is present in the vapor phase, which can be easily estimated from the free vapor space of the

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