Viscosities and Excess Molar Volumes for Acetonitrile + Methanol at 298.15, 308.15, and 318.15 K

Nirmal Saha, Bijan Das,* and Dilip K. Hazra

Department of Chemistry, North Bengal University, Darjeeling 734 430, India

Densities and viscosities have been measured for the binary mixtures of acetonitrile and methanol as a function of mole fraction at temperatures of 298.15, 308.15, and 318.15 K. The excess molar volumes V^E derived from the experimental density data and the deviation of the viscosity of mixtures from the ideal mole fraction rule $\Delta\eta$ are negative at all the temperatures investigated. The V^E and $\Delta\eta$ values have been fitted to a Redlich–Kister-type polynomial relation to estimate the coefficients and standard deviations. The results are used to interpret the nature of interactions.

Introduction

In recent years, there has been an increased interest (Aminabhavi et al., 1994; Comelli and Francesconi, 1993; Crabtree and O'Brien, 1991; Das and Hazra, 1993; Das et al., 1994; Douhéret et al., 1990; Fuangfoo and Viswanath, 1993; Marchetti et al., 1991; Monfort, 1983; Moumouzias et al., 1991; Nagata, 1985) in the study of thermodynamic and transport properties of binary liquid mixtures. These properties have been extensively used to understand the molecular interactions between the components of the mixture, to develop new theoretical models, and also for engineering applications in the process industry. In the present study, the densities and viscosities have been determined for the binary system of acetonitrile + methanol over the entire range of composition at 298.15, 308.15, and 318.15 K. The experimental results of this study have been used to calculate the excess molar volumes (V^E), and the behavior of the liquid mixtures has been interpreted on the basis of these results.

Experimental Section

Acetonitrile (E. Merck, India, 99% pure) was distilled with P_2O_5 and then redistilled with CaH_2. The density, ρ_o, (0.776 86 g·cm^{-3} at 298.15 K) and the viscosity, η_o, (0.345, 0.313, and 0.289 mPa·s at 298.15, 308.15, and 318.15 K) agree well with literature values: 0.776 851 g·cm^{-3} (Singh et al., 1994) and 0.344, 0.314, and 0.289 mPa·s (Moumouzias et al., 1991), respectively.

Methanol (E. Merck, India, uvasol grade, 99.5% pure) was dried over 3 Å molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density, ρ_o, of 0.786 54 g·cm^{-3} at 298.15 K and a viscosity, η_o, of 0.545, 0.474, and 0.419 mPa·s at 298.15, 308.15, and 318.15 K. These values are in good agreement with the literature values which are 0.786 54 g·cm^{-3} and 0.542, 0.474, and 0.417 mPa·s (Doe et al., 1984), respectively.

The purities as checked by gas chromatography were found to be better than 99.5% for acetonitrile and 99.8% for methanol.

The densities, ρ, were measured with an Ostwald–Sprengel-type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 308.15, and 318.15 K with doubly distilled water and benzene. The temperature of the bath was controlled to ±0.01 K. The reproducibility of density measurements was $\pm 3 \times 10^{-5}$ g·cm^{-3}.

The kinematic viscosities, ν, were measured by means of a suspended level Ubbelohde viscometer. The time of efflux was measured with a stopwatch to ±0.1 s. The viscometer was kept in a vertical position in a water thermostat controlled to ±0.01 K. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The efflux time for water at 298.15 K was about 540 s. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \tag{1}$$

$$\eta = \nu\rho \tag{2}$$

where t is the efflux time, ρ is the density, and C and K are the characteristic constants of the viscometer. The values of the constants C and K, determined by using the density and viscosity values of water (Stokes and Mills, 1965) and benzene (Gill and Sekhri, 1982), were found to be 1.648×10^{-5} cm^2 s^{-2} and $-0.023\,316\,47$ cm^2, respectively. The estimated error of the viscosity measurements was ±0.2%.

In all cases the experiments were performed at least in five replicates for each composition and at each temperature, and the results were averaged.

Results

The experimental results of densities and viscosities at various mole fractions and at three temperatures are reported in Table 1.

The excess volumes have been calculated by the following equation:

$$V^E = V - (V_1x_1 + V_2x_2) \tag{3}$$

The deviation of the viscosity from the mole fraction average is calculated from

$$\Delta\eta = \eta - (\eta_1x_1 + \eta_2x_2) \tag{4}$$

x_1 and x_2 are the mole fractions of acetonitrile and methanol, respectively, V, V_1, and V_2 are the molar volumes, and η, η_1, and η_2 are the measured absolute viscosities of the mixture, acetonitrile, and methanol, respectively. The molar volume V is defined by the relationship

$$V = (M_1x_1 + M_2x_2)/\rho \tag{5}$$

where M_1 and M_2 are the molecular weights of pure

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Table 1. Expeimental Density (ρ), Absolute Viscosity (η), and Excess Molar Volume (V^E) for Acetonitrile (1) + Methanol (2) at 298.15, 308.15, and 318.15 K

x_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})
			298.15 K				
0.0000	0.786 54	0.545	0.000	0.5496	0.782 78	0.349	−0.132
0.0495	0.786 82	0.509	−0.047	0.5999	0.782 12	0.343	−0.121
0.0999	0.787 00	0.479	−0.089	0.6494	0.781 48	0.340	−0.110
0.1494	0.787 02	0.455	−0.123	0.6997	0.780 84	0.336	−0.099
0.1995	0.786 82	0.434	−0.145	0.7450	0.780 26	0.334	−0.088
0.2450	0.786 47	0.418	−0.156	0.7995	0.779 54	0.333	−0.072
0.2998	0.785 87	0.400	−0.157	0.8496	0.778 87	0.335	−0.055
0.3451	0.785 33	0.387	−0.156	0.8998	0.778 18	0.338	−0.037
0.3997	0.784 66	0.374	−0.151	0.9500	0.777 59	0.340	−0.024
0.4489	0.784 05	0.364	−0.146	1.0000	0.776 86	0.345	0.000
0.4950	0.783 47	0.357	−0.140				
			308.15 K				
0.0000	0.777 18	0.474	0.000	0.5496	0.772 89	0.320	−0.173
0.0495	0.777 50	0.451	−0.057	0.5999	0.772 11	0.314	−0.161
0.0999	0.777 53	0.436	−0.099	0.6494	0.771 33	0.310	−0.147
0.1494	0.777 59	0.412	−0.142	0.6997	0.770 39	0.307	−0.122
0.1995	0.777 49	0.395	−0.176	0.7450	0.769 83	0.305	−0.117
0.2450	0.777 16	0.380	−0.194	0.7995	0.768 98	0.305	−0.098
0.2998	0.776 55	0.364	−0.203	0.8496	0.768 18	0.306	−0.078
0.3451	0.775 94	0.352	−0.202	0.8998	0.767 35	0.307	−0.055
0.3997	0.775 16	0.341	−0.199	0.9500	0.766 50	0.309	−0.028
0.4489	0.774 44	0.333	−0.193	1.0000	0.765 64	0.313	0.000
0.4950	0.773 73	0.326	−0.185				
			318.15 K				
0.0000	0.767 74	0.419	0.000	0.5496	0.763 04	0.294	−0.200
0.0495	0.768 06	0.403	−0.062	0.5999	0.762 16	0.289	−0.185
0.0999	0.768 29	0.390	−0.121	0.6494	0.761 30	0.285	−0.169
0.1494	0.768 23	0.376	−0.163	0.6997	0.760 44	0.282	−0.153
0.1995	0.768 10	0.361	−0.201	0.7450	0.759 65	0.280	−0.136
0.2450	0.767 77	0.347	−0.223	0.7995	0.758 65	0.280	−0.110
0.2998	0.767 19	0.333	−0.239	0.8496	0.757 79	0.281	−0.089
0.3451	0.766 51	0.323	−0.238	0.8998	0.756 90	0.281	−0.064
0.3997	0.765 61	0.313	−0.232	0.9500	0.755 96	0.284	−0.034
0.4489	0.764 78	0.306	−0.224	1.0000	0.754 98	0.289	0.000
0.4950	0.763 99	0.300	−0.214				

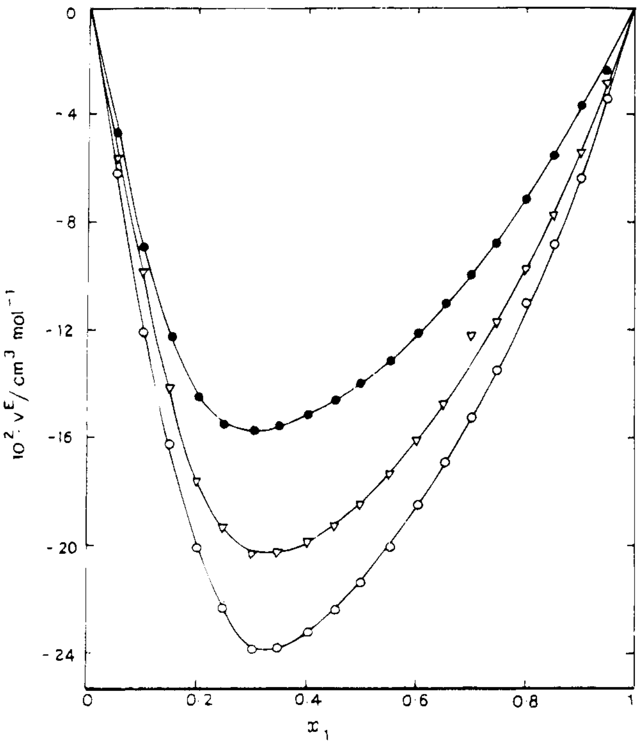

Figure 1. Variation of the excess molar volume for acetonitrile (1) + methanol (2) at 298.15 K (●), 308.15 K (△), and 318.15 K (○).

substances and ρ is the density of the mixture.

The excess molar volumes at 298.15, 308.15, and 318.15 K are presented in Table 1.

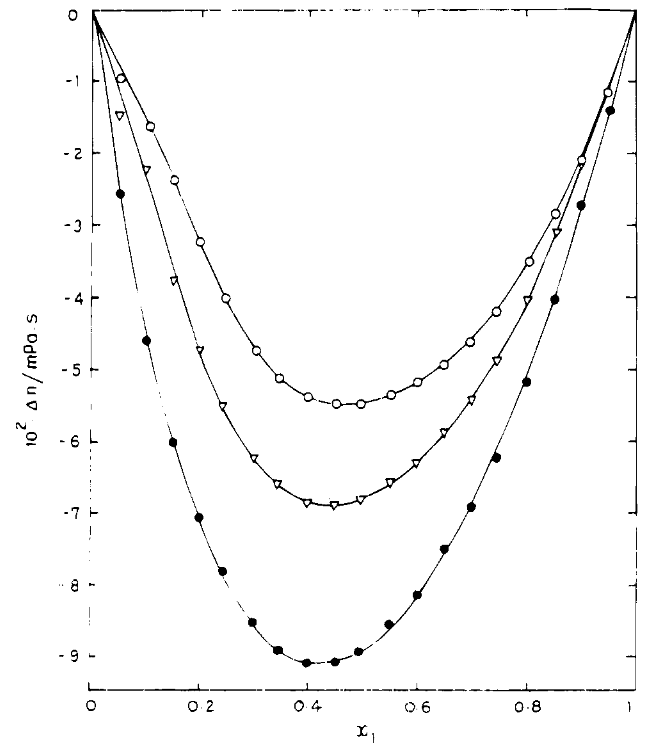

Figure 2. Variation of the viscosity deviation for acetonitrile (1) + methanol (2) at 298.15 K (●), 308.15 K (△), and 318.15 K (○).

Graphical representations of V^E and $\Delta\eta$ as functions of the mole fraction of acetonitrile are given in Figures 1 and 2, respectively.

Table 2. Coefficients of Eq 6 and the Standard Deviations

function	T/K	A_0	A_1	A_2	A_3	A_4	$\sigma(F)$
V^E/(cm^3· mol^{-1})	298.15	−0.5556	−0.4066	−0.3832	0.1209	0.1905	0.0036
	308.15	−0.7351	−0.4520	−0.3765	0.1612	0.2316	0.0034
	318.15	−0.8545	−0.5499	−0.4612	0.2559	0.3210	0.0021
$\Delta\eta$/(mPa·s)	298.15	−0.3573	−0.0851	−0.0451	−0.0607	−0.0574	0.0007
	308.15	−0.2769	−0.0468	0.0408	0.0298	−0.0445	0.0016
	318.15	−0.2253	−0.0017	0.0748	0.0354	−0.0865	0.0013

Each of these functions, $F = V^E$ and $\Delta\eta$, has been fitted to the Redlich−Kister relation (Redlich and Kister, 1948)

$$F = x_1(1 - x_1)\sum_{j=0}^{n} A_j(1 - 2x_1)^j \tag{6}$$

where A_0, A_1, A_2, ... are adjustable parameters and were evaluated by the method of least squares. The values of these parameters along with the standard deviation

$$\sigma(\mathrm{F}) = [\sum(F_{\mathrm{obsd}} - F_{\mathrm{calcd}})^2/(N - P)]^{1/2} \tag{7}$$

are recorded in Table 2. In eq 7, N is the total number of experimental points and P is the number of parameters.

Discussion

The V^E values are negative over the entire range of mole fractions and become more negative as the temperature increases. The minimum lies at a mole fraction of about 0.30 acetonitrile.

Methanol is known to be extensively self-associated through hydrogen-bonding in the pure state (Pikkarainen, 1988). In the case of acetonitrile, there is a lack of strong specific intermolecular forces, while dipole−dipole forces predominate (Moumouzias et al., 1991).

The negative V^E values for the mixtures containing acetonitrile and methanol appear to be caused by the breakdown of the hydrogen bonds in methanol and formation of specific complexes between the unlike molecules through hydrogen bonds. Infrared spectral studies (Mitra, 1962; Zhukova, 1958) also show the existence of hydrogen-bonding between acetonitrile and methanol in their mixtures which is in agreement with the present observation.

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