

CHAPTER V

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

Introduction

In recent years, there has been an increased interest¹⁻¹¹ 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 methanol + acetonitrile over the entire range of composition at 298.15, 308.15, and 318.15 K respectively. The experimental results of this study have been used to calculate the excess molar volumes (V^E), and the behaviour of the liquid mixtures has been interpreted on the basis of these results. This study will help interpret the behaviour of electrolytes in these mixed solvents.

Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with P_2O_5 and then redistilled with CaH_2 . The density, ρ_o , (0.77686 g.cm⁻³ at 298.15 K) and the viscosity, η_o , (0.345; 0.313, and 0.289 m Pa.s at 298.15, 308.15, and 318.15 K respectively) agree well with literature values:¹⁰ 0.776851 g.cm⁻³ and 0.344, 0.314, and 0.289 m Pa.s, respectively.

Methanol (E. Merck, India, uvasol grade, 99.5% pure) was dried over 3Å molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density, ρ_o , of 0.78654 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 respectively. These values are in good agreement with the literature values¹³ which are 0.78654 g.cm⁻³ and 0.542, 0.474, and 0.417 m Pa.s, 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 25cm^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, acetonitrile and methanol. The temperature of the bath was controlled to ± 0.01 K. The reproducibility of density measurements was $\pm 3 \times 10^{-5} \text{g.cm}^{-3}$.

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 :

$$\nu = C t - K / t \quad (1)$$

$$\eta = \nu \rho \quad (2)$$

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 water¹⁴ and benzene¹², were found to be $1.648 \times 10^{-5} \text{cm}^2 \text{s}^{-2}$ and -0.02331647cm^2 , respectively. The calibration constants were also checked with acetonitrile and methanol. The estimated error of the viscosity measurements was $\pm 0.2\%$.

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 :

$$V^E = V - (V_1x_1 + V_2x_2) \quad (3)$$

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

$$\Delta\eta = \eta - (\eta_1x_1 + \eta_2x_2) \quad (4)$$

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

$$V = (M_1x_1 + M_2x_2) / \rho \quad (5)$$

where M_1 and M_2 are the molecular weights of pure 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.

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

Each of these functions, $F = V^E$ and $\Delta\eta$, has been fitted to the Redlich-Kister relation¹⁵

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

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

$$\sigma(F) = \left[\sum (F_{\text{obsd}} - F_{\text{calcd}})^2 / (N - P) \right]^{1/2} \quad (7)$$

are recorded in Table 2. In equation (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 of acetonitrile.

Methanol is known to be extensively self-associated through hydrogen-bonding in the pure state¹⁶. In the case of acetonitrile, there is a lack of strong specific intermolecular forces, while dipole-dipole forces predominate¹⁰.

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^{17,18} also show the existence of hydrogen-bonding between acetonitrile and methanol in their mixtures which is in agreement with the present observation.

References

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

x_2	$\rho / (\text{g}\cdot\text{cm}^{-3})$	$\eta / (\text{mPa}\cdot\text{s})$	$V^E / (\text{cm}^3\cdot\text{mol}^{-1})$
T = 298.15 K			
0.0000	0.786 54	0.545	0.000
0.0495	0.786 82	0.509	-0.047
0.0999	0.787 00	0.479	-0.089
0.1494	0.787 02	0.455	-0.123
0.1995	0.786 82	0.434	-0.145
0.2450	0.786 47	0.418	-0.156
0.2998	0.785 87	0.400	-0.157
0.3451	0.785 33	0.387	-0.156
0.3997	0.784 66	0.374	-0.151
0.4489	0.784 05	0.364	-0.146
0.4950	0.783 47	0.357	-0.140
0.5496	0.782 78	0.349	-0.132
0.5999	0.782 12	0.343	-0.121
0.6494	0.781 48	0.340	-0.110
0.6997	0.780 84	0.336	-0.099
0.7450	0.780 26	0.334	-0.088
0.7995	0.779 54	0.333	-0.072
0.8496	0.778 87	0.335	-0.055
0.8998	0.778 18	0.338	-0.037
0.9500	0.777 59	0.340	-0.024
1.0000	0.776 86	0.345	-0.000

T = 308.15 K

0.0000	0.777 18	0.474	0.000
0.0495	0.777 50	0.451	-0.057
0.0999	0.777 53	0.436	-0.099
0.1494	0.777 59	0.412	-0.142
0.1995	0.777 49	0.395	-0.176
0.2450	0.777 16	0.380	-0.194
0.2998	0.776 55	0.364	-0.203
0.3451	0.775 94	0.352	-0.202
0.3997	0.775 16	0.341	-0.199
0.4489	0.774 44	0.333	-0.193
0.4950	0.773 73	0.326	-0.185
0.5496	0.772 89	0.320	-0.173
0.5999	0.772 11	0.314	-0.161
0.6494	0.771 33	0.310	-0.147
0.6997	0.770 39	0.307	-0.122
0.7450	0.769 83	0.305	-0.117
0.7995	0.768 98	0.305	-0.098
0.8496	0.768 18	0.306	-0.078
0.8998	0.767 35	0.307	-0.055
0.9500	0.766 50	0.309	-0.028
1.0000	0.765 64	0.313	0.000

T = 318.15 K

0.0000	0.767 74	0.419	0.000
0.0495	0.768 06	0.403	-0.062
0.0999	0.768 29	0.390	-0.121
0.1494	0.768 23	0.376	-0.163
0.1995	0.768 10	0.361	-0.201
0.2450	0.767 77	0.347	-0.223
0.2998	0.767 19	0.333	-0.239
0.3451	0.766 51	0.323	-0.238
0.3997	0.765 61	0.313	-0.232
0.4489	0.764 78	0.306	-0.224
0.4950	0.763 99	0.300	-0.214
0.5496	0.763 04	0.294	-0.200
0.5999	0.762 16	0.289	-0.185
0.6494	0.761 30	0.285	-0.169
0.6997	0.760 44	0.282	-0.153
0.7450	0.759 65	0.280	-0.136
0.7995	0.758 65	0.280	-0.110
0.8496	0.757 79	0.281	-0.089
0.8998	0.756 90	0.281	-0.064
0.9500	0.755 96	0.284	-0.034
1.0000	0.754 98	0.289	0.000

Table 2. Coefficients of Equation (6) and the Standard Deviations

Function	T / K	A ₀	A ₁	A ₂	A ₃	A ₄	σ (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
Δη / (m.Pa.s)	318.15	-0.8545	-0.5499	-0.4612	0.2559	0.3210	0.0021
	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

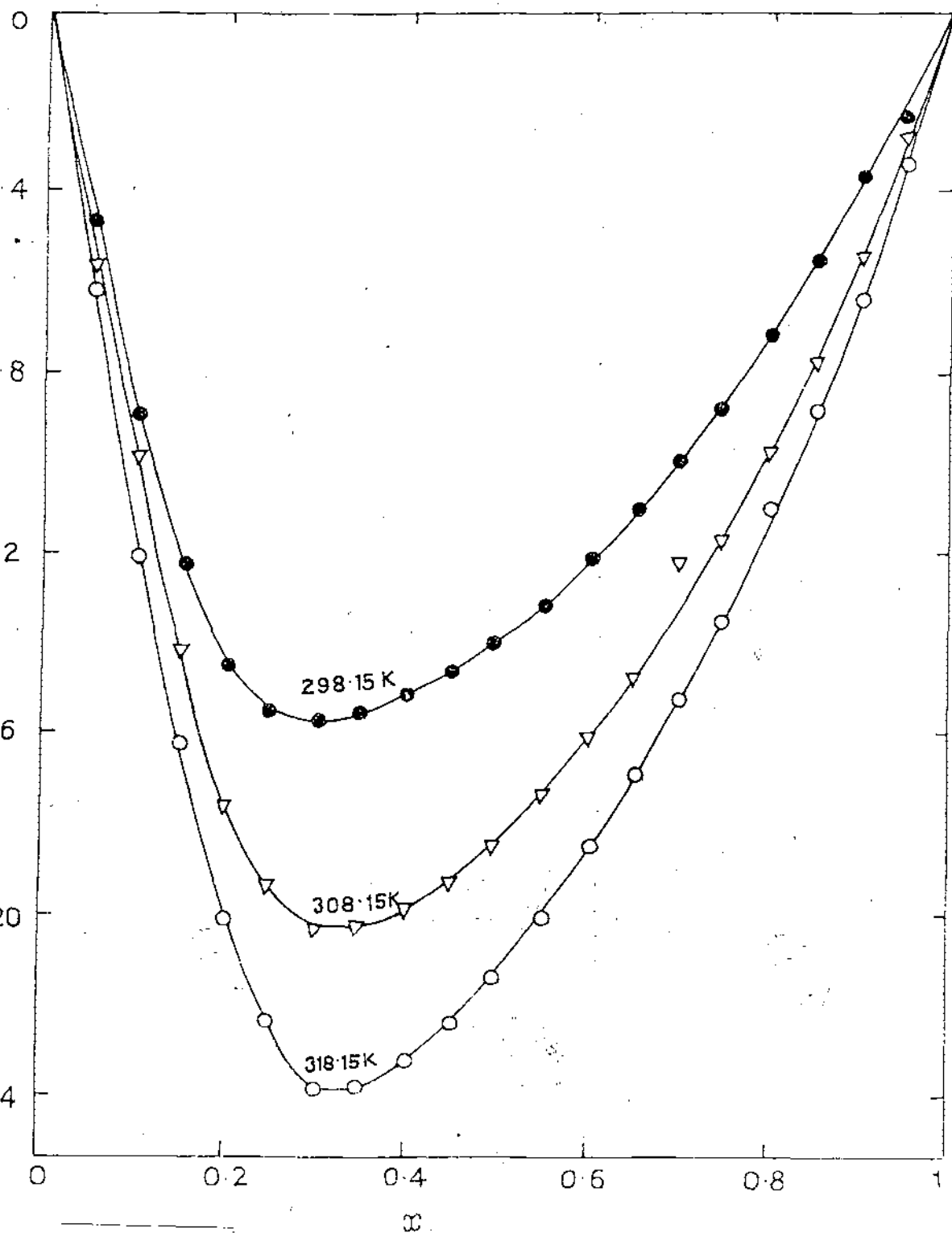


Figure 1. Excess molar volumes for methanol+acetonitrile mixtures at 298.15, 308.15 and 318.15 K.

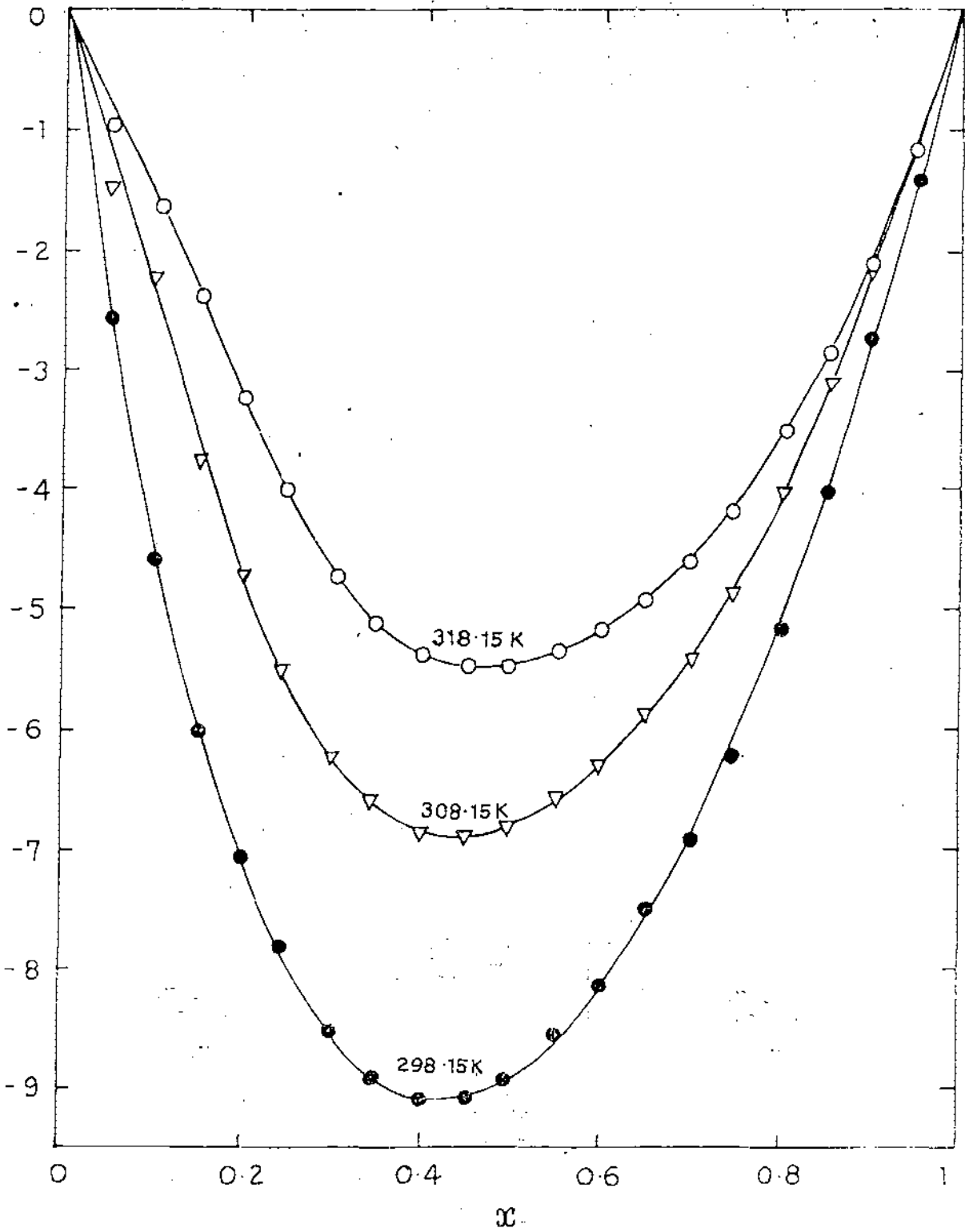


Figure 2. Viscosity deviations for methanol + acetonitrile mixtures at 298.15, 308.15 and 318.15 K.