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Viscosities and Excess Molar Volumes for 2-Methoxy-1-ethanol + Water at Different Temperatures

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Excess molar volumes (V^E) and viscosities (η) have been measured for 2-methoxy-1-ethanol + water at 25, 35, and 45 °C. The values of V^E have been found to be negative over the entire range of compositions, and the viscosity versus mole fraction curves show maxima at aboutt 0.3 mole fraction 2-methoxy-1-ethanol. The results indicate the predominance of hydrogen-bonding interactions between these two unlike molecules.

Introduction

Recently, there has been an increased interest (*1-6*) in the thermodynamic and transport properties of binary liquid mixtures. These have been extensively used to obtain information as to the intermolecular interactions and geometrical effects in these systems. We have presented here some of the properties of 2-methoxy-1-ethanol + water mixtures at different temperatures. Although 2-methoxy-1-ethanol finds a wide range of applications (*7*), namely, as a solvent and solubilizing agent in many industries, there are relatively few studies of its aqueous solutions (*2, 7*). In the present study, the excess molar volumes (V^E) and viscosities (η) have been determined over the entire composition range and at three temperatures. Attempts have been made to explain the behavior of the liquid mixtures from these properties.

Experimental Section

The purification of 2-methoxy-1-ethanol (GRE Merck, >99.5% purity) has been described earlier (*8*). All solutions were prepared by mass with deionized distilled water (specific conductance $<1 \times 10^{-6}$ S cm^{-1}).

The densities were measured with an Ostwald-Sprengal-type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 35, and 45 °C with doubly distilled water. The temperature of the bath was controlled to ±0.01 °C. The reproducibility of density measurements was $\pm 3 \times 10^{-5}$ g cm^{-3}.

The kinematic viscosities were measured by means of a suspended Ubbelohde viscometer. The time of efflux was measured with a stopwatch capable of recording ±0.1 s. The viscometer was always kept in a vertical position in a water thermostat controlled to ±0.01 °C. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge (accuracy ±0.005 °C). The efflux time for water at 25 °C was about 500 s. The viscometer needed no correction for kinetic energy. 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 (*9*) and benzene (*10*), were found to be 1.648×10^{-5} cm^2 s^{-2} and $-0.023\,316\,47$ cm^2, respectively. The accuracy of the viscosity measurements was ±0.05%.

Table I. Experimental Density (ρ) and Absolute Viscosity (η) for 2-Methoxy-1-ethanol (1) + Water (2) at 25, 35, and 45 °C

x_1	ρ/(g cm^{-3})	η/(mPa s)	x_1	ρ/(g cm^{-3})	η/(mPa s)
		25 °C			
0.0000	0.997 07	0.890	0.5001	0.985 77	2.616
0.0834	1.004 76	1.894	0.5219	0.984 29	2.571
0.1366	1.007 05	2.365	0.6161	0.978 34	2.367
0.1500	1.007 52	2.442	0.6806	0.974 55	2.232
0.2131	1.005 32	2.768	0.7514	0.970 70	2.076
0.2601	1.003 01	2.876	0.8181	0.967 49	1.930
0.3005	1.000 12	2.904	0.8844	0.964 50	1.786
0.3558	0.99597	2.886	1.000	0.960 02	1.541
0.4352	0.990 28	2.751			
		35 °C			
0.0000	0.994 06	0.722	0.5001	0.977 13	2.001
0.0623	0.997 84	1.242	0.5219	0.975 92	1.960
0.1500	1.000 10	1.803	0.6161	0.970 53	1.818
0.2131	0.997 49	2.067	0.6806	0.967 32	1.726
0.2601	0.994 87	2.149	0.7514	0.963 94	1.624
0.3005	0.991 89	2.164	0.8181	0.960 97	1.526
0.3558	0.987 44	2.150	0.8844	0.958 22	1.443
0.4352	0.981 44	2.077	1.0000	0.953 56	1.258
		45 °C			
0.0000	0.990 17	0.598	0.5001	0.968 70	1.615
0.0251	0.991 30	0.737	0.5219	0.967 21	1.602
0.0623	0.992 87	0.950	0.6161	0.961 77	1.513
0.1500	0.993 16	1.325	0.6806	0.958 54	1.444
0.2131	0.989 88	1.505	0.7514	0.955 40	1.360
0.2601	0.986 69	1.585	0.8181	0.952 83	1.281
0.3005	0.983 63	1.626	0.8844	0.950 60	1.191
0.3558	0.979 14	1.655	1.0000	0.947 15	1.040
0.4352	0.973 05	1.653			

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 I.

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

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

where x_1 and x_2 are the mole fractions of 2-methoxy-1-ethanol and water, respectively; V, V_1, and V_2 are the molar volumes

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Table II. Excess Molar Volumes (V^E) and Viscosity Deviations ($\delta\eta$) for 2-Methoxy-1-ethanol (1) + Water (2) at 25, 35, and 45 °C

x_1	V^E/cm^3 mol^{-1}	$\delta\eta$/mPa s	x_1	V^E/cm^3 mol^{-1}	$\delta\eta$/mPa s
		25 °C			
0.0000	0.000	0.000	0.5001	−0.932	1.400
0.0834	−0.421	0.950	0.5219	−0.908	1.341
0.1366	−0.660	1.386	0.6161	−0.782	1.076
0.1500	−0.720	1.454	0.6806	−0.671	0.898
0.2131	−0.878	1.739	0.7514	−0.533	0.696
0.2601	−0.964	1.816	0.8181	−0.400	0.507
0.3005	−0.994	1.818	0.8844	−0.255	0.320
0.3558	−1.005	1.764	1.0000	0.000	0.000
0.4352	−0.984	1.576			
		35 °C			
0.0000	0.000	0.000	0.5001	−0.806	1.011
0.0623	−0.285	0.486	0.5219	−0.793	0.958
0.1500	−0.650	1.000	0.6161	−0.691	0.765
0.2131	−0.798	1.230	0.6806	−0.613	0.639
0.2601	−0.873	1.287	0.7514	−0.505	0.500
0.3005	−0.899	1.281	0.8181	−0.390	0.365
0.3558	−0.896	1.237	0.8844	−0.265	0.247
0.4352	−0.855	1.121	1.0000	0.000	0.000
		45 °C			
0.0000	0.000	0.000	0.5001	−0.692	0.795
0.0251	−0.110	0.127	0.5219	−0.663	0.774
0.0623	−0.277	0.324	0.6161	−0.546	0.643
0.1500	−0.605	0.661	0.6806	−0.458	0.545
0.2131	−0.735	0.813	0.7514	−0.357	0.430
0.2601	−0.790	0.872	0.8181	−0.262	0.322
0.3005	−0.811	0.895	0.8844	−0.170	0.202
0.3558	−0.802	0.900	1.0000	0.000	0.000
0.4352	−0.750	0.863			

and η, η_1, and η_2 are the measured absolute viscosities of the mixture, 2-methoxy-1-ethanol, and water, 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 substances and ρ is the density of the mixture.

The excess volume and the viscosity deviation at 25, 35, and 45 °C are presented in Table II.

Graphical representations of V^E and η as functions of the mole fraction of 2-methoxy-1-ethanol are given in Figures 1 and 2, respectively.

The properties V^E and $\delta\eta$ were fitted, respectively, to the following equations (*11*):

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x_1(1 - x_1)\sum_{j=0}^{n} A_j(1 - 2x_1)^j \tag{6}$$

and

$$\delta\eta/(\text{mPa s}) = x_1(1 - x_1)\sum_{j=0}^{n} B_j(1 - 2x_1)^j \tag{7}$$

where $A_0, A_1, A_2, ...$ and $B_0, B_1, B_2, ...$ are adjustable parameters and were evaluated by the method of least squares. The values of these parameters along with the standard deviation

$$\sigma(X) = [\sum(X_{\text{obsd}} - X_{\text{calcd}})^2/(N - M)]^{1/2} \tag{8}$$

are recorded in Table III. In eq 8, N is the total number of experimental points and M is the number of parameters.

The Kirkwood correlation factor (g_k) for pure 2-methoxy-1-ethanol was calculated from the following expression (*12*, *13*):

$$g_k = \frac{9kT}{4\pi N_0\mu_0^2}\frac{M}{\rho_0}\frac{(\epsilon_0 - \epsilon_\alpha)(2\epsilon_0 + \epsilon_\alpha)}{\epsilon_0(\epsilon_\alpha + 2)^2} \tag{9}$$

where the terms have their usual significance. The value of ϵ_α was set equal to $1.1n^2$ where n is the refractive index of the substance. The values for the refractive indices of 2-methoxy-1-ethanol at 25, 35, and 45 °C were taken from the literature (*14*).

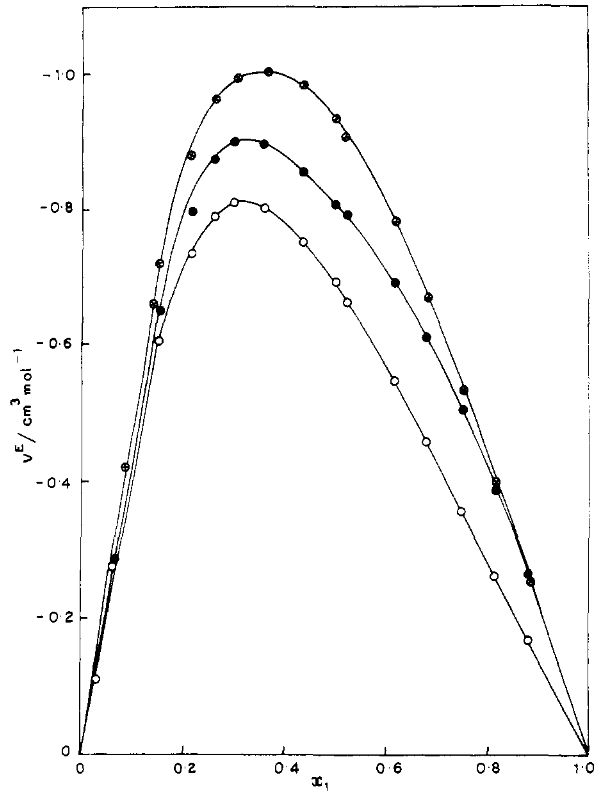

Figure 1. Variation of the excess molar volume for 2-methoxy-1-ethanol (1) + water (2) at 25 °C (⊗), 35 °C (●), and 45 °C (○).

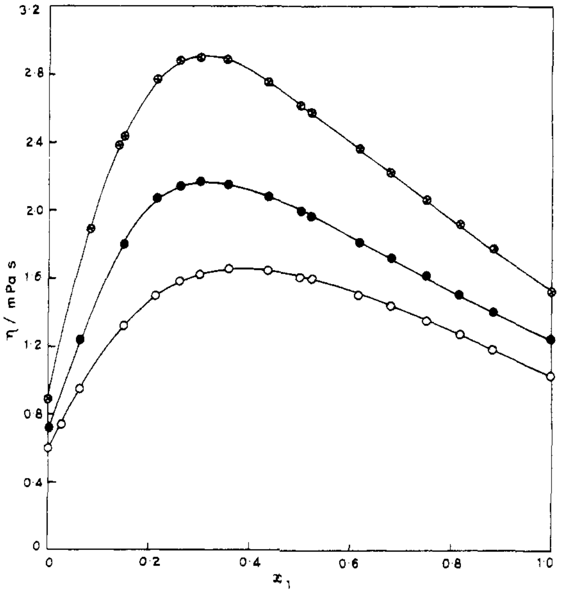

Figure 2. Variation of viscosity for 2-methoxy-1-ethanol (1) + water (2) at 25 °C (⊗), 35 °C (●), and 45 °C (○).

Discussion

From Figure 1 we see that the V^E values are negative over the entire range of mole fractions and become less negative as the temperature increases. The minimum lies at a mole fraction of about 0.3 2-methoxy-1-ethanol. Several effects may contribute to the value of V^E, and three different effects may be considered as being important: (a) breakup of

Table III. Coefficients of Equations 6 and 7 and the Standard Deviations

property	t/°C	A_0	A_1	A_2	A_3	A_4	$\sigma(V^E)$/(cm^3 mol^{-1})
V^E	25	−3.6919	−2.2503	−1.6736	0.3688	1.8862	0.011
	35	−3.2129	−2.0215	−2.4469	0.6917	2.5024	0.010
	45	−2.7231	−2.4157	−1.9182	0.6831	1.9718	0.009
property	t/°C	B_0	B_1	B_2	B_3	B_4	$\sigma(\delta\eta)$/(mPa s)
$\delta\eta$	25	5.6013	5.9122	5.2017	−0.1987	−3.2311	0.008
	35	3.9784	4.3256	3.7737	−0.9943	−2.7967	0.015
	45	3.1499	2.3658	1.8116	−0.3356	−1.7357	0.008

hydrogen bonds and dipolar interactions in 2-methoxy-1-ethanol and intermolecular hydrogen-bonded interactions in water, (b) interstitial accommodation of one component into the other, and (c) the possible hydrogen-bond interactions between unlike molecules. Let us now consider each of these effects separately.

IR studies indicate that intramolecular hydrogen bonding exists in 2-methoxy-1-ethanol molecules in the liquid state (*15*, *16*). Moreover, the values of the Kirkwood correlation factors, g_k, for pure 2-methoxy-1-ethanol in the temperature range studied are not much greater than unity (the g_k values of 2-methoxy-1-ethanol are 1.483, 1.478, and 1.463 at 25, 35, and 45 °C, respectively). This indicates that 2-methoxy-1-ethanol is a relatively unstructured liquid and that there are strong but not specific dipole–dipole forces.

In the mixtures containing 2-methoxy-1-ethanol and water, one of the effects which may contribute to V^E is the disruption of (i) the intramolecular hydrogen bonds and intermolecular dipolar interactions in 2-methoxy-1-ethanol and (ii) the hydrogen bonds present in self-associated water molecules.

Secondly, the effect which gives a negative contribution to V^E is the difference in molecular sizes between the two components. The molar volumes of 2-methoxy-1-ethanol and water at 25 °C are 79.27 and 18.07 cm^3 mol^{-1}, respectively, which might allow the components to fit into each others' structures, so that a reduction in volume occurs.

A third effect whose contribution to V^E is also expected to be negative is the existence of hydrogen-bond interactions between unlike molecules.

The actual value of V^E would depend upon the balance between the two opposing contributions. The experimental values indicate that the negative contributions predominate in this mixture.

Figure 2 shows that the viscosity η passes through a maximum at a mole fraction of 0.3 2-methoxy-1-ethanol which also gives an indication of the presence of specific interaction between 2-methoxy-1-ethanol and water molecules (*17*, *18*).

Thus, in the present study the negative V^E values for 2-methoxy-1-ethanol + water indicate the predominance of hydrogen-bonding interactions between them over the other effects. The specific interaction between these unlike molecules has further been manifested by the maxima in the viscosity versus composition curves.

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