Excess Molar Volumes and Viscosities for Glycol Ether−Water Solutions at the Temperature 308.15 K: Ethylene Glycol Monomethyl, Diethylene Glycol Monomethyl, and Triethylene Glycol Monomethyl Ethers

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Excess molar volumes (V_m^E) and viscosities (η) have been determined as a function of mole fraction for binary liquid mixtures of water with ethylene glycol monomethyl ether (2-methoxyethanol), $CH_3O(CH_2)_2OH$, diethylene glycol monomethyl ether (2-(2-methoxyethoxy)ethanol), $CH_3O(CH_2)_2O(CH_2)_2OH$, and triethylene glycol monomethyl ether (2-[2-(2-methoxyethoxy)ethoxy]ethanol), $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$, at 308.15 K. Densities (ρ) of the mixtures have been calculated from the results. The excess volumes are negative over the entire composition range for the systems studied. The results for V_m^E and η are discussed in terms of interactions of water with an amphiphilic molecule.

Introduction

In recent years much effort has been made with the measurement, analysis, and interpretation of the excess thermodynamic properties of the aqueous mixtures of nonionic amphiphiles, mainly the alkyl poly(ethylene glycol) monoethers (Pal and Singh, 1994; Pal and Singh, 1995b; Pal et al., 1994a; Douhéret et al., 1990), which has the generic formula $C_mH_{2m+1}(OCH_2CH_2)_nOH$. Excess thermodynamic properties, which depend on the composition, temperature, and pressure of the system, are of great importance in helping to understand the nature and extent of the patterns of molecular aggregation that exist in a (water + an amphiphile) mixture (Douhéret and Pal, 1988; Douhéret et al., 1989), resulting from intermolecular interactions. In fact, the interaction between the molecules can be established from a study of the characteristics abrupt departure from ideal behavior of some physical properties such as volume, viscosity, dielectric constant, refractive index, and related properties that reflects the real behavior of the solutes in such solvents. A knowledge of these properties is very important in many practical problems concerning heat transport, mass transport, and fluid flow. A search in the literature indicated the absence of any thermodynamic and spectroscopic data for these mixtures, and hence the investigation has been made.

Our previous studies focused upon aqueous solutions of homologous series of poly(ethylene glycol) monoethers. A particularly interesting family of this homologous series is that of the 2-alkoxyethanols and 2-(2-alkoxyethoxy)ethanols for which different measurements like ultrasonic speeds, dielectric constants, and densities of the aqueous mixtures of these systems have been made and reported in the literature (Pal and Singh, 1994; Douhéret et al., 1990; Douhéret and Pal, 1988; Douhéret et al., 1989).

The present work concerns the study of the changes arising from the variation of the polar head group(s) for species with the same alkyl tail. We report here the excess molar volumes (V_m^E) and viscosities (η) for binary mixtures of H_2O (1) + $CH_3O(CH_2)_2OH$ (2), H_2O (1) + $CH_3O(CH_2)_2O(CH_2)_2OH$ (2), and H_2O (1) + $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) at 308.15 K.

Experimental Section

Materials. 2-Methoxyethanol (AR grade, 99.5 mol %) was purified by the standard methods (Riddick et al., 1986). The purity of the final sample was checked by density determination at 298.15 K. The density of the purified sample of 2-methoxyethanol at 298.15 K was found to be 0.9602 g·cm^{-3}, in good agreement with literature values (Douhéret et al., 1990; Riddick et al., 1986). 2-(2-Methoxyethoxy)ethanol (E. Merck, FRG, 98 mol %) and 2-[2-(2-methoxyethoxy)ethoxy]ethanol (Aldrich, 95 mol %) were the same as used in earlier studies (Pal and Singh, 1994; Pal and Singh, 1995b). Densities of 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, and 2-[2-(2-methoxyethoxy)ethoxy]ethanol at 308.15 K were 0.9515 [lit: 0.9529, Reddy et al., 1994], 1.0092, and 1.0343 g·cm^{-3}. Prior to the measurements, all liquids were partially degassed and stored over 0.4 nm molecular sieves to reduce the water content. Water was deionized and distilled in glass. Its conductivity was always less than 1.0×10^{-6} Ω^{-1}·cm^{-1}.

Apparatus and Procedure. Excess volumes were measured using a continuous-dilution dilatometer as described by Dickinson et al. (1975). Before the measurements were begun, the dilatometer was tested with 1,2-ethanediol + water at the working temperature. The operational procedures and the experimental setup have been described previously (Pal and Singh, 1994; Pal et al., 1994b; Pal and Singh, 1995a). The excess molar volumes are reproducible to ±0.003 cm^3·mol^{-1}. A thermostatically controlled, well-stirred water bath whose temperature was controlled to ±0.01 K was used for all the measurements. The composition of each mixture was obtained from the mass of the components, with a precision of ±0.05 mg. Corrections were made for buoyancy. The mole fraction error is estimated to be less than 2×10^{-4}. Each run covered just over half of the mole-fraction range so as to give an overlap between the two runs.

Viscosities of the pure components and the mixtures were determined at 308.15 K with a calibrated Ubbelohde suspended level viscometer. The viscometers were calibrated by using high-purity benzene, toluene, and carbon tetrachloride at the working temperature. The flow-time measurements were made with an electronic stopwatch having a precision of ±0.01 s. Viscosities are reproducible

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Table 1. Excess Molar Volumes, V_m^E, of Glycol Ether + Water Mixtures at 308.15 K

x_2	$V_m^E/cm^3 \cdot mol^{-1}$	x_2	$V_m^E/cm^3 \cdot mol^{-1}$	x_2	$V_m^E/cm^3 \cdot mol^{-1}$	x_2	$V_m^E/cm^3 \cdot mol^{-1}$
			H_2O (1) + $CH_3O(CH_2)_2OH$ (2)				
0.0107	−0.062	0.2293	−0.863	0.4905	−0.954	0.7901	−0.473
0.0298	−0.167	0.2578	−0.905	0.5311	−0.906	0.8168	−0.391
0.0588	−0.319	0.2980	−0.967	0.5529	−0.889	0.8721	−0.281
0.0815	−0.417	0.3305	−0.988	0.6054	−0.819	0.9055	−0.221
0.0922	−0.475	0.3500	−0.997	0.6256	−0.790	0.9508	−0.123
0.1417	−0.643	0.3979	−1.008	0.6724	−0.701	0.9797	−0.046
0.1689	−0.729	0.4257	−0.990	0.7121	−0.631		
0.2053	−0.816	0.4644	−0.975	0.7651	−0.514		
			H_2O (1) + $CH_3O(CH_2)_2O(CH_2)_2OH$ (2)				
0.0148	−0.087	0.2406	−0.983	0.4906	−0.859	0.7647	−0.365
0.0322	−0.200	0.3324	−1.001	0.5513	−0.779	0.8096	−0.291
0.0580	−0.376	0.3632	−0.986	0.5869	−0.709	0.9042	−0.140
0.0994	−0.614	0.3981	−0.971	0.6110	−0.675		
0.1401	−0.782	0.4358	−0.931	0.6812	−0.539		
0.1854	−0.900	0.4789	−0.877	0.7167	−0.459		
			H_2O (1) + $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)				
0.0133	−0.131	0.1889	−1.079	0.3780	−1.113	0.6444	−0.690
0.0319	−0.281	0.2133	−1.125	0.4151	−1.060	0.6610	−0.662
0.0514	−0.442	0.2371	−1.145	0.4358	−1.039	0.6974	−0.609
0.0724	−0.610	0.2534	−1.149	0.4780	−0.989	0.7341	−0.532
0.0966	−0.758	0.2746	−1.154	0.4917	−0.960	0.7801	−0.438
0.1157	−0.855	0.2960	−1.156	0.5245	−0.908	0.8461	−0.309
0.1296	−0.913	0.3257	−1.141	0.5542	−0.851	0.9026	−0.194
0.1484	−0.984	0.3394	−1.137	0.5751	−0.822	0.9350	−0.115
0.1738	−1.051	0.3532	−1.119	0.6229	−0.729	0.9553	−0.088

Table 2. Experimental Viscosities, η, for Glycol Ether + Water Mixtures at 308.15 K

x_2	η/mPa·s	x_2	η/mPa·s	x_2	η/mPa·s
		H_2O (1) + $CH_3O(CH_2)_2OH$ (2)			
0.0000	0.71903	0.3260	2.342	0.6928	1.787
0.0461	1.143	0.3709	2.319	0.7288	1.724
0.0881	1.520	0.4014	2.284	0.7680	1.658
0.1239	1.829	0.4504	2.217	0.9214	1.423
0.1871	2.124	0.4974	2.140	1.0000	1.326
0.2442	2.284	0.5691	2.010		
0.2938	2.341	0.6414	1.878		
		H_2O (1) + $CH_3O(CH_2)_2O(CH_2)_2OH$ (2)			
0.0000	0.71903	0.1286	2.872	0.7694	3.235
0.0130	0.914	0.1865	3.333	0.9087	2.996
0.0426	1.445	0.3088	3.876	0.9891	2.874
0.0580	1.730	0.4518	3.836	1.0000	2.865
0.0793	2.131	0.5434	3.625		
0.0999	2.476	0.6518	3.448		
		H_2O (1) + $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)			
0.0000	0.71903	0.3020	6.380	0.6208	5.830
0.0226	1.317	0.3364	6.428	0.6681	5.716
0.0554	2.514	0.3687	6.422	0.6996	5.651
0.0964	3.669	0.3952	6.376	0.7750	5.463
0.1278	4.537	0.4200	6.331	0.8279	5.355
0.1726	5.437	0.4712	6.215	0.8744	5.266
0.2157	5.977	0.5057	6.123	0.9499	5.134
0.2434	6.176	0.5471	6.022	1.0000	5.055

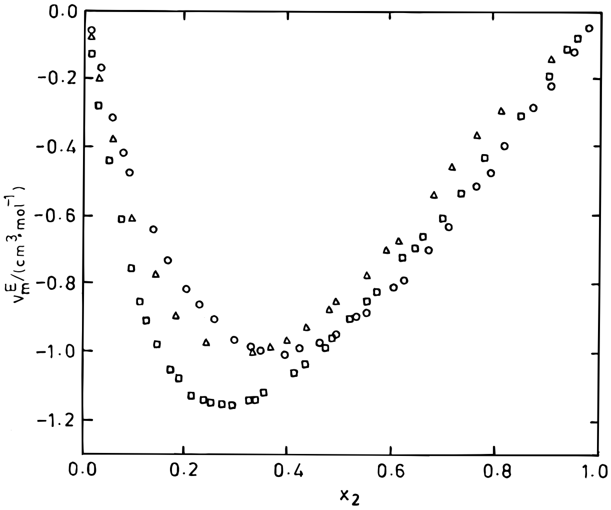

Figure 1. Mole fraction of glycol ether versus excess volumes for H_2O (1) + $CH_3O(CH_2)_2OH$ (2) (○), + $CH_3O(CH_2)_2O(CH_2)_2OH$ (2) (△), and +$CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) (□) at 308.15 K.

to ±0.003 mPa·s. Densities of the pure components were measured with a double-armed pycnometer having a total volume of approximately 15 cm^3. The reproducibility of the density was found to be 3 × 10^{-4} $g \cdot cm^{-3}$. The density and viscosity of water at 308.15 K were taken from the literature (Riddick et al., 1986; Kell, 1967).

Results and Discussion

The excess volumes and viscosities for water + 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, and 2-[2-(2-methoxyethoxy)ethoxy]ethanol at 308.15 K at various mole fractions are reported in Tables 1 and 2. The plots of excess molar volume (V_m^E) against the mole fraction of the glycol ether are given in Figure 1.

Densities of liquid mixtures were computed from the excess volume and composition according to the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V_m^E + x_1 v_1 + x_2 v_2} \tag{1}$$

where x_1 and x_2 are the mole fraction, M_1 and M_2 represent molecular masses, and v_1 and v_2 are the molar volumes of water (1) and alkoxyethanols (2), respectively.

The plots of viscosity (η) against the mole fraction of the glycol ether are given in Figure 2.

The excess volume was fitted to the Redlich and Kister (1948) relation

$$V_m^E/cm^3 \cdot mol^{-1} = x_1 x_2 \sum_{j=1}^{n} a_{j-1}(x_2 - x_1)^{j-1} \tag{2}$$

where a_{j-1}'s are adjustable parameters and were evaluated by the method of least squares. The values of the parameters along with the standard deviations $s(V_m^E)$

$$s(V_m^E) = [\sum (V_{m,exptl}^E - V_{m,calcd}^E)^2/(n-p)]^{1/2} \tag{3}$$

Table 3. Values of the Parameters of Eq 2 and the Standard Deviation at 308.15 K

	a_0	a_1	a_2	a_3	a_4	a_5	$s(V_m^E)/cm^3 \cdot mol^{-1}$
H_2O (1)							
+$CH_3O(CH_2)_2OH$ (2)	−3.7933	1.8092	−0.2121	0.4286	−0.2420	−0.5116	0.007
+$CH_3O(CH_2)_2O(CH_2)_2OH$ (2)	−3.3951	2.6514	−1.3120	3.1851	0.1052	−3.7400	0.009
+$CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	−3.7670	3.0317	−2.6010	2.1936	0.1833	−1.0968	0.009

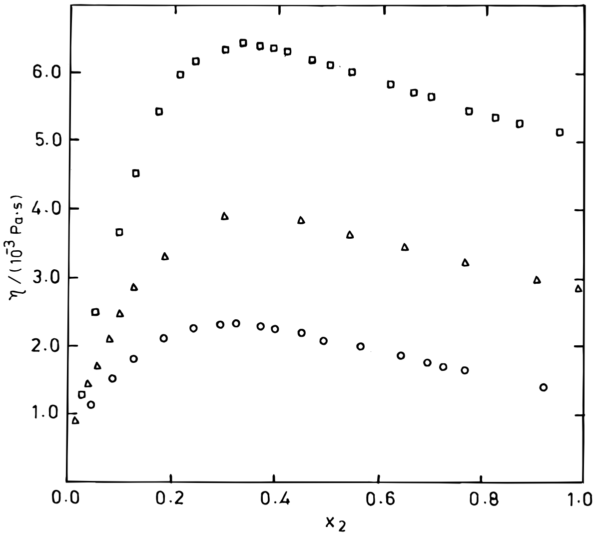

Figure 2. Mole fraction of glycol ether versus viscosities for H_2O (1) + $CH_3O(CH_2)_2OH$ (2) (○) + $CH_3O(CH_2)_2O(CH_2)_2OH$ (2) (△), and + $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) (□) at 305.15 K.

where n is the total number of experimental points and p is the number of adjustable parameters are recorded in Table 3.

The V_m^E values for water (1) + 2-methoxyethanol (2) reported by Reddy et al. (1994) at 308.15 K are uniformly more negative than ours at mole fraction $x_2 > 0.5$ but agree with our V_m^E values at a lower mole fraction range. Our viscosity values for each set of mixture composition exhibit a pleasing level of internal consistency. There are systematic differences between the viscosity values for the water + 2-methoxyethanol obtained in this laboratory and those reported by Reddy et al. (1994) obtained using an Ostwald viscometer. The maximum value of η lower than ours at $x_2 = 0.3$ is 0.3 mPa·s.

Excess molar volumes (V_m^E) are negative for all the systems studied at 308.15 K. Figures 1 and 2 show that there is a sharp change in V_m^E and η in the water-rich region. The negative V_m^E and rather large values of η over the entire range of mole fraction may be attributed mainly to the association through intermolecular hydrogen bonding between the water and the ether molecules. The addition of alkoxyethanol molecules gives rise to a slight enhancement of the three-dimensional water lattice in the water-rich region, followed by a progressive destructuring; the ether functions do not seem to play a prominent role (Kusano et al., 1973; Harada, et al., 1978), since the possibility of intramolecular hydrogen bond formation between alkoxyethanol molecules may be negligible in such high concentrations of water. The presence of the etheric oxygen enhances the ability of the −OH group of the alkoxyethanols (Buckley and Brochu, 1972) to form hydrogen bonds with the water molecules which results in a contraction in volume. The order of strength of the hydrogen bonding owing to increased molecular weight and size is as follows: triethylene glycol monomethyl ether > diethylene glycol monomethyl ether > ethylene glycol monomethyl ether. The sharp changes in V_m^E and η at low mole fractions of amphiphile would imply more order and hence more structure or clustering in an aqueous environment. This leads to substantial increases in the viscosities of the amphiphile + water mixtures and a corresponding decrease in their excess molar volumes. Equally evident is the fact that considering the differences of the molar volumes of the components, such clustering might also arise from interstitial accommodation of amphiphile molecules occupying a void space in a more structured water lattice, thereby giving rise to a marked changes in their V_m^E and η values at the water-rich region.

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