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Dielectric Constants and Densities of Aqueous Mixtures of 2-Alkoxyethanols at 25 °C

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Densities and dielectric constants are reported for the four binary systems water + 1,2-ethanediol, + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol, over the whole composition range, at 25 °C. The dielectric molar susceptibilities and the molar orientational polarizabilities were calculated. The plots of dielectric properties vs composition emphasize the prominent role of the lengthening of the hydrocarbon chain. Results support previous conclusions of a thermodynamic study of the water (1) + 2-butoxyethanol (2) system, where trends in the composition dependence resembling micellization were observed in the water-rich region (0.00 < x_2 < 0.04). Similar trends indicative of structural reorganization appear to exist in the 2-butoxyethanol-rich region ($x_2 \simeq$ 0.45–0.85).

Introduction

In an earlier study of the thermodynamic properties of alkoxyethanols, $H(CH_2)_nOC_2H_4OH$, in water, it was assumed that the binary system water–2-butoxyethanol ($n = 4$) appears to be a true solution over the entire concentration range, but behaves as if microphases coexist in the water-rich region (*1*). The changes vs concentration of nonthermodynamic properties often give more evidence of the structural character of binary systems. Since the magnitude of the static dielectric constant of a liquid system is determined by the permanent electric moments and the polarizabilities of its individual molecules and by the nature of their mutual orientation, measurements of such a property ought to be an useful tool, for investigating intermolecular forces and the local order which these forces produce in a dense mixture of polar fluids. Consequently, dielectric constants of the binary systems water–alkoxyethanol (n = 0, 1, 2, 4) were measured at 25 °C over the whole composition range. Densities of these mixtures are needed to calculate some related dielectric properties. Since previous investigations (*1–6*) contain few data beyond the equimolal mixtures, measurements have been performed to cover in more detail the intermediate and organic solvent-rich regions.

Experimental Section

Materials. Water was first deionized by means of ion-exchange resins and then distilled. Its conductivity was always less than $1.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. All reagents were from Fluka AG, Buchs, Switzerland, excepting the 1,2-ethanediol from Prolabo, Paris, France. The manufacturer's estimate of the purity of 1,2-ethanediol was greater than 99.8 mol % and its water content was less than 0.2 mol %. The estimates of purity of 2-alkoxyethanols were respectively greater than 99.5% (2-methoxy- and 2-ethoxyethanol) and 98% (2-butoxyethanol). All chemicals were stored and protected from atmospheric moisture and CO_2 as far as possible.

All solutions were prepared by weight with a precision of 0.1 mg, from thoroughly degassed samples of deionized and distilled water and of alkoxyethanol, and then corrected for buoyancy. This corresponds to the mole fraction values being reliable to within 1×10^{-4}.

Apparatus and Procedures. Measurements of density and dielectric constant were made over the whole composition range. Densities of mixtures were measured with a flow-type oscillating tube densimeter (Sodev Inc., Model 02 D, Sherbrooke, Québec, Canada). The densimeter was calibrated assuming a linear relationship between the density of the liquid under consideration and the square of the oscillator period. Water and air at very low pressure ($<10^{-3}$ atm), assimilated to vacuum, were used as standards to fix the value of the calibration constant; no significant change of this constant was observed over several months. The densimeter was thermostated to within ±0.002 K with a Setaram temperature controller. The temperature was checked with a calibrated Hewlett-Packard Model 2801-A quartz thermometer and was estimated to be accurate to within 0.01 K, with a long-term stability of about ±0.002 K. Each sample measurement was bracketed by two water measurements, water serving as the reference fluid to determine samples densities. All the measurements were carried out at 298.15 K. The solutions were passed through the densimeter by gravity. In these conditions, differences in densities ($\rho - \rho_0$) of the sample and the reference fluid can be determined with a reproducibility of $\pm 5 \times 10^{-6}$ g cm^{-3}.

Dielectric constant measurements were carried out at 1.8 MHz, by the heterodyne beat method, with a Wissenschaftliche Technische Werskstätten Dekameter (Model DK 03). (W.T.W., Weilheim/Oberbayern, West Germany). The thermostated (±0.03 K) measuring cells were MFL-3/s and MFL-2/s type. The sample cells were of the covered coaxial capacitor type with vacuum capacitances of 2.0 (MFL-3/s) and 0.5 pF (MFL-2/s). They are adequate to cover the dielectric constant range of water + alkoxyethanol at 298.15 K ($\epsilon \simeq$ 9–80). It was checked that a good overlapping was obtained when passing from MFL-3/s (ϵ = 20–85) to MFL-2/s (ϵ = 7–23) measuring cells, the difference lying always within the experimental accuracy of the equipment. Reproducibility of measurements was approximately equal to ±0.05 dielectric constant unit. The cells were calibrated with standard pure liquids: water, methanol, acetone, 1-propanol (MFL-3/s); acetone, 2-propanol, 1-butanol, 1,2-dichloroethane, and ethyl acetate (MFL-2/s). The calibration was checked at each two or three measurements; no significant change was observed throughout the whole experiment.

Results and Discussion

Experimental values for density (ρ) and dielectric constant (ϵ) at 298.15 K for mixtures of $((1 - x_2)H_2O + x_2H(CH_2)_nOC_2H_4OH)$ with n = 0, 1, 2, and 4 are listed in Table I, where x_2 refers to the mole fraction of the alkoxyethanol.

Densities and Excess Molar Volumes. Densities were converted to excess molar volumes V_m^E, assuming ideal mole fraction additivity of V_m.

The smoothing equation

$$V_m^E = \phi_2(1 - \phi_2)\sum_i A_{i-1}(1 - 2\phi_2)^{i-1} \qquad i = 1, 2, \ldots \qquad (1)$$

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Table I. Measured Densities and Dielectric Constants of Mixtures of H_2O (1) + $H(CH_2)_nO\text{-}CH_2\text{-}CH_2OH$ (2) at 298.15 K

x_2	ρ/g cm^{-3}	ϵ	x_2	ρ/g cm^{-3}	ϵ	x_2	ρ/g cm^{-3}	ϵ	x_2	ρ/g cm^{-3}	ϵ
$H_2O + HO\text{-}CH_2\text{-}CH_2OH$											
0	0.997048	78.35	0.0798	1.02672	72.41	0.3000	1.07349	60.34	0.6971	1.10184	46.96
0.0098	1.00108	77.52	0.0900	1.02994	71.80	0.3495	1.07942	58.12	0.7463	1.10354	45.77
0.0198	1.00514	76.76	0.1001	1.03296	71.07	0.4005	1.08449	56.15	0.7958	1.10505	44.71
0.0306	1.00935	76.00	0.1196	1.03843	69.79	0.4461	1.08833	54.41	0.8447	1.10639	43.60
0.0403	1.01301	75.24	0.1392	1.04375	68.68	0.4978	1.09202	52.73	0.8949	1.10761	42.57
0.0501	1.01662	74.43	0.1799	1.05322	66.38	0.5481	1.09505	51.19	0.9437	1.10869	41.60
0.0599	1.01999	73.85	0.2206	1.06116	64.18	0.5968	1.09759	49.78	0.9931	1.10969	40.72
0.0701	1.02351	73.13	0.2600	1.06776	62.24	0.6471	1.09986	48.27	1	1.10982	40.61
$H_2O + CH_3O\text{-}CH_2\text{-}CH_2OH$											
0	0.997048	78.35	0.1110		61.03	0.3977	0.99300		0.7901		21.80
0.0199	0.99873		0.1303	1.00685		0.4412		34.27	0.8205	0.96740	
0.0297		72.83	0.1392		57.57	0.4589	0.98867		0.8603		20.02
0.0398	1.00083		0.1705	1.00675		0.5167	0.98455		0.8733	0.96503	
0.0505		69.46	0.1823		52.84	0.5317		30.22	0.9203		18.67
0.0599	1.00287		0.2203	1.00500		0.5798	0.98044		0.9259	0.96284	
0.0700		66.54	0.2309		48.28	0.6128		27.13	0.9599		17.85
0.0797	1.00457		0.2797	1.00147		0.6393	0.97683		0.9731		17.60
0.0813		64.95	0.2902		43.53	0.6999	0.97341		1	0.96002	17.10
0.0912		63.58	0.3393	0.99730		0.7105		24.02			
0.0983	1.00576		0.3618		38.74	0.7599	0.97029				
$H_2O + C_2H_5O\text{-}CH_2\text{-}CH_2OH$											
0	0.997048	78.35	0.0743		62.49	0.2195	0.98359		0.6698	0.94105	
0.0079	0.99685		0.0748	0.99835		0.2703	0.97699		0.6701		19.86
0.0086		76.21	0.0862		60.39	0.2722		38.02	0.7279		18.46
0.0155		74.56	0.0873	0.99794		0.3293	0.97000		0.7319	0.93740	
0.0159	0.99694		0.0999	0.99724		0.3330		33.52	0.7852		17.23
0.0249	0.99725		0.1036		57.43	0.3991		29.85	0.7906	0.93424	
0.0262		72.05	0.1173		55.27	0.4014	0.96235		0.8506	0.93121	
0.0339		70.66	0.1196	0.99563		0.4682	0.95605		0.8521		15.92
0.0348	0.99768		0.1499		50.62	0.4719		26.46	0.9014	0.92902	
0.0495		67.22	0.1500	0.99235		0.5337		24.02	0.9022		14.99
0.0505	0.99822		0.1796	0.98864		0.5417	0.94997		0.9492		14.19
0.0625	0.99844		0.1800		46.82	0.6021		21.79	0.9515	0.92681	
0.0626		64.44	0.2194		42.58	0.6128	0.94479		1	0.92502	13.38
$H_2O + C_4H_9O\text{-}CH_2\text{-}CH_2OH$											
0	0.997048	78.35	0.0250	0.99076		0.1887	0.94807		0.6385	0.90977	
0.0024		77.50	0.0251		68.50	0.2202		29.13	0.6526		13.72
0.0033	0.99632		0.0297	0.98881		0.2497	0.93948		0.6979	0.90702	
0.0051		76.59	0.0299		66.47	0.2639		25.94	0.7026		12.96
0.0066	0.99570		0.0392	0.98503		0.3008		23.70	0.7496	0.90501	
0.0076		75.61	0.0400		62.31	0.3092	0.93268		0.7514		12.29
0.0100	0.99512		0.0493		58.97	0.3521		21.26	0.8003		11.64
0.0102		74.64	0.0494	0.98124		0.3800	0.92607		0.8010	0.90298	
0.0121		74.19	0.0675	0.97509		0.4017		19.43	0.8507	0.90119	
0.0133	0.99453		0.0698		52.38	0.4778	0.92080		0.8511		11.01
0.0152		72.87	0.0903		47.12	0.4478		18.03	0.8983	0.89943	
0.0166	0.99379		0.1017	0.96545		0.5217	0.91612		0.8987		10.47
0.0176		71.92	0.1201		41.17	0.5294		16.01	0.9479	0.89787	
0.0199	0.99275		0.1398	0.95688		0.5511		15.56	0.9490		9.94
0.0202		70.82	0.1472		36.96	0.5772	0.91294		1	0.89649	9.43
0.0226		69.71	0.1802		32.88	0.6028		14.56			

Table II. Coefficients of Eq 1 and Standard Deviations $\sigma(V_m^E)$ for the Systems Water (1) + $H(CH_2)_nOCH_2\text{-}CH_2OH$ (2) at 298.15 K

n	ref	A_0	A_1	A_2	A_3	A_4	$\sigma(V_m^E)$/cm^3·mol^{-1}	N
0	this work	−1.2118	0.9865	−0.2621	0.1541	−0.0891	0.0007	30
	lit. (*4*)	−1.2329	0.9289	−0.1599	0.2025	−0.2344	0.0103	10
1	this work	−3.2606	3.1175	−1.1585	1.2640	−1.0692	0.0025	20
	lit. (*2*)	−3.2546	3.0533	−1.0496	1.3553	−1.2180	0.0062	10
	lit. (*1*)	−3.2562	3.1424	−1.3034	1.2055	−0.7635	0.0012	14
	lit. (*5*)	−3.1683	2.7859	−1.0219	1.7897	−1.5149	0.0007	9
2	this work	−3.7674	3.0926	−1.2474	2.7504	−2.2424	0.0047	28
	lit. (*2*)	−3.7545	3.1549	−1.4407	2.4683	−1.7468	0.0044	10
	lit. (*1*)	−3.7384	3.0272	−1.3255	2.8060	−2.0425	0.0032	18
	lit. (*5*)	−3.6052	2.9452	−1.2528	2.6018	−1.9010	0.0065	9
	lit. (*6*)	−3.7082	3.2530	−1.9107	2.2770	−1.0471	0.0189	10
4	this work	−1.9175	1.3262	−1.5437	3.9944	−4.3227	0.0197	28
	lit. (*2*)	−1.8907	1.6023	−1.9849	3.1901	−3.6088	0.0127	10
	lit. (*1*)	−1.8686	1.4431	−2.3798	3.6968	−2.9590	0.0136	10
	lit. (*5*)	−1.9267	1.7057	−1.8638	2.8026	−3.4342	0.0157	9

was fitted to each set of results by the method of least squares with all points weighted equally. In eq 1, ϕ_2 is the volume fraction of alkoxyethanol stated in terms of the volumes of the unmixed components at 298.15 K. Values of the coefficients

A_i in eq 1 are listed in Table II, along with the standard deviations (σ) of the representations and the number of experimental points (N). Equation 1 was also fitted to several sets of literature data. It should be emphasized that the equation derived from eq 1 by replacing ϕ_2 by x_2 is more generally used. Both equations were found to give fairly satisfactory fits for our measurements, which were carried out at regular mole fraction intervals over the entire composition range. However, only eq 1 could be applied successfully to literature data (*1*, *2*, *5*), that are mainly focused in the water-rich ($x_2 < 0.2$). The uncommonly high values of $\sigma(V_m^E)$ for the 2-butoxyethanol–water system are due to the failure of the smoothing function to handle the dramatic changes in dV_m/dx_2 within the water-rich region.

Dielectric Constants and Related Properties. Fitted values of dielectric constants were obtained as follows. Deviations of the dielectric constants from linearity on a ideal volume fraction basis were calculated by using the relation

$$\Delta\epsilon = \epsilon - (\phi_1\epsilon_1 + \phi_2\epsilon_2) \qquad (2)$$

where ϵ_1 and ϵ_2 are the dielectric constants of pure water and alkoxyethanol. Our results for $\Delta\epsilon$ were fitted with the smoothing equation previously used for excess molar volumes. Values of the coefficients A'_i, determined for each of the four mixtures are listed in Table III along with the standard deviations of the representation and N. When dealing with totally miscible binary systems, it is considered to be useful to examine the composition dependence of their excess properties. For thermodynamic properties, ideal composition dependence may be defined within the context of the widely accepted generalization of Raoult's law (*7*). For nonthermodynamic properties such as dielectric constants, one must rely upon theories which offer an intuitive basis for defining ideality (*8*, *9*).

We calculated the following molar quantities:

molar susceptibility $(\chi_e V)_m$

$$(\chi_e V)_m = (\epsilon - 1)V_m \qquad (3)$$

molar polarizability of Kirkwood (*10*), P_K

$$P_K = ((\epsilon - 1)(2\epsilon + 1)V_m/9\epsilon) \qquad (4)$$

molar orientational polarizability derived by Fröhlich (*11*), P_F

$$P_F = ((\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)V_m/\epsilon(\epsilon_\infty + 2)^2) \qquad (5)$$

V_m is the molar volume and ϵ_∞ the high-frequency limiting value of ϵ; ϵ_∞ was to be taken equal to $(n_D)^2$, the square of the Na D line refractive index. n_D values at desired mole fractions were obtained by interpolation of a fitting eq 2, applied to literature data (*5*, *12*).

Each of these quantities, $(\chi_e V)_m$, P_K, and P_F, was assumed to be mole fraction additive for an ideal mixture.

Deviations from ideal mixing may be estimated in terms of either the excess molar properties or differences between the apparent molar quantities and the properties of the pure compounds.

An apparent molar property of component 2 in a mixture is defined as

$$Z_{\phi,2} = \frac{Z - x_1 Z_1^0}{x_2} \qquad (6)$$

Detailed quantitative analysis of excess thermodynamic and dielectric quantities of these systems will be carried out in due course. That there exist some interesting features in the composition dependence of the dielectric properties is nicely revealed in plots of the apparent molar quantities vs inverse mole fraction.

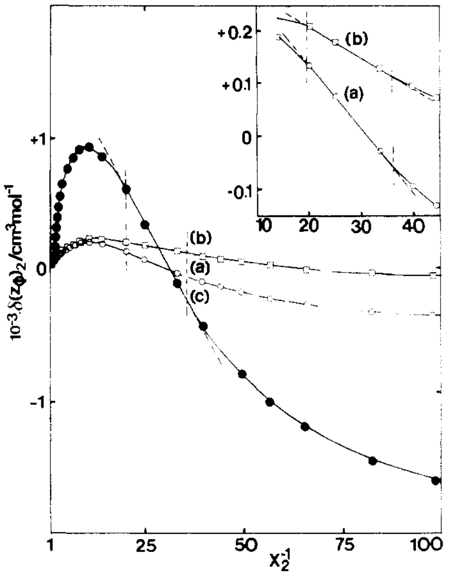

Figure 1. Differences $\delta(Z_\phi)_2 = ((Z_\phi)_2^0 - (Z_\phi)_2)$ vs reciprocal mole fraction $(x_2)^{-1}$ for $\{(1 - x_2)H_2O + x_2C_4H_9OCH_2CH_2OH\}$ at 298.15 K: (a) $Z = P_K$; (b) $Z = P_F$; (c) $Z = \chi_e V$. The insert shows the changes of graphs (a) and (b) magnified.

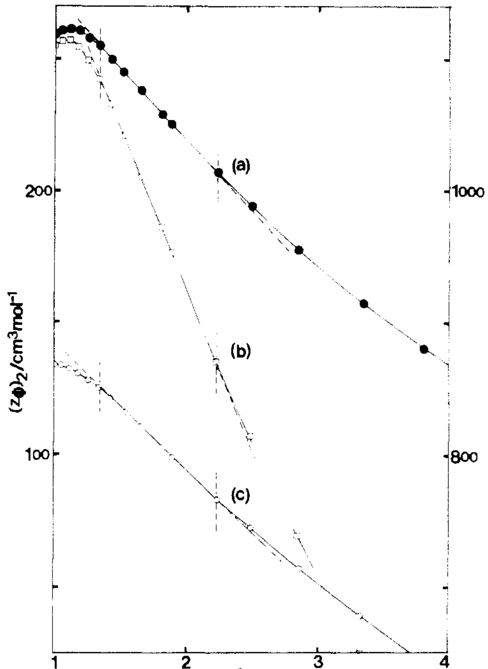

Figure 2. $(Z_\phi)_2$ vs reciprocal mole fraction $(x_2)^{-1}$ for $\{(1 - x_2)H_2O + x_2C_4H_9OCH_2CH_2OH\}$ at 298.15 K: (a) $Z = P_K$; (b) $Z = P_F$; (c) $= \chi_e V$. Scales on the axes are left ordinate for $((P_K)_\phi)_2$ and $((P_F)_\phi)_2$, right ordinate for $((\chi_e V)_\phi)_2$.

The rationale for plotting apparent molar quantities vs inverse mole fraction is based upon the findings of Douhéret and Viallard (*13*, *14*) that, for a diphasic system, such as a micellar system, apparent molar thermodynamic quantities $Z_{\phi,2}$, vary linearly with x_2^{-1}. Similar behavior is also observed for systems containing metastable microphases (pseudophase model).

This type of linear dependence is clearly manifested by the apparent molar dielectric properties of the 2-butoxyethanol–water system in the composition range $x_2 = 0.02$–0.04, as can be seen in Figure 1. This supports the conclusions of Roux et al. (*1*), based on a study of molar heat capacities where the 2-butoxyethanol–water system behaves as if microphases coexist with the water-rich mixtures. It is also of interest to note that the apparent molar dielectric quantities of 2-butoxy-

Table III. Coefficients of Eq 1 and Standard Deviations $\sigma(\Delta\epsilon)$ for the Systems Water (1) + $H(CH_2)_nOCH_2$–CH_2OH (2) at 298.15 K

n	A'_0	A'_1	A'_2	A'_3	A'_4	$\sigma(\Delta\epsilon)$	N
0	13.9172	−2.6887	0.2252			0.0486	30
1	19.2285	−1.9785	−0.0906			0.0596	20
2	15.5167	6.6099	0.7008	−6.1475	0.1949	0.0591	25
4	−11.2605	10.5111	15.0639	7.1495	12.2569	0.1111	34

ethanol vary in a linear way with x_2^{-1} in the range $x_2 \simeq$ 0.45–0.85 as can be seen in Figure 2. It is evident that these mixtures are highly structured, containing interesting metastable aggregates. No such linear regions were to be found in the plots of $Z_{\phi,2}$ vs x_2^{-1} for any system studied.

Numerous models have been proposed for the patterns of molecular aggregation that exists in mixtures of water with H-bond-forming organic species (*15*–*18*). We propose to examine the respective merits of these models in a detailed analysis of both the thermodynamic and dielectric properties of the alkoxyethanol–water systems.

Registry No. 1,2-Ethanediol, 107-21-1; 2-methoxyethanol, 109-86-4; 2-ethoxyethanol, 110-80-5; 2-butoxyethanol, 111-76-2.

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Molar Refractivities of Tetra-*n*-alkylammonium Salts and Ions

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The refractive index and density of dilute solutions of tetra-*n*-alkylammonium bromides in water and in *N*,*N*-dimethylformamide (DMF) were measured at 298.15 K. The following values of the infinite dilution molar refractivities (in cm^3 mol^{-1}) were found: NH_4Br 15 ± 2, $(CH_3)_4NBr$ 36 ± 2, $(C_2H_5)_4NBr$ 47 ± 1, $(C_2H_5)_4NI$ 61 ± 2, $(C_3H_7)_4NBr$ 73 ± 2 (in water) and 68 ± 2 (in DMF), $(C_4H_9)_4NBr$ 91 ± 2 (in both solvents), $(C_5H_{11})_4NBr$ 108 ± 2 (in water) and 110 ± 2 (in DMF), $(C_6H_{13})_4NBr$ 128 ± 3, and $(C_7H_{15})_4NBr$ 150 ± 3. They yield a slope of 19.0 cm^3 mol^{-1} per four methylene groups added in the alkyl chains, when plotted against the length of the latter. The calculated polarizabilities of the cations are proportional to their van der Waals volumes.

Introduction

The molar refractivities, R, or polarizabilities, $\alpha = 3R/4\pi N_{Av}$ (N_{Av} is Avogadro's number) of the tetra-*n*-alkylammonium cations are useful quantities, relating to their interactions with the surroundings in solutions. Although they may be calculated approximately from group contributions (*1*), very few experimental values of them have been reported.

The present study was undertaken to provide such data from the measurement of refractive index values, n_D, and densities, d, of dilute solutions of those tetra-*n*-alkylammonium bromides that are soluble in water and in *N*,*N*-dimethylformamide (DMF) at 298.15 K. These ranged from $n_C = 1$ to $n_C = 5$ in water (n_C is the number of carbon atoms in the alkyl chain) and from $n_C = 3$ to $n_C = 7$ in DMF. The n_D and d values of dilute aqueous solutions of ammonium bromide and tetraethylammonium iodide were also measured for the purpose of comparison and checking. The molar concentrations, c, of the solutions ranged from 0.005 to 0.1 M (M = mol L^{-1}).

The apparent molar refractivity of the solute is given by

$$R_D = (1000/c)[(n_D^2 - 1)/(n_D^2 + 2) - (d - cM/1000) \times (1/d_0)(n_{D0}^2 - 1)/(n_{D0}^2 + 2)] \quad (1)$$

where n_{D0} and d_0 are the refractive index and density of the solvent and M is the molar mass (in g mol^{-1}). The subscript D is used on R and n to designate values measured at the mean yellow sodium line.

The values of R_D can, in principle, depend on the solvent and on the concentration c of the solution. Infinite dilution values, R_D^{∞}, obtained by extrapolation, are best employed for the purpose of further considerations of the solute–solvent interactions.

Experimental Section

The density and refractive index measurements were made essentially as in our previous work (*2*), with a Sodev 020 densitometer and a Bausch & Lomb dipping refractometer. The temperature was held constant at 298.15 K, controlled to ±0.001 K for the density and to ±0.05 K for the refractive index measurements.

Triply distilled water and spectral grade methanol, ethanol, and DMF were employed. Solutions were prepared by weight from the solid salts and the solvent and were then diluted volumetrically. The tetra-*n*-alkylammonium bromides were pure commercial products (Eastman Kodak), except for the ethyl-substituted salt. This was prepared in aqueous solution from tetraethylammonium iodide by means of an anion exchange resin column in the bromide form.

The densitometer was calibrated with water and methanol, using their reported densities at 298.15 K: d_0 = 0.997045 g cm^{-3} for water (*3*) and d_0 = 0.785818 g cm^{-3} for methanol (*4*). The density of ethanol was then measured, the resulting d_0 = 0.78431 g cm^{-3} agreeing completely with its reported

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