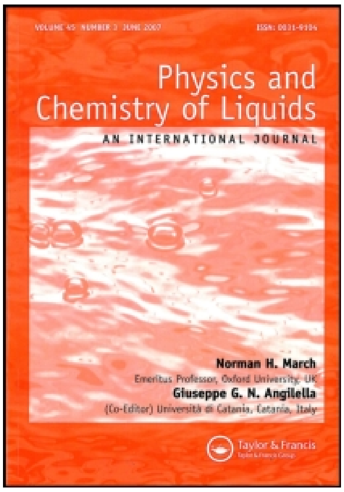

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Dielectric and Index of Refraction Properties of Binary Mixtures of Polyoxyethene Glycol Monobutyl Ethers with Water

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DIELECTRIC AND INDEX OF REFRACTION PROPERTIES OF BINARY MIXTURES OF POLYOXYETHENE GLYCOL MONOBUTYL ETHERS WITH WATER

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Dielectric constants and indices of refraction of aqueous mixtures of the homologous series of polyoxyethene glycol mono-n-butyl ethers $C_4H_9O(CH_2CH_2O)_mH$ (where $m = 1$ to 3) were measured. From the experimental data, excess dielectric permittivities, dielectric molar susceptibilities, molar and molar orientational polarizabilities were evaluated. Also excess Lorentz–Lorentz molar refractions were evaluated and the results were discussed in terms of departure from ideality and intermolecular interactions in the mixtures.

KEY WORDS: Dielectric constants, Refractive indices, Excess properties, Alkoxy alcohols.

INTRODUCTION

In an earlier study, we have reported the effect of microheterogeneity on bulk and surface properties of binary mixtures of polyoxyethene glycol monobutyl ethers with water[1]. In the mixtures of water with hydrophobic alcohols, the dependency of excess thermodynamic properties on the composition suggests the coexistence of microphases in the water rich region[2]. Several intensive physical properties of liquids, such as static dielectric constant (ε), viscosity (η) and index of refraction (n_D) were commonly used solvent parameters to interpret medium effect upon solute solubilities, acid-base equilibria, electrolytic behaviour and reaction mechanisms for polar and ionic species[3-5]. 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. Hence a study of this property should be a useful tool in the investigation of intermolecular forces and the local order which these forces produce in binary polar mixtures. Dielectric constants of the binary mixtures of water + $C_4H_9O(CH_2CH_2O)_m H$ ($m = 1$ and 2) were measured at 298 K over a whole composition range. Also the index of refraction of aqueous mixtures with $C_4H_9O(CH_2CH_2O)_mH$ (where $m = 1$ to 3) were measured at five different temperatures to evaluate the variations in electronic polarizability of the systems.

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EXPERIMENTAL SECTION

2-Butoxyethanol (ethylene glycol monobutyl ether or C_4E_1), 2-(2-butoxyethoxy) ethanol (Diethylene glycol monobutyl ether or C_4E_2) were purchased from Aldrich Chemicals of stated purity 99+%. Triethylene glycol monobutyl ether (C_4E_3) was purchased from Tokyo Kasei Chemicals. All chemicals were purified by distillation under reduced pressure and stored over molecular sieves. All mixtures were prepared by mass with a precision of 0.1 mg from thoroughly degassed nanopure water. The mole fractions are believed to be reliable to within 1×10^{-4}.

Dielectric constants were measured by changes in dielectric cell capacitance with a Sargent Model V cathode coupled oscillator. The instrument was calibrated using literature values for pure solvents[6]: methanol, acetone, nitrobenzene and acetonitrile. Dielectric constants of the pure substances and their mixtures with water at 298 K were determined employing the procedures described in the literature[7]. Reproducibility of measurements was approximately equal to ± 0.15 dielectric constant unit. The calibration was periodically checked with standard solvents during the course of the investigation and no significant change was observed throughout the course of the study. The index of refraction for the Na D-line was measured with a thermostatted Abbe-3L refractometer (Bausch and Lomb) with an error of less then 0.0001 unit. The instrument was calibrated with a glass piece of known refractive index ($n_D = 1.5125$) supplied with the instrument. The instrument was also checked by measuring the refractive index of purified water, methanol and n-hexane at known temperatures[7]. Densities were measured using a SODEV Model-02D vibrating-tube densimeter operating in a flow mode and an Anton-Paar DMA 45 vibrating-tube densimeter operating in static mode. A SODEV temperature controlled bath was used in the measurement of densities. Densities have an estimated reproducibility of 5.0×10^{-5}.

RESULTS AND DISCUSSION

The experimentally determined physical properties of the pure components at 298 K along with the literature values are listed in Table 1. The dielectric properties of $H_2O + C_4E_1$ system at 298 K were reported in the literature[8] and our value 9.47 for the dielectric constant of C_4E_1 is in excellent agreement with the literature value of 9.43 (Table 1).

To estimate the strength of intermolecular interactions between the components of the mixture, an adequate approach is to evaluate the departure from ideal behaviour of noninteracting components[9]. The departure from ideality ($\Delta\varepsilon$) is given by:

$$\Delta\varepsilon = \varepsilon - \varepsilon^{id} \tag{1}$$

where ε and ε^{id} are the experimental and ideal dielectric constants of the mixtures respectively. The ideal dielectric constants of the mixtures were computed by using Dacroocq's formula[10] in the general form:

$$\varepsilon^{id} = (1 - Y_2)\varepsilon_1 + Y_2\varepsilon_2 + 2\left[\frac{1}{\varepsilon^{id}} - \frac{(1 - Y_2)}{\varepsilon_1} - \frac{Y_2}{\varepsilon_2}\right] \tag{2}$$

Table 1 Physical properties of pure compounds at 298 K.

Compound	*Property*	*This Study*	*Literature*
C_4E_1	Dielectric constant	9.47	9.43[a]
	Density*	0.89647	0.89648[a]
	Refractive Index	1.4175	1.4177[b]
C_4E_2	Dielectric constant	10.93	—
	Density*	0.95218	0.9528[c]
	Refractive Index	1.4302	—
C_4E_3	Density*	0.98275	0.9830[c]
	Refractive Index	1.4380	—

* units: $g.cm^{-3}$, a: Ref (8), b: Ref (6), c: Ref (1).

where ε_1 and ε_2 are the dielectric constants of water and C_4E_1 or C_4E_2, respectively, Y_2 is the volume fraction defined on partial molar volume basis:[11]

$$Y_2 = \frac{X_2\bar{V}_2}{X_2\bar{V}_2 + (1 - X_2)\bar{V}_1} \tag{3}$$

where $\bar{V}_2$ and $\bar{V}_1$ are the partial molar volumes of C_4E_1 or C_4E_2 and water, respectively. The partial molar volumes $\bar{V}_1$ and $\bar{V}_2$ were obtained using the following equations[11], modified in the mole fraction scale:

$$\bar{V}_1 = M_1\left[\frac{1}{\rho}\right] - \bar{M}X_2\frac{d\left[\frac{1}{\rho}\right]}{dX_2} \tag{4}$$

$$\bar{V}_2 = M_2\left[\frac{1}{\rho}\right] - \bar{M}X_1\frac{d\left[\frac{1}{\rho}\right]}{dX_2} \tag{5}$$

and

$$\bar{M} = X_1M_1 + X_2M_2 \tag{6}$$

It was found that $\Delta\varepsilon$ values are negative and the plot of $\Delta\varepsilon$ vs. Y_2 at 298 K (Figure 1) exhibits a pronounced minimum generally centered at $Y_2 \approx 0.55$ to 0.60 and the $\Delta\varepsilon$ values are more negative for C_4E_1 than C_4E_2. The values of molar susceptibility $(\chi_e V)_m$, molar polarizability of Kirkwood[12] P_k and molar orientational polarizability derived by Frohlich[13] P_f, were calculated using the following equations respectively:

$$(\chi_e V)_m = (\varepsilon - 1)V_m \tag{7}$$

$$P_k = \left[\frac{(\varepsilon - 1)(2\varepsilon + 1)V_m}{9\varepsilon}\right] \tag{8}$$

$$P_f = \left[\frac{(\varepsilon - n_D)(2\varepsilon + n_D)V_m}{\varepsilon(n_D + 2)^2}\right] \tag{9}$$

where V_m and n_D are the molar volume and refractive index of the mixture. Excess values of these quantities (Z^E) were calculated assuming mole fraction additivity for an ideal mixture:

$$Z^E = Z - (X_1Z_1 + X_2Z_2) \tag{10}$$

The plots of the derived excess quantities (Z^E), against mole fraction of C_4E_2, exhibited negative deviations from the ideal behaviour (Figures 2–4). Refractive index data for the binary systems at all temperatures was fitted into a polynomial equation as a function of C_4E_n.

$$n_D = \sum_{i=0}^{n} A_i X_2 \tag{11}$$

The coefficients along with standard deviation calculated by the least-squares method are listed in Table 2.

Lorentz–Lorentz molar refraction (R) is related to electronic polarizability α of molecules by the expression:

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d} = \frac{4}{3}\Pi\alpha N \tag{12}$$

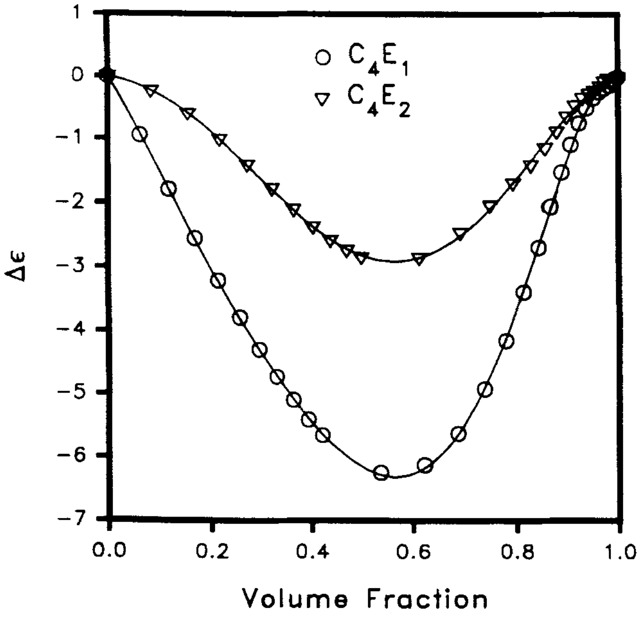

Figure 1 Plot of Δε vs. Volume Fraction of C_4E_n.

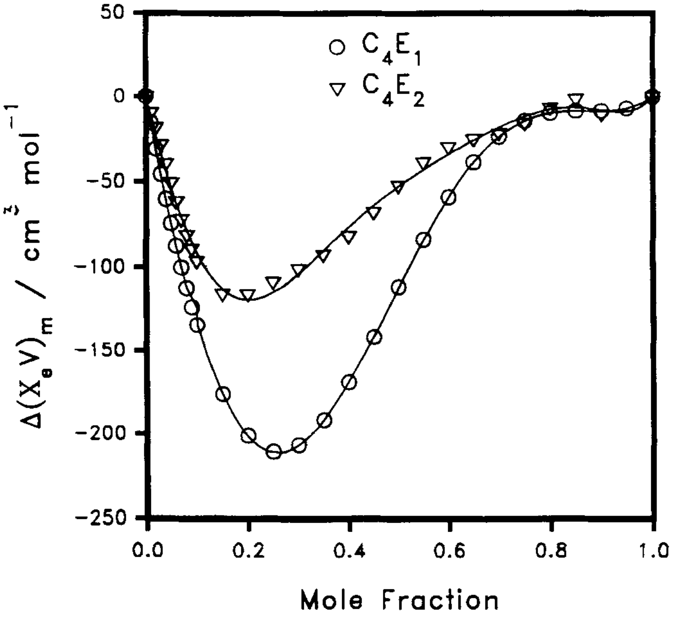

Figure 2 Plot of $\Delta(\chi_e V)_m$ vs. Mole Fraction of C_4E_n.

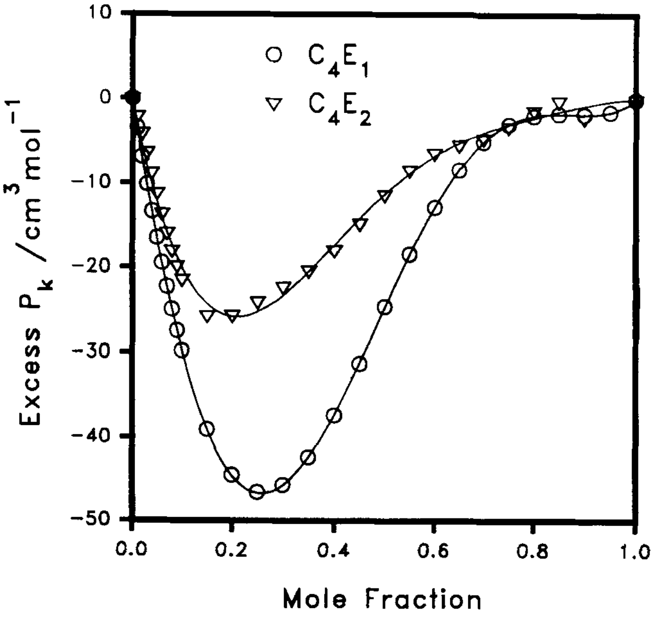

Figure 3 Plot of Excess P_k vs. Mole Fraction of C_4E_n.

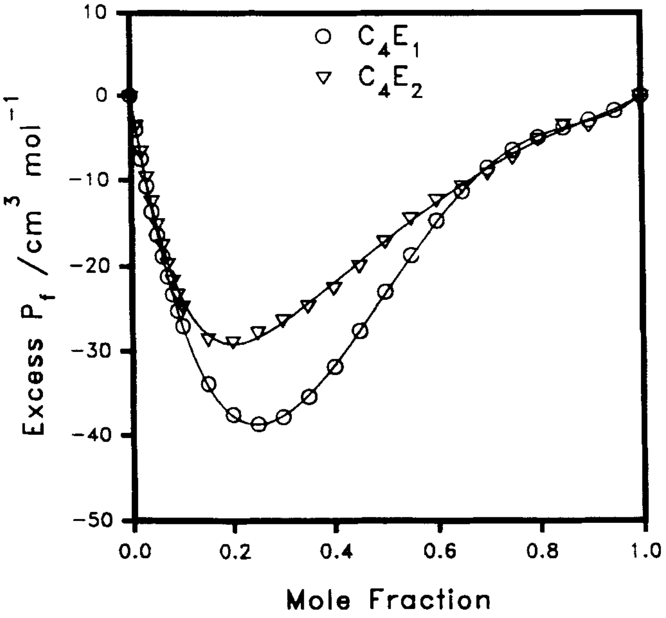

Figure 4 Plot of Excess P_f vs. Mole Fraction of C_4E_n.

where M is the molecular mass, d is the density and N is Avagadro's number. The excess molar refraction. ΔR, which represents the electronic perturbation due to orbital mixing of the molecules is a quantity of interest which has been studied extensively in the literature[14-16]. This quantity is calculated using the refractive index mixing rules as follows:

$$\Delta R = R_{mix} - (R_1 Y_1 + R_2 Y_2) \tag{13}$$

where R_1 and R_2 are molar refractions of pure components. The excess values ΔR vs. Y_2 for all the mixtures are plotted in Figure 5.

Each set of the derived excess quantities $Z^E (= \Delta\varepsilon, \Delta(\chi_e V)_m, P_K^E, P_f^E$ and $\Delta R)$ discussed above was fitted to the Redlich-Kister[16] polynomial equation of the type:

$$Z^E = C_1 C_2 \sum_{i=0}^{n} a_i (1 - 2C_2)^i \tag{14}$$

to estimate the regression coefficients a_i and standard errors σ. Here C represents the values of mole or volume fractions. These values are listed in Table 3 and the continuous curves were generated using the values of these coefficients.

The negative values of $\Delta\varepsilon$ for C_4E_1 and C_4E_2 systems with water can be attributed to the formation of polar associates with lower dipole moments[17-20]. It has been postulated that small negative deviations on this excess nonthermodynamic property ($\Delta\varepsilon \leqslant 5$) are a consequence of either a weak dipole–dipole association phenomena or

Table 2 Estimated parameters of indices of refraction for binary mixtures

m	T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	$\sigma\,(10^4)$
1	298	1.33252	0.67067	−3.23454	10.11155	−19.55975	22.28071	−13.60666	3.42301	—	2.81
	303	1.33195	0.64299	−2.91259	8.34638	−14.69931	15.31998	−8.64906	2.03526	—	1.69
	308	1.33132	0.63089	−2.83781	8.09390	−14.22875	14.80814	−8.33549	1.95141	—	2.07
	313	1.33062	0.63893	−3.10255	9.84197	−19.23205	21.95338	−13.35091	3.33213	—	3.70
	318	1.32986	0.62387	−2.98010	9.15764	−17.31272	19.23844	−11.47011	2.82262	—	1.57
2	298	1.33252	0.93497	−5.04713	16.36978	−31.63794	35.44828	−21.17808	5.20781	—	2.60
	303	1.33195	0.93148	−5.17421	17.40106	−34.84505	40.31505	−24.78309	6.25101	—	2.66
	308	1.33133	0.90060	−4.84170	15.82953	−31.10774	35.59278	−21.74649	5.46790	—	3.68
	313	1.33062	0.87885	−4.58972	14.35137	−26.80163	29.15440	−16.99900	4.09940	—	2.82
	318	1.32986	0.87238	−4.62353	14.75617	−28.13450	31.16939	−18.45064	4.50338	—	1.39
3	298	1.32503	1.40012	−9.76796	41.21404	−107.22448	172.39314	−166.40225	88.20613	−19.70577	1.53
	303	1.33194	1.18327	−7.57957	29.69382	−72.46261	110.21532	−101.34767	51.46927	−11.06768	1.09
	308	1.33131	1.18619	−7.83790	31.85817	−80.52487	126.24074	−118.98110	61.60695	−13.44518	1.82
	313	1.33061	1.18367	−8.02968	33.92983	−89.24662	144.94840	−140.77219	74.77120	−16.68283	1.88
	318	1.32985	1.16601	−7.83471	32.63648	−84.84569	136.91495	−132.72017	70.57061	−15.78694	1.88

Table 3 Estimated parameters of excess quantities for binary mixtures

*Quantity**	*System*	a_0	a_1	a_2	a_3	a_4	a_5	σ
$\Delta\varepsilon$	C_4E_1	−24.6254	9.1370	5.4611	−16.2711	13.1877		1.1
	C_4E_2	−11.2447	5.7929	9.6019	−5.2496	−0.4357		1.1
	C_4E_1	−98.6886	−258.1398	−145.7919	97.8771	42.4163	4.3761	0.10
P_K^E	C_4E_2	−45.1463	−108.5546	−127.2010	−39.2223	27.6658		1.00
	C_4E_1	−92.8731	−175.4773	−100.6885	11.4177	−26.6848		0.20
P_f^E	C_4E_2	−68.3203	−93.9907	−87.4274	−82.2253	−61.5325		0.51
	C_4E_1	−447.6845	−1159.5	−657.6976	436.5443	193.0630	24.6093	0.31
$\Delta(\chi_e V_m)$	C_4E_2	−209.9472	−411.9202	−488.7614	−740.8372	−69.6473	749.1	01.1
	C_4E_1	−43.7234	29.5445	−17.2447	30.8866	−31.5081		0.11
ΔR	C_4E_2	−65.1159	55.43341	−30.2094	−2.7468	−62.2816	86.2464	0.16
	C_4E_3	−85.9214	77.7791	−100.7694	10.3954	170.3158	133.7483	0.27

Units*: P_K^E, P_f^E, $\Delta(\chi_e V_m)$ and ΔR in cm^3. mole^{-1}.

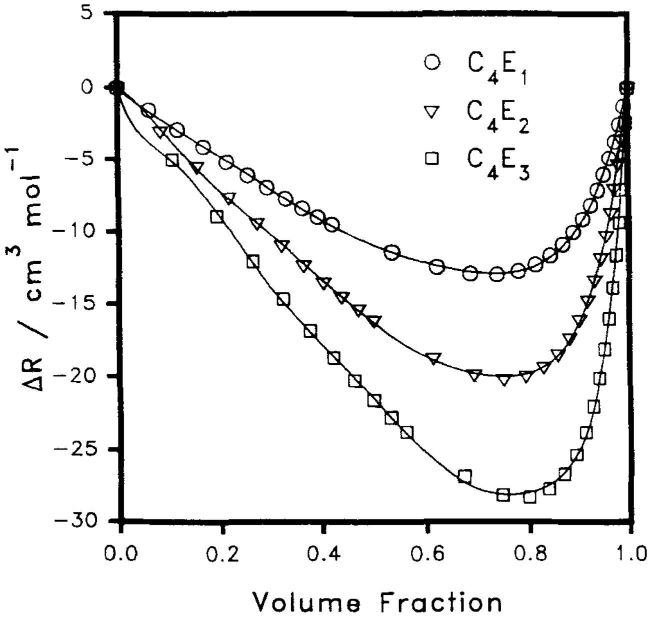

Figure 5 Plot of ΔR vs. Volume Fraction of C_4E_n.

hydrogen-bonded complexes[9]. The observed behaviour of the other excess functions $\Delta(\chi_e V)_m$, P_K^E and P_f^E also leads to the same conclusion.

It has been shown[21,22] that the quantity ΔR is an indication of the modification of the electronic polarizability of the mixtures and in most cases allows one to draw some conclusions concerning the inter and intramolecular forces operating. A negative value of ΔR has been often interpreted[23] as indicative of a tightening of the electronic system. The negative values of ΔR follow the order $C_4E_3 > C_4E_2 > C_4E_1$ (Figure 5). Incidently, the volume contraction (V_E) for these systems also follows the same order, leading to an order of modification of the electronic polarizability as follows: $C_4E_3 + H_2O > C_4E_2 + H_2O > C_4E_1 + H_2O$. Also, an increase of packing density increases the dipole concentration, leading to a lesser negative value $\Delta\varepsilon$ for $C_4E_2 + H_2O$ system compared to $C_4E_1 + H_2O$ system.

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