An Empirical Relation for the Evaluation of the Dielectric Constants of Some Miscible Aqueous-Organic Solvent Mixtures at 298.15 K

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AN EMPIRICAL RELATION FOR THE EVALUATION OF THE DIELECTRIC CONSTANTS OF SOME MISCIBLE AQUEOUS-ORGANIC SOLVENT MIXTURES AT 298.15 K

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Dielectric constants of some miscible aqueous-organic solvent mixtures at 25°C have been analyzed by an equation analogous to Tamura and Kurata equation for viscosity. The hydration numbers n_h found out from the plots of $\Delta\varepsilon$ *vs.* x_2 are explained in terms of H-bonding both in water-rich and alcohol-rich medium.

INTRODUCTION

The dielectric constants of some thoroughly miscible aqueous-organic liquid mixtures are of considerable importance in physical and pharmaceutical chemistry. These liquids are associated. The extent of hydration of water-miscible organic liquid mixtures can be determined from density, viscosity [1] and dielectric constants [2] of these mixtures. The dielectric properties of aqueous-organic solvent mixtures and aqueous solutions of nonelectrolytes have been studied by using mixture formulas of viscosity for polar spheres in non-polar media [3–13].

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Tamura and co-workers [14, 15] have analyzed the viscosity data of binary mixtures of liquids and solutions of nonelectrolytes by the following equations

$$\eta = x_1^2 \eta_1 + 2x_1 x_2 \eta_{12} + x_2^2 \eta_2 \qquad (1)$$

$$\eta = x_1 v_1 \eta_1 + 2(x_1 x_2 v_1 v_2)^{1/2} \eta_{12} + x_2 v_2 \eta_2 \qquad (2)$$

where x_i and η stand for mole fraction and viscosity and subscripts 1, 2 and 12 stand for water, organic liquid and their mixtures respectively. The volume fraction v_2 was calculated by taking the density and weight fraction of the solution and solid respectively.

Equations (1) and (2) fit well the viscosity data at 25°C. Therefore in this paper an attempt is made to analyze the dielectric constant data of some aqueous-organic solvent mixtures at 25°C by the above two equations.

MATERIALS AND METHODS

The dielectric constant data at 25°C are taken from literature [16]. They are represented graphically in Figures 1 and 2 as a function of x_2, the mole fraction of the organic components.

Examination of the figures shows that the dielectric constant of water decreases in an exponential manner which indicates the existence of interaction between the two liquids in the mixtures. The data were analyzed [17] by

$$\log \varepsilon_{12} = x_1 \log \varepsilon_1 + x_2 \log \varepsilon_2 + dx_1 x_2 \qquad (3)$$

which is analogous to the viscosity equation of Grunberg and Nissan [18].

The work of Tamura and coworkers [14, 15] has prompted us to use the viscosity equations for analysis of dielectric constant data of aqueous-organic solvent mixtures by using Eqs. (1) and (2) as

$$\varepsilon = x_1^2 \varepsilon_1 + 2x_1 x_2 \varepsilon_{12} + x_2^2 \varepsilon_2 \qquad (4)$$
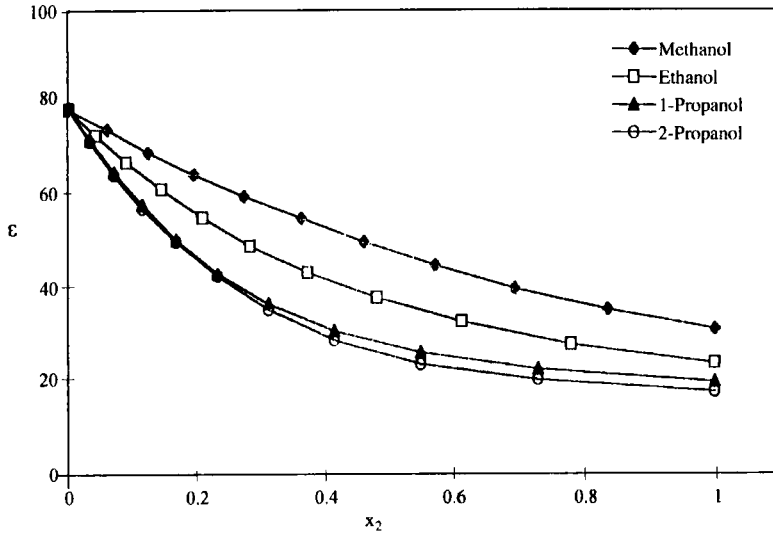
FIGURE 1 ε_{exp} as a function of x_2.
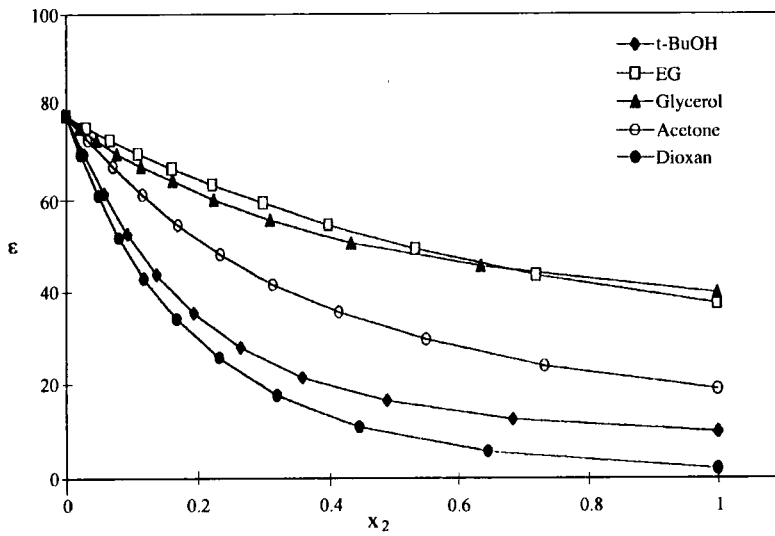
FIGURE 2 ε_{exp} as a function of x_2.

$$\varepsilon = x_1 v_1 \varepsilon_1 + 2(x_1 x_2 v_1 v_2)^{1/2} \varepsilon_{12} + x_2 v_2 \varepsilon_2 \qquad (5)$$

The volume fraction v_2 of the organic component in the mixture was calculated by Looyenga's [6, 7] method as

$$v_2 = (\varepsilon_{12}^{1/3} - \varepsilon_1^{1/3})/(\varepsilon_2^{1/3} - \varepsilon_1^{1/3}) \qquad (6)$$

$$v_1 = (1 - v_2) \qquad (7)$$

The deviations and the percent relative deviations in dielectric constants are calculated as

$$\Delta\varepsilon = \varepsilon_{12\,calc} - \varepsilon_{12\,exp} \qquad (8)$$

$$\text{Relative deviation in } \varepsilon_{12} = 100 \times \frac{\Delta\varepsilon}{\varepsilon_{12\,exp}} \qquad (9)$$

RESULTS AND DISCUSSION

The physical parameters from dielectric constants of some water miscible organic solvents at 25°C are set out in Tables I and II.

The percentage mean relative deviation values clearly show that Eqs. (4) and (5) can be applied to these aqueous-organic solvent mixtures which are thoroughly miscible and associated.

Schott [9] has pointed out while analyzing the viscosity and dielectric constant data by using Kendall equation [13] that deviations in $\Delta\eta$ and $\Delta\varepsilon$ *vs.* x_2 give a useful measure of the extent of hydration

TABLE I Physical parameters of some water-miscible organic solvents at 25°C from Eq. (4)

Organic solvent	ε_2	x_2	n_h	% Mean R.D
Methanol	31.5	0.22, 0.82	3.55, 0.22	6.4
Ethanol	24.3	0.24, 0.90	3.17, 0.11	16.59
1-Propanol	20.1	0.23	3.35	31.17
2-Propanol	18.0	0.23	3.35	33.8
t-Butanol	9.9	0.21	3.76	58.7
Ethylene Glycol	37.7	0.22, 0.85	3.35, 0.18	7.66
Glycerol	40.1	0.22	3.55	10.90
Acetone	19.1	0.23	3.35	21.79
Dioxan	2.1	0.20	4.0	88.57

TABLE II   Physical parameters of some water-miscible organic solvents at 25°C from Eq. (5)

Organic solvent	x_2	n_h	% Mean R.D
Methanol	0.19, 0.80	4.26, 0.25	4.0
Ethanol	0.14, 0.76	6.14, 0.32	7.06
1-Propanol	0.11, 0.73	8.09, 0.37	8.23
2-Propanol	0.11, 0.73	8.09, 0.37	9.6
t-Butanol	0.14, 0.72	6.14, 0.39	20.4
Ethylene Glycol	0.17, 0.73	4.8, 0.37	4.2
Glycerol	0.14, 0.70	6.14, 0.43	2.9
Acetone	0.17, 0.75	4.8, 0.33	10.03
Dioxan	0.16	5.25	48.86

of the organic components in the miscible mixtures. The deviations of the experimental dielectric constants of both the Eqs. (4) and (5) as a function of x_2 are shown in Figures 3–6.

Examination of Figures 3 and 4 indicate that methanol, ethanol and ethylene glycol show both maxima and minima in the mixtures and rest of the organic components show only maxima. Examination of Figures 5 and 6 indicate that all the organic components show both maxima and minima excepting dioxan, which shows only a maxima. The mole fractions x_2 of all the organic components corresponding to maxima and minima are shown in Tables I and II. Compositions of these mole fractions indicate the extent of hydration represented by the hydration number n_h as

$$n_h = x_1/x_2 \tag{10}$$

The hydration numbers of the organic components in the mixture are set out in Tables I and II.

The percentage relative deviations of Eq. (4) are much higher than that of Eq. (5). The hydration numbers obtained by Eq. (4) (Tab. I) are almost same for all the organic components whereas the hydration numbers obtained by Eq. (5) are different from solvent to solvent.

In alcohol–water mixtures the existence of maxima and minima is observed in water-rich regions and alcohol-rich regions respectively [19] which is reflected in the measurement of Walden product and measurement of relaxation times [20]. In aqueous-alcohol solutions, the structure of solutions increases with increasing amount of alcohols
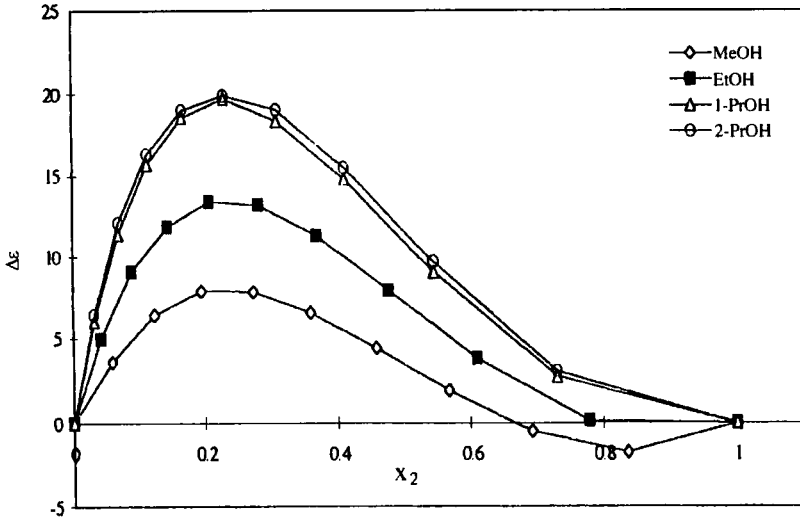
FIGURE 3 $\Delta\varepsilon$ as a function of x_2 for Eq. (4).
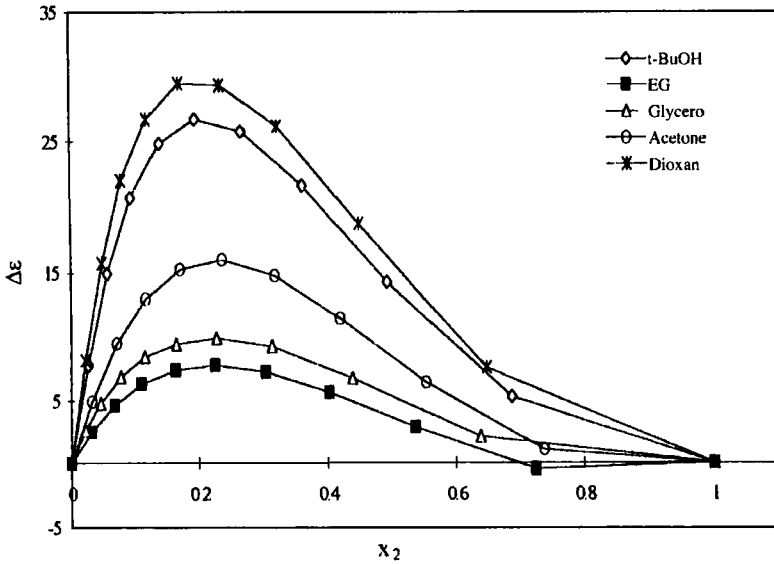
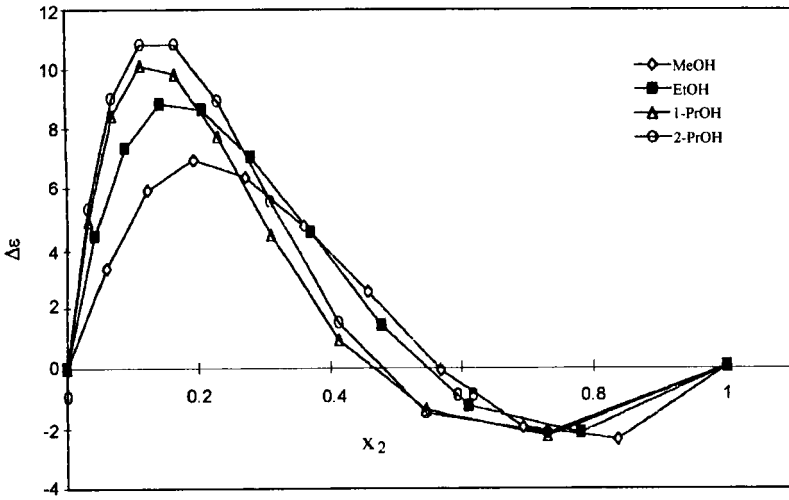FIGURE 4 $\Delta\varepsilon$ as a function of x_2 for Eq. (4).

FIGURE 5 $\Delta\varepsilon$ as a function of x_2 for Eq. (5).
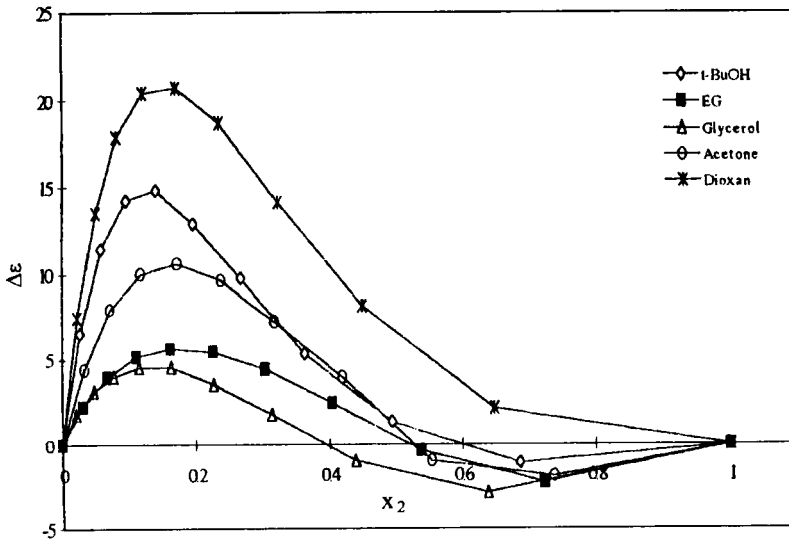

FIGURE 6 $\Delta\varepsilon$ as a function of x_2 for Eq. (5).

[21] and decreases at high alcohol content. It is well known that association of alcohols is governed by the association equilibria:

$$(ROH)_n + ROH \rightleftharpoons (ROH)_{n+1} \qquad (11)$$

It has been shown qualitatively that water re-establishes a three-dimensional H-bonded arrangement in aqueous-alcoholic mixtures which enforces hydrophobic association of the cosolvent molecules [22] represented by

$$(ROH)_{aq} + (ROH)_{aq} \rightleftharpoons (HOR \cdot ROH)_{aq} \qquad (12)$$
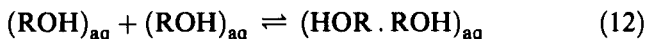
Presumably the equilibria (11) and (12) take place in alcohol-rich and water-rich medium resulting in low and high hydration numbers n_h respectively.

On the basis of the above analogy we conclude that Eq. (5) fits the dielectric constant data of aqueous-organic solvent mixtures well because of low percentage relative deviation and existence of maxima and minima with two hydration numbers which explains the equilibria represented by Eqs. (11) and (12).

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