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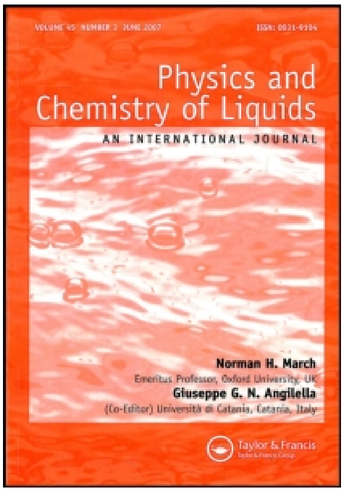

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DIELECTRIC CONSTANTS OF SOME MISCIBLE AQUEOUS-ORGANIC SOLVENT MIXTURES

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The dielectric constants of some aqueous-organic solvent mixtures have been analysed by an equation analogous to Grunberg and Nissan equation. The hydration numbers are found out at the maxima and minima of the plots of $\Delta\varepsilon$ versus x_2. The extent of hydration of organic solvents is discussed in the light of structure of the solvents. It is shown that the equations can be very well applied to aqueous-organic solvent mixtures. An interaction parameter d is defined to fit the dielectric constant data of the mixtures which bears a linear relationship with ε_2.

Keywords: Dielectric constants; aqueous-organic solvent mixtures; hydration number; water structure

INTRODUCTION

The dielectric constants of mixtures of polar – polar liquids is of great importance in physical and pharmaceutical chemistry. These liquids are associated to some extent. The probabilities of the occurrence of A-A, B-B and A-B interactions are expected when two polar liquids A and B are mixed together. The extent of hydration of water-miscible organic liquids can be determined from density, viscosity and dielectric constants of these mixtures.

Hasted [1] has reviewed the dielectric properties of aqueous-organic solvent mixtures and aqueous solutions of non-electrolytes. Certain more modern mixture formulas for polar spheres in non-polar media [2–6] almost give rise to identical results for the volume fraction.

Schott [7] has found out the deviations of experimental dielectric constants using

$$\log \varepsilon_{12} = x_1 \log \varepsilon_1 + x_2 \log \varepsilon_2 \qquad (1)$$

analogous to Kendall equation [8] for viscosity, where x and ε stand for mole fraction and dielectric constants and the subscripts 1, 2 and 12 stand for water, organic liquid and their mixtures respectively. This equation is analogous to that of Arrhenius [9] equation for viscosity and therefore it has a theoretical basis, Grunberg and Nissan [10] modified equation (1) with an interaction parameter d for viscosity as

$$\log n_{12} = x_1 \log n_1 + x_2 \log n_2 + x_1 x_2 d. \qquad (2)$$

The parameter d can be both positive and negative and is a measure of the strength of interaction between two liquids in the solution [11].

The interactions as shown above is not taken care of in equation (1). Survey of literature reveals that the dielectric constant data is not analysed accoding to Grunberg and Nissan equation. Therefore in this paper an attempt is made to analyse the dielectric constant data of some aqueous-organic solvent mixtures by a method analogous to that of Grunberg and Nissan at 25°C.

MATERIALS AND METHODS

The dielectric constant data at 25°C are taken from literature [12]. The data are shown graphically in Figures 1 and 2 as a function of molefraction of the organic components.

The plots indicate that the dielectric constant of water gradually decreases with addition of the organic liquid. The decrease is not linear but exponential. The nature of the curves indicates the existence of interaction between the two liquids. Hence an interaction parameter should explain the non-linearity of the plots. Basing on this analogy the Grunberg-Nissan equation (eqn.(2)) for viscosity [10] can be extended to dielectric constants of solvent mixtures as

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

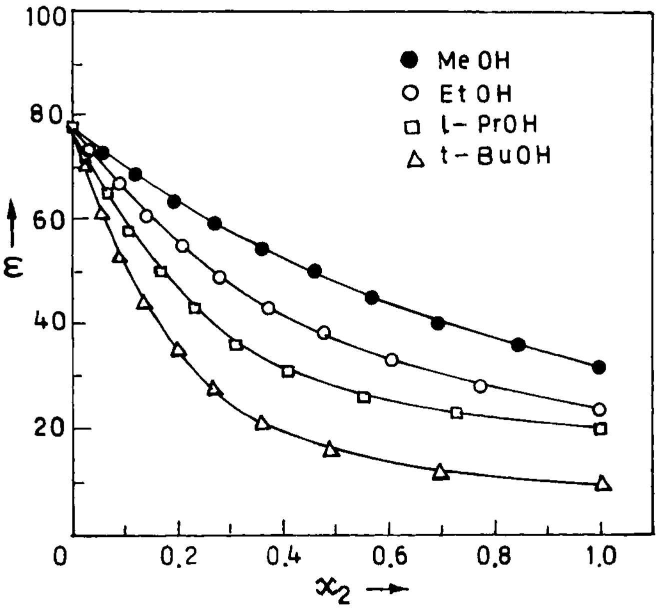

FIGURE 1 ε_{exp} as a function of x_2.

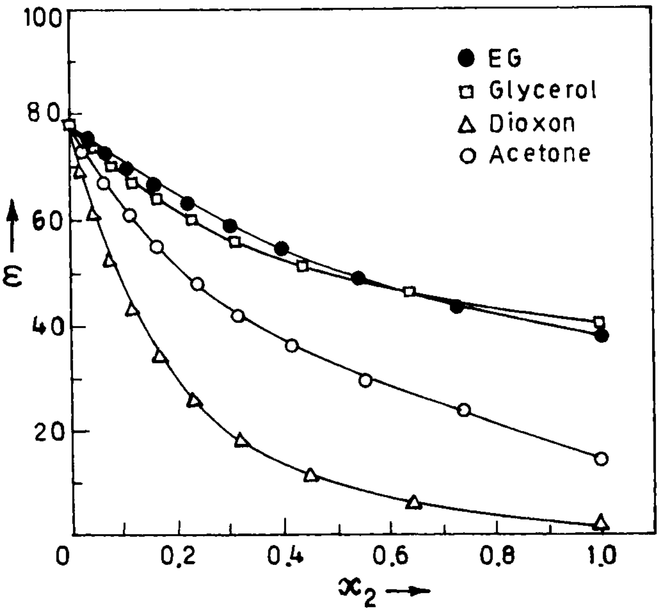

FIGURE 2 ε_{exp} as a function of x_2.

Eqn. (2) is used to calculate the dielectric constants of the mixtures at various compositions. Deviations in dielectric constants are defined as

$$\Delta\varepsilon = \varepsilon_{12\,\text{calc}} - \varepsilon_{12\,\text{exp}} \tag{4}$$

while percent relative deviations in dielectric constants are calculated as

$$\text{Relative deviation in } \varepsilon_{12} = 100 \times \frac{\Delta\varepsilon}{\varepsilon_{12\text{exp}}} \tag{5}$$

RESULTS AND DISCUSSION

The mean of the deviations calculated by eqn. (4) and (5) is given in Table I. The low values of the percent relative deviation clearly show that eqn. (3) can be universally applied to aqueous-organic solvent mixtures which are thoroughly miscible.

The interaction parameter d for different organic solvents is given in Table I. The empirical parameter d is calculated for each composition by the equation.

$$d = \frac{\log(\varepsilon_{\text{cal}}/\varepsilon_{\text{exp}})}{x_1 x_2} \tag{6}$$

TABLE I Physical Parameters from dielectric constants of some water miscible organic solvents at 25°C

Organic Solvent	ε	d	x_2	n_h	*% mean R.D.*
Methanol	31.5	−0.044	0.19,0.69	4.26,0.45	0.70
Ethanol	24.3	−0.230	0,28,0.48	2.57,1.08	2.27
1-Propanol	20.1	−0.525	0.31	2.23	4.58
2-Propanol	18.0	−0.540	0.42	1.38	4.85
t-butanol	9.9	−0.816	0.20	4.00	6.22
Glycerol	40.1	+0.150	0.11,0.23	8.10,3.30	6.29
Ethylene glycol	37.71	+0.060	0.40	1.50	3.63
Acetone	19.1	−0.450	0.42	1.38	12.33
Dioxan	2.1	−1.050	0.20	4.00	3.70

The mean of the d-values was taken for further calculation. It provides a useful measure of the interactions between pairs of miscible liquids reaching a maximum or minimum at the composition of strongest interaction. It is negative for alcohols, acetone and dioxan containing one or no hydroxy groups (groups-I) and positive for glycerol and ethylene glycol (group-II) containing polyhydroxy groups. This confirms the views of Fort and Moore [11]. The plot of d versus ε_2 is shown in Figure 3.

Which shows that d bears a linear relationship with ε_2 empirically as

$$d = 0.03\varepsilon_2 - 1.07 \tag{7}$$

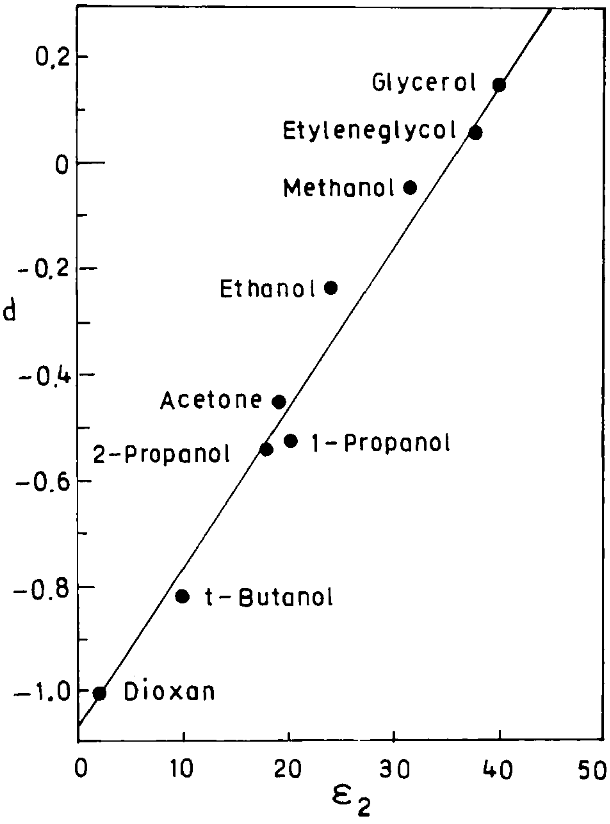

FIGURE 3 d as a function of ε_2.

The empirical parameter d takes into account the interactions A-A, B-B and A-B. The negative values of d for group-I solvents indicate that the interaction A-B dominates over A-A and B-B and for group II compounds the reverse is true. Becuase of the greater interactions between A and B, the water structure gets disrupted by the addition of organic solvents which results in the negative value of d.

The deviations of the experimental dielectric constants are plotted in Figures 4 and 5 as function of x_2.

The figures reveal that there exists maxima in cases of methanol, ethanol, 1-propanol, 2-propanol, *t*-butanol, ethylene glycol, glycerol and minima in case of acetone and dioxan in the solvent mixtures. In case of methanol, ethanol and glycerol there exists two maxima in the aqueous solvent mixtures. Compositions corresponding to these

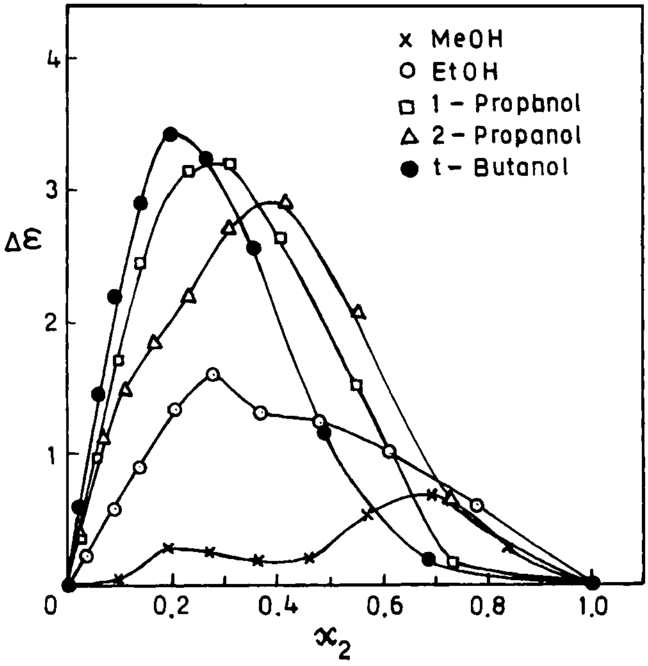

FIGURE 4 $\Delta\varepsilon$ as a function of x_2.

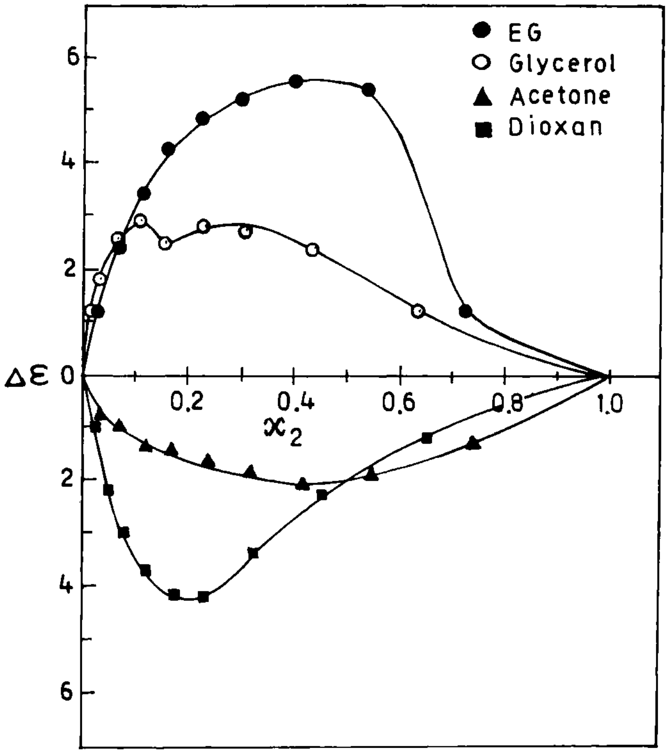

FIGURE 5 $\Delta\varepsilon$ as a function of x_2.

maxima and minima determine the extent of hydration and thus the hydration number n_h can be calculated from

$$n_h = x_1/x_2 \tag{8}$$

The vlaues of n_h are set out in Table I. In case of methanol, ethanol and glycerol, there are two hydration numbers: one for the water-rich region and the other for the organic solvent-rich region. It is well known that association of alcohols is governed by the association equilibria:

$$(\mathrm{ROH})_n + \mathrm{ROH} \rightleftharpoons (\mathrm{ROH})_{n+1} \tag{9}$$

Organic liquids interact with water through hydrogen bonds as OH...O. Because of the association equilibrium (Eqn.-9) there exists two maxima in case of methanol, ethanol and glycerol due to two values of n. The water-alcohol mixtures are treated as heterogeneous mixtures. The pure alcohol is conceived as containing vary long molecular chains which can penetrate into the three dimensional network structure of water and the water structure gets disrupted at higher concentrations of organic solvents,

Thus one can get the value of d from eqn. (7) using the known value of the dielectric constant ε_2 of the organic component and utilise this value in eqn.(3) to calculate the dielectric constants of water- organic solvent mixtures at various compositions.

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