Research Note

A SIMPLE MODEL FOR THE ESTIMATION OF DIELECTRIC CONSTANTS OF BINARY SOLVENT MIXTURES

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Abstract

A simple and reliable method for quick estimation of the dielectric constant of a binary solvent mixture is proposed. The validity of the proposed method has been tested for a broad range of binary solvent mixtures.

Dielectric constants play a particular role in the characterization of solvents. They govern the magnitude of all electrostatic interactions in solution and, therefore, greatly influence the rates of chemical reactions as well as the chemical equilibria in solutions [1]. The dielectric constants for solution dipole moment studies are commonly determined by resonance or heterodyne methods [2, 3].

Recently, there has been increasing interest in the study of physico-chemical phenomena in binary mixed solvent systems and in their interpretation in terms of solutes' preferential solvation by one of the mixed solvent components [4-8]. In this connection, having information about the polarity of the solvent mixture, as expressed by its dielectric constant, is of fundamental importance. The dielectric behavior of solvent mixtures according to the Kirkwood-Frohlich statistical theory has been discussed previously [9]. However, there are some practical difficulties associated with such approaches to the polarity of mixed solvents.

In this communication, we propose a rather simple model for quick estimation of the dielectric constant of a binary solvent mixture. The validity of the method has been tested for a wide variety of solvent mixtures.

In this model, we suppose that a binary mixture of solvents S_1 and S_2 with respective weight percents w_1 and w_2 are inserted between the two charged plates of a capacitor of area A and distanced. It seems then reasonable to take this capacitor to be a parallel combination of two smaller capacitors with respective areas of A_1 and A_2 and distance d so that

$$A= A_1 + A_2 \quad (1)$$

in which A_1 and A_2 are areas occupied by solvent components S_1 and S_2 in their binary mixture. The total capacitance of the system can be written as

$$C= C_1 + C_2 \quad (2)$$

or

$$\varepsilon A/d= \varepsilon_1 A_1/d + \varepsilon_2 A_2/d \quad (3)$$

where ε, ε_1 and ε_2 are the dielectric constants of the solvent mixture, pure S_1 and pure S_2, respectively. Rearrangement of Equation (3) results in

$$\varepsilon= \varepsilon_1 A_1/A + \varepsilon_2 A_2/A \quad (4)$$

If we assume that the fractions of area occupied by S_1 and S_2 (i.e., A_1/A and A_2/A) are proportional to the weight percents w_1 and w_2 of the solvent components, we get

Keywords: Binary solvents; Dielectric constant; Weight percent

Table 1. The observed and expected equations for different binary solvent mixtures

Solvent System	Observed Equation	Regression Coefficient	Expected Equation	Ref.
Water-Acetone	$\varepsilon = 79.5 - 0.599\ w_2$	0.9998	$\varepsilon = 78.5 - 0.594\ w_2$	10, 11
Water-Acetonitrile	$\varepsilon = 78.1 - 0.431\ w_2$	0.9986	$\varepsilon = 78.5 - 0.425\ w_2$	12
Water-Dioxane	$\varepsilon = 78.5 - 0.844\ w_2$	0.9999	$\varepsilon = 78.5 - 0.763\ w_2$	13, 14
Water-Ethanol	$\varepsilon = 77.5 - 0.553\ w_2$	0.9987	$\varepsilon = 78.5 - 0.542\ w_2$	15, 16
Water-Methanol	$\varepsilon = 79.0 - 0.458\ w_2$	0.9998	$\varepsilon = 78.5 - 0.459\ w_2$	17
Water-Tetrahydrofuran	$\varepsilon = 78.5 - 0.742\ w_2$	0.9988	$\varepsilon = 78.5 - 0.709\ w_2$	18, 19
Water-Propanol	$\varepsilon = 78.6 - 0.594\ w_2$	0.9924	$\varepsilon = 78.5 - 0.581\ w_2$	20
Water-Ethylene Glycol	$\varepsilon = 80.3 - 0.373\ w_2$	0.9922	$\varepsilon = 78.5 - 0.378\ w_2$	21
Water-Glycerol	$\varepsilon = 80.6 - 0.348\ w_2$	0.9846	$\varepsilon = 78.5 - 0.361\ w_2$	21, 22
Acetone-Dioxane	$\varepsilon = 20.4 - 0.183\ w2$	0.9999	$\varepsilon = 20.5 - 0.183\ w_2$	23
Actonitrile-Dioxane	$\varepsilon = 36.2 - 0.316\ w_2$	0.9992	$\varepsilon = 36.0 - 0.338\ w_2$	23, 24
Ethanol-Acetonitrile	$\varepsilon = 24.1 + 0.114\ w_2$	0.9986	$\varepsilon = 24.3 + 0.118\ w_2$	12
Methanol-Acetonitrile	$\varepsilon = 32.6 + 0.033\ w_2$	0.9973	$\varepsilon = 32.7 + 0.053\ w_2$	12, 25
Dimethylformamide-Dioxane	$\varepsilon = 36.4 - 0.361\ w_2$	0.9989	$\varepsilon = 36.7 - 0.345\ w_2$	26
Formamide-Dioxane	$\varepsilon = 107.9 - 1.283\ w_2$	0.9986	$\varepsilon = 109.5 - 1.073\ w_2$	27
Ethanol-Methanol	$\varepsilon = 23.9 + 0.077\ w_2$	0.9967	$\varepsilon = 24.3 - 0.083\ w_2$	28
Formamide-Acetamide	$\varepsilon = 109.5 - 0.351\ w_2$	0.9996	$\varepsilon = 109.5 - 0.360\ w_2$	29
Methanol-Dioxane	$\varepsilon = 32.9 - 0.335\ w_2$	0.9995	$\varepsilon = 32.7 - 0.305\ w_2$	30

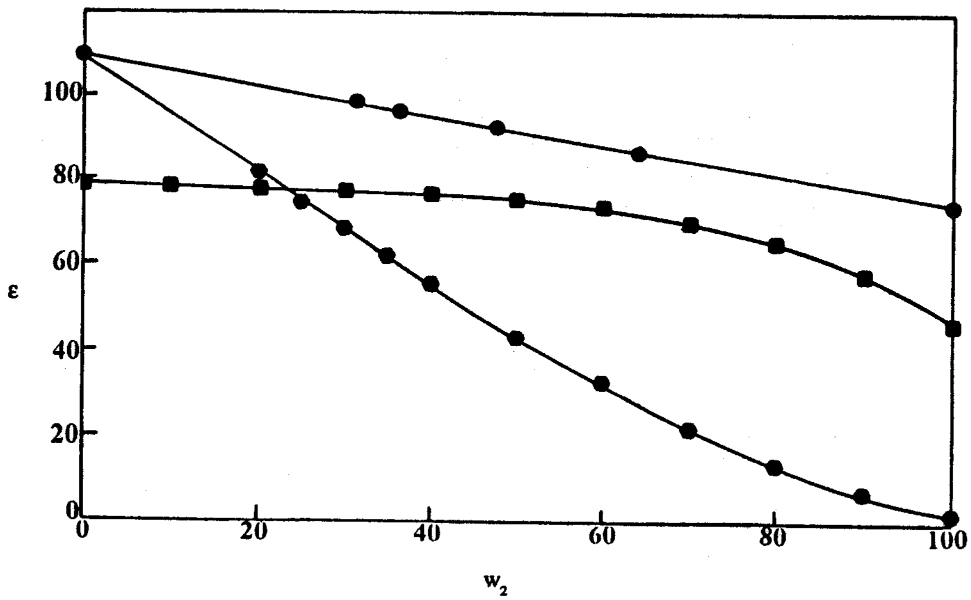

Figure 1. Plots of mixed solvent dielectric constant vs. weight percent of the second component for formamide-acetamide (●, 29), formamide-dioxane (◆, 27) and water-dimethylsulfoxide (■, 31) systems

$$\varepsilon = \varepsilon_1 w_1/100 + \varepsilon_2 w_2/100 \quad (5)$$

Knowing that

$$w_1 + w_2 = 100 \quad (6)$$

the relationship between the dielectric constant of the solvent mixture, ε, and the weight percent of one of the mixture components, w_2, will be

$$\varepsilon = \varepsilon_1(100 - w_2)/100 + \varepsilon_2 w_2/100 \quad (7)$$

or

$$\varepsilon = \varepsilon_1 - (\varepsilon_1 - \varepsilon_2)w_2/100 \quad (8)$$

According to Equation (8), a plot of the solvent mixture's dielectric constant vs. the weight percent of one of the solvent components should result in a straight line with the slope of $(\varepsilon_1 - \varepsilon_2)/100$ and intercept of ε_1.

In order to test the validity of Equation (8) in the estimation of the dielectric constants of binary solvent mixtures, the reported measured values for the dielectric constants of 20 different binary solvent systems were plotted vs. the weight percent of one of the solvent components in each case. With the exception of water-dimethylsulfoxide and formamide-dioxane systems, in all other cases, a fairly linear plot was obtained. The resulting regression equations are compared with the corresponding expected equations, according to the Equation (8), in Table I. As it is seen, there is a satisfactory agreement between the resulting regression equations and the corresponding expected equations, emphasizing the validity of Equation (8) in prediction of the dielectric constants of different mixed solvents.

The nonlinear plots of ε vs. w_2 for water-dimethylsulfoxide and formamide-dioxane mixtures as well as a typical linear graph (for formamide-acetamide system) are shown in Figure 1. The deviations from linear behavior observed in these two cases could be related to the specific association of dimethylsulfoxide and formamide molecules, at a given composition range of the corresponding binary mixtures, which results in rather distinct and unusual change in their polarities [33, 34].

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