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Dielectric studies on binary polar mixtures of propanoic acid with esters

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Abstract

It is interesting to see the nature of intermolecular interactions between associative and non-associative polar liquids. Binary polar–polar liquid mixtures of ethyl acetate, ethyl benzoate, ethyl acrylate, ethyl butyrate, *n*-butyl acetate and benzyl benzoate, each with propanoic acid were subjected to dielectric studies at temperatures 25 °C, 35 °C and 45 °C. Static permittivity (ε_o) and dielectric constant at high frequency (ε_∞) were found through dielectric measurements for different concentrations of each system. The Bruggeman dielectric factor, Kirkwood correlation factor and the excess permittivity were determined. Deviations from the linearity of various models suggest molecular association through hydrogen bonding between the polar–polar constituents of the mixtures. The formation of cyclic and linear α-multimers in the above systems were identified. The results and their temperature dependence were interpreted accordingly.

Keywords: Permittivity; Propanoic acid; Hydrogen bond; Kirkwood correlation factor

1. Introduction

The dielectric study of binary polar–polar liquid mixtures provides information regarding intermolecular interactions, both in hetero and homo modes, and the consequent structural rearrangement of molecules. Propanoic acid is an associated polar liquid with an –OH group as well with a C=0 bond. Esters are non-associated polar liquids with C=0 group. It is interesting to see the nature of interactions between propanoic acid and ester molecules.

This paper reports a dielectric study of the binary polar–polar liquid mixture of propanoic acid with each of the following six esters at temperatures 25 °C, 35 °C and 45 °C: (1) ethyl acetate (2) ethyl benzoate (3) ethyl acrylate (4) ethyl butyrate (5) *n*-butyl acetate and (6) benzyl benzoate.

The results for various concentrations and temperatures are discussed using three linear models based on the modified Bruggeman equation, the Kirkwood correlation factor and the excess permittivity.

2. Materials and methods

The dielectric constants were determined at 1 kHz using a VLCR-7 meter supplied by Vasavi Electronics, Secunderabad, India. A water circulated thermostat was used to maintain the temperature at 25 ± 1 °C, 35 ± 1 °C and 45 ± 1 °C. The refractive indices were measured using an Abbe refractometer. Densities were determined using a 10 ml specific gravity bottle and a K-Roy microbalance. The error in the measurement of density was ±0.0002 gm/cc. The uncertainties in the measurement of dielectric constants and refractive indices were ±0.0005 and ±0.0002 respectively. The chemicals used were purified by standard procedures.

3. Theory

The structural rearrangement of molecules and the emerging fluid structure when two polar liquids are mixed could be readily studied by dielectric measurements by virtue of the influence of local order and the overall dipole moment. The static permittivity of the two component mixture may lie somewhere between two extreme corre-

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sponding to static permittivity of the two liquids. In order to understand the dipole interaction in the mixture of two polar liquids, various mixture formulae have been proposed [1]. The non-linear behaviour of a binary mixture of polar liquids as a function of mole fraction at different temperatures could be studied using various linear models [2].

3.1. The modified Bruggeman model

According to the Bruggeman mixture formula of static permittivity, the Bruggeman dielectric factor f_B is given by [3],

$$f_B = \left(\frac{\varepsilon_{om} - \varepsilon_{o2}}{\varepsilon_{01} - \varepsilon_{O2}}\right)\left(\frac{\varepsilon_{ol}}{\varepsilon_{om}}\right)^{1/3} = [1 - X_2] \tag{1}$$

where the mole fraction X_2 is used in place of volume fraction. In fact, mole fraction X_2 is a qualitative measure of volume fraction of the solute. ε_{om}, ε_{o1} and ε_{o2} respectively are the values of static permittivity corresponding to mixture, solvent and solute. This Bruggeman equation assumes that orientation of the solvent molecules does not change in the mixture. This is only true for the non-polar solvent. When both the solvent and the solute happen to be polar liquids, the Bruggeman equation has to be modified as [4,5]

$$f_B = 1 - [a - (a-1)X_2]X_2 \tag{2}$$

where 'a' is the interaction parameter.

The numerical fitting parameter 'a' signifies change in volume, that is, the change in the orientation of the constituent molecules and thus measures the extent of the dipole interaction of the constituent polar liquids of the binary mixture in terms of size of molecules and their occupation of volume [5]. This dipole–dipole interaction may be between the –OH group of acid with C=O of the ester.

3.2. The Kirkwood model

The short-range interaction between dipoles could be described by the Kirkwood correlation factor. The Kirkwood theory of dielectric polarization follows the statistical mechanical approach. This was later modified by Froehlich [6]. The Kirkwood–Froehlich treatment takes care of short-range correlations like hydrogen bonding through the introduction of the dimensionless correlation parameter 'g'.

For a pure polar liquid, the Kirkwood correlation factor 'g' may be obtained by the expression [7],

$$\frac{4\pi N\mu^2\rho}{9kTM}g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_o + \varepsilon_\infty)}{\varepsilon_o(\varepsilon_\infty + 2)^2} \tag{3}$$

where μ is dipole moment, ρ is density at temperature T, M is molecular weight, k is Boltzman constant, N is Avogadro's number, ε_o is static dielectric constant and ε_∞ is the dielectric constant at high frequency, often represented by the square of refractive index.

For the mixture of two polar liquids (1) and (2), Eq. (3) is modified by Kumbharkhane et al., with the following assumptions [8–10].

Assuming that for the mixture, g^{eff}, is the effective Kirkwood correlation factor in the mixture, the Kirkwood equation for the mixture may be expressed as

$$\frac{4\pi N}{9kT}\left[\frac{\mu_1^2\rho_1}{M_1}X_1 + \frac{\mu_2^2\rho_2}{M_2}X_2\right]g^{\text{eff}} = \frac{(\varepsilon_{om} - \varepsilon_{\infty m})(2\varepsilon_{om} + \varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m} + 2)^2} \tag{4}$$

X_1 and X_2 are mole fractions of liquids (1) and (2) respectively in the mixture. The suffixes m, 1 and 2 represent mixture, liquid 1 (propanoic acid) and liquid 2 (the respective ester) respectively. g^{eff} changes from g_1 to g_2 as X_2 increases from zero to one.

Assuming that g_1 and g_2 are affected by an amount g_f in the mixture, the corrective Kirkwood correlation factor g_f for the mixture is given by the following Kirkwood equation for the mixture [6].

$$\frac{4\pi N}{9kT}\left[\frac{\mu_1^2\rho_1 g_1}{M_1}X_1 + \frac{\mu_2^2\rho_2 g_2}{M_2}X_2\right]g_f = \frac{(\varepsilon_{om} - \varepsilon_{\infty m})(2\varepsilon_{om} + \varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m} + 2)^2}. \tag{5}$$

The value of g_f remains close to unity, if there is no heterogeneous interaction between the liquids (1) and (2). The deviation from unity indicates the interaction between molecules of liquids (1) and (2). [11].

3.3. The excess permittivity

The information related to the heterogeneous interaction may also be obtained by the value of excess permittivity [12]. The excess permittivity ε^E is defined as

$$\varepsilon^E = (\varepsilon_o - \varepsilon_\infty)_m - \left[(\varepsilon_o - \varepsilon_\infty)_1 X_1 + (\varepsilon_o - \varepsilon_\infty)_2 X_2\right]. \tag{6}$$

The excess permittivity provides qualitative information about multimer formation in the mixture [13].

4. Results and discussion

The values of dipole moment for the liquids studied were taken from the literature [14,15].

The determined values of static dielectric constant (ε_o) and dielectric constant at high frequency (ε_∞) for solutions of different concentrations of ethyl acetate, ethyl benzoate, ethyl acrylate, ethyl butyrate, *n*-butyl acetate and benzyl benzoate, each in propanoic acid at different temperatures (25 °C, 35 °C and 45 °C), are presented in Tables 1 and 2.

The static dielectric constant for the mixtures increases towards the dielectric constant of the respective ester. Increase of dielectric constant is due to the transition of spherical molecular aggregates into elongated aggregates giving rise to parallel orientation of the dipoles. Similar