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Studies on Dielectric Behaviour of Some Long Chain Alcohols and Their Mixtures With a Non-Polar Solvent at Various Concentrations

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Abstract. Dielectric constant, refractive index and the Kirkwood linear correlation factor of 1-propanol, 1-butanol and 1-pentanol in mixtures with carbon tetrachloride at various concentrations have been measured at fixed frequency (100 KHz) at 303.15 K. For the study of dielectric properties of polar molecules in a non-polar solvent at different concentrations, polarization per unit volume and excess free-energy of mixing were evaluated at this temperature. In order to study the association of polar molecules in such a non-polar solvent, the Kirkwood correlation factor (g) between molecular pairs, which exists due to the hydrogen bond association suggesting the presence of some dimensions in the liquid phase with a number of dimmers, was determined. The refractive index and dielectric constant measurements are expected to shed some light on the configuration of molecules in various mixtures, and give some idea about the specific interactions between components, which decrease with the increase in the concentrations of alcohol. All the three mixtures showed different behaviour for the value of correlation factor (g) as a function of concentration. The response of 1-pentanol was broadly identical to that of small chain alcohols. The different behaviour of the correlation factor (g) was interpreted in terms of the Kirkwood-Frohlich theory, as it takes into account, explicitly, such types of short and long range interactions of a mixture of polar molecules with non-polar solvents.

Keywords: polar and non-polar molecules, polarization, KF linear correlation factor, short range dipolar interaction, binary mixture, long range dipolar interaction

Introduction

Relative permittivity of binary liquid mixtures of some associated liquids with a non-polar solvent (non-polarizable system) is generally used to evaluate the Kirkwood-Frohlich linear correlation factor (g), the excess molar polarization (Δp), and excess free-energy of mixing (Δf) (Ray *et al.,* 2000). The results so obtained have been used to interpret the molecular structure in such types of liquid mixtures. The technique has been reported to be used to study small chain alcohols (Sebesan *et al.,* 1979). However, little work has been reported on long chain alcohols. There has been a significant interest during the last two decades to characterize the intermolecular forces underlying therein. There is a need, therefore, to investigate the physical and chemical properties of long chain molecules in liquid mixtures and particle suspension in a host medium with regard to their dielectric response.

Characterization of dielectric properties of pure polar fluids and their mixtures is a major dimension of study in the area of liquid physics. New models to describe the general behaviour of polar mixtures (alcohol/water) have been developed (Sato *et al.,* 2002). Within this context, the dielectric relaxation mechanism of 2-propanol + water mixture has been investigated using time domain reflectometry for the entire range of concentrations. The connection between the dielectric properties and molecular structure for permittivity of liquids involves short range and long range dipolar interactions, which have been calculated by Garabadu and Swain (1993).

The activation enthalpies (ΔH) and entropies (ΔS) have been calculated against concentrations of a polar liquid (1-propyl alcohol) in benzene, which increases with increase in the concentration of polar molecules (Swain, 1984). Kirkwood (1939) had earlier suggested that the static permittivity of a polar fluid could be calculated by using statistical mechanics. It was considered that in a way, a sample consists of (n) number of molecules contained in a spherical region of the fluid, while the remaining molecules were assumed to constitute a continuum extending to infinity with permittivity (ε) and dipole moment (μ). By the application of this assumption, the intermolecular interaction between the (n) number of molecules can be considered. Taking (n) as very large, the approximation of such an assumption can be reduced to a desired degree. Suppose, the spherical region has a permittivity (ε_α) due to molecular polarization, then the point dipoles with dipole moment (μ) replace each polar molecule. The orientation of each molecule, due to the short range forces, forms a

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correlation factor (g), which is defined in the following equation (Chakrabarty *et al.,* 2000).

$$\overset{i = n}{g = \Sigma \cos \theta ij} \qquad (1)$$

where:

θij = the angle between the orientation of the molecules averaged over the whole medium
n = number of molecules

It has been observed in literature that considerable number of liquids can be described by the hard sphere model, and can be compared with computer simulation (Swain and Ray, 1986; Swain, 1984; Perram and Anastasiou, 1981). This is due to the partial compensation between different factors among which can be included the presence of real (not ideal) multipoles, and the non-spherical shape of molecules and their flexibility. Hence, the linear correlation factor (g) is a shape-dependent parameter that helps in a qualitative interpretation of liquid structures. In liquid mixtures where (g) is less than 1, the predominance of β-multimers with anti-parallel dipole orientation indicates the shape of molecules (Swain and Ray, 1986). A brief account of the approach, which will be used to measure the static permittivity of polar liquids (long chain alcohols), 1-propanol alcohol, 1-butyl alcohol and 1-pentanol, and their mixtures with carbon tetrachloride is discussed in the present paper. Kirkwood (1939) and Oster (1946) have earlier discussed the dielectric polarization of polar liquids, through the role of the hindered molecular rotation.These studies have shown that permittivity can be expressed by means of short range forces, which constitute a part of the two-particles correlation function (Neinhuis and Deutch, 1971), which is despite the fact that the molecular interactions can strongly influence the two-particles correlation function.

Calculations. The value of (g) for polar liquids has been calculated in three mixtures. This is a well known Kirkwood linear correlation equation, which relates the dipole moment of the molecules and the value of (g) to the static permittivity of polar liquids (ε_s), once the dipole moment of the gas phase (μ_g) is known (Nath and Dubey, 1980).

$$g = \frac{(\varepsilon_0 - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} - \frac{4\pi N \mu_g^2}{9KTV\varepsilon_0} \qquad (2)$$

where:

ε_0 = permittivity of free space
K = Boltzman constant = 1.38065031 x 10^{-23} m^2kg/sec^2/kelven
ε = dielectric constant of liquid mixtures
N = Avogadro number = 6.022x10^{23}/mole
V = one molal volume
T = absolute temperature
n = number of molecules/volume of the polar fluid
μ_g = gas phase dipole moment of polar molecules

The value of u_g for CCl_4 is 0.54 Debye, and for 1-propanol is 1.113 Debye, for 1-butanol is 1.313 Debye and for 1-pentanol is 1.443 Debye. Equation (2) was used for the calculation of Kirkwood correlation factor (g). The molal volume of mixtures used in equation (2) was estimated from the molal volume of the pure components and the measurements of excess volumes for the three systems (Nath and Dubey, 1980).

For a polar liquid, the value of $g \geq 1$ shows that the molecules tend to align with parallel dipole moments, which depends on its concentration and high dipole moment. It indicates the predominance of α-multimers with parallel dipole orientation. When the molecules tend to order themselves with anti-parallel dipoles, the value of (g) will be smaller than 1. The value of (g) decreases, goes through a minimum, increases again, and at further dilution becomes 1. In liquids where (g) is less than 1, it indicates the predominance of β-multimers with anti-parallel dipole orientation. The value of (g) is unity for normal liquids, while it departs from unity in abnormal or associated liquids (Bottcher, 1973).

Calculation of dipole moment of the molecules. The minimum value of (g) corresponds to concentration where the Clausius Mossotti relation holds for the mean value of the local field (ε + 2 /3) (Cole, 1965).

$$\varepsilon - 1 = \frac{n/\varepsilon_0(\varepsilon+2)(\alpha+\mu_g^2)}{3KT} \qquad (3)$$

where:

ε_0 = static permittivity
α = polarizability
μ_g = molecular dipole moment
T = absolute temperature
K = Boltzman constant
Other symbols are the same as used for equation (2)

Materials and Methods

Chemicals. All the chemicals used were of Analar grade (BDH). These were dehydrated by the usual methods and fractionally distilled prior to their use. Conventional procedures were followed for standardization of the set-up for purification of the samples.

Refractive index measurements. The refractive index measurements were carried out by using a thermostated Abbe's refractometer at 303.15 K. The value of (n) refractive index was determined for sodium D-lines, the wavelengths being λ = 5892 Å and 5898 Å. Values of the refractive indices of the two components, n_{12} alcohols and their mixtures with CCl_4 were put to the empirical equation:

$$n_{12} = x\, n_1 + (1 - x)\, n_2 + x\,(1 - x)\, A \qquad (4)$$

where:

n_{12} = value of refractive index of the mixture
n_1 and n_2 = values of the refractive indices of the individual components of the mixture
A = a constant, which is the characteristic of the system (Nath and Dubey, 1980)
n = mole fraction of component 1 (alcohols)

The following refractive indices were observed at the temperature of 303.15 K: 1-propanol = 1.3830; 1-butanol = 1.3968; 1-pentanol= 1.3397. These values are in good agreement with those reported in the literature. The expression derived by Winkelmann and Quitzesch (1976) was used to calculate Δf (excess free-energy).

Measurement of dielectric constants. The method of capacitance variation in a tuned circuit, a square law mirror voltmeter being used as the resonance indicator, was applied for the measurement of dielectric constant. The dielectric constant is measured as the ratio of change in capacitance $\Delta c/\Delta c_0$. The test set consisted of an oscillator, which was inductively coupled to a tuned LC test circuit. Observations were taken for measuring the dielectric constant (ε_s) of the liquid, when there was resonance in the circuit. The resonance curve was first determined when the liquid was not in between the metallic electrodes. The sample was then poured in between moving electrodes and was set to get resonance. Since the liquid had high permittivity, a parallel supplementary capacitor of 100 pf was also placed to reach a point of resonance. To prevent losses from evaporation, the capacitance jig was kept within an air tight desiccator (Ahmad *et al.,* 2001).

For the evaluation Δf and Δp, the Winkelmann Quitzsch (1976b) equation was used for excess thermodynamic function in a binary mixture.

Results and Discussion

Since the Kirkwood correlation factor (g) is a measure of the degree of alignment of molecules in the liquid, it is related with dielectric constant or permittivity and refractive index of a fluid by equation (2). In order to ascertain the degree of orientation of a dipole in the pure polar liquid and their binary mixtures with a non-polar solvent, the value of (g) was determined using equation (1). These values have been recorded in Tables 1-3. It has been demonstrated how the correlation factor (g) was involved in the orientation of the neighboring molecules, which diminished the contribution of individual molecular dipoles.

The value of (g) increases in more dilute solutions, where the dipoles become free from each other and they are completely unhindered in their rotation at infinite dilution (Sabesan *et al.,* 1979). The value of (g) in pure 1-propanol, 1-butanol and 1- pentanol was greater than 1, and was maximum at the highest concentration of the polar molecules, which is in accordance with the Oster's theoretical curve (Oster, 1946). The minimum value of (g) occurred at the lowest concentration of

Table 1. Variations in the dielectric constant (ε_s), Kirkwood linear correlation factor (g), polarization per mole (Δp) and free energy of mixing (Δf: Joule/mole) for 1-propanol in mixture with CCl_4 (solvent) in a range of concentrations at 303.15 K (frequency = 100 KHz; refractive index of 1-propanol = 1.3830)

Concentration of 1-propanol (mole fraction)	ε_s	g*	Δp* (cm^3/mole)	Δf* (Joule/mole)
0.06	2.212	3.01	4.08	45.38 0.11
2.820	2.75	5.62	73.12	
0.221	3.502	2.63	7.57	131.44
0.330	4.773	2.22	9.05	169.99
0.441	4.954	2.05	10.53	209.33
0.550	5.501	1.95	7.65	231.88
0.66	7.722	2.65	5.59	225.44
0.77	9.535	3.05	4.97	207.11
0.88	12.243	3.75	2.77	154.55

* = calculated values

Table 2. Variations in the dielectric constant (ε_s), Kirkwood linear correlation factor (g), polarization per mole (Δp) and free energy of mixing (Δf: Joule/mole) for 1-butanol in mixture with CCl_4 (solvent) in a range of concentrations at 303.15 K (frequency = 100 KHz; refractive index of 1-butanol = 1.3968)

Concentration of 1-butanol (mole fraction)	ε_s	g*	Δp* (cm^3/mole)	Δf* (Joule/mole)
0.05	2.231	4.01	3.55	37.21
0.11	2.447	3.77	4.73	53.22
0.22	2.743	3.21	6.91	178.88
0.33	3.121	2.97	9.24	217.31
0.44	3.854	3.33	8.11	268.22
0.55	4.422	2.47	7.44	300.11
0.66	7.888	3.832	5.11	200.21
0.77	11.75	4.53	3.77	198.44

* = calculated values

Table 3. Variations in the dielectric constant (ε_s), Kirkwood linear correlation factor (g), polarization per mole (Δp), and free energy of mixing (Δf: Joule/mole) for 1-pentanol in mixture with CCl_4 (solvent) in a range of concentrations at 303.15 K (frequency = 100 KHz; refractive index of 1-pentanol = 1.4080)

Concentration of 1-propanol (mole fraction)	ε_s	g*	Δp* (cm^3/mole)	Δf* (Joule/mole)
0.05	2.241	2.02	3.67	50.17
0.1	2.587	1.87	6.74	113.43
0.22	3.764	1.65	7.89	145.66
0.33	4.276	1.73	8.97	221.17
0.44	5.665	2.15	9.11	243.55
0.55	7.311	2.33	8.31	365.77
0.66	9.776	3.42	6.22	251.33
0.77	11.223	4.67	3.33	201.44
0.88	12.754	5 88.	2.62	145.55

* = calculated values

the polar component, since it was necessary to dilute the liquid mixture in order to allow the dipoles to orient themselves in their anti-parallel position. At further dilution, the tendency to arrange themselves was decreased. For a polar liquid, the value of $g \geq 1$ depends on its concentration and has high dipole moment. The value decreases, goes through a minimum increase again and at further dilution becomes 1. When the value of (g) is greater than 1, it indicates the predominance of α-multimers with parallel dipole orientation. In liquids where (g) is less than 1, it indicates the predominance of β-multimers with anti-parallel dipole orientation. The value of (g) is unity for normal liquids, while it departs from unity in abnormal or associated liquids (Bottcher, 1973).

The Winkelmann Quitzsch equation (Winkelmann and Quitzsch, 1976a; 1976b) was used for the evaluation of excess thermodynamic function in binary mixtures and to calculate free energy of mixing (Δf) that takes in to account the contribution due to both short-range and long-range dipolar interactions between both like and unlike molecules (Ray *et al.,* 2000). The value of (Δf) was positive in all the mixtures studied, attaining maximum at nearly equi-molar range of concentration. This value has been used for the evaluation of excess free energy (Δf) in the polar and non-polar mixtures (Swain and Ray, 1986). The results so obtained have been used to interpret liquid structure in such mixtures.

Conclusion

In brief, under similar conditions within the effect of polarization, the following were noted on the application of Onsager

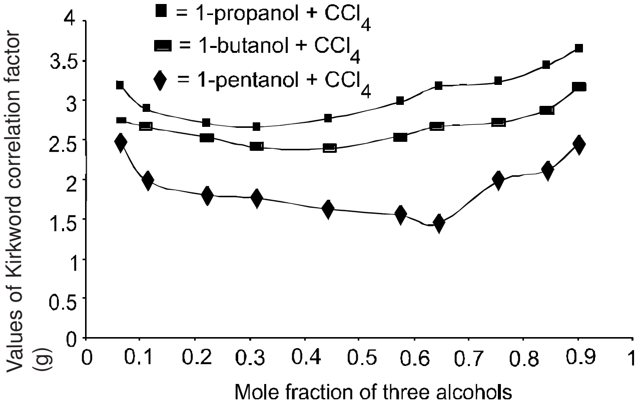

Fig. 1. The variation of Kirkwood correlation factor (g) with concentrations of three alcohols in mixture with CCl_4 at 303.15 K.

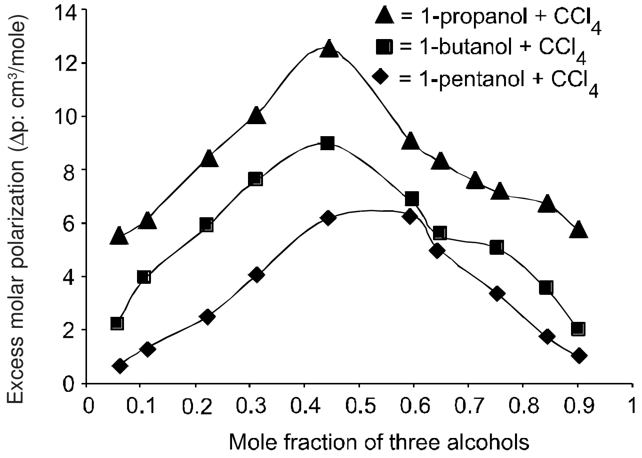

Fig. 2. The variation of excess molar polarization (Δp) with mole fractions of three alcohols in mixture with CCl_4 at 303.15 K.

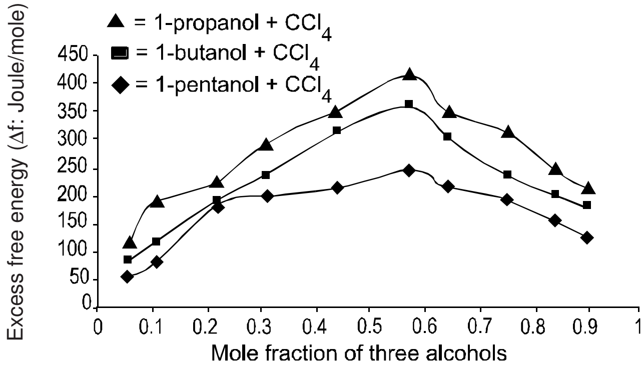

Fig. 3. The variation of excess free energy (Δf) with mole fractions of the alcohols in mixture with CCl_4 at 303.15 K.

Kirkwood theory of dielectric polarization of polar liquids in mixture with non-polar molecules. The dielectric constant or permittivity (ε) in mixture of major concentration predominates. In polar mixture, the value (ε) is a linear function of mole fraction. The value of (g) was calculated for solutions of polar molecules in a non-polar solvent, CCl_4.

Based on the observations obtained, it has been concluded that permittivity can be expressed in terms of short range forces, which is a part of two-particles correlation function, though it is affected by molecular interaction. The linear correlation parameter (g), whose value is different from unity, is a measure of the hindering effect of a molecule and its neighbours which has been calculated for solutions of polar molecules in a non-polar solvent. The value of (g) is a direct measure of the nature and extent of molecular association. When the value of $g \simeq 1$, it means that the hydrogen bonding can be neglected (Bottcher, 1973). This provides a way of correlating the macroscopic properties of a fluid within the properties of molecules and their interactions (Wakino *et al.,* 1993). The trend of variations in the value of Δp (excess molar polarization), as evident froms Tables 1-3, was positive over the entire range of concentration in the mixture of 1-propanol, 1-butanol and 1-pentanol. This happens for mixtures where $g > 1$ throughout.

The value of Δf in all the mixtures was positive, attaining maximum at nearly equimolar range of concentration. There was no perceptible difference in the magnitude, except in the case of a long chain mixture. This observation confirms the earlier findings on (g), where it was noted that in the mixtures with pentanol initially α-multimers were converted to β-multimers. In the other set of mixtures involving long chain alcohol mixtures, there was a predominance of β-multimers in the alcohol-deficient region, which was due to the formation of β-multimers. This is expected to result in the release of internal energy, making Δf positive (Garabadu and Swain, 1993). For the alcohol rich region, there was a reinforcement of correlation, resulting in a number of multimers, hence there was a fall in the value of Δf.

This comparative study has shown that Winkelmann and Quitzsch (1976) expression explained the molar interaction and association in the binary mixtures of polar liquids more suitably. This W.Q. equation divided the excess molar polarization in two parts, namely, $\Delta p_{W.Q.}$ and $\Delta p_{D.D.}$, which indicated an application of Winkelmann and Quitzsch (1976) model on dielectric properties.

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