

Dielectric studies of binary mixtures of polar liquids in non-polar solvents—Excess correlation factor and excess free energy of mixing

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Abstract

A study of the dielectric properties of binary mixture of polar liquids, namely, *n*-butanol, *t*-butanol, *t*-butanol in non-polar solvents such as benzene, tetrachloromethane and *n*-heptane has been made. Two new parameters, excess correlation factor (g_g) and excess free energy (ΔF_H) have been evaluated. These parameters have been used to throw light on the dynamic characteristics of molecular association in these binary mixtures of polar-non-polar liquids.

Key words: Dielectric study, binary mixtures, polar liquids, non-polar solvent, excess correlation factor, excess free energy of mixing.

1. Introduction

The study of dielectric properties of binary mixture of polar liquids is an interesting field of investigation. To obtain qualitative information on the molecular association in the mixture different equations have been proposed by Onsager¹, Decriocq² and Kirkwood³. Recently, Winkelmann and Quitzsch^{4, 5} have developed the expression for the correlation factor, excess free energy of mixing and excess molar polarisation taking into account the long- and the short-range interaction among similar and dissimilar molecules for the polar liquid mixtures. Swain and Roy⁶ have evaluated Kirkwood³ correlation factor (g_m) and excess free energy of mixing (ΔF_I) using modified Winkelmann and Quitzsch's equation for the binary mixture of polar and non-polar liquids.

From the experimental study of dielectric properties of polar liquids by Swain, Davis and others⁷⁻¹¹ it is observed that the correlation factor of the binary mixture is a measure of solute and solvent interaction and as such the excess free energy of

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mixing depends on this parameter. Hence, a similar type of variation is expected between the correlation factor (g_m) and excess free energy of mixing (ΔF_I) in a binary mixture of polar and non-polar liquids. However, Swain and Roy⁶ found that there is a distinct variation in the trend of g_m and ΔF_I , thus indicating the independence of the two parameters. Hence, this experimental result does not reflect the actual dynamic characteristics of the molecular association among the solute and solvent molecules. Hence, by modifying Kirkwood expression³ we have defined new terms, excess correlation factor (δg) and excess free energy of mixing (ΔF_{II}) utilizing the concept of Davis and Douheret and evaluated these terms (δg and ΔF_{II}) in the same binary mixtures to throw light on the nature of molecular interaction. Since no such investigation is found in the literature, we have undertaken this aspect.

2. Theory

To study solute-solvent interaction in the binary mixture of polar and non-polar liquids, Swain and Roy⁶ have used the Kirkwood correlation factor (g_m);

$$g_m = \frac{9KT\epsilon_0(2\epsilon_m + \epsilon_{\infty B})^2}{N\mu_{gB}^2 X_B(\epsilon_{\infty B} + 2)^2(2\epsilon_m + 1)} \left[V_m \frac{\epsilon_m - 1}{\epsilon_m} - \frac{3X_A V_A(\epsilon_A - 1)}{2\epsilon_m + \epsilon_A} - \frac{3X_B V_B(\epsilon_{\infty B} - 1)}{2\epsilon_m + \epsilon_{\infty B}} \right] \quad (1)$$

where X_A and X_B denote the mole fraction of non-polar and polar liquids, V_m , V_A and V_B , the molar volume of mixture, non-polar liquid and polar liquid, respectively, ϵ_m and ϵ_B , the dielectric constant of mixture and polar liquid, respectively, $\epsilon_{\infty B}$, the square of refractive index of polar liquid, μ_{gB} , the gas-phase dipole moment of the polar liquid, N , Avogadro's number, K , Boltzmann constant, ϵ_0 vacuum permittivity and T , the temperature in Kelvin. Again, Swain and Roy⁶ have evaluated the excess free energy using the equation

$$\Delta F_I = -\frac{N}{2} [R_{fB} - R_{fB}^c] X_B \mu_{gB}^2 [X_B (g_{BB} - 1) + 1] \quad (2)$$

where

$$R_{fB}^c = \frac{2N}{9V_B\epsilon_0} \frac{(\epsilon_B - 1)(\epsilon_{\infty B} + 2)}{(2\epsilon_B + \epsilon_{\infty B})}$$

$$R_{fB} = \frac{2N}{9V_B\epsilon_0} \frac{(\epsilon_m - 1)(\epsilon_{\infty B} + 2)}{(2\epsilon_m + \epsilon_{\infty B})}$$

From the experimental result of Swain and Roy⁶ we have observed that g_m increases with increase in the mole fraction of polar liquid in the mixture. On the other

hand, the excess free energy of these mixtures increases and then decreases with the increase of mole fraction of polar liquids. From the study of dielectric behaviour of polar liquids, many authors^{7, 8, 11} have shown that the correlation factor is negative and excess free energy of mixing is positive for associative and non-associative liquid mixtures. Further, Swain⁸ has observed that the nature of angular correlation is reflected from the excess thermodynamic parameters. Since there is a maxima in ΔF_I in Swain and Roy's⁶ observation we must expect a dip/heap in the curve g_m . In view of these, we proceed to formulate a new term, the excess correlation factor, δg , and accordingly the expression for excess free energy of mixing is formulated.

In the binary mixture of polar and non-polar liquids, the non-polar molecules are slightly polarised. So the effective dipole moment and the gas-phase dipole moment of the non-polar molecules in the mixture are negligibly small. According to Oster and Kirkwood¹², the correlation factor for the non-polar liquid in the mixture can be expressed as:

$$g = \lim_{\mu_x \rightarrow 0} \frac{\mu_{eff}}{\mu_x} \rightarrow 0 \frac{\mu_{eff}^2}{\mu_g^2} = 1. \quad (3)$$

So the excess correlation function δg whose magnitude is taken as a departure from the ideality in the light of Davis-Douheret⁹ theory can be written as:

$$\delta g = g_m - (X_A + X_B g_{BB}). \quad (4)$$

The expression for excess free energy of mixing in eqn (2) mainly depends on $\epsilon_B \sim \epsilon_m$. Hence, ΔF_I s have similar type of variation for all the mixtures and the maxima occurs at equal concentration of solute and solvent. Therefore, the result does not reflect any specific structural correlation between the solute and solvent molecules. So we have substituted the excess correlation function δg in place of g_{BB} in eqn (2). The excess free energy of mixing for the binary mixture of polar and non-polar liquids can be expressed as:

$$\Delta F_{II} = -\frac{N}{2} [R_{fB} - R_{fB}^0] X_B \cdot \mu_{gB}^2 [X_B (\delta g - 1) + 1]. \quad (5)$$

3. Result and discussion

We have calculated δg and ΔF_{II} at 307°K with the help of experimental results obtained by Swain and Roy⁶. The values of δg and ΔF_{II} for the binary mixtures of butanols and benzene are presented in Table I for ready reference and the experimental data of the binary mixtures of butanols in benzene, CCl₄, and *n*-heptane are displayed in Figs 1(a) to (f). The excess correlation function δg is similar to that of Winkelmann and Quitzsch ($g_{AB} - 1$). According to Swain^{7,8} ($g_{AB} - 1$) is negative

Table 1

Excess correlation function and excess free energy of mixing of the binary mixtures at 307 K

Mole fraction of alcohol (X_A)	\bar{g}_m^-	δg	$\Delta F_H^*/J/\text{mole}$	$\Delta F_H/J/\text{mole}$
1	2	3	4	5
(i) <i>n</i> -butanol + benzene				
0.084	-.90	-.290	3.13	2.34
0.142	-.94	-.381	31.62	19.26
0.200	-.98	-.472	73.05	35.519
0.250	1.14	-.425	111.23	45.700
0.300	1.29	-.388	146.79	51.088
0.360	1.43	-.384	193.16	54.454
0.420	1.65	-.299	224.47	52.288
0.460	1.78	-.260	246.13	50.698
0.600	2.18	-.176	224.70	28.040
(ii) <i>i</i> -butanol + benzene				
0.078	-.86	-.333	3.03	2.275
0.128	-.97	-.346	33.48	21.065
0.190	1.10	-.369	78.45	39.465
0.250	1.23	-.387	114.79	46.356
0.300	1.40	-.341	166.12	56.964
0.360	1.64	-.249	200.18	58.284
0.430	1.90	-.162	239.04	58.019
0.600	2.41	-.072	218.68	31.479
(iii) <i>t</i> -butanol + benzene				
0.079	-.70	-.387	2.81	2.288
0.146	-.74	-.432	4.89	3.300
0.211	-.79	-.459	27.83	15.419
0.240	-.96	-.323	39.49	20.991
0.270	1.03	-.289	51.04	25.224
0.338	1.12	-.279	78.97	32.062
0.400	1.22	-.252	102.97	34.906
0.500	1.38	-.210	130.38	32.390
0.600	1.64	-.068	118.69	17.789

* Source: Swain and Roy⁶

and excess free energy of mixing is positive for the binary mixture of associative-non-associative polar liquids. In our present paper, since the non-polar liquids approach the nature of non-associative liquid in the mixture, the negative value of δg and positive nature of ΔF_H confirm the correctness of our mathematical formulation. With increase in solute concentration (polar liquids) ΔF_H increases, and attains the maximum value in the range 0.3 to 0.4 mole fraction of solute and then decreases. This is probably due to the fact that β -multimers (antiparallel orientation of dipole moment) in the mixture is characterised by reduction of internal energy in comparison

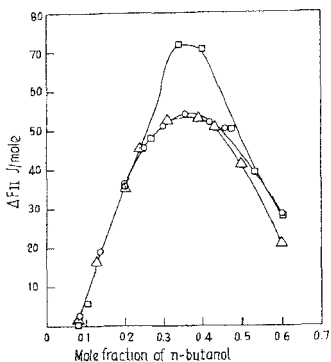


Fig. 1(a). Variation of excess free energy of mixing with mole fraction of *n*-butanol in binary mixtures at 307°K. Plots: \circ — \circ *n*-butanol + benzene, Δ — Δ *n*-butanol + CCl_4 , \square — \square *n*-butanol + *n*-heptane.

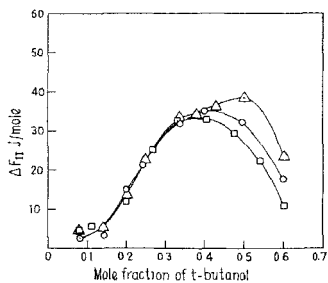


Fig. 1(c). Variation of excess free energy of mixing with mole fraction of *t*-butanol in binary mixtures at 307°K. Plots: \circ — \circ *t*-butanol + benzene, \square — \square *t*-butanol + CCl_4 , Δ — Δ *t*-butanol + *n*-heptane.

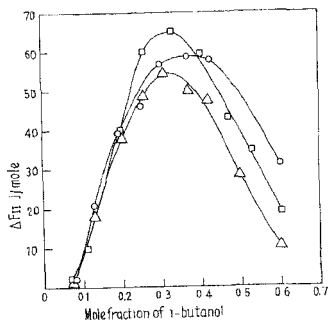


Fig. 1(b). Variation of excess free energy of mixing with mole fraction of *i*-butanol in binary mixtures at 307°K. Plots: \circ — \circ *i*-butanol + benzene, Δ — Δ *i*-butanol + CCl_4 , \square — \square *i*-butanol + *n*-heptane.

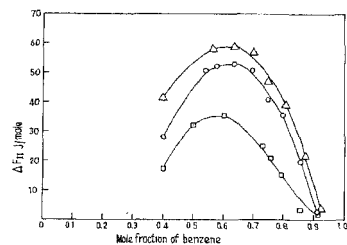


Fig. 1(d). Variation of excess free energy of mixing with mole fraction of benzene in binary mixtures at 307°K. Plots: \circ — \circ *n*-butanol + benzene, Δ — Δ *i*-butanol + benzene, \square — \square *t*-butanol + benzene.

to α -multimers (parallel orientation of dipole moments) in the polar liquids. With further increase in the concentration of solute the conversion of β -multimers to

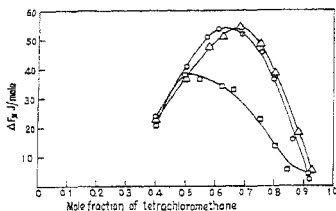


Fig. 1(e). Variation of excess free energy of mixing with mole fraction of tetrachloromethane in the binary mixtures at 307°K. Plots: \circ — \circ *n*-butanol + CCl_4 , Δ — Δ *i*-butanol + CCl_4 , \square — \square *t*-butanol + CCl_4 .

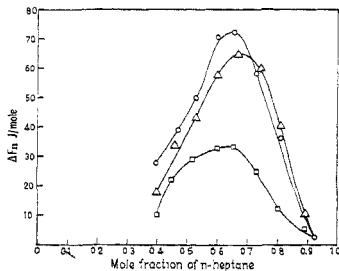


Fig. 1(f). Variation of excess free energy of mixing with mole fraction of *n*-heptane in binary mixtures at 307°K. Plots: \circ — \circ *n*-butanol + *n*-heptane, Δ — Δ *i*-butanol + *n*-heptane, \square — \square *t*-butanol + *n*-heptane.

α -multimers reverses the trend and ΔF_{II} starts diminishing. Again as per our prediction in the theory, we have also observed a dip in the variation of δg .

In Fig. 1 (a) and (b), we observe the maxima of ΔF_{II} to be in the order *n*-heptane > benzene > CCl_4 . In the straight chain alkane, the conformation can be manifold. It can take from highly coiled (unstable) to a zigzag (planar) conformation. When a solute like *n*-butanol is added to *n*-heptane there is a little tendency on the part of the non-polar solvent (*n*-heptane molecule) to disrupt the hydrogen bonding in *n*-butanol or *i*-butanol. The interaction between solvent and solute becomes less (*i.e.*, mixability is minimum) and therefore the departure from ideal behaviour is maximum. On the other hand, the conformation of benzene and CCl_4 is unique, the former being hexagonal (planar) and the latter tetrahedral. The π -electron cloud in benzene solvent interacts with the *n*- or *i*-butanol (solute) and disrupts the intermolecular hydrogen bond existing between them. Hence, mixability becomes more and the departure from ideal behaviour is less compared to *n*-heptane. Although CCl_4 is non-polar, there are four polar C—Cl bonds directed towards the four corners of a tetrahedron. Each bond dipole ($\text{C}^{\delta-}-\text{Cl}^{\delta+}$) interacts with the H-bonds of the solute (*i.e.*, *n*- or *i*-butanol) and disrupts them. Hence, mixability is being facilitated at four directions of each solvent molecule. Therefore the departure from ideal behaviour is minimum. The above explanation holds good both for *n*- and *i*-butanols used as solutes. But when *t*-butanol is used as solute the order of mixability is different (Fig. 1c). The mixability is maximum in *n*-heptane followed by benzene and minimum in CCl_4 . The trend may be attributed to steric effect associated with *t*-butanol. Also the degree of H-bonding in this liquid is minimum. When it is added to *n*-heptane, probably the non-polar solvent molecules with their manifold conformations penetrate through the intermolecular voids of the bulky *t*-butanol molecules which have less intermolecular attraction between themselves. On the contrary, when

when *t*-butanol is added to CCl₄ the bulky three-dimensional (tetrahedral) CCl₄ molecules cannot penetrate into the bulky *t*-butanol molecules so as to disrupt the intermolecular H-bonds between them. Hence, the mixability is minimum and the departure from the ideal behaviour is maximum. Benzene remains unaltered in its action towards *t*-butanol as compared with *n*-butanol and *i*-butanol. The π -electron cloud of benzene interacts more or less equally with three types of alcohols.

It is seen from Figs 1d and e that benzene or tetrachloromethane as common solvent (ΔF_{11}) maxima is in the order *i*-butanol > *n*-butanol > *t*-butanol. It is probably due to the value of linear correlation factor which are in the order of *i*-butanol > *n*-butanol > *t*-butanol⁷.

On the other hand, with *n*-heptane as the common solvent the situation is different, i.e., it is in the order *n*-butanol > *i*-butanol > *t*-butanol (Fig. 1f). The reason may be due to the fact that there is little tendency of this non-polar solvent to disrupt the hydrogen bonding in three alcohols. Since the degree of hydrogen bonding is the maximum in *n*-butanol and the least in *t*-butanol, the interaction between the solvent and the solute molecules becomes minimum in the case of *n*-butanol and maximum in *t*-butanol. As a result, the departure from ideal behaviour is maximum in the case of *n*-butanol and minimum in *t*-butanol.

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