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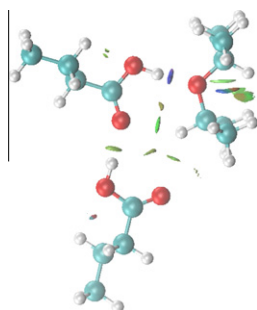
A probe on the intermolecular forces in diisopropyl ether–n-butyric acid mixture by dielectric, FTIR studies and quantum chemical calculations

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HIGHLIGHTS

- ▶ Non-linearity of ϵ_m Vs X_2 curve due to hetero H-bond formation – to be corrected.
- ▶ No evidence for g^{eff} to be the index of H-bonding ability of solute/solvent.
- ▶ Positive ϵ^E values – increase in the number of effective dipoles also seems invalid.

GRAPHICAL ABSTRACT



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ABSTRACT

The results of FTIR spectral measurement on equimolar diisopropyl ether–butyric acid binary mixture and quantum chemical calculations on the complex molecule have been presented. Dielectric studies have been carried out on the binary mixture over the entire composition range and at four different temperatures 303 K, 308 K, 313 K and 318 K. n-Butyric acid seems to prefer less polar ether to interact with it. It appears that the usual interpretation of variation of static dielectric constant and positive deviation of excess permittivity from ideal mixture behavior needs to be relooked.

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Introduction

Dielectric studies is one of the sensitive tools for studying the structural modifications taking place in liquid mixtures. It has been used to investigate the heterogeneous interactions and orientational correlations between molecular dipoles [1–6] in a fluid from the dielectric parameters such as permittivity, Kirkwood correlation factor, and excess permittivity. Review of literature shows that these dielectric parameters have been interpreted in different ways.

The effective Kirkwood Correlation factor g^{eff} has been used to describe the angular correlation [3–10] of dipoles in liquid mix-

tures. But Gabrielyan and Markarian [11] have interpreted the magnitude of g^{eff} as the H-bonding ability of one of the mixture constituents. It has been reported [8,12,13] that positive values of ϵ^E is due to the parallel alignment of dipoles of liquid mixtures. According to Undre et al. [14], the positive ϵ^E in the mixture of N, N-dimethylacetamide with the associative ethanolamine is due to the formation of monomeric or polymeric structures with increase in the total number of dipoles.

The non-linear variation of static dielectric constant with solute concentration has been attributed to the formation of H-bond between unlike molecules in some works [5,15,16] and to the presence of heterointeraction in some other works [15,17]. So from the dielectric parameters, one can give an unclear picture about the intermolecular forces that are operative in liquid mixtures. In the present work we have made an attempt to give more precise interpretation of dielectric parameters using dielectric studies on

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polar–polar liquid mixtures combined with FTIR studies and quantum chemical calculations. The polar liquids selected for the investigation are an aprotic diisopropyl ether and associative n-butyric acid.

Materials and methods

FTIR and dielectric studies

The n-butyric acid and diisopropyl ether of AR grade were purchased from SRL Pvt. Ltd., Mumbai and used as such without any further purification. FTIR spectra of pure acid and its equimolar binary mixture with diisopropyl ether was recorded using Jasco 460 plus FTIR spectrophotometer at room temperature. The static dielectric constant was obtained at a frequency of 1 kHz using a digital VLCR-7 meter supplied by Vasavi Electronics, Secunderabad, India. The uncertainty in the static dielectric constant is less than 2%. The temperature was maintained at 303 ± 0.1 K, 308 ± 0.1 K, 313 ± 0.1 K and 318 ± 0.1 K using a water circulating thermostat supplied by Raaga Industries, Chennai, India. Refractive indices were measured using an Abbe's refractometer. All the mass measurements were made using K-Roy microbalance having an accuracy of 0.0001 g. The uncertainty in refractive index is ± 0.0001 .

Computational details

DFT calculations were performed using Gaussian03w program package [18]. For the optimization of molecular structures and vibrational frequency calculations, the B3LYP functional [19,20] with the basis set 6-31 + G (d,p) was used.

Theory

The averaged effective angular Kirkwood correlation factor g^{eff} of heterogeneous molecules in a mixture of two polar liquids can be evaluated from the equation [21,22]

$$\frac{4\pi N}{9kT} \left(\frac{\mu_1^2 \rho_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2}{M_2} X_2 \right) g^{eff} = \frac{(\epsilon_m - \epsilon_{\infty m})(2\epsilon_m + \epsilon_{\infty m})}{\epsilon_m(\epsilon_{\infty m} + 2)^2} \quad (1)$$

where, the suffixes m , 1, and 2 represent mixture, liquid 1 and liquid 2, X and μ are the mole fraction and the gas phase dipole moment of the respective molecules. The corrective Kirkwood correlation factor g_f for a binary mixture can be calculated using the equation [23,24]

$$\frac{4\pi N}{9kT} \left(\frac{\mu_1^2 \rho_1 g_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} X_2 \right) g_f = \frac{(\epsilon_m - \epsilon_{\infty m})(2\epsilon_m + \epsilon_{\infty m})}{\epsilon_m(\epsilon_{\infty m} + 2)^2} \quad (2)$$

The excess dielectric constant which is another useful parameter stating the composition dependent dielectric behavior is defined as [25]

$$\epsilon^E = (\epsilon_m - \epsilon_{\infty m}) - [(\epsilon_{01} - \epsilon_{\infty 1})X_1 + (\epsilon_{02} - \epsilon_{\infty 2})X_2]. \quad (3)$$

The excess Helmholtz free energy ΔF^E almost equal to the excess Gibb's free energy for a matter in condensed phase is given by [26]

$$\begin{aligned} \Delta F^E = & -\frac{N}{2} \left[\sum_{r=1,2} X_r \mu_r^2 (R_r - R_{fr0}) + \sum_{r=1,2} X_r^2 \mu_r^2 (g_{rr} - 1)(R_r - R_{fr0}) \right. \\ & \left. + X_1 X_2 \mu_1 \mu_2 (g_{12} - 1)(R_{f1} + R_{f2} - R_{f10} - R_{f20}) \right] \\ & = \Delta F_0^E + \Delta F_{rr}^E + \Delta F_{12}^E \quad (4) \end{aligned}$$

Here, the first term ΔF_0^E represents the excess dipolar energy due to long range electrostatic interaction, the second term ΔF_{rr}^E represents the excess energy due to short range interaction be-

tween identical molecules and the third term ΔF_{12}^E gives the excess dipolar energy due to short range interaction between dissimilar molecules.

The terms R_{fr0} and R_{fr} , which give the reaction field parameters in the pure liquid and that in the mixture respectively, are given by [27]

$$R_{fr0} = \frac{8\pi N}{9V_r} \frac{(\epsilon_m - 1)(\epsilon_{\infty} + 2)}{(2\epsilon_m + \epsilon_{\infty r})} \quad (5)$$

$$R_{fr} = \frac{8\pi N}{9V_r} \frac{(\epsilon_m - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_m + \epsilon_{\infty r})} \quad (6)$$

with ϵ_r , the static dielectric constant of the pure liquid.

The values of excess permittivity and excess free energy for our system have been fitted to Redlich–Kister equation [28,29]

$$Y^E = (X_A X_B) \sum_i B_i (X_A - X_B)^i \quad (7)$$

where, Y^E is either ϵ^E or ΔF^E . The coefficients B_i have been used as guidelines to draw the smooth curves.

Results and discussion

FTIR studies and quantum chemical calculations

Carboxylic acid dimers are usually characterized by mainly three type of bands: (i) strongly bonded, very broad O–H stretching band centering near 3000 cm^{-1} superimposed on the C–H stretching bands [30], (ii) two C=O stretching bands, asymmetric at $1720\text{--}1706 \text{ cm}^{-1}$ [31] and symmetric at $1680\text{--}1640 \text{ cm}^{-1}$ [30] and (iii) out of plane O–H...O hydrogen deformation band, broader and medium intensity, at $960\text{--}875 \text{ cm}^{-1}$ [30].

In the experimental FTIR spectrum of pure butyric acid (Fig. 1), the asymmetrical C=O stretching mode appears at 1712 cm^{-1} with the absence of the IR inactive symmetrical C=O stretching band and the out of plane O–H...O hydrogen deformation band is at 934 cm^{-1} with a shoulder at 886 cm^{-1} . When butyric acid is mixed with diisopropyl ether, the FTIR spectrum (Fig. 1) shows three prominent changes: (i) disturbed shape and intensity of the O–H stretching band, (ii) two C=O stretching absorptions, indicating that the carbonyl bonds of pure acid dimer are now under different chemical environment, one at 1738 cm^{-1} belonging to the acid molecule bonded with another acid molecule and the other at 1713 cm^{-1} belonging to the acid molecule H-bonded with ether, and (iii) two distinct blue shifted out of plane O–H...O hydrogen deformation bands at 936 and 904 cm^{-1} , the former with reduced and the later with increased intensities in comparison with that in pure acid dimer. All these confirm that the intermolecular H-bond of diisopropyl ether oxygen is with the carboxylic hydrogen of open butyric acid dimer. This type of heterostructure is also identified in 1,4-dioxane + butyric acid mixture [32] in which the O–H stretching band is significantly broader than in the present system and this means that the ether–acid H-bond is relatively stronger in the former case. The stretching absorption of the C=O free from H-bond interaction and the O–H...O hydrogen deformation band in 1,4-dioxane + butyric acid mixture [32] are at 1733 and 934 cm^{-1} , respectively. These modes absorb at higher wavenumbers (1738 and 936 cm^{-1}) in the present work where the H-bond is relatively weak.

The structure of the H-bonded hetero unit is optimized (Fig. 2) and the vibrational frequency has been calculated for this structure. The butyric acid closed dimeric ring has also been optimized (Fig. 3) for the frequency calculation. The structural parameters of pure acid dimer and the H-bonded heterostructure have been given in Table 1. The length of C=O, C–O and O–H bonds of one acid

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