

Dielectric relaxation study of aqueous amides in non-polar solute using picoseconds time domain technique

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Abstract. The dielectric permittivity of amide - 1, 4-dioxane (DX) for various concentrations has been studied in the frequency range from 10 MHz to 30 GHz using the time domain reflectometry (TDR) method. A hydrogen bonded theory suggested by Luzar is applied to compute correlation terms for the mixtures. Static permittivity for the mixtures can be explained using the Luzar model by assuming the formation of two types of hydrogen bonded dimmers, one between amide-amide (pair 1) and other between amide-1, 4-dioxane (pair 2). The numbers of these pairs are also estimated as a function of concentration.

Keywords: Dielectric permittivity, Relaxation time, Time domain reflectometry (TDR)

1. Introduction

Amide represents an important class of bio-organic solvent. The hydrogen bond formation ability of these solvents is useful in understanding the peptide linkage in complex bio-systems [1-3]. The study of hydrogen bonding molecular interactions of binary mixtures is currently a significant challenge in the research field of science and technology. Hydrogen bond constitutes a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. "Hydrogen Bonding in Biological Structures" can be used in many ways by biophysicists [4]. The study of the H-bonds of the type O=H --- O=C occupies a position of considerable importance as it relates to the study of biopolymers [5]. In the case of amides, N, N-dimethylformamide (DMF) is able to form the H-bonded network structures with dipolar aprotic and protic solvents [6]. *Malathi M. et al.* have studied mutual interaction of amides with non polar solvents to understand the conformational stability of protein molecules [7]. Thenappan and Sankar were studied hydrogen-bonded complexes of alcohol with N, N-dimethylformamide (DMF) [8]. DMF is a widely used solvent for many recently developed synthetic procedures because of its powerful solvating properties [9]. N-methylacetamide (NMA) is the most frequently used analog compound for the peptide unit in proteins. Paul Firman and S. Sahoo were studied the mixture of N-methylacetamide (NMA) with non-polar solvent [10, 11]. The non polar solvent 1, 4-dioxane (DX) is used as a laboratory reagent and as a solvent for the production of cellulose acetate, ethyl cellulose, benzyl cellulose, dyes, oils, fats and polyvinyl polymers. The intermolecular interaction plays an important part in intermolecular recognition processes essential to most of biological systems. It also found that Physical and chemical phenomenon of binary systems are closely related to the intermolecular interactions.

In the present work, we report a comparative dielectric relaxation study of amide (DMF and NMA) with non polar solute (DX) at various concentrations at 25°C employing Time Domain Reflectometry (TDR) in the frequency range of 10 MHz-30 GHz. The complex permittivity spectra of DMF-DX and NMA-DX have been fitted to Debye model and Davidson – Cole model respectively. The static permittivity, dielectric

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relaxation time and Kirkwood correlation factor has been obtained. The experimental results of static dielectric constant have been used to estimate the average number of hydrogen bonds between solvent – solvent and solute – solvent molecules.

2. Experimental

2.1. Materials

N, N-dimethylformamide (DMF) and N-methylacetamide (NMA) was obtained commercially from s d fine-chem Ltd. (AR Grade 99%). The solutions were prepared by mixing the 1, 4-dioxane (DX) and amides in volume.

2.2. Measurements

The densities of solutions were measured using specific gravity bottle and weighting were carried out by using electronic balance. The uncertainties of the measured values of densities were $\pm 10^{-4}$ g/cm³. The dielectric complex permittivity of the mixtures was measured by TDR [12]. The Tektronix model no. DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used. The details of the apparatus and data analysis procedures of the TDR have been reported previously [13].

3. Results and Discussion

Fig.1 (a, b) shows frequency dependent complex permittivity spectra for DMF–DX and NMA–DX at 25⁰C. It can be seen from Fig. 1 (b) that the position of the peak is shifted towards lower frequency for NMA system.

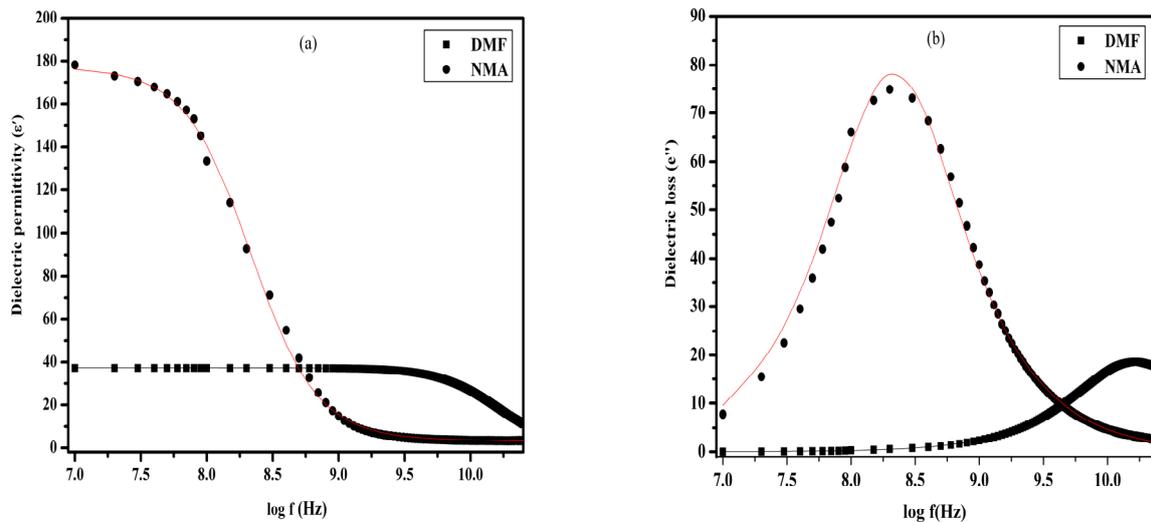


Fig. 1: Frequency dependent (a) dielectric permittivity (ϵ') & (b) dielectric loss (ϵ'') for DMF and NMA at 25⁰C.

The complex permittivity spectra measured using TDR is fitted by the non-linear least squares fit method to the Havriliak - Negami expression [14, 15]:

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{[1 + (j\omega\tau)^{1-\alpha}]^{\beta}} \quad (1)$$

where ϵ_0 is the static dielectric constant, ϵ_{∞} is the permittivity at high frequency, τ is relaxation time and α & β are the distribution parameters. Equation (1) includes the Debye ($\alpha = 0$, $\beta = 1$), Cole-Cole ($0 \leq \alpha \leq 1$ and $\beta = 1$) and Davidson – Cole ($\alpha = 0$ and $0 \leq \beta \leq 1$). For the system DMF-DX, the values of α and β are found to be 0 and 1, respectively; whereas NMA-DX system, β is less than 1.

3.1. Kirkwood correlation factor

The contribution of hydrogen bonds to dielectric properties of the mixture can also be studied by using the hydrogen bonding model as suggested by Luzar [16]. We have used the Luzar model to explain static permittivity of the mixture. Considering only the hydrogen bond contribution to dipole-dipole correlation, the dielectric constant for binary mixtures can be determined using Kirkwood- Frohlich equation [17]

$$\frac{(\epsilon_{0i} - \epsilon_{\infty i})(2\epsilon_{0i} + \epsilon_{\infty i})}{9\epsilon_{0i}} = \frac{4\pi}{9kT} \sum_{i=1}^2 g_i \rho_i \mu_i^2 \quad (2)$$

where $i=1$ and 2 represent solute and solvent, respectively. Here μ_i is the corresponding dipole moment in the gas phase, ρ_i is the density, k is Boltzmann constant, T is the temperature and g_i is the Kirkwood correlation factor for the i^{th} liquid component. It is also impossible to separate the average correlation factor g_1 and g_2 from single value of the static dielectric constant without any assumptions. Luzar suggested theoretical model based on mean field approximation for hydrogen bonded mixture [16]. The correlation factor g_1 and g_2 are calculated by following equations:

$$g_1 = 1 + Z_{11} \cos \phi_{11} + Z_{12} \cos \phi_{12} (\mu_2 / \mu_1) \quad (3)$$

$$g_2 = 1 + Z_{21} \cos \phi_{21} (\mu_1 / \mu_2) \quad (4)$$

where $Z_{11} = 2\langle n_{\text{HB}}^{11} \rangle$, $Z_{12} = \langle n_{\text{HB}}^{12} \rangle$ and $Z_{21} = \langle n_{\text{HB}}^{21} \rangle X_{\text{DX}} / (1 - X_{\text{DX}})$ are the average number of hydrogen bond with solvent - solvent and solvent - solute pairs respectively. ϕ_{11} and ϕ_{21} are the average angles between neighboring dipoles of solvent and solute molecule. Since 'g' is measure of the molecular association between a reference molecule and its nearest neighbors, the departure of 'g' from unity can be indicative of molecular association. The values of g_1 and g_2 for different DMF-DX & NMA-DX mixtures are computed by using the parameters given in Table 1 and are shown in Fig.2. The values of g_1 and g_2 depend on the concentration of DX in DMF-DX & NMA-DX mixtures. This model gives a good qualitative account of the static dielectric constant of the binary mixtures (DMF-DX & NMA-DX) along with the experimental values determined from Time Domain Reflectometry technique (TDR) in our laboratory, and are shown in Fig.3 respectively. The value of static dielectric constant & relaxation time at 25°C for DMF and NMA are reported in Table.2. In case of secondary amine (NMA) the single bond character is decreases and double bond character is increased. Due to this the rotation of molecules are slower and relaxation time is more as compared to DMF.

Table 1. Molecular parameters used in computation of the Static Dielectric Constant (ϵ_0)

| Molecular parameters | Symbols | |
|--|-------------------|--------|
| Dipole moment of DMF in Debye | (μ_1) | 3.22 |
| Dipole moment of NMA in Debye | (μ_1) | 6.05 |
| Dipole moment of DX in Debye | (μ_2) | 0.75 |
| Polarizability of DMF in Å^3 | (α_1) | 4.08 |
| Polarizability of NMA in Å^3 | (α_1) | 7.82 |
| Polarizability of DX in Å^3 | (α_2) | 5.68 |
| Binding energy of Amide – Amide in kJ/mol | (E_{11}) | -14.39 |
| Binding energy of Amide – DX in kJ/mol | (E_{12}) | -18.25 |
| Statistical volume ratio for Amide - Amide | (α_{11}) | 28 |
| Statistical volume ratio for DX-DX | (α_{12}) | 40 |

Table 2. Static dielectric constant and relaxation time at 25°C.

| | N, N-dimethylformamide | N-methylacetamide |
|---|------------------------|-------------------|
| Static dielectric constant (ϵ_0) | 37.22 | 179.54 |
| Relaxation time (τ) | 10.43 | 736.40 |

The average number of hydrogen bonds $\langle n_{\text{HB}}^{11} \rangle$, $\langle n_{\text{HB}}^{12} \rangle$ and $\langle n_{\text{HB}}^{21} \rangle$ per DX molecule for $1i$ pairs ($i=1, 2$) has been determined using following relation [16]:

$$\langle n_{\text{HB}}^{1i} \rangle = n_{1i} \omega^{1i} / n_1 \quad (5)$$

where $\omega^{1i} = 1/[1 + \alpha^{1i} \exp(\beta E^{1i})]$ is the probability of bond formation between solvent and solute. n_1 is the number density of solvent molecules, $\beta = 1/kT$, and α^{1i} are the statistical volume ratios of the two sub volumes of the phase space related to the non hydrogen-bonded and hydrogen bonded pairs. These hydrogen bonded pairs have only two energy levels, E_{11} and E_{12} , for 11 and 12 pair formed bonds, respectively. The values of $\langle n_{\text{HB}}^{11} \rangle$ and $\langle n_{\text{HB}}^{12} \rangle$ depend on the number densities of the hydrogen-bonded pairs between solvent - solvent and solvent - solute molecules respectively. Fig.4. shows a plot of the average number of hydrogen bonds between amide-amide and amide-1, 4-dioxane against the mole fraction of 1, 4-dioxane.

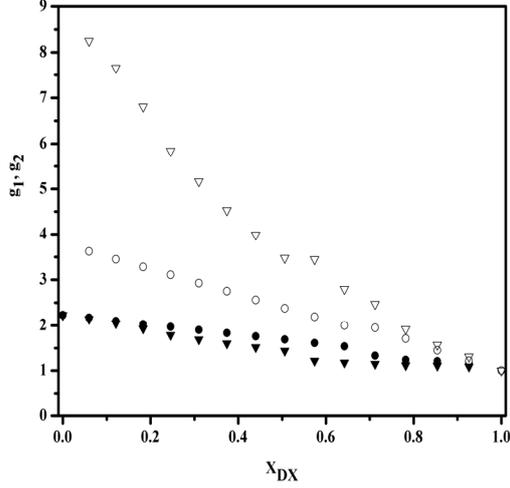


Fig. 2: Mole fraction of 1, 4-dioxane dependence of the g_1 (closed symbols) & g_2 (open symbols) \blacktriangledown - N-methylacetamide \bullet - N-dimethylformamide at 25°C.

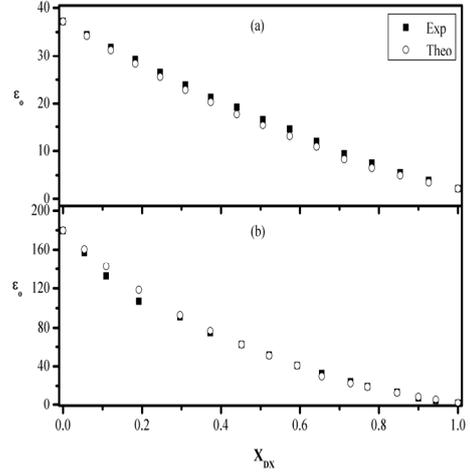


Fig. 3: Comparison of experimental and theoretical static dielectric constant for (a) DMF-DX & (b) NMA-DX at 25°C.

We calculated the average number of hydrogen-bonded solvent - solvent pairs $[n_{\text{HB}}^{11}]_V$ and solvent - solute pairs $[n_{\text{HB}}^{12}]_V$ per unit volume ($/\text{cm}^3$) using the following equations[18]

$$[n_{\text{HB}}^{11}]_V = \frac{C_{\text{SOLVENT}} \rho_{\text{mix}} N_A}{M_{\text{SOLVENT}}} n_{\text{HB}}^{11} (/ \text{cm}^3) \quad \text{and} \quad [n_{\text{HB}}^{12}]_V = \frac{C_{\text{SOLVENT}} \rho_{\text{mix}} N_A}{M_{\text{SOLVENT}}} n_{\text{HB}}^{12} (/ \text{cm}^3) \quad (6)$$

where C_{SOLVENT} is the weight fraction of solvent, ρ_{mix} (g/cm^3) is the density of mixture, N_A is the Avogadro number, as 6.02×10^{23} (/mol) and M_{SOLVENT} is the molecular weight of solvent.

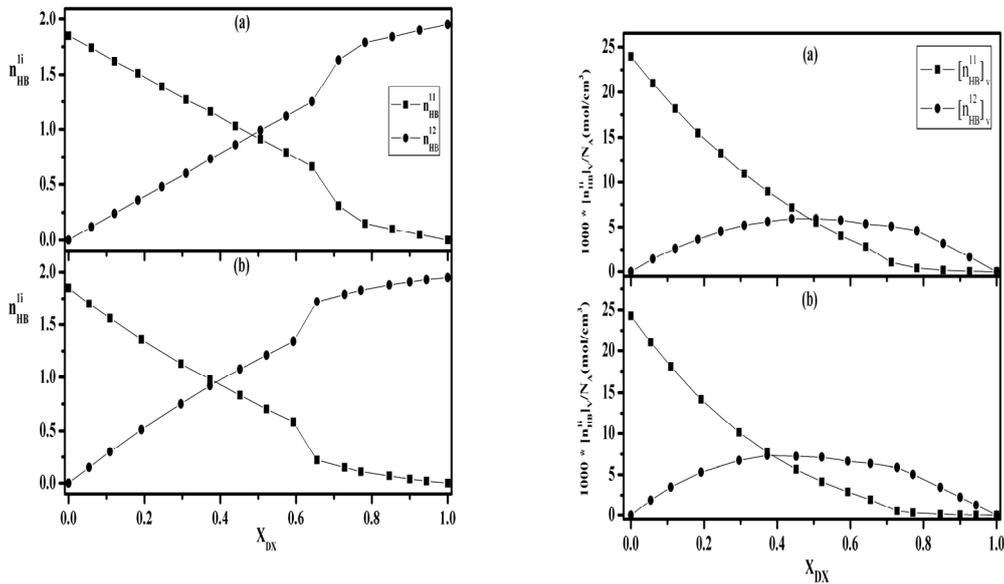


Fig. 4: Plots of the average number of hydrogen bonds [n_{11} pair & n_{12} pair] for (a) DMF–DX and (b) NMA–DX vs. mole fraction of 1, 4-dioxane (X_{DX}) at 25°C.

Fig. 5: Plots of the number of hydrogen bonds per unit volume against X_{DX} for (a) DMF–DX & (b) NMA–DX at 25°C.

Fig.5 shows the plots of $[n_{HB}^{11}]_V$ and $[n_{HB}^{12}]_V$ against mole fraction of 1, 4-dioxane (X_{DX}). The value of $[n_{HB}^{11}]_V$ increases with increasing X_{DX} and that of $[n_{HB}^{12}]_V$ has a maxima at concentration $X_{DX} \approx 0.50$ for DMF-DX and $X_{DX} \approx 0.37$ for NMA-DX. These results provide information regarding the intermolecular interaction of solvent - solvent and solvent – solute molecules.

4. Conclusions

The temperature dependent complex permittivity spectra of amide - 1, 4-dioxane mixtures have been studied using time domain reflectometry technique in the frequency range 10 MHz to 30 GHz. The deviation from ideality in Kirkwood correlation factor provides information regarding hydrogen bonding interactions in mixtures. The number of hydrogen bonds of DMF–DX & NMA–DX molecules increases with increasing DX concentration and maximum at $X_{DX} \approx 0.50$ & $X_{DX} \approx 0.37$, respectively. The Kirkwood correlation factors and relaxation times of NMA-DX system are found to be larger than the corresponding values of DMF-DX system, indicating stronger hydrogen bonding in NMA-DX system. By using recently developed Luzar theory one may get quantitative information about solute-solvent interactions.

5. References

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