

## Dielectric relaxation and molecular interaction study of aqueous amides

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Dielectric permittivity spectra of amides (DMF and DMA) over entire concentrations with aqueous solution have been measured with different frequency ranges at 25 °C. The permittivity spectra of amide-water mixtures at lower frequencies (20 Hz to 2 MHz) have been measured using Agilent Precision LCR meter E4980A and the same have been measured at higher frequencies using time domain reflectometry technique in the frequency range of 10 MHz to 30 GHz. The permittivity spectra have been fitted in Cole-Davidson model in order to evaluate the dielectric parameters. Further the Excess permittivity, Kirkwood correlation factor, Bruggeman factor have been calculated to study the molecular interactions in amides with water molecules. The study has been extended to confirm the molecular interactions among the unlike molecules using the volumetric properties.

**Keywords:** Dielectric permittivity, LCR meter, Time domain reflectometry, Excess properties, Molecular interaction

### 1 Introduction

The study of dielectric dispersion and absorption spectra of binary liquid mixture provides information regarding molecular interaction through hydrogen bonding in the liquid mixture<sup>1</sup>. Therefore the dielectric relaxation spectroscopy (DRS) is commonly applied to the systems in which hydrogen bonds play an important role such as aqueous or alcoholic mixtures<sup>2</sup>. Water is the basic of all living organisms. It is a polar and strong hydrogen bonding liquid. The dielectric relaxation of pure water is of the Debye type<sup>3</sup>. Amides are the simplest molecules having a peptide linkage. Due to high polarity, strong solvating power and large liquid state range, amides are the important class of organic solvents<sup>4-5</sup>. N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) are the di-substituted alkyl amides having formula  $\text{H C(O)N(CH}_3)_2$  and  $\text{CH}_3 \text{ C(O)N(CH}_3)_2$ , respectively. Amides possess the donor-acceptor  $-\text{CO-NH}-$  peptide bond and most of them form the self association through H-bond<sup>6</sup>. Dynamics and the dielectric studies of amides in pure as well as in different binary mixtures of polar and non polar solvent have been extensively carried out<sup>7-16</sup>. The dielectric studies carried out by Sengwa *et al*<sup>13-17</sup> studied the hetero molecular interactions in amides with polar and non-polar solvent using the excess dielectric constant. The peak values of

excess dielectric constants attributed as a formation of 1:1 complexes in the mixtures of DMF, DMA with DMSO and Dioxane (Dx) whereas DMF and DMA form 2:1 and 1:2 complexes with Dimethylethanolamine, respectively<sup>15,16</sup>. The study also reveals unlike molecule hydrogen bond interaction strength is stronger in amide-Dx in comparison with amide-DMSO. Apart from DMSO and Dx, water molecules have both hydrogen bond acceptor and donor sites. Therefore, it is important to study the dielectric dispersion in amide-water binary mixtures. In this paper, the attempt is made to study the dielectric properties of mixed solvents of DMF and DMA with water over entire concentration range. The dielectric measurement have been carried out in different frequency ranges 20 Hz to 2 MHz using Precision LCR meter and 10 MHz to 30 GHz using time domain reflectometry technique. The complex aggregates in unlike molecules through H-bonds have been discussed using Kirkwood correlation factor, excess dielectric constant, excess volumetric properties and Bruggeman factor.

### 2 Experimental

#### 2.1 Materials

DMF, DMA and water were obtained commercially (Fisher Scientific India Pvt Ltd). Purity of the DMF is 99%, DMA is 99.5% and de-ionized water with HPLC grade. They were used without

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further purification. The solutions were prepared at different mole fractions of water in DMF and DMA.

## 2.2 Measurements and data analysis

The measurements of dielectric dispersion of amide-water at frequency range from 20 Hz to 2 MHz have been carried out using Agilent precision LCR meter E4980A and Agilent 16452A liquid dielectric test fixture. The static dielectric constants for pure liquids and entire concentrations of binary mixtures were determined by using ‘capacitive measurement method’ with a short compensation at 2 MHz. The detailed measurement techniques have been described in literature by Sengwa *et al*<sup>17</sup>. It is observed that for the various concentrations of DMF-water and DMA-water (Fig. 1(a and b)), the real part of dielectric constants became constant in the frequency range of 30 kHz–0.2 MHz and then remain constant up to frequency 2 MHz. Below the frequency range of 30 kHz to 0.2 MHz the real part of dielectric constants increases due to contribution of ionic conduction process, and also at very low frequency region there is large increase in the values due to electrode polarization phenomenon. Therefore, the static dielectric constant measurements are suitable above these frequencies. In present study 2 MHz frequency is used.

The measurements of dielectric spectra in the frequency range of 10 MHz to 30 GHz have been carried out by the time domain reflectometry

technique<sup>18</sup>. The Tektronix model number DSA8200 digital serial analyzer sampling mainframe along with the sampling module 80E08 has been used for the time domain reflectometry. The data analysis to determine complex permittivity spectra  $\epsilon^*(\omega)$  using nonlinear least squares fit method were discussed elsewhere<sup>19</sup>. Figures 2 and 3 show the example of frequency dependent complex permittivity spectra for amide–water mixtures at 25°C.

The binary mixtures for the density measurements were prepared in 5 cm<sup>3</sup> flasks by measuring the masses of the components with an electronic balance. The maximum error in the density measurement was  $\pm 5 \times 10^{-5}$  g·cm<sup>-3</sup>. The measured densities are in good agreement with literature values<sup>20</sup> and are given in Table 1.

## 3 Results and Discussion

The complex permittivity spectra  $\epsilon^*(\omega)$  measured from the TDR technique of the amide–water mixtures were fitted in well known CD model using non linear least squares fit method to determine the dielectric relaxation parameters<sup>21</sup>.

Using CD model the dielectric parameters such as the static dielectric constant  $\epsilon_0$ , permittivity at high frequency  $\epsilon_\infty$ , relaxation time  $\tau$  and  $\beta$  is the Cole-Davidson distribution parameter were obtained. Its value lies such that  $0 \leq \beta \leq 1$ . The dielectric parameters obtained from both the measurement in this study are in good agreement with available

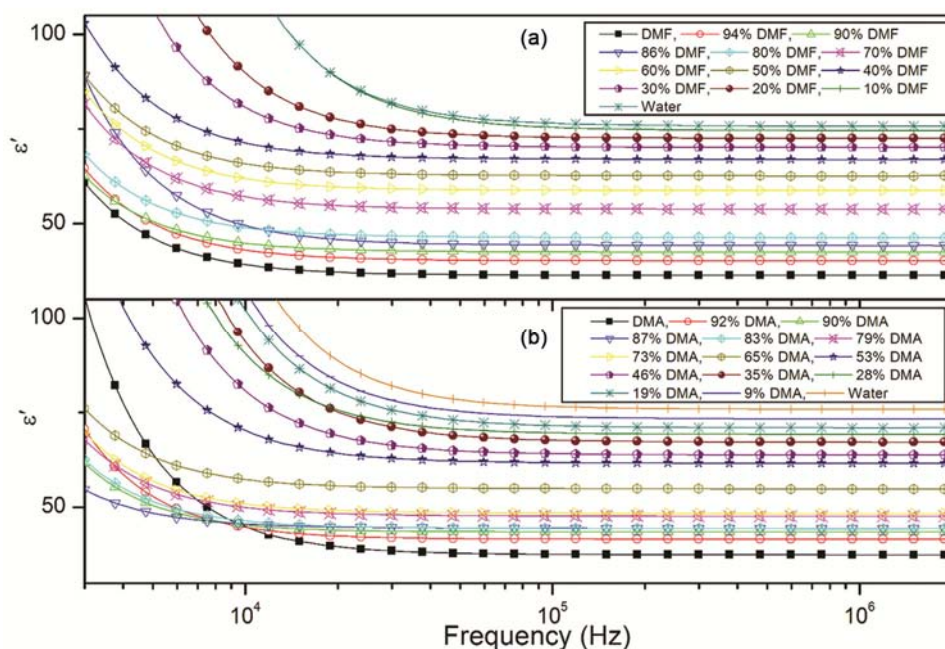


Fig. 1 — Dielectric permittivity spectra for (a) DMF-water and (b) DMA-water mixtures at 25 °C

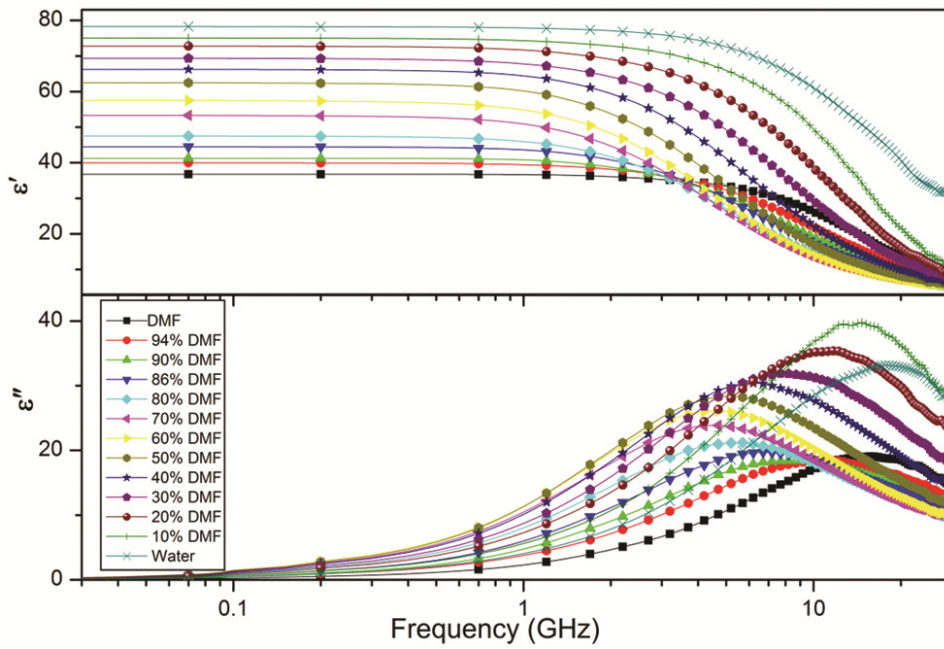


Fig. 2 — Complex permittivity spectra for DMF-water mixtures at 25 °C

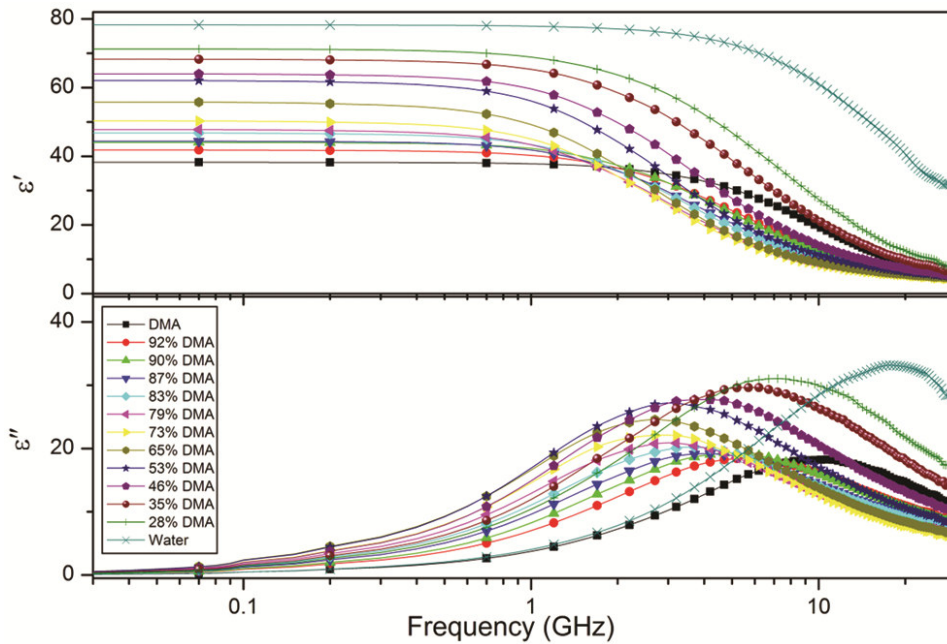


Fig. 3 — Complex permittivity spectra for DMA-water mixtures at 25 °C

literature data<sup>8,9</sup> and are given in Table 1. Figures 4 and 5 give an idea about the behavior of dielectric constant and relaxation time with respect to mixture compositions. In Fig. 4 the values of the static dielectric constant plotted as a function of water mole fraction ( $X_w$ ). The straight dashed lines show the ideal behavior and calculated from the additive equation:

$$\epsilon_{0m} = X_w \epsilon_{0W} + (1 - X_w) \epsilon_{0A} \quad \dots (1)$$

where  $\epsilon_{0m}$ ,  $\epsilon_{0W}$  and  $\epsilon_{0A}$  are the dielectric constants of mixture, water and amide, respectively. The experimental  $\epsilon_0$  values show deviation from the ideal behavior which may be attributed to hetero-molecular interaction in unlike species. Figure 5 is plotted as log

Table1 — Various parameters for the pure liquids measured and evaluated at 25 °C

Liquid	Dielectric constant		Relaxation time $\tau$ (ps)	Density	Kirkwood correlation factor $g$	
	TDR $\epsilon_0$	LCR			TDR	LCR
DMF	37.75	37.45	10.40	0.9383	1.01	1.00
		37.31 <sup>a</sup>	10.77 <sup>b</sup>	0.9438 <sup>c</sup>		1.01 <sup>d</sup>
DMA	38.19	38.55	16.13	0.9321	1.48	1.49
		38.25 <sup>a</sup>	15.80 <sup>b</sup>	0.9364 <sup>c</sup>		1.50 <sup>d</sup>
Water	78.32	78.09	8.21		2.82	2.81

<sup>a</sup>Ref. 7, <sup>b</sup>Ref. 8, <sup>c</sup>Ref. 19, <sup>d</sup>Ref. 13

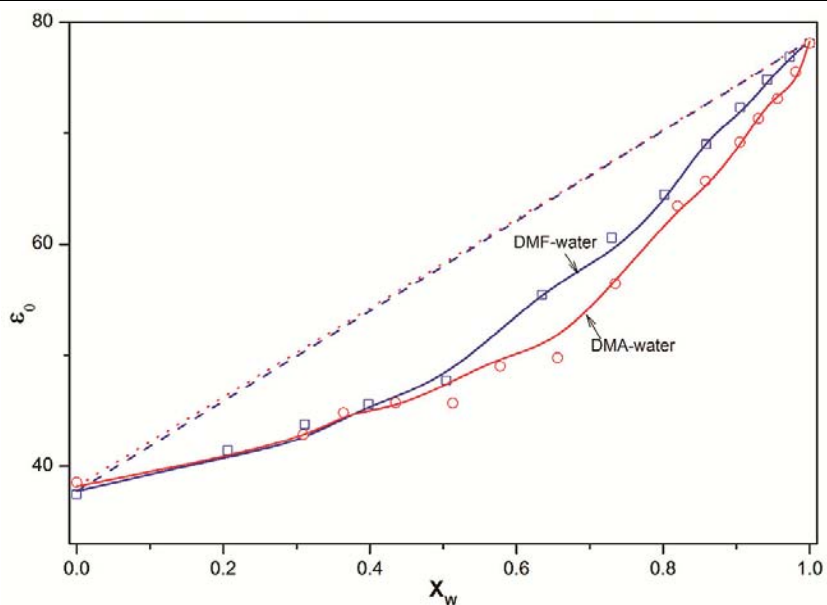


Fig. 4 — Static dielectric constant vs mole fraction of water  $X_w$ , solid lines, open symbols and dash lines are for the values of  $\epsilon_0$  from TDR, LCR and ideal behavior, respectively for amide-water mixtures

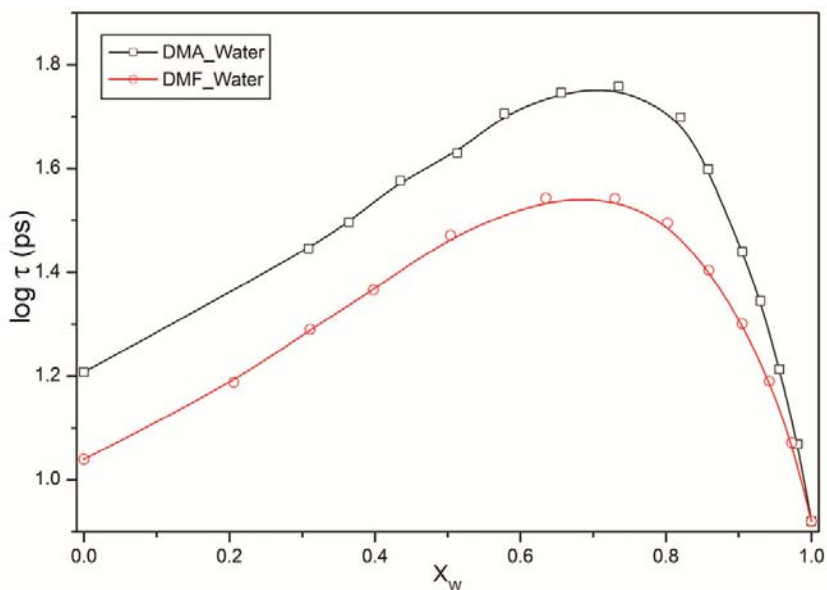


Fig. 5 — log of relaxation time ( $\log \tau$ ) vs  $X_w$  for amide-water mixtures

$\tau$  vs  $X_w$  which shows a nonlinear nature. Initially, as amount of water increases in amides the relaxation times increase up to  $X_w=0.7$ . Further increase in water concentration in binary mixture that is in water rich region the relaxation time monotonously decreases. If we compare two amides studied here, DMA molecule has additional hydrophobic ( $-\text{CH}_2$ ) site than DMF. Therefore, an increase in molecular size may lead to increase in peak values of relaxation times for the DMA-water than DMF-water.

### 3.1 Excess properties

#### 3.1.1 Excess dielectric constant

The excess dielectric constant  $\epsilon_0^E$  values of the binary mixtures of amide-water are obtained by the mole-fraction mixture law<sup>8</sup>. The excess dielectric constant provides qualitative information about multimers formation in the mixtures. The excess dielectric constant values remain negative for whole concentration range plotted in Fig. 6. These negative  $\epsilon_0^E$  values for amide-water mixtures show the experimental evidence of some molecular interaction among the unlike molecules such that the total number of effective dipoles get reduced. The plot exhibits a pronounced minimum which suggests the formation of complex structure in amide-water through H-bonds. It is observed from Fig. 6 that the minima for DMF-water occurs at  $X_w \sim 0.5$  and that for DMA-water at  $X_w \sim 0.65$ . The mole fraction of water  $X_w$  corresponding to the minimum in  $\epsilon_0^E$  value provides the stoichiometric ratio of stable adduct complexation. Here it is found that for DMF:water is 1:1 and same for the DMA-water is 1:1.85. Peak magnitude of  $\epsilon_0^E$  for

DMF-water mixture is less as compared to DMA-water. It reveals that unlike molecule hydrogen bond interaction strength is stronger in DMA-water in comparison with DMF-water mixture.

#### 3.1.2 Excess volumetric properties

Extending our discussion to study the molecular interactions in amide-water further using the measured densities of these binary mixtures around 25 °C, the excess molar volume  $V^E$  of solutions have been obtained using an expression<sup>22,23</sup>. The values of excess molar volume  $V^E$  for binary mixtures of DMF and DMA with water have been plotted in Fig. 7. It is seen that excess molar volumes  $V^E$  are negative over the entire concentration range for all DMF and DMA mixtures. The values of  $V^E$  in these mixtures become more negative with addition of  $-\text{CH}_2$  group, from DMF to DMA. The value of  $V^E$  decreases with increase in concentration of water, pass through a minima and then increase further with increase in the concentration of water. The negative values of  $V^E$  can be attributed to several types of interactions among the solute and solvent molecules. The effect which gives a negative contribution to  $V^E$  is due the difference in molecular size between the solute and solvent molecules which may allow accommodation of amide molecules in the structured water lattice, a void space. Also the contraction in volume might be due to breaking of homogeneous structure of like molecules and interaction among the unlike molecules (amide-water) which may form new hydrogen bonds. The excess properties (dielectric constant and volumetric) are plotted in Figs 6

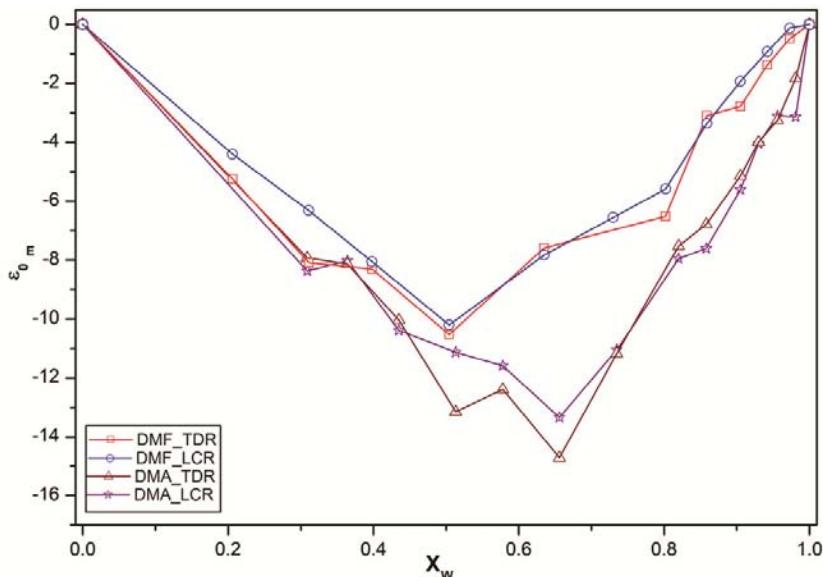


Fig. 6 — Excess dielectric constant  $\epsilon_0^E$  vs  $X_w$  for amide-water mixtures



and 7. These plots are showing the negative values which suggest the significant structural changes in DMF and DMA molecules in presence of water. Excess molar volume values also show similar nature to excess dielectric values, the peak  $V^E$  value for DMA-water is more negative than DMF-water.

### 3.2 Kirkwood Correlation factor

The Kirkwood Frohlich equation for pure liquid gives the useful information regarding the orientation of electric dipole. The deviation of  $g$  value from unity is a measure of degree of short range dipolar ordering

due to hydrogen bond interactions<sup>24</sup>. We have taken  $\epsilon_\infty$  values<sup>25</sup> from refractive index ( $\epsilon_\infty = n^2$ ) data at 25 °C. The  $g$  value for pure DMF is around unity which suggests that there is no orientational correlation among the DMF molecules whereas for DMA it is around 1.50 reveals that the DMA molecules are having parallel orientation of dipoles. The molecular interaction between associating polar liquids can be described by effective Kirkwood correlation factor  $g^{eff}$  in binary mixtures by modified Kirkwood equation<sup>24</sup>. The  $g^{eff}$  values for entire concentrations and temperature range studied here are shown in Fig. 8.

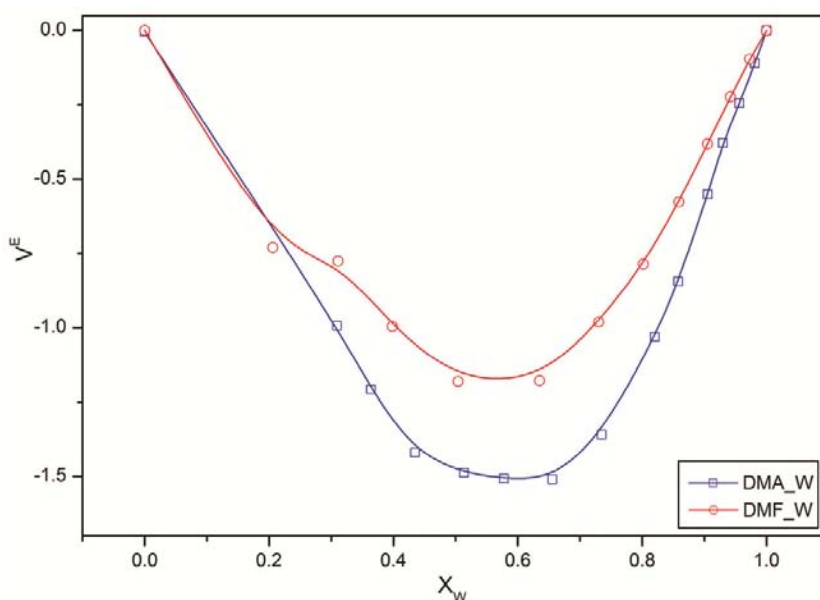


Fig. 7 — Excess molar volume  $V^E$  vs  $X_W$  for amide-water mixtures

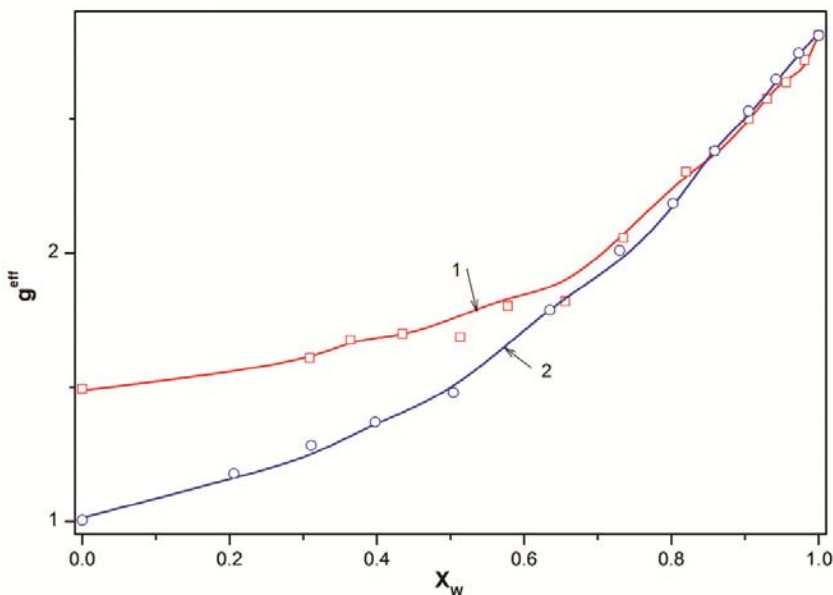


Fig. 8 — Kirkwood correlation factor  $g^{eff}$  as a function of  $X_W$  for amide-water mixtures

The  $g^{eff}$  values for pure liquids like water and DMA are greater than unity, which suggest that the molecular dipoles have parallel orientation among themselves. There is an increasing tendency of  $g^{eff}$  values with respect to the concentration of water. This trend suggests that the heterogeneous interaction between the molecules of the constituent polar liquids and in such a way that they form multimers with increasing parallel orientation of electric dipoles.

### 3.3 Bruggeman factor

The static permittivity of binary mixtures can be obtained by using the Bruggeman mixture formula<sup>26</sup>. Bruggeman expression predicts a linear relationship between the Bruggeman factor  $f_B$  and the volume fraction of water but the experimental values of  $f_B$  show a non linear behavior (Figs 9 and 10). To explain the non linear relationship, modified Bruggeman mixture formula has been used<sup>27</sup>.

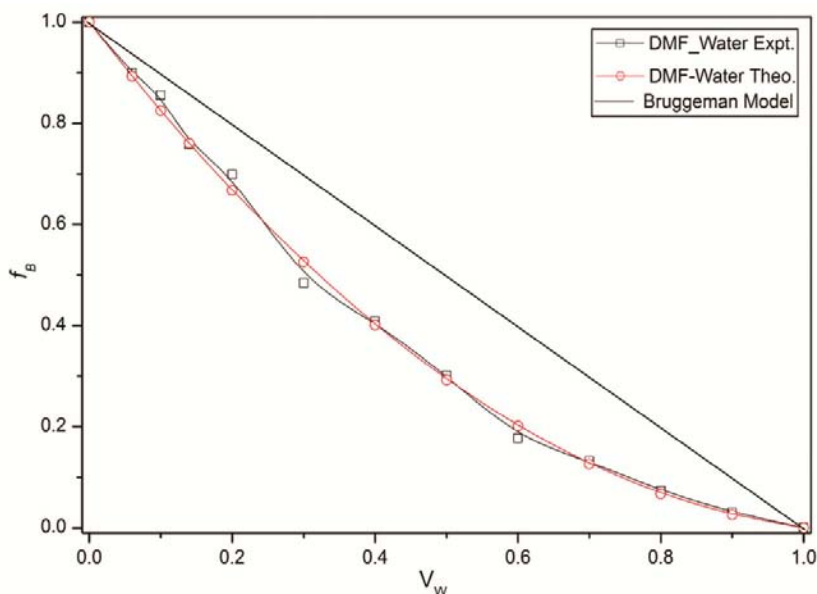


Fig. 9 — Bruggeman factor  $f_B$  for DMF-water mixtures

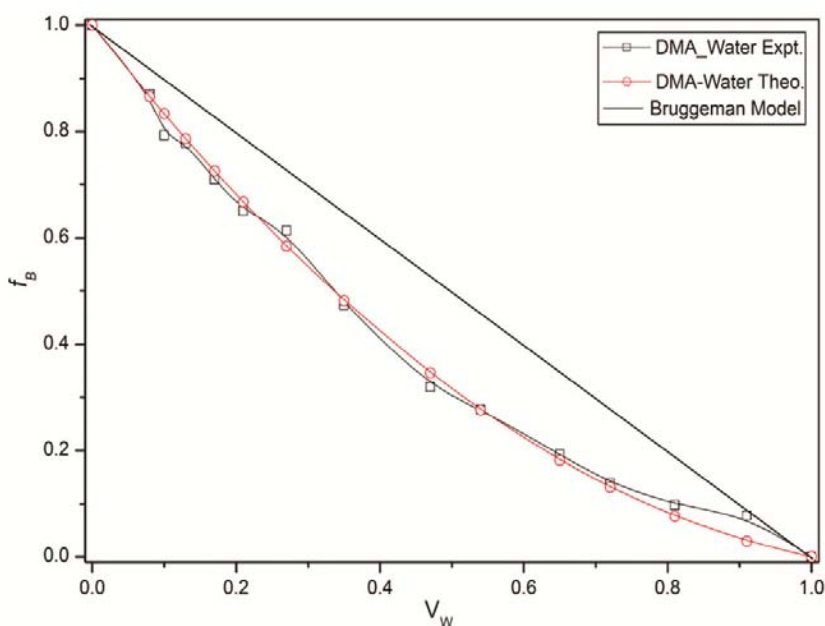


Fig. 10 — Bruggeman factor  $f_B$  for DMA-water mixtures

In which 'a' is arbitrary parameter, the value of  $a=1$  means the ideal mixture with no interaction between solute and solvent. In Figs 9 and 10 solid lines represent the ideal behavior according to Bruggeman mixture formula. Experimental values represent the deviation from ideal behavior of mixture which shows the solute-solvent molecular interaction between amide-water mixtures. The calculated value of 'a' is determined using least square fit method. For DMF-water mixture and DMA-water it is found to be 1.83 and 1.74, respectively at 25 °C.

#### 4 Conclusions

The dielectric behavior of amide-water mixtures is studied at 25 °C. The dielectric parameters studied here shows non linear behavior. The negative values of excess properties for entire concentrations of amide-water attributed as structural changes in pure liquids due to heterogeneous molecular interaction among the unlike molecules. Kirkwood correlation factor for amide-water suggests the formation of multimers with parallel ordered structure. Bruggeman factor for the binary mixtures of amide-water confirms the deviation from ideal behaviour.

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