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Computation of Dielectric Constants of N, N-Dymethylformamide with Propylene Glycol and Water at Different Temperatures

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Abstract: Dielectric constants of binary mixtures of polar liquids have been evaluated at different concentrations and temperatures. The chemicals used were N, N-Dymethylformamide (DMF) as a solvent and Propylene Glycol (PLG), Water (H_2O) as solutes. Excess dielectric constant, Kirkwood correlation factor and Bruggeman factor of the binary solutions has also been reported in the study. The measurements have been carried out using a wet sensor which is based on Frequency Domain Reflectometry (FDR) technique. The results show that the dielectric constant of the binary mixtures depends on the molecular size of the solute. The study also shows the DMF-PLG interaction is more favorable than that of DMF- H_2O interaction.

Keywords: Dielectric constant; Polar liquids; Excess properties; N, N- Dymethylformamide; Propylene Glycol; Water.

I. INTRODUCTION

Thermophysical properties of pure liquids such as dielectric constant, viscosity, density and refractive index and their mixtures are essential for accurate design and optimal operation of many industrial processes. With the development of measuring techniques and instruments, these properties can now be obtained in an easy, fast and precise way, which allows systematic and accurate investigations of these properties [1]. The variation of these properties with composition and temperature gives important data about intermolecular interactions and the structure. There are wide range of possible interactions between the components of a mixture, such as hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole induced dipole interactions [2].

The dielectric study of materials provides vital information about dielectric parameters and molecular interaction, which are of direct technological importance. The knowledge of dielectric properties of materials and their frequency and temperature dependence is of great importance in various areas of science and engineering in both basic and applied research. Dielectric properties obtain can be related to a physical parameter of interest. It has been demonstrated that properties such as moisture control, bacterial content, mechanical stress and other seemingly unrelated parameters are related to the dielectric properties or permittivity of the material [3-5].

Accurate measurement of these properties can provide scientists and engineers with valuable information that allows them to properly incorporate the material into its intended applications or to monitor a process for improved quality control. The permittivity is the fundamental property of the material and is independent of the measurement technique. The interpretation of dielectric behavior of a material in terms of its molecular structure is a scientific objective. The dielectric properties are essential and useful in a vast area of physical and biological sciences, engineering technologies [7-10].

In the present study, dielectric constants of N, N-Dymethylformamide with propylene glycol and water have been reported at 298, 308 and 318K temperatures. The Excess Dielectric Constant (ε^E), Kirkwood correlation factor (g^{eff}) and Bruggeman factor (f_B) of the binary mixtures have also been reported to study their structure, hydrogen bonding and intermolecular interactions.

II. EXPERIMENTAL

The chemicals used in the present investigation are in spectroscopic grade with 99.9% purity and were used without further purification. The solutions were prepared by mixing N, N-Dymethylformamide (DMF) with Propylene Glycol (PLG) and N, N-Dymethylformamide with Water (H_2O) at eleven different volume percentages of PLG and Water as 0 to 100% in steps of 10%. The temperature controller system with water bath has been used to maintain the constant temperature within an accuracy limit of ± 2°C. The sample cell is inserted into a constant temperature bath and the water of constant temperature using a temperature controller system is circulated.

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Measurement of Dielectric Constant

The dielectric constants of the binary mixtures were measured using a wet sensor make by Delta-T Devices Ltd. UK, which is based on the principle of frequency domain reflectometry (FDR) technique. When power is applied to the sensor, it creates a 100 MHz frequency signal. This signal is then applied to a pair of stainless steel rods, which transmit an electromagnetic field in to the mixture. The field passes easily through the mixture resulting in stable voltage output that acts as a simple sensitive measure of the dielectric constant. The measurements were recorded with a calibrated meter which is connected to the wet sensor through a cable. When probes of the sensor inserted into the mixture, pressing the read button on the meter, the dielectric constant reading will display on it. There is facility to store the readings in the meter. Each measurement was repeated at least three times and the average value of that reading was taken as a dielectric constant. The accuracy of measurement in dielectric constant was ± 4%.

Study of Excess Permittivity

The information related to the excess permittivity of the binary solution was obtained from the excess properties [11] of the mixture. The excess permittivity is defined as

$$\varepsilon^{\mathrm{E}} = (\varepsilon_{\mathrm{O}})_m - [(\varepsilon_{\mathrm{A}} \cdot \mathrm{X}_{\mathrm{A}}) + (\varepsilon_{\mathrm{B}} . \mathrm{X}_{\mathrm{B}})], \qquad (1)$$

Where X is the volume fraction and suffix m, A, B represents a mixture, liquid A (DMF) and liquids B (PLG or water) respectively. Excess permittivity provides qualitative information about the formation of new structure in the mixture as follows:

i) $\varepsilon^E = 0$: indicates that solution A and B do not interact.
ii) $\varepsilon^E < 0$: indicates that solution A and B interact is in such a way that the effective dipole moment gets reduced.
iii) $\varepsilon^E > 0$: indicates that solution A and B interact in such a way that the effective dipole moment increases.

Study of Kirkwood Correlation Factor

The Kirkwood correlation factor [12] provides information regarding the orientation of the electric dipoles in polar liquids.

For a pure polar liquid, the Kirkwood correlation factor “g” may be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9KTM} g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}, \qquad (2)$$

Where μ is dipole moment, ρ is density at temperature T, M is molecular weight, K is Boltzman constant, N is Avogadro’s number, ($\in_s$) is the static dielectric permittivity and ε_∞ is the dielectric permittivity at high frequency, often represented by the square of the refractive index.

Modified forms of this equation have been used to study the orientations of electric dipoles in the binary mixtures are given by Kumbharkhane et al [13, 14] two such equations used are as follows:

$$\frac{4\pi N}{9kT}\left(\frac{\mu^2{}_M\rho_M}{M_M}X_M + \frac{\mu^2{}_F\rho_F}{M_F}X_F\right)g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{[\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2]}, \qquad (3)$$

Where “g^{eff}” is the Kirkwood correlation factor for the binary mixtures. g^{eff} varies between g_M and g_F.

$$\frac{4\pi N}{9kT}\left(\frac{\mu^2{}_M\rho_M g_M}{M_M}X_M + \frac{\mu^2{}_F\rho_F g_F}{M_F}X_F\right)g^f = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2}), \qquad (4)$$

g_M and g_F are assumed to be affected by an amount “g^f” in the mixture. $g^f = 1$ for an ideal mixture and deviation from unity may indicate the interaction between the two components of the mixture.

Study of Bruggeman Factor

Static permittivity of two mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids a various mixture formula has been proposed [15].

Bruggeman mixture formula [16, 17] can be used as first evidence of molecular interactions in the binary mixture. The effective volume of the solute gets modified by solute – solvent interactions and is best illustrated by the non-linearity of Bruggeman formula. The static dielectric constant ($\in_s$) of the mixtures is related to the Bruggeman mixture formula with the volume fraction of solute which indicates the interaction between solvent and solute. This formula states that static dielectric permittivity of binary mixture ($\in_{sm}$), solute ($\in_{sB}$) and solvent ($\in_{sA}$) can be related to volume fraction of solvent (V) which indicates the interaction between solvent and solute in the mixture and it is given by [18]

$$f_{BM}=\left[\frac{\epsilon sm-\epsilon sB}{\epsilon sA-\epsilon sB}\right]\left[\frac{\epsilon sA}{\epsilon sm}\right]^{\frac{1}{3}}=1-V, \qquad (5)$$

Where ‘V’ is the volume fraction. In fact, mole fraction is a qualitative measure of the volume fraction of the solute. εsm, εsA and $\varepsilon sB$are static dielectric constant values of mixture, solution A (solvent) and solution B (solute) respectively. According to above equation linear relationship is expected in the Bruggeman factor **(**F_{BM}) and (V). Any deviation from this linear relation indicates molecular interaction [19]. When both the solvent and the solute happen to be polar liquids, the Bruggeman equation has to be modified as;

$$f_{BM}=1-[a-(a-1)V\,]\,V, \qquad (6)$$

Where ‘a’ is the interaction factor. The relative change in value of ‘a’ reveals the amount of interaction between solute and solvent as follows:

i) a >1: indicates that the effective microscopic volume of solvent gets more than the actual volume. The solute exerts a repulsive force on the system.

ii) a <1: indicates that the effective microscopic volume of solvent gets less than the actual volume. The solute exerts an attractive microscopic force on the system.

iii) a =1: indicates that there is no change in effective microscopic volume of the system and that corresponds to the ideal Bruggeman mixture factor.

III. RESULTS AND DISCUSSIONS

The variation in dielectric constant (ε_s) of the binary mixtures of DMF-PLG and DMF- Water are shown in Fig.1 and 2 respectively.

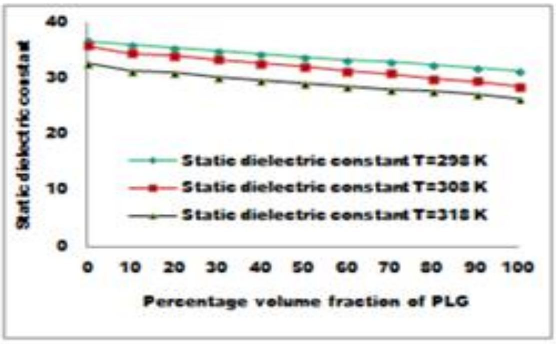

Fig. 1. Static dielectric constant for various compositions of mixtures of DMF- PLG at 298, 308 and 318 K.

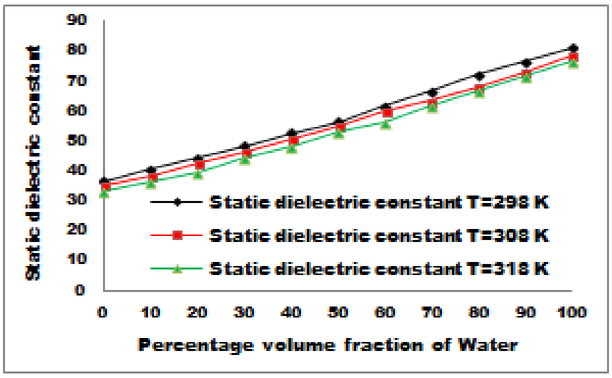

Fig. 2. Static dielectric constant for various compositions of mixtures of DMF- H_2O at 298, 308 and 318 K.

The variation in dielectric constant is different for both the binary mixtures. The dielectric constant of the binary mixtures decreases with increase in temperature and it is same for both the binary mixtures. The decrease in dielectric constant with increase in temperature is due to rapid fall in orientation polarization, because an increased thermal motion reduces the alignment of the permanent dipoles [20].

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The dielectric permittivity of (DMF- PLG) binary mixture (Fig. 1) decreases with an increase in volume fraction of PLG for entire volume fraction range. The decrease in dielectric permittivity with an increase in volume fraction of PLG may be due to increase in size and shape of the complex molecules after hydrogen bonding interaction. This could be attributed to the decrease in the number of dipoles in the complex, which may lead to decrease in the volume of the rotating molecules. The other reason may be due to the bigger molecular structure of the solute (PLG). When the higher molecular dimension solute (PLG) is added to solvent (DMF) the resultant dipole moment of the binary mixture decreases, which will decrease its mobility in the mixture that will results in a decrease in dielectric permittivity [21].

The dielectric permittivity of DMF- H_2O binary mixture (Fig. 2) increases with increase in volume fraction of water for entire volume fraction range. The increase in dielectric permittivity with an increase in volume fraction of water may be due to decrease in size and shape of the complex molecules. This could be attributed to the increase in the number of dipoles in the complex, which may lead to an increase in the volume of the rotating molecules. The other reason may be due to the smaller molecular structure of the solute (Water) than that of the solvent (DMF). Due to smaller molecular structure of the solute (Water) its mobility in the mixture will increase and that will results in increase in dielectric permittivity.

The experimental study of binary mixtures shows the dielectric constant of the mixtures depends on the molecular structure of the solute. If the molecular structure of the solute is bigger than that of solvent, the dielectric constant of the binary mixtures decreases and vice - versa [22, 23].

Excess permittivity (ε^E) provides significant information regarding interaction between the polar-polar liquid mixtures. Excess dielectric permittivity of the binary mixtures was calculated using equation (1). Excess permittivity (ε^E) of the binary mixtures of DMF-PLG and DMF – H_2O at 298, 308, and 318K is given in Table 1 and 2 respectively.

Table 1. Variation in estimated values of excess dielectric constant of DMF- PLG binary mixtures at different temperatures

Percentage volume of PLG in DMF	Excess dielectric constant T=298 K	Excess dielectric constant T=308 K	Excess dielectric constant T=318 K
00	0	0	0
10	-0.17	-0.58	-0.60
20	-0.19	-0.34	-0.42
30	-0.14	-0.26	-0.44
40	-0.27	-0.16	-0.54
50	-0.13	-0.07	-0.50
60	-0.25	-0.02	-0.42
70	0.01	0.22	-0.29
80	0.10	0.33	0.19
90	0.16	0.31	0.09
100	0	0	0

Table 2. Variation in estimated values of excess dielectric constant of DMF- H_2O binary mixtures at different temperatures.

Percentage volume of Water in DMF	Excess dielectric constant T=298 K	Excess dielectric constant T=308 K	Excess dielectric constant T=318 K
00	0	0	0
10	-1.08	-1.42	-1.38
20	-1.62	-1.34	-2.15
30	-1.59	-1.79	-2.04
40	-1.99	-1.54	-2.15
50	-2.67	-2.23	-1.87
60	-1.76	-1.30	-2.88
70	-1.46	-2.27	-1.43
80	-0.28	-1.73	-1.10
90	-0.12	-1.02	-0.28
100	0	0	0

As given in Table 1, the excess permittivity is negative in DMF rich region and positive in PLG rich region for the studied temperatures. This indicates that in DMF rich region, the mixture of DMF-PLG solutions interacts in such a way that the effective dipole moment decreases. The negative values of (ε^E) suggest that the effective number of dipoles in the mixture might be smaller than the corresponding average number in the pure liquids, probably due to the creation of new structure leading to a lower macroscopic permittivity.

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Excess permittivity is positive in PLG rich region. This indicates that in PLG rich region the mixture of DMF-PLG solutions interacts in such a way that the effective dipole moment increases. The positive values of (ε^E) suggest that the effective number of dipoles in the mixture might be greater than the corresponding average number in the pure liquids, probably due to the creation of new structure leading to a higher macroscopic permittivity.
The excess permittivity is negative for entire volume fraction range of DMF - H_2O binary mixture (Table 2) at the studied temperatures. These negative values of (ε^E) suggest that the effective number of dipoles in the mixture might be smaller than the corresponding average number in the pure liquids, probably due to the creation of new structure leading to a lower macroscopic permittivity. The results are in agreement with the earlier results of Navarkhele et al [24].
In the mixture, the dipole pairs are formed and orient in parallel and antiparallel direction in the binary mixtures that is studied from Kirkwood angular correlation factor. The Kirkwood angular correlation factor (g^{eff}) of the binary mixtures of DMF-PLG and DMF- H_2O is calculated and illustrated graphically in Figs. 3 and 4 respectively.

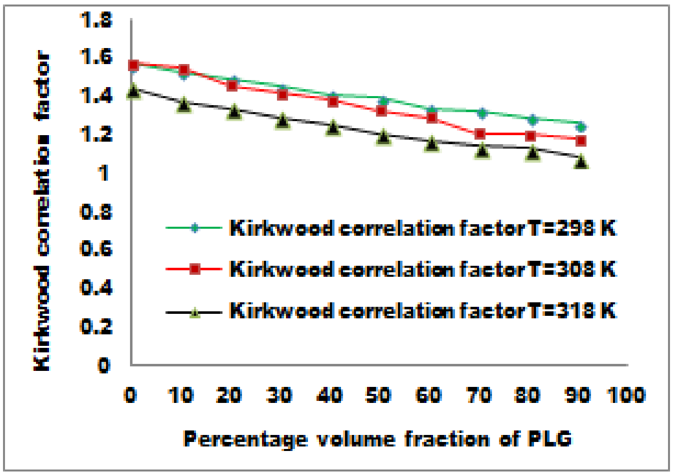

Fig. 3. Kirkwood correlation factor (g^{eff}) for various compositions of mixtures of DMF-PLG at 298, 308 and 318 K.

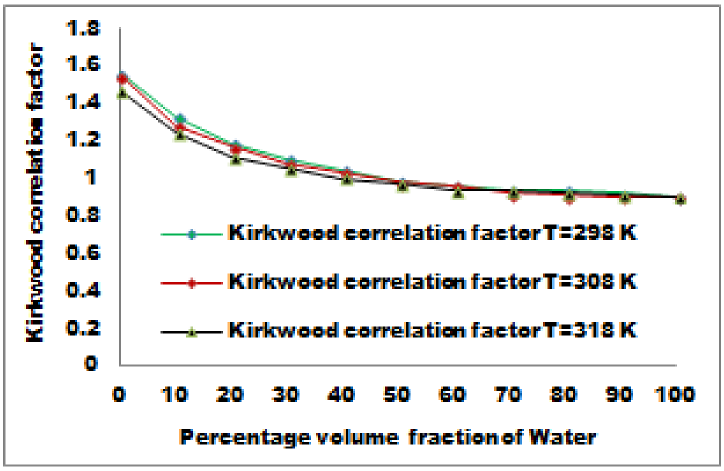

Fig. 4. Kirkwood correlation factor (g^{eff}) for various compositions of mixtures of DMF- H_2O at 298, 308 and 318 K.

From Fig. 3 it is seen that, the g^{eff} values of DMF-PLG binary mixtures is greater than 1 ($g^{eff} > 1$) for entire volume fraction range and at the studied temperatures; indicates parallel orientation of electric dipole in the DMF molecules. The g^{eff} values of DMF- H_2O binary mixtures are greater than 1 ($g^{eff} > 1$) in DMF rich region (Fig. 4) and ($g^{eff} < 1$) in water rich region for the studied temperatures. $g^{eff} > 1$ indicates parallel orientation of electric dipoles in the DMF molecules. $g^{eff} < 1$ in water rich region indicate antiparallel orientation of electric dipoles of water molecules. The addition of water to DMF causes breaking of antiparallel orientation of water molecules. The results are in agreement with the earlier results of Hosamani et al [25].

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Bruggeman factor values of DMF-PLG and DMF- H_2O binary mixtures at 298 308, and 318K are graphically given in Fig. 5 and 6 respectively.

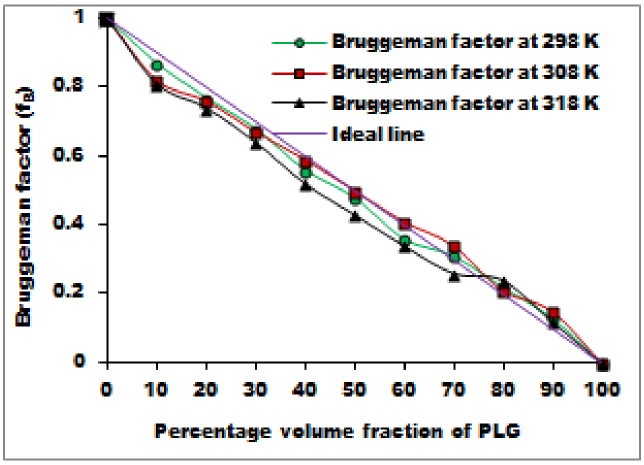

Fig. 5. Bruggeman factor (f_B) for DMF-PLG at 298, 308 and 318 K.

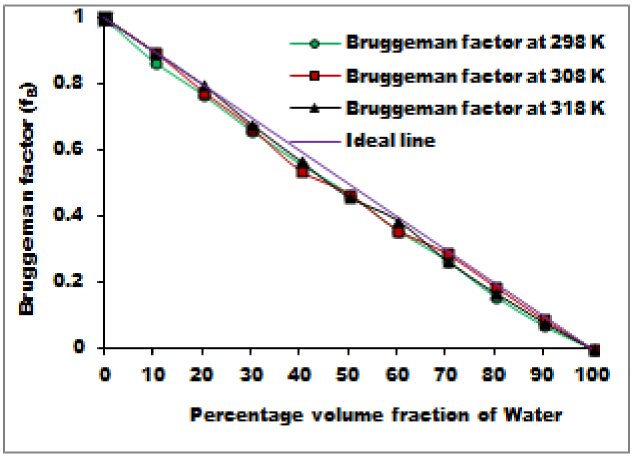

Fig. 6. Bruggeman factor (f_B) for DMF- H_2O at 298, 308 and 318 K.

From Fig. 5 it is noted that, there is more deviation from the linear relation of binary mixtures has been take place at the studied temperatures, which give the evidence of presence of molecular interactions and hydrogen bonding in the said binary mixtures. It is also observed that the values of ‘a’ are smaller than 1 ($a < 1$), indicating that the effective microscopic volume of solvent (DMF) gets less than the actual volume, and the solute (PLG) exerts an attractive microscopic force in the system.

From Fig. 6 it is seen that a very small deviation from the linear relation of the binary mixtures has been occurred at the studied temperatures, which show weaker molecular interaction and hydrogen bonding in the said binary mixtures. In this binary mixtures, the values of ‘a’ are greater than 1 ($a > 1$), indicates that the effective microscopic volume of solvent (DMF) gets more than the actual volume, and the solute (water) exerts an repulsive microscopic force in the system.

Bruggeman factor study of the binary mixtures of DMF-PLG and DMF- H_2O (Figs. 5 and 6) shows that there is higher deviation from linear relation for DMF-PLG than that of DMF- H_2O binary mixtures, indicates that the DMF-PLG interaction is more favorable than that of DMF – H_2O interaction [26].

IV. CONCLUSION

The dielectric constant of the binary mixtures depends on the molecular structure of the solute. If the molecular structure of the solute is bigger than that of solvent; the dielectric permittivity of the binary mixtures decreases and vice – versa Excess permittivity is negative in DMF rich region and positive in PLG rich region of the DMF-PLG binary mixture. It is negative for entire volume fraction range of DMF-Water binary mixtures.

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In DMF-PLG binary mixture the dipole pairs are formed and orient in parallel direction for entire volume fraction range. In DMF- H_2O binary mixture the electric dipoles are formed and orient in parallel direction in DMF rich region and in antiparallel direction in water rich region for the studied temperatures which is confirmed from the (g^{eff}) values.
The Bruggeman factor study of the binary mixtures shows the deviation from the linear relations, which give the strong evidence of presence of molecular interactions and hydrogen bonding in the binary mixtures.
In DMF- H_2O binary mixtures there is a very small deviation from the linear relations than that of DMF-PLG binary mixtures; this show weaker hydrogen bonding in DMF- H_2O binary mixtures. The Bruggeman factor study show, DMF (solvent) favors PLG (solute) for interaction and hydrogen bonding than that of Water (solute).

Conflicts of interest

This is an original research work carried by the author using a FDR sensor working at 100 MHz frequency.
There are no conflicts to declare.

Captions to the Figures

Fig. 1. Static dielectric constant for various compositions of mixtures of DMF- PLG at 298, 308 and 318 K.
Fig. 2. Static dielectric constant for various compositions of mixtures of DMF- H_2O at 298, 308 and 318 K.
Fig. 3. Kirkwood correlation factor (g^{eff}) for various compositions of mixtures of DMF-PLG at 298, 308 and 318 K.
Fig. 4. Kirkwood correlation factor (g^{eff}) for various compositions of mixtures of DMF- H_2O at 298, 308 and 318 K.
Fig. 5. Bruggeman factor (f_B) for DMF- PLG at 298, 308 and 318 K.
Fig. 6. Bruggeman factor (f_B) for DMF- H_2O at 298, 308 and 318 K.

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