

Dielectric Relaxation in Dimethyl Sulfoxide/Water Mixtures

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Dielectric spectra of dimethyl sulfoxide (DMSO)/water mixtures, over the entire concentration range, were measured using the transmission line method at frequencies from 45 MHz to 26 GHz and at temperatures of 298–318 K. The relaxation times of the mixtures showed a maximum at an intermediate molar fraction of DMSO. A water structure “breaking effect”, manifested by a reduced average number of hydrogen bonds per water molecule, was observed in dilute aqueous solutions based on the dielectric relaxation dynamics analysis. The increase in the dielectric relaxation time in DMSO/water mixtures was attributed to the spatial (steric) constraints of DMSO molecules on the hydrogen bond network, rather than being due to hydrophobic hydration of the methyl groups. The interactions between water and DMSO molecules in DMSO-rich mixtures are also discussed.

Introduction

In this paper, we present and discuss results of a dielectric relaxation study of aqueous solutions of dimethyl sulfoxide (DMSO). The interest in DMSO is due, in part, to the wide use of DMSO-H₂O as a mixed-solvent, e.g. in reaction media. DMSO is a multifunctional molecule with a highly polar S=O group and two hydrophobic CH₃ groups. The partial negative charge on the oxygen atom of DMSO molecule favors the formation of hydrogen bonds with water molecules, while the nonpolar CH₃ groups may give rise to hydrophobic hydration and hydrophobic association of DMSO molecules. Many observations (1-4) suggest that DMSO forms hydrogen bonds with water molecules throughout the whole composition range of DMSO/water mixtures. It is generally concluded that in the DMSO mole fraction range of 0.3-0.4 DMSO interactions with water, due to hydrogen bonding, are at a maximum.

Dielectric relaxation studies of DMSO/water mixtures have been the subject of several investigations (5-9). Kaatze et al. (5) measured the dielectric spectra of aqueous DMSO solutions over the complete composition range at 25 °C between 1 MHz and 40 GHz. A strong increase of relaxation time was observed with increasing DMSO concentration for the mixtures in the water-rich region. Similar behavior was also observed by Lyashchenko et al. (6) and Puranik et al. (8). This increase in relaxation time was explained to be due to hydrophobic hydration effects, simply as an analogy to the increased dielectric relaxation times typically found in hydrated macromolecules.

However, this analogy ignores the effects of strong H-bonds between water and DMSO molecules and may not be directly transferable. Buchner et al. (10) applied the absolute reaction rate theory to determine the dielectric activation enthalpy and entropy for water from the dielectric relaxation times and to understand the molecular dynamics in water. A similar approach has also been used in the investigation of alcohol/water systems (11). The same method seems to be applicable to DMSO/water mixtures. Therefore, a main goal of this paper is to investigate the dielectric relaxation in the DMSO/water mixtures in hope of better understanding the dielectric mechanism of this system.

Along these lines, it is also interesting to investigate the dielectric relaxation of highly concentrated DMSO solutions, since dimethyl sulfoxide is a self-associating liquid. Infrared and Raman studies (12,13) suggest the existence of dimers and higher “polymers” in liquid DMSO, which could be traced to a distinct anti-parallel ordering of DMSO molecular dipoles, as observed by static permittivity measurements (5) and by molecular dynamics simulation (14). In highly concentrated solutions, insufficient water molecules are available to completely hydrate each DMSO molecule. One would thus expect that it is the solute-solute association that leads to the formation of microphases in these solutions. However, one also expects that other molecular complexes will be formed as well, e.g., through the hydrogen bonding between DMSO and water; for example, a recent MD simulation (15,16) revealed the existence of 1H₂O-2DMSO clusters (an association of a pair of DMSO molecules through their oxygen atoms linked by one water molecule) in DMSO-rich mixtures.

In view of the conflicting interpretations from previous studies concerning the structure of dimethyl sulfoxide/water mixtures, it was deemed appropriate to investigate the temperature dependence of the dielectric spectra of aqueous DMSO solutions over the whole composition range. Accordingly, in this study, we measured the dielectric relaxation spectra over a wide frequency range of 45 MHz - 26 GHz and at temperatures ranging from 25 to 45 °C. The aim of this paper is to explore the relative contributions of the hydrophobic and hydrophilic groups of DMSO to modifying water structure, and to elucidate the structure of DMSO/water mixtures as a function of concentration.

Experimental

Dimethyl sulfoxide (DMSO, Sigma-Aldrich, 99.97%) was used as received. Double distilled and deionized water (>18 MΩ, Millipore) was used in all the experiments. The DMSO/water mixtures at different DMSO mole fractions (x_{DMSO}) were prepared by mixing appropriate amounts of solute and solvent.

The complex permittivity spectra of the DMSO/water mixtures in the frequency range from 45 MHz to 26 GHz were measured with a transmission line using a traveling-wave method. The wave transmitted through a liquid-filled coaxial line in the form of transmitted S-parameter (S_{21}) was measured by an HP8510C vector network analyzer. This technique was previously developed to measure the dielectric properties of hydrated polymer electrolyte membranes in the authors' laboratory (17,18). The DMSO/water mixture sample was placed in a vertically positioned coaxial line (7 mm outer diameter and 10 cm long). A thin layer of dielectric plug (vacuum grease, in this case, whose dielectric properties are close to that of air and have negligible influence in solving for

dielectric spectra of DMSO/water mixtures) was placed in the probe connector to prevent liquid leakage. Before measurement, the system was calibrated with an open, a short, and a known load (50Ω). Calibration of the S_{21} magnitude was made by performing a simple through connection with air as the dielectric medium. Due to the high dielectric loss of the DMSO/water mixtures, several sample lengths varying from 10 cm to 1 cm, were used to obtain the optimal measurement of the complete dielectric spectrum. Detailed explanation for the apparatus, the measurement procedure, and the accuracy of the data, as well as of the technique validation for liquid media, are discussed elsewhere (18).

Dielectric measurements were carried out at temperatures over the range of 25–45 °C at intervals of 5 °C. The coaxial line was heated by using a heating tape and the temperature was controlled by a temperature controller to a precision of ± 0.5 °C. The uncertainties of the complex permittivity values depend on the accuracy of the scattering parameters and on the magnitude of the ϵ' and ϵ'' , themselves. Typical errors of less than 3% for ϵ' and ϵ'' were obtained. The experimental dielectric spectra were fitted by a complex nonlinear least-square routine to various models represented by the generalized Havriliak-Negami function (19)

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

where ϵ_s is the static permittivity; ϵ_{∞} is the high-frequency limiting permittivity; τ is the relaxation time; α ($0 \leq \alpha \leq 1$) and β ($0 \leq \beta \leq 1$) are shape parameters describing symmetric and asymmetric distribution of relaxation times, respectively. Three well-known models can be considered as limiting cases of this general equation: they are the Debye equation ($\alpha=0, \beta=1$), the Cole-Cole equation ($0 \leq \alpha < 1, \beta=1$), and the Davidson-Cole equation ($\alpha=0, 0 < \beta \leq 1$).

Results and Discussion

The Cole-Cole representation of the permittivity spectra of the DMSO/water mixtures at selected DMSO mole fractions (from 0 to 1) and in temperatures of 298 – 318 K (25 – 45 °C) are shown in Figure 1. The permittivity spectra, $\epsilon^*(\omega)$, of the mixtures at various compositions were analyzed by simultaneously fitting $\epsilon'(\omega)$ and $\epsilon''(\omega)$ to Eq. 1 with adjustable α and β . The best results, i.e., the minimum variance of the fit and a consistent set of relaxation parameters as a function of composition and temperature, are obtained using the Davidson-Cole function ($\alpha=0$ in Eq. 1). This is in agreement with prior literature (5,8). The dielectric spectrum of pure water in this frequency range is described as being a Debye relaxation (20,21).

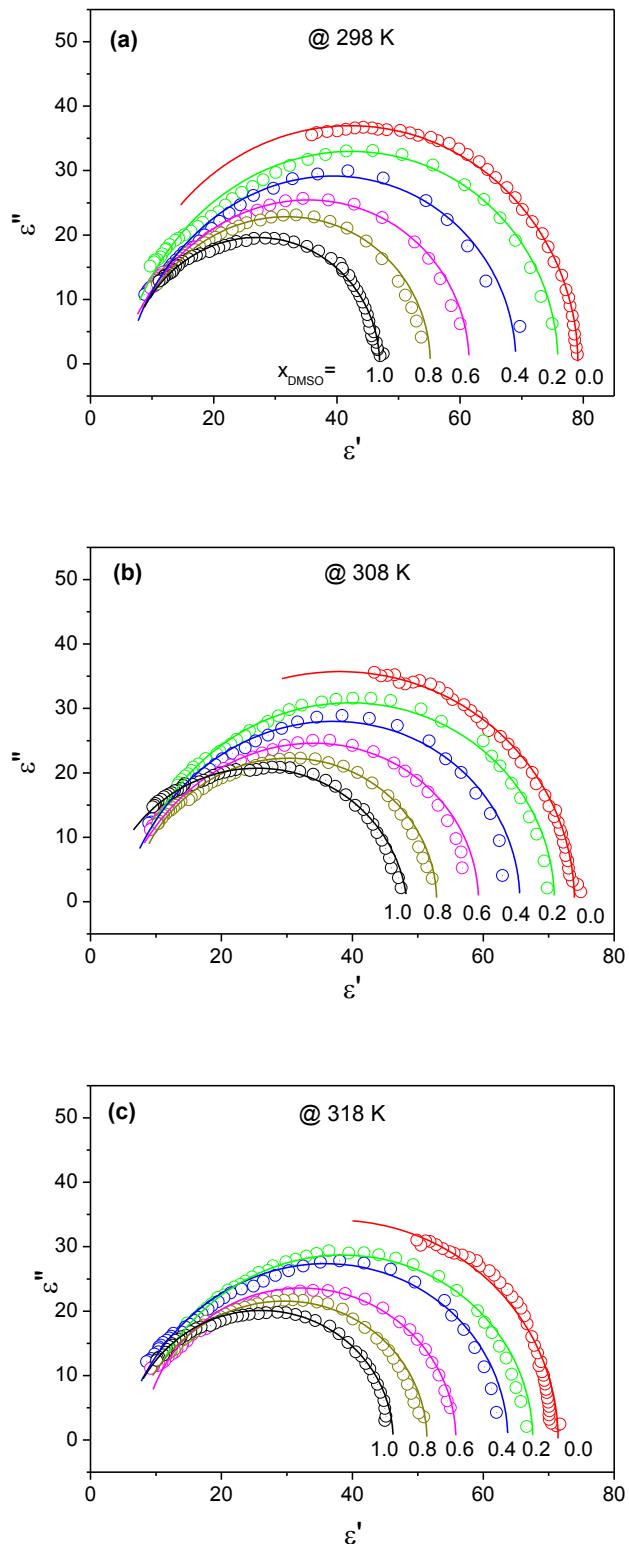


Figure 1. Cole-Cole diagrams of permittivity spectra (ϵ' and ϵ'') of DMSO/water mixtures at 298 – 318 K at selected concentrations (0 to 100 mol.% DMSO, in steps of 20%, the numbers in the figure provide the mole fraction of DMSO). The solid lines are the best fits with a Davidson-Cole function.

The corresponding dielectric parameters, i.e., relaxation time (τ) and the spread of the relaxation time distribution (β), obtained through Davidson-Cole function fits from a larger number of DMSO/water concentrations are shown in Figures 2 and 3. At each temperature, τ increases with x_{DMSO} at small DMSO contents and reaches a maximum when x_{DMSO} is in the range of 0.3-0.4, which also corresponds to a local maximum of β (Figure 3). As DMSO concentration further increases, the τ of the mixtures decreases smoothly to the relaxation time of pure DMSO.

Previous studies (5,6) have attributed the increase in the relaxation time with DMSO concentration to hydrophobic hydration caused by the nonpolar methyl groups, in an analogy to hydrophobic hydration in macromolecules. However, this analogy ignores the effects of the strong hydrogen bonds between DMSO and water molecules, a contribution that can be delineated through further analysis of the obtained dielectric relaxation times.

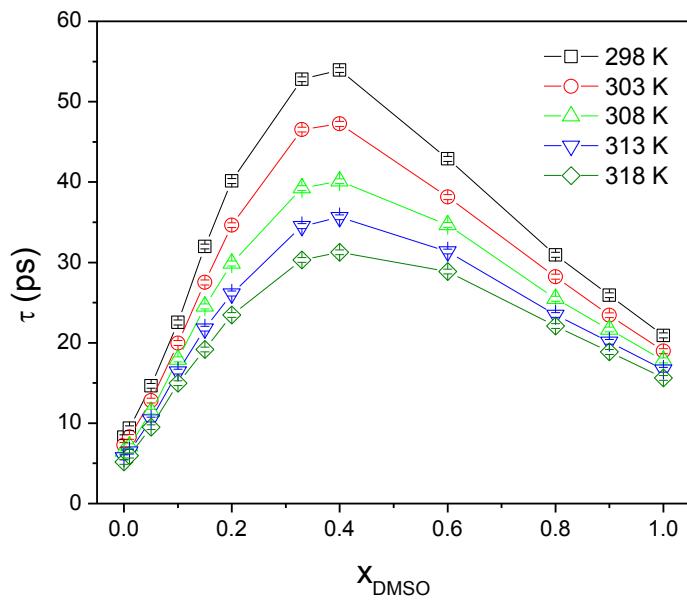


Figure 2. Plot of the relaxation time (τ) from fitted Davidson-Cole functions versus the DMSO mole fraction for the full range of DMSO/water mixtures (data shown over a temperature range of 298 – 318 K at an interval of 5 K).

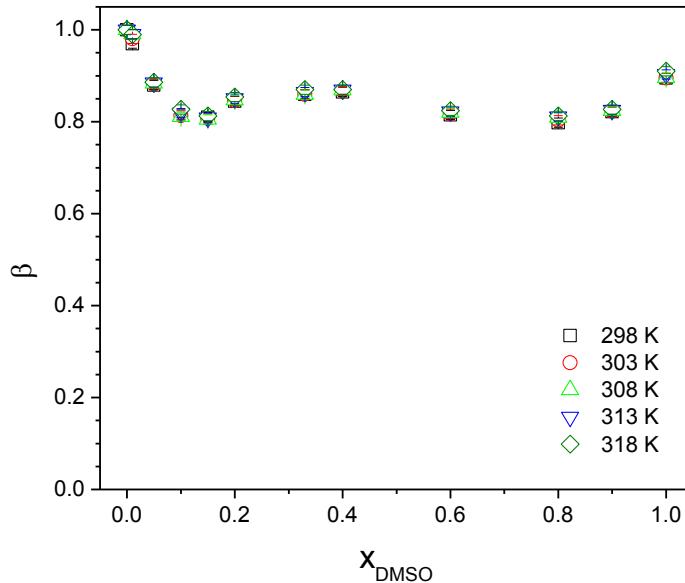


Figure 3. Plot of the relaxation time distribution parameter (β) from fitted Davidson-Cole functions ($\alpha = 0$) shown as a function of the DMSO mole fraction for the full range of DMSO/water mixtures (the temperature range was 298 – 318 K at an interval of 5 K).

The dielectric relaxation can be treated as a rate process involving a path over a potential barrier (10,11). The corresponding energy of activation, $\Delta G^{0,\neq}$, as well as its enthalpy ($\Delta H^{0,\neq}$) and entropy ($\Delta S^{0,\neq}$) contributions, for such a dielectric relaxation process can be calculated from the relaxation time by using the Eyring equation

$$\Delta G^{0,\neq} = \Delta H^{0,\neq} - T\Delta S^{0,\neq} = RT \ln\left(\frac{k_B T \tau}{h}\right) \quad [2]$$

where T is the absolute temperature, and h , k_B , and R are the Planck constant, the Boltzmann constant, and the ideal gas constant, respectively. These energy terms, particularly $\Delta H^{0,\neq}$ and $\Delta S^{0,\neq}$, provide important information for the molecular interactions and dynamics of the components and their mixtures. Figure 4 shows the $\Delta H^{0,\neq}$ and $\Delta S^{0,\neq}$ of the mixtures, as a function of the DMSO mole fraction. Three different regions, separated by boundaries at $x_{\text{DMSO}} \sim 0.1$ and $x_{\text{DMSO}} \sim 0.6$, are apparent from the dependencies of activation enthalpy and entropy on composition (Figure 4). The mixtures in each region display different dielectric relaxation mechanism.

A. Low DMSO concentration region ($0 \leq x_{\text{DMSO}} \leq 0.1$)

The activation enthalpy ($\Delta H^{0,\neq}$) and entropy ($\Delta S^{0,\neq}$) for water were calculated to be 15.9 kJ/mol and 20.7 J/mol.K, respectively, values which are in good agreement with literature data (6,10). Buchner et al. (10) further related the $\Delta H^{0,\neq}$ value to the average number of hydrogen bonds per water molecule (n_{HB}), by assuming that only water molecules with a single H-bond are mobile,

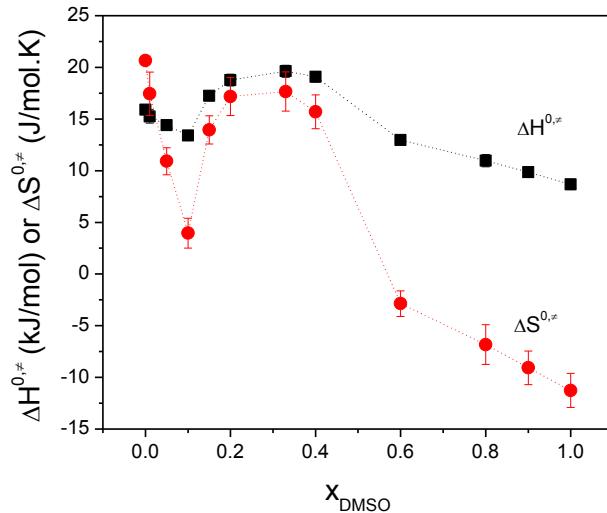


Figure 4. Concentration dependence of the activation enthalpy ($\Delta H^{0,\ddagger}$) and entropy ($\Delta S^{0,\ddagger}$) plotted against the DMSO molar fraction of the DMSO/water mixture.

$$n_{HB} = \frac{\Delta H^{0,\ddagger}}{\Delta H_{HB}} + 1 \quad [3]$$

where ΔH_{HB} is the strength of the hydrogen bond, ~ 10.9 kJ/mol (22); the 1 added in Eq. 3 reflects the assumption that “mobile” water molecules have one intact hydrogen bond. Thus, a value of 2.5 is obtained for the average number of hydrogen bonds per water molecule in the liquid state at 298 K, which is close to the literature value (23,24).

When a small amount of DMSO ($0 \leq x \leq 0.1$) is added to water, $\Delta H^{0,\ddagger}$ and $\Delta S^{0,\ddagger}$ decrease from the pure water value (Figure 4). Applying Eq. 3 the average number of H-bonds were calculated for these dilute solutions, with the results being summarized in Table 1. An apparent reduction in n_{HB} in these mixtures is observed, denoting a cooperative relaxation of the hydrogen bond network facilitated by the presence of DMSO. Such a “structure breaking” effect of DMSO –originating from the strong hydrogen bonding between DMSO and water– is clearly displayed in the dielectric measurements. This result is consistent with neutron diffraction studies (25-27), IR spectroscopy studies (3,28) and temperature of maximum-density measurements (29).

The water structure “breakdown” caused by small amounts of DMSO can be accounted for by hydrogen-bonding between water and DMSO molecules. Due to the ability for DMSO to accept two hydrogen bonds (14), the short-range water structure can be maintained in the presence of DMSO molecules. However, the total hydrogen bonds are decreased, and the percentage of water molecules that are hydrogen-bonded to each other is substantially reduced, owing to the steric constraints of DMSO’s two methyl groups, which prevent the formation of hydrogen bonds on these sites, as also shown by the reduced n_{HB} values in the mixtures obtained from the dielectric measurements. Since DMSO forms stronger hydrogen bonds with water than water does with itself (1,2,30),

the hydrogen-bonding between water molecules are energetically more favorable to break or reform compared to the H-bonds between DMSO and water. Thus, the dielectric relaxation observed in dilute DMSO/water mixtures is essentially the same process as it is in pure water, i.e., through the reorientation of the H-bonds between water molecules. The spatial steric constraints imposed by DMSO molecules on the hydrogen bond network have at least two consequences: (a) reducing the proportion of H-bonds that are energetically favorable and (b) leading to longer waiting times for a destabilized hydrogen to rejoin the network by forming a new hydrogen bond. Both of these effects will result in longer relaxation times, as was observed in these dilute mixtures.

Table I. Activation parameters ($\Delta H^{0,\ddagger}$ and $\Delta S^{0,\ddagger}$) and average number of H-bonds (n_{HB}) during the relaxation process of dilute DMSO/water mixtures (T: 298 – 318 K).

Mole Fraction	$\Delta H^{0,\ddagger}$, kJ/mol	$\Delta S^{0,\ddagger}$, J/mol.K	n_{HB}
0	15.91 \pm 0.15	20.67 \pm 0.40	2.46
0.01	15.25 \pm 0.45	17.45 \pm 2.10	2.42
0.05	14.41 \pm 0.40	10.92 \pm 1.30	2.31
0.1	13.40 \pm 0.45	3.95 \pm 1.45	2.23

B. Intermediate DMSO concentration region ($0.15 \leq x_{DMSO} \leq 0.4$)

As shown in Figure 4, $\Delta H^{0,\ddagger}$ reaches a maximum value (20 kJ/mol) at $x_{DMSO} = 0.33$. This concentration also corresponds to the existence of minima or maxima in several other thermodynamic properties (3,4), which can again be explained by the hydrogen bonding behavior within the mixtures: As the DMSO concentration increases, the fraction of H-bonds between DMSO and water molecules increases, while the fraction of water-water H-bonds concomitantly decreases. In view of the two hydrogen bond accepting ability of the DMSO oxygen atom, the ratio of these two types of H-bonds should reach a maximum at $x_{DMSO} = 0.33$, which corresponds to the stoichiometric complex H_2O -DMSO- H_2O . At this concentration, each water molecule will be hydrogen-bonded to a DMSO molecule, and the mixture will behave like a homogeneous liquid, as reflected by the maximum β value in Figure 3. The higher activation enthalpies in this second concentration region can then be due to the change of the relaxing species, from water to DMSO, which have higher H-bond strengths, and consequently would result in a maximum relaxation time, as a result of the increased strength and the longer lifetime of these H-bonds.

C. Pure DMSO and DMSO rich region ($0.6 \leq x_{DMSO} \leq 1$)

In the concentrated DMSO solutions, the complete hydration of DMSO becomes impossible, because of the shortage of water molecules. The interaction between DMSO molecules is then expected to contribute significantly to the measured properties in this region. For these concentrated solutions, negative entropies of activation were obtained, and the activation enthalpy decreased to less than the strength of one hydrogen bond (Figure 4).

In pure DMSO liquid, a distinct anti-parallel ordering of the molecular dipoles has been previously reported by static permittivity measurements (5), as well as by molecular dynamics simulation (14). The dipole correlation, expressed by the Kirkwood correlation factor g_K (31), for pure DMSO can be calculated according to the Kirkwood-Frohlich equation (31),

$$\varepsilon_s - \varepsilon_\infty = \frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_\infty} \frac{4\pi N}{3k_B TV} \frac{(\varepsilon_\infty + 2)^2 \mu^2}{9} g_K \quad [4]$$

where ε_s and ε_∞ have same meaning as above; N is the number of particles; V is the volume; and μ is the magnitude of the dipole moment. Using the gas state dipole moment for μ , 3.91 D (30), a value of 0.5 is obtained for g_K of DMSO at 25 °C from the permittivity data, indicating anti-parallel ordering of neighboring dipoles (5).

Clusters of DMSO are expected to exist in highly concentrated aqueous solutions, due to the same dipolar interactions. The value of g_K for the DMSO/water mixtures can be calculated from Eq. 4, by approximating the average dipole moment in each mixture with $\mu = \sqrt{x_w \mu_w^2 + x_{DMSO} \mu_{DMSO}^2}$. Figure 5 shows the Kirkwood correlation factor g_K for the DMSO-rich mixtures at 25, 35, and 45 °C (298, 308, and 318 K). The g_K values of the mixtures are all smaller than 1, and smoothly decrease to 0.5 (complete anti-parallel dipole correlation) as the DMSO concentration increases to that of pure DMSO. The significance of g_K for dilute solutions is less important in dilute solutions than in these concentrated solutions, due to the prevailing water-water hydrogen bonding, and is not shown in this figure.

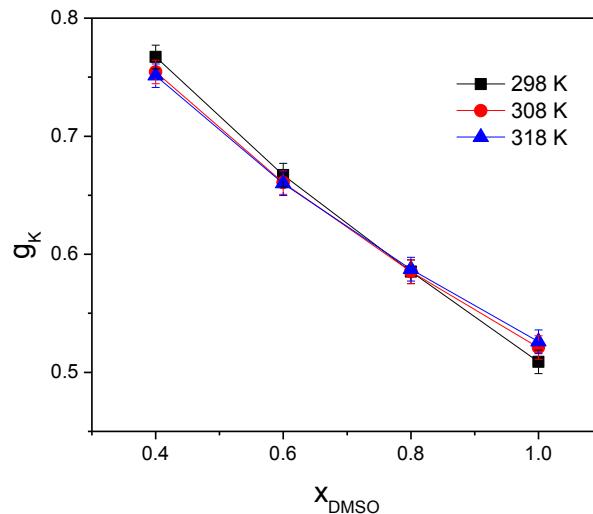


Figure 5: The Kirkwood correlation factor (g_K) as a function of DMSO mole fraction for concentrated DMSO/water mixtures at 298, 308, and 318 K.

Conclusions

The temperature-dependence of the dielectric relaxation behavior at microwave frequencies of DMSO/water-mixtures was investigated over the whole composition range. These mixtures exhibit different relaxation dynamics as the DMSO concentration is varied, as revealed from an analysis of the corresponding relaxation time. At small DMSO mole fractions ($x_{DMSO} \leq 0.1$), the average number of hydrogen bonds per water molecule is decreased with increasing DMSO concentration in the mixtures, indicating a water “structure break” by DMSO molecules; the corresponding increase in the relaxation time for these mixtures –which was previously attributed to the hydrophobic hydration of the DMSO methyl groups– can thus naturally be explained by the steric constraints imposed by DMSO molecule on the water hydrogen bond network. At intermediate DMSO mole fractions, hydrogen-bonded H₂O-DMSO-H₂O complexes are suggested in the mixtures, manifested by a maximum activation enthalpy and entropy at a DMSO mole fraction of 0.33. In concentrated DMSO solutions, an anti-parallel arrangement of dipoles is obtained, indicating that dipolar forces also contribute significantly to the dielectric relaxation in DMSO-rich mixtures.

Acknowledgments

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