Dielectric Relaxation in Dimethyl Sulfoxide/Water Mixtures Studied by Microwave Dielectric Relaxation Spectroscopy

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Received: June 24, 2009; Revised Manuscript Received: August 17, 2009

Dielectric spectra of dimethyl sulfoxide (DMSO)/water mixtures, over the entire concentration range, have been 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 show a maximum at an intermediate molar fraction of DMSO. The specific structure of mixtures in different concentration regions was determined by the dielectric relaxation dynamics, obtained from the effect of temperature on the relaxation time. A water structure “breaking effect” is observed in dilute aqueous solutions. The average number of hydrogen bonds per water molecule in these mixtures is found to be reduced compared to pure water. The increase in the dielectric relaxation time in DMSO/water mixtures is 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 interaction between water and DMSO by hydrogen bonding reaches a maximum at a DMSO molar fraction of 0.33, reflected by the maximum activation enthalpy for dielectric relaxation in this concentration, suggesting the formation of a stoichiometric compound, H₂O–DMSO–H₂O. In highly concentrated solutions, negative activation entropies are observed, indicating the presence of aggregates of DMSO molecules. A distinct antiparallel arrangement of dipoles is obtained for neat DMSO in the liquid state according to the Kirkwood correlation factor (gK = 0.5), calculated from the static permittivity. The similarity of the dielectric behavior of pure DMSO and DMSO-rich mixtures suggests that dipole–dipole interactions contribute significantly to the rotational relaxation process in these solutions.

1. Introduction

Water is a highly self-associated liquid with an open, low coordination number structure; the coordination number is about 4.8 at 20 °C.¹ A number of models have been proposed to account for the physical properties of water.²,³ Nevertheless, water remains an anomalous liquid where no single model is able to explain all of its properties.⁴ Ionic, polar, and hydrophobic solutes perturb the structure of water in different ways with profound consequences on their solubility, hydration thermodynamics, and their association with other solutes. Solute-induced perturbations in the water structure are, in turn, less understood than the structure of water itself and have long been a subject of controversy in chemistry, biology, and physiology.⁵

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 solvents and reaction media. DMSO is a polyfunctional 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 the hydrogen bonds with water molecules, whereas the nonpolar CH₃ groups may give rise to hydrophobic hydration and hydrophobic association of DMSO molecules. Many observa-

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The aim of this paper is to explore the relative contributions of dielectric relaxation spectra over a wide frequency range of 45 MHz to 26 GHz and at temperatures ranging from 25 to 45 °C. The dielectric mechanism of the DMSO/water mixtures, several sample lengths, varying from 10 to 1 cm, were prepared by mixing appropriate amounts of solute and solvent. The complex permittivity spectra of the DMSO/water mixtures were fitted in a complex nonlinear least-squares routine by using various models represented by the Havriliak–Negami function:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}\beta}$$

where $\varepsilon_s$ is the static permittivity, $\varepsilon_\infty$ is the high-frequency limiting permittivity, and $\tau$ is the relaxation time. $\alpha (0 \leq \alpha \leq 1)$ and $\beta (0 \leq \beta \leq 1)$ are shape parameters describing symmetric and asymmetric distribution of relaxation times, respectively. Three well-known models are 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 ($\alpha = 0$, $0 < \beta \leq 1$).
atures of 25–45 °C (298–318 K) are shown in Figures 1 and 2, where Figure 1 shows the permittivity spectra of the mixtures over the entire concentration range at 298 K and Figure 2 shows the spectra of the mixture of 0.15 at 298, 308, and 318 K. The plot in Figure 2b is commonly called a Cole–Cole plot. The dielectric spectrum of pure water in this frequency range is usually described as being a Debye relaxation.46–49 The relaxation times and static permittivity obtained by fitting the experimental data with a single Debye relaxation model are in accordance with the literature data46–49 to within ±0.5%. The permittivity spectra of pure DMSO are best fit by a Davidson–Cole function. This is in agreement with the literature.33,36 In order to check more complicated spectral functions that might be related to more specific solution models, as shown in the case of diethyl sulfoxide/water mixtures,51 we also attempted to fit by a sum of multiple dispersion steps, where for each relaxation process a band shape defined by Debye, Cole–Cole, Davidson–Cole, or Havriliak–Negami function can be selected. However, for DMSO/water mixtures, even a sum of two simple Debye relaxation processes, assuming a discrete contribution from water and pure DMSO, has been proven to be invalid. This was also pointed out by Kaatze et al.33 The authors are aware that the use of Davidson–Cole spectral function is less theoretically based than the functions like Debye. However, recognizing a previous fitting procedure described in the literature,33,36 we believe that the Davidson–Cole function is the most appropriate way for displaying the frequency dispersion of the data.

Figure 1. Complex permittivity spectra ($\varepsilon'$ and $\varepsilon''$) of DMSO/water mixtures at 25 °C at concentrations of (a) $0 \leq x_{\text{DMSO}} \leq 0.33$ and (b) $0.4 \leq x_{\text{DMSO}} \leq 1$. The numbers in the figure represent the mole fraction of DMSO. The solid lines are the best fit with a Davidson–Cole function.

Figure 2. (a) Complex permittivity spectra of a DMSO/water mixture with the concentration of $x_{\text{DMSO}} = 0.15$ at 298, 308, and 318 K; (b) Cole–Cole diagram of $\varepsilon'$ and $\varepsilon''$. Open symbols represent experimental data. The solid lines are calculated from the Davidson–Cole relaxation spectral function.
The dielectric parameters obtained from the dielectric relaxation spectra of mixtures through the Davidson–Cole function are collected in Table 1 and also shown in Figures 3 and 4. From Figure 3, the spread of the relaxation time ($\tau$) sharply decreases when small amounts of DMSO are added to water or when a small amount of water is added to DMSO. On further addition of DMSO, a maximum value is obtained at $x_{\text{DMSO}}$ in the range of 0.3–0.4. The change in $\beta$ values may reflect a variation in the relaxing species or a perturbation of the molecular structure of the system. The decrease of $\beta$ in the low DMSO concentration region suggests that the structure of the mixtures deviates significantly from that of pure water. The maximum $\beta$ at $x_{\text{DMSO}} = 0.3$–0.4 may indicate the formation of DMSO/2H$_2$O complexes, for which $x_{\text{DMSO}} = 0.33$.

**TABLE 1: Dielectric Parameters of the Davidson–Cole Relaxation Spectral Function (Eq 1 with $\alpha = 0$) for DMSO/Water Mixtures**

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\varepsilon_1$ ($\pm 0.4$)</th>
<th>$\tau$ (ps) ($\pm 0.3$)</th>
<th>$\beta$ ($\pm 0.01$)</th>
<th>$\varepsilon_\infty$ ($\pm 0.2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.89</td>
<td>8.25</td>
<td>1</td>
<td>5.2</td>
</tr>
<tr>
<td>0.01</td>
<td>78.11</td>
<td>9.37</td>
<td>0.97</td>
<td>4.65</td>
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<tr>
<td>0.05</td>
<td>78.02</td>
<td>14.65</td>
<td>0.882</td>
<td>4.26</td>
</tr>
<tr>
<td>0.1</td>
<td>76.79</td>
<td>22.53</td>
<td>0.816</td>
<td>4.27</td>
</tr>
<tr>
<td>0.15</td>
<td>75.16</td>
<td>31.98</td>
<td>0.81</td>
<td>3.91</td>
</tr>
<tr>
<td>0.2</td>
<td>74.64</td>
<td>40.13</td>
<td>0.845</td>
<td>3.74</td>
</tr>
<tr>
<td>0.3</td>
<td>72.54</td>
<td>27.51</td>
<td>0.808</td>
<td>3.48</td>
</tr>
<tr>
<td>0.33</td>
<td>75.64</td>
<td>40.13</td>
<td>0.845</td>
<td>3.74</td>
</tr>
<tr>
<td>0.4</td>
<td>72.26</td>
<td>34.64</td>
<td>0.848</td>
<td>3.76</td>
</tr>
<tr>
<td>0.01</td>
<td>72.26</td>
<td>34.64</td>
<td>0.848</td>
<td>3.76</td>
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<tr>
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<td>0.4</td>
<td>72.26</td>
<td>34.64</td>
<td>0.848</td>
<td>3.76</td>
</tr>
</tbody>
</table>

**Figure 3.** Plot of relaxation time distribution parameter ($\beta$) of the Davidson–Cole function displayed as a function of mole fraction of DMSO for DMSO/water mixtures over the temperatures of 298–318 K at interval of 5 K.

**Figure 4.** Plot of relaxation time ($\tau$) of the Davidson–Cole function displayed as a function of mole fraction of DMSO for DMSO/water mixtures over the temperatures of 298–318 K at interval of 5 K.
Dielectric Relaxation in DMSO/Water Mixtures

The dielectric relaxation time, $\tau$, as a function of the composition of the solution is shown in Figure 4. For each temperature, $\tau$ increases with $x_{\text{DMSO}}$ at small DMSO content, reaches a maximum when $x_{\text{DMSO}}$ is in the range of 0.3–0.4, and then decreases to the pure DMSO value. Previous studies have attributed the increase in the relaxation time with DMSO concentration to hydrophobic hydration caused by the nonpolar methyl groups, in an analogy with hydrophobic hydration in macromolecules. However, this analogy ignores the effects of the strong hydrogen bonds between DMSO and water molecules. Therefore, the dielectric relaxation time information needs further analysis.

The dielectric relaxation can be treated as a rate process involving a path over a potential barrier.\(^{38,39,52,53}\) The energy of activation for the dielectric relaxation process, $\Delta G^{\text{q,0}}$, can be calculated from the dielectric relaxation time by using the Eyring equation

$$\Delta G^{\text{q,0}} = RT \ln \left( \frac{k_B T \tau}{h} \right)$$  \hspace{1cm} (2)

where $T$ is the absolute temperature, and $h$, $k_B$, and $R$ are Plank’s constant, Boltzmann’s constant, and the molar gas constant, respectively. A plot of $\Delta G^{\text{q,0}}$ versus $T (\Delta G^{\text{q,0}} = \Delta H^{\text{q,0}} - T \Delta S^{\text{q,0}})$ can yield the enthalpy $\Delta H^{\text{q,0}}$ and entropy $\Delta S^{\text{q,0}}$ of activation for the dielectric relaxation process. These parameters characterize the molecular interactions and dynamics of the components and their mixtures.

Figure 5 displays the free energy of activation ($\Delta G_q^{0,0}$) for the dielectric relaxation process in the DMSO/water mixtures as a function of the solution composition at 298, 308, and 318 K.

![Figure 5](image1)

**Figure 5.** Free energy of activation ($\Delta G_q^{0,0}$) for the dielectric relaxation process in the DMSO/water mixtures as a function of the solution composition at 298, 308, and 318 K.

Figure 6 shows that $\Delta G_q^{0,0}$ can yield the enthalpy $\Delta H_q^{0,0}$ and entropy $\Delta S_q^{0,0}$ of activation plotted against the molar fraction of DMSO.

![Figure 6](image2)

**Figure 6.** Free energy of activation ($\Delta G_q^{0,0}$) for the dielectric relaxation process in the DMSO/water mixtures as a function temperature. The numbers in the figure denote the mole fractions of DMSO.

Figure 7 shows that $\Delta G_q^{0,0}$ displays an extremely nonlinear dependence on composition, as shown in Figure 7. The following section will discuss the dielectric relaxation mechanism of the mixtures in each region.

4. Discussion

4A. Low-DMSO Region (0 ≤ $x_{\text{DMSO}}$ ≤ 0.1). The activation enthalpy ($\Delta H_q^{0,0}$) and entropy ($\Delta S_q^{0,0}$) for pure water are calculated to be 15.9 kJ/mol and 20.7 J/mol·K, respectively. These values are in good agreement with data in the literature.\(^{34,38}\) Buchner et al.\(^{38}\) related the $\Delta H_q^{0,0}$ value to the H-bond probability in water. Assuming that only water molecules with one H-bond are mobile, they estimated the average number of hydrogen bonds per water, $n_{\text{HB}}$, as

$$n_{\text{HB}} = \frac{\Delta H_q^{0,0}}{\Delta H_{\text{HB}}} + 1$$  \hspace{1cm} (3)

where $\Delta H_{\text{HB}}$ is the strength of the hydrogen bond, ∼10.9 kJ/mol.\(^{34}\) Adding 1 in eq 3 is based on the fact that these “mobile”
molecules usually 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 of 2.4,55 obtained with molecular dynamics simulation, and of 2.8,56 obtained from density data.

When a small amount of DMSO (0 ≤ x ≤ 0.1) is added to water, ΔH^0,8 and ΔS^0,8 of the DMSO/water mixtures decrease from the values of pure water to a minimum at x_{DMSO} = 0.1 (Figure 7). The decrease of ΔH^0,8 and ΔS^0,8 in the mixtures can be attributed to two phenomena: a change in hydrogen-bond strength or a decrease in the average number of hydrogen bonds. IR spectra measurements10 show that the addition of DMSO did not change the distribution of hydrogen-bond energies of water. It is thus concluded that the reduction of ΔH^0,8 and ΔS^0,8 is due to the decrease of average number of hydrogen bonds. Applying the similar method in eq 3 the average numbers of H-bonds were also calculated for the dilute solutions, with the results being summarized in Table 2. The reduction ofΔH^0,8 and ΔS^0,8 in the mixtures means that the cooperative relaxation of the hydrogen-bond network is facilitated by the presence of DMSO. In other words, the DMSO molecules decrease the potential barrier for reorientation of the system dipole.

A hydrogen-bonding configuration has been proposed by Soper and Luzar13 to account for the neutron diffraction results. A similar configuration is redrawn in Figure 8, where a water molecule is replaced by a DMSO molecule. Due to the ability for DMSO to accept two hydrogen bonds,23 the short-range water structure remains in the presence of DMSO molecules. Owing to the steric constraints of two methyl groups, which prevent the further formation of hydrogen bonds on these sites, the total hydrogen bonds are decreased and the percentage of water molecules that are hydrogen-bonded to each other are substantially reduced compared to that in pure water (Figure 8). This allows interpreting the reduced n_{HB} values in the mixtures obtained from the dielectric measurement. Since DMSO forms stronger hydrogen bonds with water than water does with itself6,8,57 the hydrogen bonding between water molecules is energetically more favorable to break or reform compared to the H-bond between DMSO and water. Thus, dielectric relaxation in DMSO/water mixtures is essentially the same process as it is in pure water, 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: reducing the proportion of H-bonds that are energetically favorable and leading to longer waiting time for destabilized hydrogen to rejoin the network by forming new hydrogen bonds. Both of these two effects will result in higher relaxation times. This accounts for the increase in relaxation times in mixtures.

This structure-breaking effect due to the strong hydrogen bonding between DMSO and water is clearly manifested also in the dielectric measurements. This result is consistent with many other studies.10,19,23 Among them, the measurement of the temperature of maximum density provides a direct indication of water structure. Passage of the density through a maximum at 3.98 °C with increasing temperature is a unique property of water that can be attributed to a breakdown of the open hydrogen-bonded “flickering clusters” to form dense, nonstructured water, superimposed upon the increase in molar volume of both components as the temperature is raised. When a solute is added to water to form an ideal solution (one that does not have a specific impact on the structure of water) the temperature of maximum density (T_m) changes by an amount that is readily calculated from the properties of the system assuming ideal behavior. Subtraction of this change from the measured change in T_m yields a component that unequivocally reflects the impact of the solute on the unique structure of water. If the difference is positive, the solute buttresses the structure of water and is deemed to be a “structure maker”; if it is negative, the solute is a “structure breaker”. DMSO at low concentration is found to be a water structure breaker.10 On the other hand, in a neutron and X-ray diffraction experiment, Stafford et al.7 observed an increase in the RDF (radial distribution function) intensities in dilute DMSO solutions and explained it as the promotion of

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**Table 2: Activation Parameters (ΔH^0,8, ΔS^0,8) and the Average Number of H-Bonds That Must Be Broken during the Relaxation Process in the Temperature Range of 298–318 K**

<table>
<thead>
<tr>
<th>mole fraction</th>
<th>ΔH^0,8, kJ/mol</th>
<th>ΔS^0,8, J/mol·K</th>
<th>n_{HB}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.91 ± 0.15</td>
<td>20.67 ± 0.40</td>
<td>2.46</td>
</tr>
<tr>
<td>0.01</td>
<td>15.25 ± 0.45</td>
<td>17.45 ± 2.10</td>
<td>2.42</td>
</tr>
<tr>
<td>0.05</td>
<td>14.41 ± 0.40</td>
<td>10.92 ± 1.30</td>
<td>2.31</td>
</tr>
<tr>
<td>0.1</td>
<td>13.40 ± 0.45</td>
<td>3.95 ± 1.45</td>
<td>2.23</td>
</tr>
<tr>
<td>0.15</td>
<td>17.25 ± 0.45</td>
<td>13.94 ± 1.40</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>18.77 ± 0.55</td>
<td>17.18 ± 1.85</td>
<td></td>
</tr>
<tr>
<td>0.33</td>
<td>19.63 ± 0.55</td>
<td>17.66 ± 1.90</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>19.08 ± 0.50</td>
<td>15.70 ± 1.65</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>12.96 ± 0.40</td>
<td>-2.86 ± 1.20</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>10.98 ± 0.50</td>
<td>-6.83 ± 1.90</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>9.86 ± 0.50</td>
<td>-9.07 ± 1.60</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>8.67 ± 0.50</td>
<td>-11.26 ± 1.65</td>
<td></td>
</tr>
</tbody>
</table>

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**Figure 8.** Schematic view of hydrogen bonding in pure water (a) and DMSO/water mixture (b). Solid lines represent intramolecular bonds; dashed lines represent hydrogen bonds.
the water structure by the presence of DMSO molecules. However, this increase may reflect mostly concentration changes rather than the influence of the second component. The contribution from nonpolar methyl groups, if there is any, may only appear in extremely dilute solutions.

4.B. Region 0.15 < x < 0.4. As shown in Figure 7, the most outstanding feature for the dynamics of the mixtures in the concentration region of 0.15 < x < 0.4 is that the activation enthalpy in this region is higher than that for pure water (Figure 7). ΔH^q15 reaches a maximum (20 kJ/mol) at x = 0.33, which is 1.3 times higher than that of pure water. This concentration also corresponds to the existence of minima or maxima in several thermodynamic properties. The explanation for this phenomenon lies in the hydrogen-bonding configuration in the mixtures. According to Figure 8, the fraction of H-bond formed between DMSO and water molecules increases as the DMSO concentration increases, whereas the fraction of H-bond between water molecules decreases. The ratio of these two types of H-bonds will reach a maximum at a particular concentration. In view of the two hydrogen-bond accepting ability of the DMSO oxygen atom, the ratio will reach maximum at x = 0.33, where the stoichiometric complex H2O–DMSO–H2O forms. 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 in Figure 3. The rotational relaxation of this mixture, without doubt, involves the hydrogen bond between DMSO and the water molecule. The higher activation enthalpies in the second region, in comparison with the bulk water, are then due to the change of the relaxation species, which have higher hydrogen-bond strengths. The maximum relaxation time in this region could be a result of the stronger hydrogen bonding and longer lifetime of these H-bonds.

The existence of stoichiometrically well-defined hydrogen-bonded DMSO/water aggregates is suggested here based on the arguments of ΔH^q15 and ΔS^0.4. Such aggregates are expected to add distinct contributions to the dielectric spectrum. However, there is no evidence of a distinct contribution to the dielectric relaxation in the spectra of these mixtures. This is not clearly understood. The explanation may be that the radii of the different aggregates in the system essentially have a continuous distribution. However, an alternative interpretation may involve the lifetimes of the different relaxation species. The relaxation times of aqueous DMSO solutions may reflect the production rate of certain mobile species, including mobile water and DMSO molecules.

4.C. Pure DMSO and DMSO-Rich Region 0.6 < x ≤ 1. In sharp contrast to the above two regions, negative entropies of activation (ΔS^0.4) are obtained for the concentrated solutions, as seen in Figure 7. At the same time, the activation enthalpy decreases to less than the strength of a hydrogen bond (10.9 kJ/mol). In the concentrated solutions, the complete hydration of DMSO becomes impossible, because of the shortage of water molecules. The interaction between DMSO molecules is thus believed to contribute significantly to the properties in this region.

In pure DMSO liquid, a distinct antiparallel ordering of the molecular dipoles has been observed by static permittivity measurements and by molecular dynamics simulation. The dipole correlation, expressed by the Kirkwood correlation factor g_k, for pure DMSO can be calculated according to the Kirkwood–Frohlich equation

\[ ε_s - ε_∞ = \frac{3ε_s}{2ε_s + ε_∞} \frac{4πN}{3k_B T} \left( ε_∞ + 2γ^2μ^2 \right) \frac{9}{g_k} \]  

where ε_s, ε_∞ have the same meaning as above. N is the number of particles, V is the volume, and μ is the magnitude of the dipole moment. Taking the gas-state dipole moment, 3.91 D, for μ, a value of 0.5 is obtained for g_k of DMSO at 25 °C from the permittivity data, indicating antiparallel ordering of neighboring dipoles. The dipolar interaction energy between neighboring dipoles can be further calculated as a rough approximation as

\[ E = \frac{μ_1μ_2}{4πε_0 r^3} \]  

where r is the distance between two neighboring DMSO molecules, which is approximately a molecular diameter. With a molecular diameter of 5.6 Å, one obtains E = 6.4 kJ/mol from eq 5. The activation enthalpy determined by the dielectric measurements is close to 9 kJ/mol (Table 2). Taking into account the oversimplification of the mean spherical molecule model, higher dipolar interaction energy is obtained in practice. It is thus concluded that antiparallel dipole–dipole interactions contribute significantly to the formation of local order in liquid DMSO.

The clusters of DMSO would be expected to exist in highly concentrated solutions due to the same dipolar interactions. In theory, the Kirkwood correlation parameter for the concentrated solutions could also be determined through eq 4. However, the precise determination of g_k for the liquid mixtures is very difficult owing to the complex interaction between the components. As a rough approximation, the average dipole moment is taken as μ = (μ_H2O + x_DMSOμ_DMSO)/2. The value of g_k for the DMSO/water mixtures can thus be calculated from eq 4. Figure 9 shows the Kirkwood correlation factor g_k for the DMSO-rich mixtures at 25, 35, and 45 °C. g_k values of the mixtures are smaller than 1, indicating the similar dipole correlation to that in pure DMSO. The significance of g_k for dilute solutions is less important than in concentrated solutions, due to the prevailing hydrogen bonding in dilute solutions, and is not shown in this figure. Obviously, antiparallel ordering is also significant in highly concentrated aqueous solutions.

5. 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 in different concentration regions, as revealed from an analysis of the relaxation time. At small DMSO mole fractions (x_DMSO ≤ 0.10), both the activation enthalpy and entropy decrease from the pure water values to minimum values at x_DMSO = 0.1. The average number of hydrogen bonds per water molecule in the mixtures is calculated to decrease accordingly, assuming that the presence of a small amount of DMSO does not significantly change the strength of hydrogen bonding. A hydrogen-bonding configuration in DMSO/water mixtures is suggested, where a water molecule in a hydrogen-bonding network is replaced by a DMSO molecule. Through this configuration, the breakdown of water structure is introduced. The increase in the relaxation time in the mixtures does not appear to be due to the hydrophobic hydration of the methyl groups; instead it is due
to the spatial steric constraints imposed by DMSO molecule on the hydrogen-bond network. At intermediate DMSO mole fractions \(0.15 \leq x_{\text{DMSO}} \leq 0.6\), a stronger hydrogen bonding is suggested to form between DMSO and water molecules than between water molecules, based on the higher activation enthalpies in these mixtures than in pure water. The activation entropy becomes negative. The negative activation entropy implies the self-association of DMSO molecules in these mixtures, such that the rotational activated complex is a more ordered structure than is the initial fraction of DMSO for the concentrated DMSO/water mixtures at 298, 308, and 318 K.

Figure 9. Kirkwood correlation factor \(g_k\) as a function of mole fraction of DMSO for the concentrated DMSO/water mixtures at 298, 308, and 318 K.

References and Notes


JP9059246