RELATIONSHIPS BETWEEN THE DIELECTRIC AND STRUCTURAL PROPERTIES OF SUPERCOOLED LiCl:RH₂O SOLUTIONS

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ABSTRACT

The relation between the dynamics of dielectric relaxation, the glass-forming ability and properties in the supercooled state of LiCl : RH₂O solutions are investigated, via measurements of the dielectric spectra between 45 MHz and 20 GHz and temperatures between 210 K and 300 K and concentrations R ≤ 20. For high concentration glass-forming solutions, a close correspondence between the temperature dependencies of the Cole-Cole relaxation time τ_C, the conductivity, and the viscosity, is observed. τ_C(T) is well-described by a power law form (T - T_MC)', with T_MC ~ 205 K and γ ~ 2, a form motivated by mode-coupling theory. The data suggest that non-Debye response at room temperature is associated with the ability to vitrify at low temperatures. A microscopic basis for the avoidance of crystallization is provided by obtaining from the dielectric data the mean radius available to a water molecule, which is shown to approach 1.9 Å in the highly concentrated solutions. This suggests strong confinement of water molecules by the ions, which prevents macroscopic crystallization from occurring when cooled.

INTRODUCTION

Robert Cole influenced generations of scientists interested in the dielectric properties of matter. Cole firmly believed in the importance of the knowledge available from dielectric studies, and that such information could only come from sound and reliable experimentation accompanied by thoughtful analysis [1]. The authors of this
paper feel privileged to have interacted with Cole during the last few years. When we apprised him of our early work on ionic solutions, he gently pointed out our ignorance of the results of the paper by Hubbard and Onsager [2]. His persistent questions spurred us to reexamine our results in new contexts. It was during our attempt to seek his opinion regarding the outcome of our further research that we learnt of his untimely demise.

The present paper concerns the dielectric properties of ionic aqueous solutions, a topic to which Robert Cole made important contributions and in which he recognized outstanding issues [1]. In LiCl : RH₂O, we explore the relationship of the dielectric relaxation to structural relaxation, based upon a comprehensive set of results on the temperature (T), concentration (c) and frequency (ω) dependence of the dielectric response at frequencies between 45 MHz and 20 GHz. We focus here not on the solute, but on the influence of the solute on the solvent (i.e. water). Because of its importance in chemical and biological processes, water has been subject to numerous studies. Although considerable progress has been achieved in understanding the observed properties, which are often anomalous, in terms of microscopic mechanisms, a satisfactorily complete picture is yet to be achieved. It is thus of value to carry out new studies, and to interrelate results with other properties, to add to the phenomenological picture. This paper examines results on one well-known anomalous feature of water, viz. the dielectric response, and explores connections to other transport properties.

Dielectric relaxation is a powerful probe of the local environment of relaxing constituents, such as ions and dipoles. Since the dielectric relaxation frequency f₁ (≈ 1/2πτ₁) ~ 19 GHz (8.5 ps) at 25 C in water, the spectral range upto 20 GHz is essential to observe the relaxation in aqueous systems at high temperatures. Also, as noted by Cole [1], electrode polarization effects are suppressed at the higher frequencies. At room temperature in aqueous solutions, we have established earlier [3] that the dielectric response above about 2 GHz is dominantly sensitive to the "free" water (i.e. solvent), with the solute and the hydration shell (presumably) relaxing at much lower frequencies [3,4]. Thus very high frequency studies are a probe of solvent perturbations due to the solute (this is true in non-aqueous systems also). We utilize this fact to probe via dielectric spectroscopy, the influence of dissolved ionic salts on the local environment around the relaxing water dipoles in the solution.

The LiCl : RH₂O system is particularly interesting because of the wide range of
salt solubility and for the rich variety of phenomena observed as one tunes the concentration. Partially for these reasons, it is also one of the most widely studied by several techniques [5 - 12]. One very important feature is the ability to be vitrified for concentrations \( R \leq 12 \) [6]. Such solutions do not freeze but undergo a well documented glass transition at \( T_g \sim 140 \text{ K} \). The general question of how a liquid avoids crystallization and instead can be supercooled into a glassy state remains an important issue [13,14].

The dynamical response of supercooled liquids to different kinds of stress (electric, shear, etc.) has been studied extensively and some general trends have been recognized. At very high temperatures \( T >> T_F >> T_g \), the dielectric relaxation time generally obeys an Arrhenius temperature dependence, followed by a Vogel-Fulcher-Tammann behavior closer to \( T_g \). Another general trend is the tendency to exhibit a spread of relaxation times, typically described by a stretched exponential time dependence to sudden application of stress. An attempt to provide a microscopic basis for the dynamical response of supercooled liquids has been made on the basis of a mode coupling theory of density fluctuations. The initial theory exhibited an ergodic-nonergodic transition which shared many features with the liquid-glass transition. An improved model [15] predicts that the transition takes place at temperature \( T_{MC} > T_g \). Above \( T_{MC} \), relaxation phenomena (eg. dielectric, viscosity) are predicted to obey a power law dependence

\[
\tau \propto \eta \sim (T-T_{MC})^{-\gamma}
\]

in which \( \gamma \sim 2 \), and when \( T_g < T < T_{MC} \) the temperature dependence of various relaxations have the Vogel-Fulcher-Tammann form. An early test of a phenomenological version of the mode coupling theory was carried out by Sridhar & Taborek [5] using conductivity relaxation measurements on \( \text{LiCl : 7H}_2\text{O} \) at low temperatures, while more recently there have been studies of the dielectric relaxation of several glass formers [16-18].

At a fixed ambient temperature of 25 C, a detailed study of dielectric properties as a function of concentration [7] of \( \text{LiCl} \) in water has been carried out in our earlier work. A "low frequency" ( \( \sim 1 \) to \( 4 \) GHz) plateau \( \varepsilon_0 \) in \( \varepsilon'(\omega) \) was observed, which decreased with increasing concentration from the pure water value of \( \sim 78.5 \), saturating
at about 20 for \(c = 20\) to 29 mol\% (\(R = 3.4\)). The data were fit to a Cole-Cole expression plus a dc conductivity contribution \(\sigma_0\) to the imaginary part of the dielectric constant

\[
\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\left[1 + (i\omega\tau_c)^{-\alpha}\right] - i \left(\sigma_0/\varepsilon_\infty\omega\right)
\]

(2)

where \(\varepsilon_\infty = 8.85 \times 10^{-12}\) F/m is the permittivity of vacuum. It was found that \(\tau_c\) decreased slightly from 8.5 ps of water to a minimum \(\sim 7\) ps and then increased again. A remarkable feature of the LiCl/H\(_2\)O data is the deviation that occurs in all the quantities for \(c \geq 15\) mol\% (\(R < 7\)). The "dc" conductivity \(\sigma_0\) goes through a maximum, \(\varepsilon_\infty\) gradually saturates, \(\tau_c\) has a minimum and the parameter \(\alpha\) increases from zero. These results raise the interesting question whether the (low temperature) glass-forming ability of LiCl/H\(_2\)O solutions is related to the non-Debye behavior observed at room (i.e. high) temperature.

Later the same measurements were completed on RbCl/H\(_2\)O and CsCl/H\(_2\)O solutions [19]. All the dielectric spectra of RbCl and CsCl aqueous solutions appear to be Debye-like apparently up to the solubility limits, during which the "dc" conductivity of the solution monotonically increases with the concentration, while \(\tau_c\) \((-\tau_D\)) decreases. For all three ionic aqueous systems, the decrease of the relaxation time of the solution \(\tau_c\) from that of pure water was found to be proportional to the solution conductivity \(\sigma_0\). Earlier work by Sridhar and Taborek [5] showed that the temperature dependence of the "dc" conductivity of 15 mol\% LiCl/H\(_2\)O solution tracks that of the solution viscosity. This established an intimate connection between the conductivity properties and the structural relaxation associated with the viscosity.

A similar connection has not been made with regard to the dielectric relaxation time, and is addressed in this work. In addition we address the following questions: How does the characteristic relaxation time of a glass forming ionic solution scale with temperature and relate to the "dc" conductivity? To what extent do the ions disturb the hydrogen bond network in water, and can one extract microscopic parameters relevant to the vitrifying ability from the dielectric results?

II. EXPERIMENTS AND RESULTS

The measurement technique is described in ref. [20,21], and consists of a coaxial line dipped in the liquid. Reflection coefficients are measured with a HP8510 network
analyzer, and deconvolved to extract $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$. The temperature was varied by cooling in a jacket surrounded by liquid nitrogen. Temperature was controlled with

**TABLE I**

Dielectric relaxation time $\tau_c$ and Conductivity $\sigma_0$ for LiCl : RH$_2$O, R = 20, 7 and 5.

<table>
<thead>
<tr>
<th>Solution</th>
<th>T (K)</th>
<th>$\tau_c$(ps)</th>
<th>$\sigma_0$(1/Ωm)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl : 20H$_2$O</td>
<td>296</td>
<td>8.69</td>
<td>13.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>10.7</td>
<td>11.2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>13.3</td>
<td>8.5</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>19.0</td>
<td>6.0</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>262</td>
<td>22.8</td>
<td>5.0</td>
<td>0.03</td>
</tr>
<tr>
<td>LiCl : 7H$_2$O</td>
<td>293</td>
<td>7.22</td>
<td>17.1</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>289</td>
<td>7.12</td>
<td>16.2</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>7.67</td>
<td>15.1</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>8.05</td>
<td>13.9</td>
<td>0.04</td>
</tr>
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<td></td>
<td>278</td>
<td>9.39</td>
<td>12.2</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>10.4</td>
<td>10.5</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>11.4</td>
<td>9.0</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>15.6</td>
<td>7.2</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>258</td>
<td>18.1</td>
<td>6.0</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>253</td>
<td>23.3</td>
<td>4.7</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>248</td>
<td>29.6</td>
<td>3.6</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>37.8</td>
<td>2.8</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>238</td>
<td>50.3</td>
<td>2.0</td>
<td>0.12</td>
</tr>
<tr>
<td>LiCl : 5H$_2$O</td>
<td>298</td>
<td>7.63</td>
<td>14.8</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td>11.03</td>
<td>9.0</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>12.35</td>
<td>7.2</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>253</td>
<td>16.84</td>
<td>5.0</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>49.78</td>
<td>2.1</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>225</td>
<td>99.93</td>
<td>1.0</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>223</td>
<td>130.7</td>
<td>0.9</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>217.1</td>
<td>0.6</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>212</td>
<td>284.2</td>
<td>0.44</td>
<td>0.38</td>
</tr>
</tbody>
</table>
an Omega controller. The rapid data acquisition (1 sec) enables data to be taken on the fly, and is much quicker than the times required for equilibration. Samples were prepared by dissolving reagent grade LiCl in de-ionized water.

The temperature dependencies of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for LiCl : $\mathrm{RH}_2\mathrm{O}$ (R=5,7,20) solutions were measured and fitted by the Cole-Cole expression Eqn. (2). As the temperature decreases, the static dielectric constant of the solution $\varepsilon_{\infty}$, the relaxation time $\tau_c$ and the relaxation time distribution factor $\alpha$ all increase, while the "dc" conductivity decreases. The fit parameters $\tau_c$, $\sigma_0$ and $\alpha$ are listed in Table I for various concentrations. The expansion and contraction of the teflon inside the coax affected accurate determination of $\varepsilon_{\infty}$ and $\varepsilon_{\infty}$ of the solutions at lower temperatures. $\varepsilon'$ and $\varepsilon''$

---

Fig. 1. (a) Real and (b) imaginary part of the dielectric constant versus frequency for LiCl:5$\mathrm{H}_2\mathrm{O}$ solutions at $T = 272\mathrm{K}$ (x's), 253K (o's), 235K (+'s) and 212K (diamonds).
versus frequency at several temperatures and the corresponding fits are plotted in Fig. 1 (a) and (b) for the LiCl : 5H₂O sample.

The measurement temperature range of the LiCl : 20H₂O sample was limited by crystallization of the sample. For R=5 and 7 samples, the rapid increase of the relaxation time restricted the accuracy of lower temperature range measurements.

The dielectric spectra of all solutions, become increasingly non-Debye upon cooling to low temperature. At the same time, the characteristic relaxation times of all solutions increase rapidly and the conductivity dramatically decreases. The data for τ_c and σ_0 were fitted to both a power law form :

\[ \tau_c = \tau_0 \left[ T_{\infty MC} - (T - T_{\infty MC}) \right]^{\gamma} \]  \hspace{1cm} (3)

\[ \sigma_0 = \sigma_{00} \left[ (T - T_{\infty MC}) / T_{\infty MC} \right]^{\delta} \]  \hspace{1cm} (4)

and the Vogel-Fulcher-Tammann form :

\[ \tau_c = A_1 \exp \left( B_1 / (T - T_0) \right) \]  \hspace{1cm} (5)
\[ \sigma_0 = A_\sigma \exp \left( -B_\sigma / (T-T_{\sigma 0}) \right) \] (6)

The value of the relevant fitting parameters are listed in Table II for the power law and Table III for VFT. Reasonably good fits were obtained to both the above forms which can be seen from the values of \( \delta_{\text{PL}} \) and \( \delta_{\text{VFT}} \) - this may possibly be due to the relatively narrow temperature range. The power law fit is motivated by earlier observations on the T-dependence of the viscosity [8] and the conductivity [5] and also has justification from the mode-coupling theory. Data and power law fits for \( \tau_c \) are shown in Fig. 2 and for \( \sigma_0 \) are shown in Fig. 3.

Fig. 3. "dc" conductivity \( \sigma_0 \) versus temperature for LiCl:RH\textsubscript{2}O, R=5 (x's), R=7 (o's) and R=20 (+'s) samples. Solid lines are the corresponding power law fits.

<table>
<thead>
<tr>
<th>Solution</th>
<th>( \gamma )</th>
<th>( T_{\tau \text{MC}} ) (K)</th>
<th>( \delta_{\text{PL}} )</th>
<th>( \theta )</th>
<th>( T_{\sigma \text{MC}} ) (K)</th>
<th>( \delta_{\text{PL}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl : 20H\textsubscript{2}O</td>
<td>1.52</td>
<td>223</td>
<td>0.01</td>
<td>1.82</td>
<td>215</td>
<td>0.01</td>
</tr>
<tr>
<td>LiCl : 7H\textsubscript{2}O</td>
<td>1.98</td>
<td>209</td>
<td>0.01</td>
<td>2.04</td>
<td>210</td>
<td>0.01</td>
</tr>
<tr>
<td>LiCl : 5H\textsubscript{2}O</td>
<td>1.95</td>
<td>204</td>
<td>0.03</td>
<td>2.07</td>
<td>198</td>
<td>0.05</td>
</tr>
</tbody>
</table>
TABLE III

Vogel-Fulcher-Tammann fits for LiCl/H₂O solutions

<table>
<thead>
<tr>
<th>Solution</th>
<th>B₁(K)</th>
<th>T₀₁(K)</th>
<th>δ_{VFT}</th>
<th>B₀(K)</th>
<th>T₀₀(K)</th>
<th>δ_{VFT}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl : 2H₂O</td>
<td>319</td>
<td>171</td>
<td>0.01</td>
<td>441</td>
<td>155</td>
<td>0.01</td>
</tr>
<tr>
<td>LiCl : 7H₂O</td>
<td>370</td>
<td>163</td>
<td>&lt;0.01</td>
<td>381</td>
<td>164</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>LiCl : 5H₂O</td>
<td>341</td>
<td>159</td>
<td>0.01</td>
<td>458</td>
<td>143</td>
<td>0.02</td>
</tr>
</tbody>
</table>

III. DISCUSSION

(1) Choice of fitting function

The polarization decay function φ(t) for the glass forming liquids is generally described in terms of a Kohlrausch-Williams-Watts form [22]

\[
φ(t) = \exp \left[-\left(\frac{t}{\tau}\right)^\gamma\right]
\]

(7)
in the temperature range of interest. Numerical evaluations have shown that in the frequency domain, the Cole-Davidson dielectric function corresponds closest to the KWW stretched exponential response in the time domain. A random-walk model has been proposed [23,24] to interpret the KWW behavior. The Havriliak-Nagami function [25] is also used to fit the dielectric spectra of glass forming materials.

However, the main difference between Cole-Cole, Cole-Davidson and Havriliak-Nagami functions is the shape of the dielectric spectrum, not the location of the absorption peak. Also, they are all different manifestations of non-Debye behavior. What we are interested in here are the temperature dependence of the characteristic relaxation time and the trend of deviation from Debye response. Therefore, the choice of a particular form among the various non-Debye functions is not important for the present work.

(2) Temperature dependence of LiCl:RH₂O (R < 7)

One feature of the glass forming solutions with R = 5 and 7, is that the power law fits to the relaxation time \(\tau_c(T)\) and the "dc" conductivity \(\sigma_0(T)\) yield a
characteristic temperature $T_{MC}$ around 205K, which is about 65K higher than the glass transition temperature 140K. The 65K difference is close to that predicted by the mode coupling theory, which suggests that there is a ergodic-non-ergodic transition at a temperature 30-50K higher than the glass transition temperature. Although, we cannot distinguish which type of fit is better for our data, we note that the characteristic temperatures of ~160K extracted from the VFT fits, are above $T_g$ instead of below, as is the more common experience.

The present result is consistent with results for the viscosity of a R ~ 7 solution by Taborek et al. [8], which obey a power law fit with power $\mu \sim -2.08$ and $T_{\eta_0} = 207$K. Although the transition is not a sharp point, it appears to be a significant temperature which marks the boundary between two types of viscous behavior: power law for $T > T_{\eta_0}$ and approximately Arrhenius for $T < T_{\eta_0}$.

The second feature which emerges from the results is the close correspondence between the dielectric relaxation time and the conductivity for the glass-forming solutions of R = 7 and 5. Combining the viscosity measurements made by Taborek et al. and the conductivity results by Sridhar and Taborek on a R ~ 7 sample, it is very appealing to speculate that, for glass forming solutions,

$$\tau_c(T) \propto \frac{1}{\sigma_0(T)} \propto \eta(T)$$

(8)

This is apparently true in our data for the high concentration (R < 7) solutions, but is inapplicable to the water rich sample R=20.

We have shown elsewhere that alkali-halide ACI additives to water modify the dynamic response of the solution by shortening the Debye dielectric relaxation time with increasing concentration as

$$\tau_{solution} = \tau_{water} - \beta \sigma_0$$

(9)

This was established at 25 C by varying ion size of A. The fact that the dielectric relaxation time of the solution is not simply that of unperturbed water molecules is further confirmed by the temperature dependence reported here. By fitting the dielectric
relaxation data of supercooled pure water from -21C to 32C, provided by Bertolini et al.[24], we obtain

\[
\tau_{\text{water}}(T) = 2.0 \times 10^4 (T - 211)^{2.26}
\]  

(10)

Fig. 4. Dielectric relaxation \( \tau_c \) (o's) and Cole-Cole parameter \( \alpha \) (+'a) as a function of concentration mol\% \((= 1/R)\) for LiCl/H\(_2\)O at room temperature.

whose exponent (2.26) is much bigger than that of the LiCl:20H\(_2\)O sample \((\gamma = 1.52)\).

(3) Connection to supercooling properties of LiCl/H\(_2\)O

Fig. 4 summarizes the dielectric parameters of LiCl/H\(_2\)O at \( T \sim 25C \). Shown are the dielectric relaxation time \( \tau_c \) and the Cole-Cole parameter \( \alpha \) as a function of concentration.

Two significant features of the data are apparent:

(a) For \( c \leq 10 \) mol \% \((R > 10)\), the relaxation is Debye like \((\alpha = 0)\), and \( \tau_c - \tau_D \) decreases with increasing \( c \). These concentration also freeze, but at depressed temperatures.

(b) For \( c \geq 15 \) mol\% \((R < 6.7)\), the relaxation is non-Debye \((\alpha > 0)\) and \( \tau_c \) increases with increasing \( c \). Also these higher concentrations can be supercooled.
Thus there appears to be a plausible connection between the Debye-like dielectric response of the liquid at high temperatures, and the ability to supercool it. This connection is possible because the dielectric response is dominated by the free water, and we assume that freezing is also determined by the ability for extended hydrogen bond networking in water [27]. (The concentrations are still too low to view the solution as a molten salt, since the solubility limit at 25°C is about 30 mol%).

Each ion gathers around it a cloud of water molecules, and the dielectric measurements suggest that the hydration layer is strongly bound. The solutions may be regarded (as we do in our analysis), as composed of two components: a matrix of hydrated ions in a medium of water. If the concentration is sufficiently low, the hydrated ions are well separated, and the water "medium" is identical to bulk water, except that it is divided into connected pieces due to the presence of the hydrated ions. The primary evidence for this is the weak effect on τD, and the continued Debye-like response (α = 0) until concentrations c > 10 mol% are attained. The disturbance of the H-H network by the existence of ions is equivalent to raising the solution temperature for low concentrations. We conclude that for c ≤ 10 mol%, the structure of the free
water in the solution is basically unaffected, and the strong water-water correlations, such as the H-H bonds, continue to be present.

Further evidence for this picture comes from measurements of the dielectric response of mixtures of water with strongly associated liquids such as glycerol, propanol, ethylene glycol, etc. Even small additions of these strongly hydrogen bonded liquids dramatically affects both $\tau_p$ and $\alpha$. (Details of measurements on these liquids will be presented elsewhere [28]). This is because these molecules strongly disrupt the hydrogen bonding of the water molecules, to the extent that the solution cannot be regarded as a two component mixture, but rather as a microscopically disordered liquid. The main point which we wish to utilize here is the observation, common to both the liquid mixtures and the ionic solutions, is that a non-Debye response in water signals disruption of the long-range correlations, arising from the hydrogen bonding.

When the ionic concentration is increased, the ionic separation decreases to the point where the local water-water interactions are affected, and the two component picture breaks down. This is signaled by $\alpha > 0$ for $c \geq 10$ mol%. Within the frame-work described above, the rigid ions act to confine the "free" water molecules, preventing communication with another "free" water molecule, thus disrupting the H-H bond network. From our measurements of $\varepsilon_0$, we can directly determine the water-water separation distance at which the hydrogen bond network is disrupted.

The $\varepsilon_0$ results of our earlier work [7] at room temperature for solutions of different concentrations directly yield the microwave dielectric excluded volume in the solution, i.e. the volume not available to the free water, and then the effective radius of the space around an ion available to free water molecules can be estimated by

$$r_{fw} = \left[\frac{3}{4\pi} \left(1 - \frac{c}{c/N_0/2}\right)\right]^{\frac{1}{3}}$$  \hspace{1cm} (11)

$r_{fw}$ is plotted vs. mol% concentration in Fig. 5, and is seen to decrease with increasing concentration.

As Fig. 5 shows, each water molecule is increasingly confined as the ionic concentration increases, due to the presence of the ions. Around 10 mol% (R=10), the radius of the available space for a free water molecule falls to about 2 Å, which is
comparable to the average radius of the volume a bulk water molecule occupies at 4C, estimated as \[3*18/(4\pi N_0)\]^{1/3} = 1.9 Å.

The confinement picture and the relation to the Debye relaxation suggests that the interplay between the translational properties and the re-orientational relaxation is important. This appears to have theoretical foundations, based upon recent work by Bagchi and Chandra [29]. Using a hydrodynamic continuum model, they show an interesting trend from Debye to non-Debye relaxation as the diffusion time crosses the reorientational time. Thus in liquids where translational contribution to polarization relaxation is significant, the response is Debye, whereas in liquids where the orientational mechanism of polarization relaxation dominates, the dielectric relaxation is non-Debye. This picture is qualitatively consistent with the observations in this paper. Although a quantitative analysis remains to be carried out, the approach taken in this work is novel, in that it provides an interesting way of tuning diffusion times by varying additive concentration in solutions.

The connection to crystallization becomes apparent if one recognizes that crystallization of water takes place through a macroscopic H-bonded network, and is accompanied also by an increase in volume. The strong confinement of individual water molecules by the ions not only disrupts a macroscopic network, but also the strong electrostatic forces prevent needed volume expansion from occurring, thus preventing crystallization in the high concentrations solutions.

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