Ion size effects on the dynamic and static dielectric properties of aqueous alkali solutions

Yan-Zhen Wei, Ping Chiang, and S. Sridhar

Department of Physics, Northeastern University, Boston, Massachusetts 02115

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Dielectric spectroscopy studies of aqueous ionic solutions ACl/H2O (A = Li, Rb, Cs) were carried out at frequencies between 45 MHz and 20 GHz, using recently developed coaxial measurement techniques. The behavior of the static dielectric constant \( \varepsilon_0 \) and the dielectric relaxation time \( \tau_D \) of the solutions were studied as functions of ion size and concentration. For moderate concentrations both \( \varepsilon_0 \) and \( \tau_D \) decrease linearly with solution conductivity. While the behavior of \( \varepsilon_0 \) can be understood in terms of either static or Hubbard-Onsager kinetic polarization models, the experimental results for \( \tau_D \) are at present not understood quantitatively in terms of these models. However we point out the good correlation of the \( \tau_D \) data with empirical viscosity results, which suggests an alternative explanation based upon the solution viscosity, modified by ion size effects, which play an important role in the dielectric response. We also discuss the various length scales relevant to dielectric and conductivity processes in the solutions.

Dielectric spectroscopy can be a powerful probe of microscopic processes in a liquid, particularly when carried out over a broad range of frequency. The frequency dependence of the dielectric function \( \varepsilon(\omega) \) of a liquid (pure, solution or mixture), reflects the dynamic response of the constituents of the liquid, whether ionic or dipolar. An ionic solution may be considered to consist of 3 constituents: the charged anions and cations, "hydration" solvent molecules near the vicinity of the ions, and "free" solvent molecules. At high concentration, an additional component may exist in the form of ion pairs due to incomplete dissociation. The distinction between the hydration and free solvent molecules is largely a matter of the time scales involved, and the strength of the ion-solvent interaction. Furthermore, the dynamical processes are affected by the ion size and charge. These aspects are some of the issues addressed in this work.

While ionic conductivity and viscosity has been the subject of intense research, the dynamic aspects of the dielectric properties of ionic solutions have received less attention. Certain phenomena, such as the (static) dielectric decrement, are well known. Reliable experimental data on the dynamic aspects, such as the relaxation time \( \tau_D \), have not been easily available, partly because of the higher frequencies required (~10 GHz) particularly for aqueous solutions. In this paper we present detailed studies and analysis of the dielectric spectra of ACl (A = Li, Rb, Cs) in H2O. The complex dielectric functions \( \varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \) were measured between 45 MHz and 20 GHz at 25 C, using recently developed techniques, which enables the measurement of continuous spectra in this frequency range. \( \varepsilon' \) and \( \sigma = \varepsilon_\infty \omega \varepsilon'' \) (\( \varepsilon_\infty = 8.85 \times 10^{-12} \) F/m) vs frequency for RbCl/H2O for various concentrations are shown in Figs. 1(a) and 1(b) (the rise of the \( \varepsilon' \) at the low frequency end is caused by electrode polarization effects due to the ionic conductivity). Similar characteristics are observed for LiCl (Refs. 10 and 11) and CsCl aqueous solutions. The data were fit to Cole–Cole expressions, including the dc conductivity:

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau_D)^{1-\beta}} - \frac{i\sigma_0}{\varepsilon_\infty \omega}
\]

from which the parameters \( \varepsilon_0, \varepsilon_\infty, \tau_D, \sigma_0, \) and \( \beta \) were extracted (see Table I). For the moderate concentration dis-
TABLE I. The fitting parameters for the aqueous electrolyte solutions ($\beta = 0$ for all).

<table>
<thead>
<tr>
<th>Solution</th>
<th>$c$ (M)</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_m$</th>
<th>$\tau_D$ (ps)</th>
<th>$\nu_0$ (mho/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbCl/H$_2$O</td>
<td>0.54</td>
<td>70.6</td>
<td>4.5</td>
<td>7.9</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>66.0</td>
<td>5.2</td>
<td>7.6</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>55.0</td>
<td>5.0</td>
<td>6.5</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>53.7</td>
<td>5.5</td>
<td>6.4</td>
<td>27.5</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>42.4</td>
<td>6.5</td>
<td>36.0</td>
<td>43.9</td>
</tr>
<tr>
<td>CsCl/H$_2$O</td>
<td>0.33</td>
<td>74.5</td>
<td>4.4</td>
<td>8.3</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>0.49</td>
<td>72.0</td>
<td>5.2</td>
<td>8.2</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>70.5</td>
<td>5.2</td>
<td>8.1</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>68.0</td>
<td>4.8</td>
<td>7.8</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>57.6</td>
<td>4.5</td>
<td>7.0</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>46.6</td>
<td>4.0</td>
<td>6.0</td>
<td>40.4</td>
</tr>
</tbody>
</table>

The solid lines in Fig. 1 are the corresponding fits. The dc conductivity is indicated by the plateau at the low frequency end of Fig. 1 (b). The differences in conductivity between the 3 electrolyte solutions are evidence of the ion size effect. The dielectric properties, particularly at the frequencies considered here, are dominantly due to the solvent dipoles, of course modified by the presence of the ions. The perspective of this work is to study the behavior of the parameters characterizing the dielectric response, viz. $\varepsilon_{SO}$, $\varepsilon_{is}$, $\tau_D$, and $\beta$, and from it, to deduce information regarding microscopic dynamical processes in the liquid on the basis of microscopic models.

I. STATIC DIELECTRIC CONSTANT $\varepsilon_{SO}$: STATIC AND KINETIC POLARIZATION

The "static" dielectric constant, which is obtained as the low frequency plateau in the $\varepsilon'(w)$ data, decreases monotonically with increasing concentration. This phenomenon, and also the observation of the leveling off of the decrease, is known. Data for $\varepsilon_{SO} v$s $C$, the molar concentration, is shown in the inset to Fig. 2 for LiCl, RbCl, and CsCl solutions.

In an earlier paper, we had discussed the results for $\varepsilon_{SO}$ of LiCl/H$_2$O in terms of a simple "static" polarization model. The hydrated ions act as a "void" with $\varepsilon_v \sim 5$ due only to the electronic polarizability of the ion + hydration shell. The dielectric constant of this mixture of dipolar solvent molecules and the voids can be calculated with the aid of Maxwell-Wagner theory. The model satisfactorily explained the $\varepsilon_{SO}$ data for LiCl solutions at low concentrations assuming complete dissociation, and for moderate concentrations with inclusion of a dissociation parameter which was obtained from the conductivity data. The leveling off of the $\varepsilon_{SO}$ is not explained in this model, primarily because we believe the latter requires an approach including correlations, in contrast to the above simple single particle picture.

A similar analysis is carried out here for the RbCl and CsCl solutions also, and the conclusions are also similar. From the analysis, we deduce several parameters: the radius of the hydrated ions $r_D$, and the hydration number $N_{hyd}$. The latter is the average number of hydration water molecules per electrolyte molecule, and is shown in Fig. 3, assuming complete dissociation. It is apparent that $N_{hyd}$ (LiCl) > $N_{hyd}$ (RbCl) > $N_{hyd}$ (CsCl) for a given concentration, with $N_{hyd}$ of the latter two being quite close. Since the bare ionic radius progressively increases from Li to Cs (0.78, 1.48, 1.69 Å), it is clear that the hydration number is determined by the charge density at the ion surface, which progressively decreases. As a consequence the ion-water interaction is progressively weaker, with fewer water molecules bound by the Coulomb forces in the CsCl solution than in the LiCl solution.
The above static polarization model is to be contrasted with the kinetic polarization model proposed by Hubbard and Onsager (HO). In the HO model, the liquid is treated as a hydrodynamic continuum, and the kinetic ion–solvent interaction affects the capacitive admittance (i.e., \( \epsilon_{\sigma_0} \)) in two closely related ways: (1) As an ion migrates, the surrounding fluid dipoles rotate according to the laws of hydrodynamics, and although dielectric relaxation tends to restore a polarization corresponding to the local field, this process is not instantaneous and the average delay is equal to the relaxation time \( \tau_D \). (2) The force which an external field exerts on an ion does not develop its full strength immediately because the ion is driven partly by the external field and partly by the polarization which develops in response to the applied field, with the polarization field evolving with a time constant \( \tau_D \). It is clear here that the dynamical relaxation time \( \tau_D \) (and also the viscosity relaxation time \( \tau_V \)), play an essential role.

The HO model leads naturally to an intimate relation between the conductivity \( \sigma_0 \) and the dielectric decrement \( \Delta \epsilon_0 \), which can be expressed as

\[
\Delta \epsilon_0 = \Delta \epsilon(\text{dipole}) + \Delta \epsilon(\text{ion}) = - \frac{-4\pi}{\epsilon_0} \left( \frac{-\epsilon_{\text{d}} - \epsilon_{\text{w}}}{\epsilon_{\text{w}}} \right) \tau_D \sigma_0,
\]

where \( \tau_D \) is the Debye relaxation time of water, for a boundary condition of no slip when the viscous relaxation time is not comparable to the dielectric relaxation time.

The linear relation between \( \Delta \epsilon_0 \) and \( \sigma_0 \) which naturally emerges from the HO theory is confirmed by experiment, as seen in Fig. 2, the plot of \( \epsilon_{\sigma_0} \) vs. dc conductivity \( \sigma_0 \) of the solutions. The slopes obtained from least-squares fits are \(-2.1, -0.90, \) and \(-0.89 \Omega^{-1} \cdot \text{m} \) for LiCl, RbCl, and CsCl, respectively. These values may be contrasted with a slope of \(-0.88 \Omega^{-1} \cdot \text{m} \) calculated from the above equation assuming no slip, which is the continuum limit. Note that the continuum version of the HO theory does not predict any dependence on ion size—indeed this appears to have been confirmed in weakly concentrated solutions in which an apparently ion-size independent slope of \(-2.7 \Omega^{-1} \cdot \text{m} \) was obtained for several solutions.

The static model discussed above also leads to a linear relation between \( \Delta \epsilon_0 \) and \( \sigma_0 \). This is simply because, in this picture, \( \Delta \epsilon_0 \) is due to the total excluded volume due to the hydrated ions, and hence is proportional to the number of ions in the solution, as is the conductivity. This applies for low concentrations. This model then leads to

\[
\Delta \epsilon_0 = \nu_{\text{exc}} \left[ \frac{1}{\mu e} \frac{3\epsilon_{\text{w}}}{2\epsilon_{\text{w}} + \epsilon_{\text{w}}} (\epsilon_{\text{u}} - \epsilon_{\text{w}}) \right] \sigma_0.
\]

This is similar to the HO Eq. (2), with the correspondence \( (\epsilon_{\text{u}} / \mu e) \nu_{\text{exc}} \rightarrow 2\nu_{\text{D}} (p + 1) \), and \( \nu_{\text{exc}} = (4\pi/3)(r_{\text{liq}}^2 + r_{\text{Cl}}^2) \). The fitting radii for \( \text{Li}^+ \), \( \text{Rb}^+ \), \( \text{Cs}^+ \), and \( \text{Cl}^- \) are \( r_{\text{liq}} = 2.6 \text{ Å} \), \( r_{\text{Rb}} = 2.45 \text{ Å} \), \( r_{\text{Cs}} = 2.4 \text{ Å} \), and \( r_{\text{Cl}} = 3.25 \text{ Å} \), respectively. This correspondence leads to a physical definition of the dielectric radius \( r_D \) occurring in the static model: It corresponds to the radius of a sphere containing the ions and the associated hydration water molecules, which responds (i.e., rotates) rigidly at microwave frequencies to the \( E-M \) field. In Sec. III we discuss further details of this radius, and contrast it with other radial length scales characteristic of ions in a solution.

II. DYNAMICAL TIME SCALES IN A SOLUTION

The multicomponent view of an ionic solution, viz. ions, hydration shell, and quasifree solvent molecules, would suggest the presence of at least two dielectric relaxation times, one pertaining to the hydration shell \( \tau_h \) and the other pertaining to the solvent molecules \( \tau_D \). The presence of \( \tau_h \) is a major open question, of interest because of the perceived importance of the hydration layer in chemical and biological processes. Simple minded arguments would lead to the conclusion that \( \tau_h > \tau_D \), since the hydration molecules are under the strong influence of the ions, with the relative separation between \( \tau_h \) and \( \tau_D \) being determined by the ion–solvent interaction strength. In the present work, we have searched for and have not observed any signature of the hydration shell relaxation. It is possible that this occurs at such low frequencies that it is masked by ionic polarization effects.

Instead we here concentrate on the effects of the ions on the solvent dielectric relaxation time \( \tau_D \). Two features of the dielectric spectrum are noteworthy:

1. \( \tau_D \) decreases with increasing ionic concentration. (However in the case of LiCl solutions, it reaches a minimum and then increases strongly.) The data are shown in the inset of Fig. 4.

2. The pure solvent (water) and the solutions with decreasing \( \tau_D \) are essentially Debye-like. (In LiCl solutions, the high C solutions with increasing \( \tau_D \) are non-Debye. We believe that the same phenomena of increasing \( \tau_D \), non-Debye relaxation and the conductivity maxima should occur in the RbCl and CsCl solutions also, however the observation is restricted due to the limited solubility.)

![FIG. 4. Dependence of the dielectric relaxation time \( \tau_D \) on the dc conductivity \( \sigma_0 \) for LiCl (diamonds), RbCl ( + ), and CsCl (O) solutions. Inset: behavior of \( \tau_D \) with concentration \( C \), including data at high concentrations for LiCl solutions not shown in main figure.](image-url)
Any static polarization model (such as the one discussed above) does not address the issue of the behavior of \( \tau_D \), which is after all a dynamical phenomenon. We therefore considered the HO theory, which includes the influence of hydrodynamics on the dielectric properties. The result of the HO theory can be written in the form\(^{12}\)

\[
\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_{\infty} - \epsilon_{\omega}}{1 + \omega \tau_D^{\omega}} - \sum \frac{\Delta \epsilon_{\omega}}{1 + \omega \tau_D^{\omega}(1 - A_i)}
\]

\( (A_i > 0). \)\(^{(4)} \)

That is, as a result of dielectric friction, the dielectric spectrum of an electrolyte solution is the free solvent spectrum modified by decrement spectra with shorter relaxation times. However upon close graphical examination of the above expression, the resultant solution spectrum has an apparent relaxation time which is longer than the pure solvent relaxation time \( \tau_D^{\omega} \). This can be seen from the asymptotic \( \omega \to 0 \) behavior of Eq. \( (4) \). We get \( \epsilon^e(\omega) = \omega \tau_D^{\omega} [\epsilon_{\infty} + (\epsilon_{\infty} - \epsilon_{\omega} + \Delta \epsilon_{\omega})(1 - \gamma)] \). Comparing with a Debye form, there is a positive shift of the relaxation time of the solution

\[
\Delta \tau_D = \gamma \tau_D^{\omega} \sigma_0,
\]

where \( \gamma \) is a constant of the solvent. Although Eq. \( (5) \) has the observed linear dependence of \( \Delta \tau_D \propto \sigma_0 \), unfortunately the HO theory predicts the wrong sign for the effect, viz. \( \Delta \tau_D > 0 \).

Although we have been unable to arrive at a microscopic explanation of the observed decrease of \( \tau_D \), we note an important correlation with empirical results for the solution viscosity, which suggests an alternative empirical explanation. Within the Debye theory, the Debye relaxation time is given by \( \tau_D = \frac{4 \pi \eta a^2}{k_B T} \), where \( \eta \) is the viscosity and \( a \) is the molecular radius. We can rewrite the above expression as

\[
\tau_D = \left[ \frac{4 \pi \eta a^2}{k_B T} \right] \left( \frac{\eta}{\eta_{\infty}} \right),\]

where \( \eta_{\infty} = a \) is the effective molecular radius of the solvent molecule. For an electrolyte solution, the Jones-Dole empirical formula is \( \eta/\eta_{\infty} = 1 + A \sqrt{C} + BC \), where \( A \) is only related to ion-ion interactions and \( B \) represents the ion solvent interaction. Relevant values for \( B \) are \( +0.146 \) (Li), \(-0.030\) (Rb), and \(-0.046\) (Cs), \(+0.14\) (LiCl), \(-0.0360\) (RbCl), and \(-0.062\) (CsCl). \( \alpha \) should be concentration dependent and can be written as \( \alpha = 1 + \theta(C) \).

Therefore the shift of the relaxation time of the solution from that of water can be expressed as

\[
\Delta \tau_D = BC + A \sqrt{C} + \theta(C).
\]

The above observation provides a plausible explanation for the decrease of \( \tau_D \) in RbCl and CsCl as being due to the decrease in the solution viscosity. However, the LiCl data for \( \tau_D \) and \( \eta \) appear to be in contradiction. This can be resolved by noting that a size effect also enters in the form of the radius \( a \). Since the bare ionic radius of Li (0.78 Å) is much smaller than that of water (2 Å), an apparent decrease of the effective radius \( [\theta(c) < 0] \) is likely, and may be responsible for the decrease in \( \tau_D \). This size effect is less important in the case of Rb and Cs, whose sizes (1.47 and 1.67 Å) are comparable to that of water.

### III. IONIC, DIELECTRIC, STOKES, AND HUBBARD-ONSAGER RADII IN AN IONIC SOLUTION

In considering size effects in ionic solutions, we note that several length scales govern the electrical behavior of solutions. Below we present a comparison of various sizes deduced from viscosity, conductivity, and dielectric data.

**Stokes radius.** The limiting \( (C \to 0) \) conductivity \( \Lambda_0 \) leads to a Stokes radius, which is related to the drift characteristics of the ion in the viscous solution, and is given by

\[
r_{\text{Stokes}} = \frac{N_0 e^2}{6 \pi \eta \Lambda_0}.
\]

The above expression ignores dielectric friction, and leads to a value much bigger than the ion radius.

**Hubbard-Onsager radius.** The HO model naturally leads to a radial length relevant to a point ion in a solution. This may be defined as\(^{12}\)

\[
a_{\text{HO}} = \frac{e^2}{16 \pi \eta} \left( \frac{\epsilon_{\infty} - \epsilon_{\omega}}{\epsilon_{\infty}^2} \right) \tau_D^{\omega}.
\]

Note that this is characteristic of the solution only, and is independent of the ion size. For water, \( a_{\text{HO}} \approx 1.5 \) Å at 25°C.

\( a_{\text{HO}} \) provides a useful measure of the importance of dielectric friction. For Li, \( R_L \) is much less than \( a_{\text{HO}} \), so the dielectric friction is important. For Rb and Cs, the ion radii are comparable to the HO radius, suggesting that dielectric friction is less important and provides a plausible explanation for the higher limiting conductivity.

Inclusion of dielectric friction leads to a size-dependent HO radius, which is related\(^{16}\) to \( r_{\text{Stokes}} \),

\[
r_{\text{HO}} = 4 \pi a_{\text{Stokes}} / x
\]

for slip boundary conditions, where \( x \) is a function of the ion size.

All the estimated numbers for individual ions are listed in the following Table II. It is hard to give accurate HO radii...

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### TABLE II. The Stokes, HO, and dielectric radii for the ions and molecules.

<table>
<thead>
<tr>
<th></th>
<th>Li(^+)</th>
<th>Rb(^+)</th>
<th>Cs(^+)</th>
<th>Cl(^-)</th>
<th>LiCl</th>
<th>RbCl</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Lambda_0 ) ( [\text{Ref. 6}] )</td>
<td>38.7</td>
<td>77</td>
<td>77.7</td>
<td>76.4</td>
<td>115.1</td>
<td>153.6</td>
<td>155.1</td>
</tr>
<tr>
<td>( \tau_{\text{Stokes}} ) ( \text{(stick)} )</td>
<td>2.38</td>
<td>1.18</td>
<td>1.19</td>
<td>1.21</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>( \tau_{\text{Stokes}} ) ( \text{(slip)} )</td>
<td>3.57</td>
<td>1.77</td>
<td>1.78</td>
<td>1.82</td>
<td>1.2</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>( \tau_{\text{ion}} ) ( \text{(slip)} )</td>
<td>1.8</td>
<td>1.8</td>
<td>2.1</td>
<td>2.2</td>
<td>1.07</td>
<td>1.07</td>
<td>0.96</td>
</tr>
<tr>
<td>( r_D )</td>
<td>3.35</td>
<td>3.02</td>
<td>2.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

for Rb⁺ and Cs⁺ since their ionic radii are close to a_HO. 12,13
The equivalent radii for molecules are obtain from the addi-
tivity of the conductivity, e.g., the Stokes radius for slip

\[ \sigma_0 = \sigma_A + \sigma_{ci} = \frac{N e^2}{4\pi\eta} \left( \frac{1}{r_A^+} + \frac{1}{r_{ci}} \right) = \frac{N e^2}{4\pi \eta r_{\text{Stokes}}}. \] 10

where

\[ r_{\text{Stokes}} = \frac{r_A^+ r_{ci}}{r_A^+ + r_{ci}}. \] 11

Dielectric radius. The notion of a dielectric radius has
already been introduced earlier. \( r_D \) listed in Table II are di-
electric radii extracted from the static model.

From the table we see that, as regards the increase of the
cation size, all the radii of the ACI molecules decrease, which
gives strong evidence for the correlation between the ion mo-
tion in the solvent and the dielectric relaxation process.

IV. CONCLUSIONS

The perspective of this work has been to utilize dielec-
tric spectroscopy results to understand ion–solvent interac-
tions, specifically by studying ion size effects on the dielec-
tric parameters. Both the static dielectric constant and the
dynamic dielectric relaxation time of the solution are affect-
ed by the presence of the ions. Remarkably, both decrease
linearly with solution conductivity, with size-dependent
slopes. The static dielectric decrement can be understood in
terms of a semiempirical static polarization model, and also
in terms of the Hubbard–Onsager theory.

The dynamical effects of the presence of the ions, reflect-
ed in the dielectric relaxation time \( r_D \), are less well under-
stood. While the data clearly show a linear decrease of \( r_D \)
with solution conductivity, the HO theory predicts a linear
increase with conductivity. Thus a first principles explana-
tion of the behaviour of \( r_D \) is still not available. However we
show that the effect on \( r_D \) appears to be dominantly due to
changes in solution viscosity, provided one also considers
the ion size effects.

Recent theoretical developments17–19 go beyond the
continuum HO theory by incorporating translational–rota-
tional coupling and soft force–hard force correlations. It re-
mains to be seen whether inclusion of such correlations will
provide a better explanation of the results presented in this
paper.

A principal feature of the moderately concentrated solu-
tions discussed here is that the dielectric relaxation is still
Debye-like (just like that of the solvent, water), albeit with a
decreased relaxation time. This indicates that the solvent
structure and correlations are not substantially modified. At
higher concentration10 (C > 5 M) in LiCl/H2O, the relaxation
time begins to increase at the same time that the relaxation
becomes non-Debye. (This regime is not observed in
RbCl and CsCl solutions because of their limited solubility.)
The non-Debye behavior at high concentrations indicates
that the water–water correlations are severely disrupted by
the presence of the ions. The implications of the high C re-
sults as regards the dynamical correlation in water remain
the subject of future work.

ACKNOWLEDGMENTS

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sions, and for pointing out the correlation with viscosity
data. Discussions with R. H. Cole are also gratefully ac-
knowledged. This work was supported by the Petroleum Re-
search Fund, administered by the American Chemical So-
ciety.

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