

Dielectric spectroscopy up to 20 GHz of LiCl/H₂O solutions

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Detailed measurements of the complex dielectric function $\epsilon = \epsilon' - i\epsilon''$ as functions of frequency between 45 MHz and 20 GHz and concentration c are presented and analyzed for LiCl/H₂O solutions. In this frequency range, the dielectric response is due to free water molecules and the response of the bound water occurs at lower frequencies and is not observed. From the data, several parameters—the static and high frequency limiting values ϵ_0 and ϵ_∞ , the dc conductivity σ_{dc} , the dielectric relaxation time τ_d , and the hydration number n_{hyd} —are extracted. The dissociation is observed to be incomplete suggesting the presence of undissociated ion pairs. A dissociation parameter is inferred from the σ_{dc} data. A model which views the liquid as composed of free water, hydrated single ions, and hydrated ion pairs is used to analyze the ϵ_0 data. With inclusion of the dissociation parameter, the model describes the data reasonably well for $c < 5.1$ M. At higher concentrations, a unique relaxation time is not observed indicating glasslike behavior.

I. INTRODUCTION

Because of its pervasive presence, the interaction of water with ions in a variety of chemical and biological systems is of great interest. Recently the importance of hydration shells in macromolecular solutions has become increasingly appreciated. Ions are always present in such macromolecular systems (e.g., proteins, DNA) and in some cases salt solutions can induce structural transformations, as in the *B-Z* transition in DNA. Thus it is particularly useful to consider the behavior of water in simple systems, such as aqueous solutions of monatomic ionic solutes, in order to extract guidelines for understanding more complex systems. Such studies, of course, are also relevant to some of the problems of classical electrochemistry.

Dielectric spectroscopy is a powerful probe of interparticle interactions (ionic and dipolar), particularly when carried out over a wide range of frequencies. Most studies have been mainly restricted to frequencies less than about 100 MHz and there have been few continuous frequency studies at GHz and higher frequencies, primarily because of technical difficulties. Particularly in aqueous systems, GHz studies are necessary since the characteristic dielectric relaxation time of water is about 9 ps (17 GHz). In electrolytical systems, an additional need for high frequencies arises because electrode polarization masks the intrinsic bulk solution behavior of the dielectric properties at low frequencies (< 100 MHz). For this reason, while conductivity (which is dominantly ionic) is an important and well understood tool in electrochemistry, the dielectric response (which is principally due to water, either free or in hydration shells) has not been adequately addressed.

We have recently developed a new technique to accurately measure the complex dielectric constant $\epsilon'(\omega) - i\epsilon''(\omega)$ of liquids using coaxial techniques.¹ The power of the technique lies in its applicability over a wide frequency range, which is 45 MHz to 20 GHz in the present experiment. Measurements at lower frequencies down to 100 kHz are also feasible (although not required for the present work). This frequency range encompasses the relaxation

spectrum of water. The high density of frequency points, and the quality of the measurements, enables us to identify the dominant relaxation processes in these liquids and clearly determine the relaxation time and its spectrum, and the low and high frequency dielectric constants.

Aqueous solutions of LiCl are an interesting system for several reasons. Such solutions may be considered to be simple, at least conceptually, in contrast to more complicated electrolytes. However, they exhibit a rich behavior in regard to their electrical and other physical properties.² For instance, certain concentrations exhibit glassy behavior at low temperatures³ and in fact are some of the classic glass forming liquids. A particularly appealing feature is that the concentrations can be easily varied over a wide range from dilute to very concentrated solutions, and indeed as this paper shows, several interesting aspects of transport in liquids are observable as one tunes the concentration.

In this paper, we present and analyze a comprehensive set of measurements of the dielectric function $\epsilon(\omega) = \epsilon' - i\epsilon''$ at frequencies between 45 MHz and 20 GHz, and for various concentrations between 0 and 14 M LiCl in H₂O. From the data we extract several parameters ϵ_0 , σ_{dc} , ϵ_∞ and the dielectric relaxation time $\tau_d(c)$ for the solutions. The concentration dependence of these parameters is then compared to a model which considers the solution as composed of free water, dissociated cations and anions which are hydrated, and also hydrated contact ion pairs, which are present due to incomplete dissociation. The conductivity data is used to extract a parameter α describing the degree of dissociation. The deduced values of α from the conductivity data are then used in the model to calculate the dielectric constant and good agreement is found for $c < 5.1$ M.

The principal feature of this work, in addition to the detailed measurements and results obtained, is the successful quantitative description of the dielectric data. Information is also extracted regarding the hydration number per ion and the size of the contact ion pairs. At concentrations greater than 5.1 M, the dielectric response is glasslike and the single particle picture considered here is inapplicable,

and perhaps a more sophisticated approach which involves cooperative effects is necessary.³

This paper is organized as follows: In Sec. II, we discuss experimental details, and present the results for ϵ' and ϵ'' as functions of ω and c . The parameters $\epsilon_0(c)$, $\sigma_{dc}(c)$ and $\epsilon_\infty(c)$ are extracted. Cole–Cole analyses of the data are discussed and the relaxation time $\tau_d(c)$ and the Cole–Cole parameter $\beta(c)$ are obtained. In Sec. III, we discuss a model incorporating single ions and ion pairs and show that the data are well described for $c < 5.1$ M. Section IV then discusses the nature of the parameters involved and the implications of the results at higher concentrations.

II. EXPERIMENTAL TECHNIQUE AND RESULTS

The experimental technique utilizes a 0.047 in. semirigid coaxial line with a sub-miniature (SMA) connector on one end and a flat face on the other, which was dipped into the liquid. The reflection coefficient of the sample system was measured using a Hewlett Packard 8510 network analyzer between 45 MHz and 20 GHz.

The dielectric constant ϵ was determined from the probe end impedance $Z(\epsilon, \omega)$ by modeling the coax-liquid interface as a dielectric-filled capacitance. Three calibrations at the end of coaxial probe—an “open”, a short, and standard liquid,—were used for a computerized deembedding procedure. The deembedding procedure eliminates the connector and coax mismatches. Details of the technique are described in Ref. 1.

Aqueous solutions of LiCl, with concentrations varying from 0.55 M (1.0 mol%) to 13.38 M (29.0 mol%) were prepared by dissolving LiCl powder (Fisher certified) in deionized water. Concentrations ranging from 0 (pure water) to 13.38 M were studied.

The results for the real part ϵ' and σ of the dielectric constant and the conductivity, respectively, as a function of frequency for various concentrations are shown in Figs. 1(a) and 1(b). (Note that σ and ϵ'' are equivalent, since $\sigma = \omega \epsilon_v \epsilon''$, where $\epsilon_v = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum.) The apparent low frequency divergence of ϵ' is due to electrode polarization effects, which masks the bulk dielectric properties. For $f > 1$ GHz, ϵ' clearly displays a relaxational behavior associated with the bulk solution. The conductivity has a nonzero low frequency plateau attributable to the ions. The frequency dependence of σ is due to the dielectric relaxation as shown below.

We parametrize the data using a William–Watts expression, for the dielectric relaxation, and include the dc conductivity

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_d)^{1-\beta}} + \frac{i\sigma_{dc}}{\epsilon_v\omega}, \quad (2.1)$$

where τ_d is a Debye relaxation time [note that $\epsilon(\omega) = \epsilon' - i\epsilon''$ satisfies the Kramers–Kronig relation]. For $\beta = 0$, Eq. (2.1) is just the single relaxation Debye formula. A nonzero value of β implies a spread of relaxation times. The above expression fits the data very well, except for the low ω divergence of ϵ' due to electrode polarization, as shown in Figs. 1(a), 2, and 3. The results of fitting the data for the complex ϵ are shown in Table I, which displays the

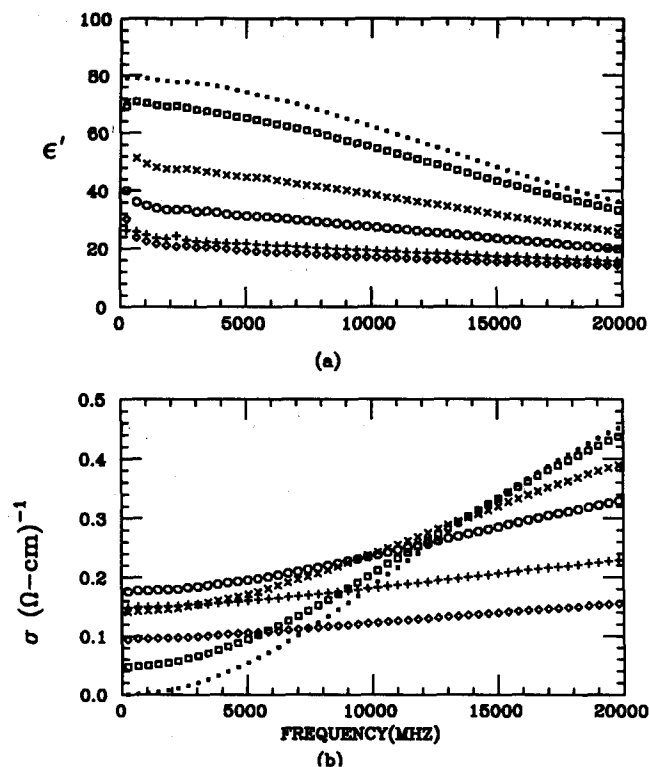


FIG. 1 (a). The real part of the dielectric constant ϵ' and (b) conductivity σ vs frequency for solutions of various concentrations $c = 0$ M (filled squares), 0.55 M (open squares), 2.65 M (\times), 5.11 M (\circ), 9.62 M ($+$), and 13.38 M (diamonds).

parameters resulting from the fit. (The dc conductivity σ_{dc} obtained directly from the measurements as the 45 MHz value of σ was subtracted from ϵ'' .) The parameters extracted are ϵ_0 , ϵ_∞ , τ_d , and β for the solution. For $c < 5.11$ M, $\beta = 0$ indicating a single relaxational process. Corresponding fits to the data are shown in Fig. 2 for these concentrations. For higher concentrations, it is apparent that a spread of relaxation times occurs, since $\beta \neq 0$. Corresponding fits of Eq. (2.1) to the higher concentration data are shown in Fig. 3 in the form of Cole–Cole plots.

The dependence of the parameters ϵ_0 , σ_{dc} , and ϵ_∞ with concentration is also displayed in graphical form in Fig. 4(a), 5(a), and 4(b). ϵ_0 decreases and ϵ_∞ increases mono-

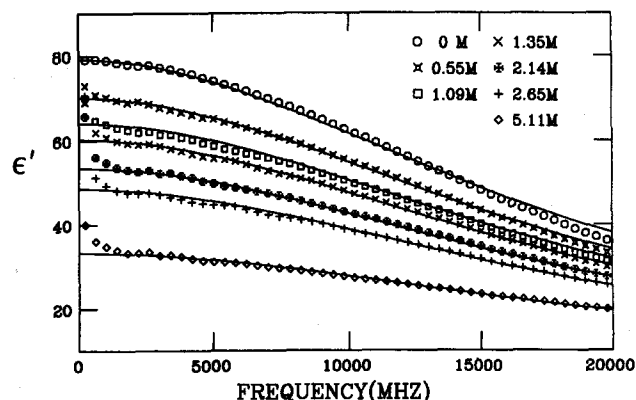


FIG. 2. ϵ' fits of the data to a single relaxation Debye model for various concentrations.

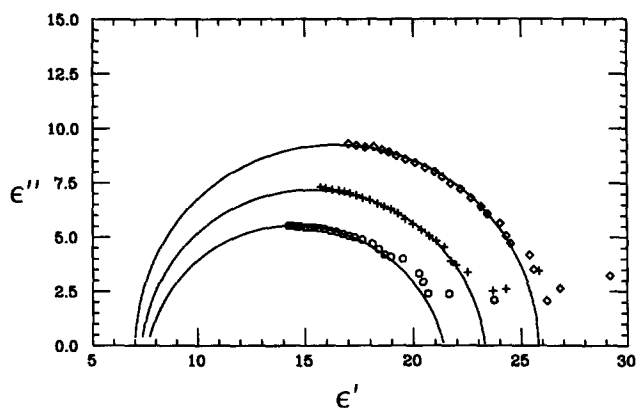


FIG. 3. Cole-Cole plots for $c = 7.2$ M (diamonds), 9.62 M (+), and 13.38 M (O). The lines represent Eq. (2.1) with parameters from Table I.

tonically with c , reaching plateaus at high concentrations. In contrast, σ_{dc} at first increases with c , reaches a maximum, and then decreases. The c dependence provides important clues to the microscopic processes which occur in the solution and the major aim of this paper is to provide an adequate model for the observed behavior.

III. MODEL OF DIELECTRIC PROPERTIES

Aqueous solutions of monovalent ions can be differentiated into different domains as the salt concentration is varied.⁴ These are *A*, a highly dilute electrolyte solution which obeys the Debye-Hückel limiting law; *B*, a concentrated aqueous electrolyte solution which satisfies extended Debye-Hückel theory; *C*, a hydrated melt; and *D*, an incompletely hydrated melt. The solutions studied in the present work may be regarded as being in domains *A* and *B*.

Experimentally, x-ray and neutron studies^{5,6} show that samples in domain *B* are mixtures of free water molecules, hydrated Li^+ cations, and Cl^- anions and perhaps ion pairs. For samples which may be located in domain *C* ($c > 5$ M), neutron diffraction⁷ and molecular dynamics studies^{8,9} show that as the concentration is increased, more and more missing water molecules in the first hydration shells are replaced by counter ions from which contact ion pairs arise.

For $c < 5.1$ M, τ_d is close to that of pure water and also $\beta = 0$ from our measurements. This indicates the dielectric properties are dominated by apparently free water molecules, which primarily interact with each other. As Fig. 4(a)

TABLE I. Dielectric parameters of LiCl/H₂O solutions.

c (M)	ϵ_0	ϵ_∞	τ_d (ps)	β
0	79.2	4.5	8.8	0
0.55	70.2	4.7	8.8	0
1.09	64.2	5.0	8.7	0
1.35	60.3	5.1	8.7	0
2.14	53.5	5.3	8.6	0
2.65	48.6	5.7	8.6	0
5.11	33.3	6.4	8.1	0
7.20	25.6	7.0	7.5	0.01
9.62	23.3	7.3	7.6	0.07
13.38	21.4	7.6	8.5	0.14

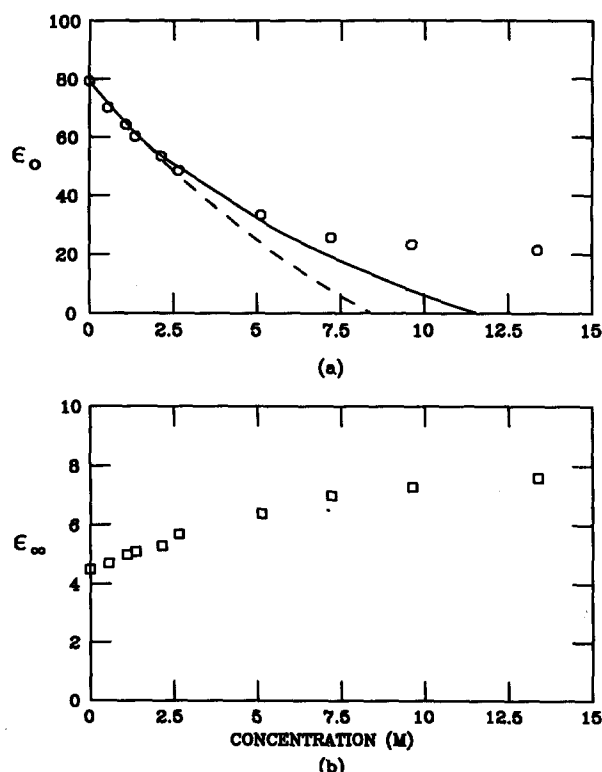


FIG. 4. (a) "Static" dielectric constant ϵ_0 vs concentration c . [The lines represent calculations for complete dissociation ($\alpha = 1$, dashed line) and incomplete dissociation ($\alpha < 1$, solid line).] (b) High frequency limiting dielectric constant ϵ_∞ vs concentration.

shows, the measured ϵ_0 is lower than that of pure water—this is due to the excluded volume of the ions and the hydration shell. As will be apparent later, the volume effect is much larger than can be attributed to the ions alone and the hydration molecules are essential. The hydration water molecules, however, appear to have a relaxation frequency significantly less than 1 GHz and hence appear "frozen" in the present frequency range. With increasing ion concentrations, as more and more water molecules form hydration shells around the ions, ϵ_0 decreases due to the loss of free water. In modeling the dielectric behavior, we make the following key assumptions, based upon the above observations:

(i) The dielectric properties are only due to free water molecules. Thus the water in the hydration shell is assumed not to contribute to the dielectric properties in the frequency range.

(ii) The "static" conductivity σ_{dc} is due only to *hydrated single* cations and anions. Further this ionic conductivity is assumed to be frequency independent.

(iii) The dissociation of LiCl is not complete and the degree of dissociation for moderate concentrations is represented by a parameter $\alpha(c)$, ($\alpha < 1$). Thus the liquid may be pictured as consisting of hydrated Li^+ and Cl^- single ions, free water molecules, and hydrated contact ion pairs. The ion pairs do not contribute to the conductivity.

A. Static conductivity

From the measured conductivity, we determine the molar conductivity Λ , which is shown in Fig. 5(b) as a function

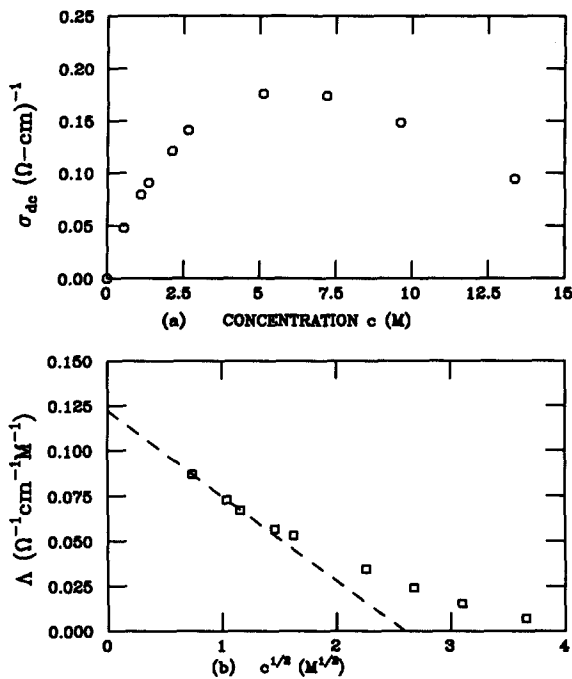


FIG. 5. (a) Conductivity σ_{dc} vs concentration c . (b) Molar conductivity vs \sqrt{c} .

of \sqrt{c} . For low concentrations, Λ follows the Kohlrausch-Debye-Hückel (KDH) law $\Lambda = \Lambda_0 - S\sqrt{c}$ shown as the dashed line in Fig. 5(b). From the low c data, the limiting conductivity Λ_0 and the coefficient S were determined. The value $\Lambda_0 = 0.122 \Omega^{-1} \text{cm}^{-1} \text{M}^{-1}$ derived from the experiment conductivity is very close to the values given by Ref. 10 $\Lambda_{\text{OLi}} = 0.03869 \Omega^{-1} \text{cm}^{-1} \text{M}^{-1}$ and $\Lambda_{\text{OCl}} = 0.07634 \Omega^{-1} \text{cm}^{-1} \text{M}^{-1}$ which give $\Lambda_0 = \Lambda_{\text{OLi}} + \Lambda_{\text{OCl}} = 0.115 \Omega^{-1} \text{cm}^{-1} \text{M}^{-1}$. S is found to be $4.71 \times 10^{-2} \Omega^{-1} \text{cm}^{-1} \text{M}^{-3/2}$.

As c increases, the values are larger than this form would predict. This is because the dissociation is not complete. In order to extend the range of validity, we make the *ad hoc* introduction of a degree of dissociation parameter α , which is concentration dependent, and fit the data to the form¹¹

$$\Lambda = \Lambda_0 - S[\alpha c(c)]^{1/2}. \quad (3.1)$$

The resulting values of α obtained using Eq. (3.1) and the earlier determined values of Λ_0 and S are shown in Table II and also in Fig. 6(a). We later use these values in a model for the dielectric data. Since the above analysis is inapplicable for $c > 7.2$ M, as is evident from Fig. 5(b), values of α for these high concentrations are not shown.

It is useful to also consider an alternative description of the static conductivity.

$$\sigma_{dc} = n_s(c)e[u_+(c) + u_-(c)], \quad (3.2)$$

$$u_{\pm}(c) = \gamma(c)u_{0\pm}, \quad (3.3)$$

where u is the mobility, u_0 is the mobility in the limit of infinite dilution, and γ is a concentration dependent factor (< 1). $n_s(c)$ is the density of singly charged ions in the solu-

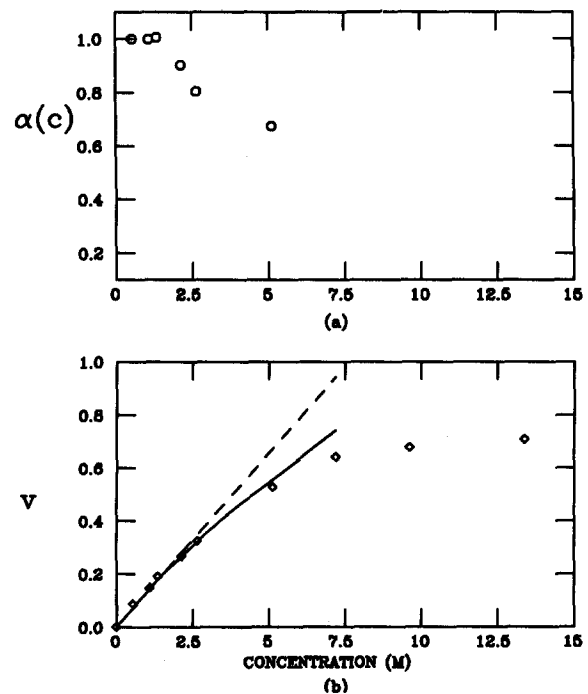


FIG. 6. (a) Degree of dissociation α vs concentration c . (b) Volume fraction ν of hydrated particles vs concentration c [The lines represent calculations for complete dissociation ($\alpha = 1$, dashed line) and incomplete dissociation ($\alpha < 1$, solid line).]

tion, which can be expressed in terms of the concentration c (M)

$$n_s = \alpha c N_0, \quad (3.4)$$

where N_0 is the Avogadro constant. Therefore,

$$\sigma_{dc} = \alpha(c)cN_0e\gamma(c)(u_{0+} + u_{0-}). \quad (3.5)$$

From Eq. (3.5), using the $\alpha(c)$ obtained above, the mobility dependence on c represented by $\gamma(c)$ can be deduced from Fig. 5(a), which is shown in Table II for $c < 5.1$ M.

B. Static dielectric constant

We now turn to an understanding of the static dielectric constant ϵ_0 .

For a dilute homogeneous dielectric mixture with inert spherical solute particles of permittivity $\epsilon_u = \epsilon'_u - i\epsilon''_u$ in a solvent of $\epsilon_{f\omega}$, the dielectric behavior can be described by the Maxwell-Wagner formula

$$\epsilon_{s0} = \epsilon_{f\omega} \frac{2(1-\nu)\epsilon_{f\omega 0} + (1+2\nu)\epsilon_u}{(2+\nu)\epsilon_{f\omega 0} + (1-\nu)\epsilon_u}, \quad (3.6)$$

where ν is the volume fraction of the solute particles.

In the ionic aqueous solutions, the "dielectric spheres" consists of the ions and ion pairs surrounded by a shell of hydration water molecules. These ions are of electronic permittivity $\epsilon_e \sim 2$ which is frequency independent. As mentioned above, the hydration water appears frozen in this frequency range and hence its permittivity is the high frequency limiting value $\epsilon_{h\infty} \sim 5$. One can show¹² that the spherical ions with $\epsilon_e \sim 2$ and the spherical shell with $\epsilon_{h\infty} \sim 5$ can be regarded as a spherical shell with $\epsilon_u \sim 5$ in the frequency range investigated, i.e., negligible error is introduced by re-

garding the ion + shell as a sphere of the same volume, but with a permittivity equal to that of the bound water molecules.

The volume fraction v can then be obtained from the above equation

$$v = \frac{(\epsilon_{w0} - \epsilon_0)(\epsilon_u + 2\epsilon_{w0})}{(2\epsilon_{w0} + \epsilon_0)(\epsilon_{w0} - \epsilon_u)} \quad (3.7)$$

using $\epsilon_u = 5$ and is plotted in Fig. 6(b).

Note that the volume fraction of free water in the solution is $1 - v$. Making the obvious assumption that the volume occupied by a water molecule is independent of the concentration, as supported by the observed linearity of the density vs concentration as shown in Table II, the volume of the hydrated water per unit volume can be found as

$$v_{\text{hyd}} = v_w - (1 - v), \quad (3.8)$$

$$v_w = d - 10^{-3}Ac, \quad (3.9)$$

where v_w is the volume of water per unit volume of the solution, d is the density of the solution, $A = 42.39$ g is the molecular weight of LiCl, and the density of water is taken as 1. Therefore the average number of hydration water per LiCl molecule is given by

$$N_{\text{hyd}} = \frac{v_{\text{hyd}}}{cV_{w,M}} \quad (3.10)$$

where $v_{w,M}$ is the molar volume of water. The dependence of N_{hyd} with concentration is listed in Table II. It decreases from about 7.6 to 2 per LiCl molecule as the concentration increases from 0.55 to 13.4 M.

The dielectric and conductivity data can be related as follows: The volume of hydrated solute v_h per unit volume of the solution can be calculated from the volume of the hydrated particles

$$v_{\text{calc}} = cN_0 \frac{4\pi}{3} \{ \alpha(c)(r_{\text{Lih}}^3 + r_{\text{Clh}}^3) + [1 - \alpha(c)]r_p^3 \}, \quad (3.11)$$

where r_{Lih} , r_{Clh} , and r_p are radii of hydrated Li^+ , Cl^- , and $\text{Li}^+ - \text{Cl}^-$ contact ion pairs and $\alpha(c)$ is the fraction of single ions in the solution which is the degree of dissociation we obtained above.

Using the parameter values $r_{\text{Lih}} = 2.6 \text{ \AA}$, $r_{\text{Clh}} = 3.25 \text{ \AA}$, $r_p = 2.9 \text{ \AA}$, with Eqs. (3.6) and (3.11) for $\epsilon_{w0} = 79.2$ and

TABLE II. Hydration numbers and dissociation parameters for LiCl/H₂O solutions.

c (M)	c (mol %)	N_{hyd}	$\alpha(c)$	$\gamma(c)$	d (g/cm ³) ^a
0.55	1.0	7.6	1.0	0.76	1.0120
1.09	2.0	6.5	1.0	0.64	1.0258
1.35	2.5	6.8	1.0	0.58	1.0324
2.14	4.0	6.0	0.90	0.54	1.0526
2.65	5.0	5.8	0.80	0.58	1.0662
5.11	10.0	4.9	0.67	0.44	1.1371
7.20	14.5	4.1	... ^c	...	1.1988 ^b
9.62	20.0	3.1	... ^c	... ^c	1.2742 ^b
13.38	29.0	2.2	... ^c	... ^c	1.3976 ^b

^a d from 0.55 to 5.11 M is obtained by interpolation using data from Ref. 19.

^b d is obtained by extrapolation using data from Ref. 19.

^c Calculation inapplicable for these concentrations.

$\epsilon_u = 5$, the calculated values of v_{calc} are shown in Fig. 6(b) (solid line) and ϵ_0 are shown in Fig. 4(a) (solid line). Experimental and calculated results coincide very well up to 5.1 M. Also shown in Fig. 6(b) (dashed line) is v_{calc} calculated from $\alpha(c) = 1$ and in Fig. 4(a) (dashed line) is ϵ_0 calculated from $\alpha(c) = 1$, which clearly are inadequate for $2.1 < c < 5.1$ M.

IV. DISCUSSION OF RESULTS

The good agreement of the model with the concentration dependent data, shows that the physical picture embodied in the assumptions (i)–(iii) in Sec. III, are applicable for concentrations up to 5.1 M. One successful feature of the model is the correlation between the conductivity and the dielectric data, via the dissociation parameter α . As is evident from Fig. 6(a), partial dissociation occurs for moderate concentrations. We now discuss the parameter values that enter the calculations.

For clarity, we retrace the logic of the analysis. From the data for σ_{dc} and hence Λ , we deduce α using Eq. (3.1). The values of α are then used in Eq. (3.11) to calculate the effective volume of the hydrated ions and ion pairs, which is then substituted in Eq. (3.6) to calculate ϵ_0 , for comparison with the measured data. For $c < 1.35$ M, $\alpha = 1$ indicating complete dissociation, and for $2.14 < c < 5.1$ M, $\alpha < 1$ indicating incomplete dissociation and hence the presence of ion pairs.

The values of $r_{\text{Lih}} = 2.6 \text{ \AA}$ and $r_{\text{Clh}} = 3.25 \text{ \AA}$, chosen to fit the data for the dilute solutions with $\alpha = 1$, agree well with the values 2.43 and 3.10 \AA for $c < 6.9$ M obtained from x-ray and neutron studies,⁵ and 2.55 and 3.34 \AA for 3.57 M from neutron studies.^{13–15} These values do not change with concentration, at least for $c < 5$ M (Ref. 6). The distance between contact $\text{Li}^+ \text{Cl}^-$ pairs obtained from molecular dynamics simulations⁸ is 2.8 \AA for 18.5 M and experimental results give 2.76 \AA for very concentrated 14.9 M solutions.⁷ For the moderate concentrations for which $\alpha < 1$, the hydrated ion pair radius $r_p = 2.9 \text{ \AA}$ is consistent with neutron scattering data and molecular dynamics studies, and indicates a partial hydration shell surrounding the ion pairs.

The dynamic hydration number of 7.6 for low concentrations, inferred from this measurement, is in agreement with that calculated in Ref. 16, which gives 7.2 (4.6 for Li^+ and 2.6 for Cl^-) in very dilute solution. In contrast, most molecular dynamic simulation studies^{8,9,16} and experimental studies^{5,15} yield coordination numbers of Li^+ between 4–5 and that of Cl^- about 6. In making this comparison, it should be kept in mind that the hydration number derived in the present experiments refers to those water molecules whose average residence time is longer than 50 ps.

An apparent discrepancy has surfaced recently between the relaxation times measured by depolarized Rayleigh scattering¹⁷ τ_R and those from dielectric measurements τ_d reported earlier by Pottel.¹⁸ In contrast to Pottel, who found an initial decrease in τ_d and then an increase, our measurements show that for $c > 5$ M (15 mol%), one cannot talk about a single τ_d , and for lower c , τ_d is essentially equal to that of free water. In the work of Ref. 17, τ_R increases monotonically with c . It is possible that the τ_R measurements are

sensitive to the hydration shell water, although it is still difficult to see why it should then depend on the concentration and not on the ion-dipole interaction, which should be c independent.

The model presented above is inadequate for concentrations exceeding 5 M. A significant clue to these high c solutions lies in the τ_d and β values, which indicate that the solution can no longer be viewed as a multicomponent liquid, but rather is glasslike. The "free" water molecules no longer interact dominantly with each other. Perhaps the proper approach to the high c solutions is to view them as connected networks of interpenetrating cages of ions, ion pairs, and water molecules. While this implies a degree of ordering, at the same time the local environment of the water molecules probably experiences substantial glasslike disorder. For a satisfactory description of the high c solutions, a theoretical approach considerably more sophisticated than presented here, such as the mode coupling analysis used in Ref. 3, may be necessary.

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