Dielectric Properties of an Electrolyte Solution at Low Reduced Temperature

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We report on the complex dielectric permittivity up to 20 GHz of solutions of tetrabutylammonium bromide in carbon tetrachloride at salt concentrations between 0.01 and 1 mol dm^{-3}, where the molar conductance increases with concentration up to molten saltlike conductances. At concentrations below about 0.1 mol dm^{-3}, the frequency dependence of the permittivity shows Debye behavior with a single relaxation time, as would be expected for the reorientation of dipolar ion pairs. The static permittivity monotonically increases with concentration. Assuming dipolar processes as the major contributors to the dielectric spectra, Kirkwood's theory yields correlation factors which rapidly decrease with increasing salt concentration, indicating strong antiparallel correlations of dipole orientations even at concentrations as low as $c = 10^{-4}$ mol dm^{-3}. Above $c = 0.1$ mol dm^{-3} the spectra broaden rapidly, while the viscosity remains low. In this range the spectra are well-represented by a Cole−Cole expression with a mean relaxation time essentially proportional to the viscosity. We suggest that at higher concentrations part of the polarization arises from a Debye−Falkenhagen-type mechanism caused by the asymmetry of the ion atmosphere in the applied field. The increasing importance of this contribution appears to result from the dissociation of ion pairs by interaction with the remainder of the screening ionic fluid, which eventually leads to a transition to molten saltlike structures.

I. Introduction

When applying corresponding states ideas to ionic fluids,[1] it is convenient to describe the behavior of charge-symmetrical electrolytes by the reduced temperature

$$T^* = \frac{4\pi\epsilon_o\epsilon_S k_B T a}{z^2 e^2} \tag{1}$$

and the reduced density

$$\rho^* = \rho a^3 \tag{2}$$

where z is the charge number of the ions, ρ their number density, a their mean hard sphere diameter, and ϵ_S the dielectric constant of the solvent. ϵ_o is the permittivity of the vacuum, and all other symbols have their usual meaning. We are interested[2−4] in solutions at low reduced temperature, $T^* \leq 0.05$ say, where theory predicts phase separation[1,5,6] which seems to correspond to liquid−liquid immiscibilities in real systems.[2,3,7] There is currently much debate on the nature of such Coulombic immiscibilities and the corresponding critical phenomena.[2−7]

Ideal ionic fluids at low T^*, say $T^* < 0.1$, should represent solutions of 1:1 electrolytes in solvents of low dielectric constant, $\epsilon_S < 5$, at room temperature.[1,2] A common feature of such systems is a minimum in the concentration dependence of the molar electric conductance Λ.[1,8] At low salt concentrations Λ shows a rapid decrease, usually interpreted as due to increasing condensation into neutral ion pairs. At higher concentrations Λ increases up to molten saltlike conductances.[9] Because the observed phase instabilities fall into a range with substantial conductances at the critical point,[2] we are interested

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in the factors determining the increasing segment of the conductance curve, typically at salt concentrations between $c = 0.01$ and 1 mol dm^{-3}.

Standard interpretation[8] attributes conductance minima to the formation of charged ion triplets and larger ionic clusters. This type of speciation ceases, however, to have meaning at high salt concentrations, where the structure of the solution must cross over to a molten saltlike pattern with alternating charges. Various alternative interpretations attribute the increasing conductance to a dissociation of previously associated ion pairs by interaction with the remainder of the electrolyte fluid.[9−12] In the context of theoretical work on phase separation and criticality in ionic fluids, the past years have seen a revival of interest in these problems.[5,6,13−15]

In seeking experimental information about ionic structures in this regime, a characterization of the frequency-dependent dielectric processes seemed of considerable interest to us. The dielectric spectrum provides valuable information concerning ionic processes. Zero-frequency extrapolation yields the static dielectric constant which, at high salt concentrations, is not measurable by conventional techniques owing to the high electrical conductivity.

Of course, one would like to have data for this sort for phase-separating systems such as solutions of tetraalkylammonium salts in alcohols which have repeatedly served as model systems.[2−4,7] Unfortunately, the alcohols themselves possess complicated dielectric spectra[16] from which the contributions arising from ionic processes are not easily separated. This holds true for most other phase-separating systems as well. The choice of a solvent without permanent dipole moments allows one to attribute the dielectric response unambiguously to ionic processes. Adopting this strategy, we report here the dielectric spectra of tetra-*n*-butylammonium bromide (Bu$_4$NBr) in carbon tetrachloride (CCl$_4$), where high solubility is achieved. Our interest has been drawn to this system by a note concerning

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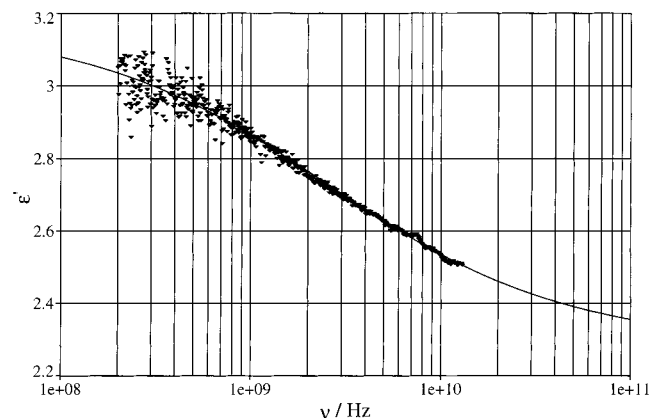*J. Phys. Chem. B, Vol. 103, No. 22, 1999* **4739**

Figure 1. $\epsilon'(\nu)$ for a solution of $c = 0.0565$ mol dm^{-3} of Bu$_4$NBr in CCl$_4$ at 298.15 K after three accumulations. The curve consists of about 1000 data points with logarithmic increments of the frequency. The figure shows the primary experimental data. Some obvious spikes have, however, been eliminated.

dielectric relaxation,[17] the results of which seemed to warrant more detailed examination.

II. Experimental Results and Data Processing

Complex dielectric spectra were recorded with a microwave network analyzer (Hewlett-Packard HP 8720C) and a probe (HP 885070B) as described elsewhere.[16] The method is based on an analysis of reflected waves and yields data triples $\{\epsilon',\epsilon'',\nu\}$ for the real (ϵ') and imaginary (ϵ'') parts of the complex permittivity $\epsilon^*(\omega)$ at frequencies $\nu = \omega/2\pi$ in the range 200 MHz $< \nu <$ 20 GHz. For a conducting system $\epsilon^*(\omega)$ is given as[18]

$$\epsilon^*(\omega) = \epsilon' - i\epsilon'' = \epsilon_\infty + \Delta\epsilon^*(\omega) + \sigma/i\epsilon_o\omega \quad (3)$$

Here ϵ_∞ is the high-frequency limit of the real part $\epsilon'(\omega)$ associated with electronic and vibrational contributions. The low-frequency limit of $\epsilon'(\omega)$ yields the static permittivity (dielectric constant)

$$\epsilon_S \equiv \epsilon'(\omega = 0) = \epsilon_\infty + \Delta\epsilon'(\omega = 0) \quad (4)$$

At low conductivity, ϵ_S can be determined independently by static techniques.

The term $i\sigma/\epsilon_o\omega$ accounts for the contribution of the electrical conductivity σ to the imaginary part $\epsilon''(\omega)$. σ can be determined by separate experiments. Because CCl$_4$ lacks a permanent dipole moment, the excess part $\Delta\epsilon^*(\omega)$ up to 20 GHz reflects ionic processes. As $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are interrelated, $\Delta\epsilon^*(\omega)$ can be viewed as a frequency-dependent excess conductivity

$$\Delta\sigma^*(\omega) = i\omega\Delta\epsilon^*(\omega) \quad (5)$$

which in conducting systems may reflect not only a contribution arising from dipolar relaxation but also contributions from ion transport in excess to those covered by the term $i\sigma/\epsilon_o\omega$.

We have measured dielectric spectra of solutions made up from dry Bu$_4$NBr (Fluka) and CCl$_4$ (Baker) between $c = 0.01$ and 1 mol dm^{-3}. Below $c = 0.01$ mol dm^{-3} the small relaxation strength did not allow measurements with the desired precision. Above $c = 1$ mol dm^{-3}, large parts of the spectrum were below the accessible frequency range. Several spectra were recorded with each sample and were accumulated. Each spectrum consisted of 1000 data points in the range 200 MHz $< \nu <$ 20 GHz. At low concentrations an analysis of $\epsilon'(\nu)$ was found to be superior to that of $\epsilon''(\nu)$. Figure 1 shows $\epsilon'(\nu)$ of a sample

TABLE 1: Parameters Describing the Complex Permittivity up to 20 GHz in Solutions of Bu$_4$NBr in CCl$_4$ at 298.15 K

c (mol dm^{-3})	x_2	n	ϵ_∞	ϵ_S	τ_o (ps)	α
0	0	1.4570	2.23	2.228		
0.0230	0.00225	1.4582	2.23	2.31	17.0	0
0.0565	0.00557	1.4592	2.24	2.32	21.3	0
0.0688	0.00677	1.4599	2.24	2.32	15.2	0
0.125	0.0125	1.4613	2.24	2.40	17.6	0.06
0.223	0.0225	1.4642	2.25	2.58	27.2	0.297
0.543	0.0597	1.4741	2.28	3.18	63.5	0.444
0.765	0.0863	1.4802	2.30	3.74	142	0.518
1.061	0.128	1.4882	2.33	4.73	406	0.569

TABLE 2: Densities, Electrical Conductances, and Viscosities of Solutions of Bu$_4$NBr in CCl$_4$ at 298.15 K

c (mol dm^{-3})	d (g cm^{-3})	$10^6 \sigma$ (S cm^{-1})	η (cP)
0.1225	1.56845	0.601	2.03
0.1954	1.55872	1.21	2.76
0.3325	1.54058	2.76	4.35
0.7391	1.48436	13.9	13.9
0.8867	1.45210	20.0	21.1
0.9917	1.44991	24.9	27.9
1.208	1.41741	34.0	51.5
1.384	1.39552	38.0	
1.495	1.37953	37.6	
1.500	1.37635	37.2	
1.608	1.35480	34.1	
1.839	1.32710	26.3	

with $c = 0.0597$ mol dm^{-3} after three accumulations. In further data processing, some obvious spikes on the spectrum were eliminated. In samples of low relaxation strength, spurious effects caused by wave reflection in the test cell led us to discard some data points above 10 GHz. A systematic bias in the data below 300 MHz was corrected by calibration. In some samples of low relaxation strength, random noise was removed by the LOESS filtering technique.[19]

For parametrization of spectra below $c = 0.1$ mol dm^{-3}, the assumption of a single Debye process with a relaxation time τ proved to be sufficient. In this case $\epsilon^*(\omega)$ is given by[18]

$$\Delta\epsilon(\omega) = \frac{\epsilon_S - \epsilon_\infty}{1 + i\omega\tau} \quad (6)$$

In the fits ϵ_∞ was kept fixed at $\epsilon_\infty = 1.05\ n^2$, where n is the refractive index at the wavelength of the sodium D-line.

For $c > 0.1$ mol dm^{-3} the spectra could be adequately represented by the Cole–Cole expression which presumes a symmetrical distribution of relaxation times around a principal time τ, namely,

$$\Delta\epsilon(\omega) = \frac{\epsilon_S - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (7)$$

where α describes the width of the spectrum. For $\alpha \rightarrow 0$ eq 7 reduces to eq 6. Other options[18] were examined, which for simplicity are not given here in detail. A bimodal spectrum with two discrete relaxation times did not adequately fit the primary data. A Cole–Davidson distribution of relaxation times[18] was found to be inadequate as well. An independent determination of the dielectric constant at 2 MHz at $c = 0.15$ mol dm^{-3} yielded agreement with the fitted value of ϵ_S. Thus, no low-frequency processes with notable amplitudes seem to be missed.

Table 1 summarizes the spectral parameters. The symbol c is the molar concentration, while x_2 is the mole fraction of the salt, and ϵ_S, ϵ_∞, τ_o, and α are the parameters of the Cole–Cole distribution. Table 2 lists auxiliary data for data evaluation and interpretation. d is the density measured with an Anton Paar
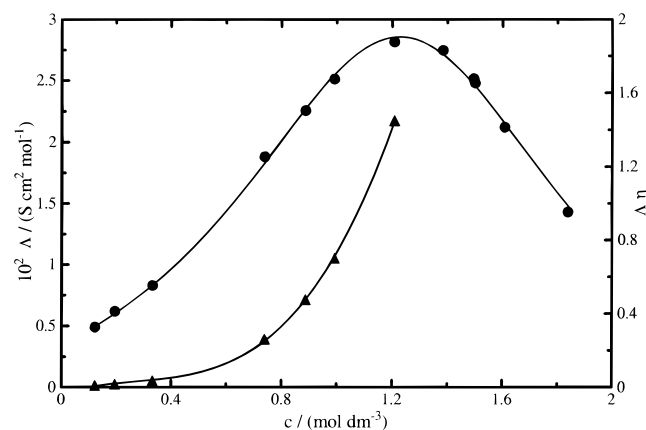
Figure 2. Molar conductance $\Lambda = \sigma/c$ (filled circles) and Walden product $\Lambda\eta$ (triangles) of solutions of Bu$_4$NBr in CCl$_4$ at 298.15 K. The figures for the Walden product refer to the conventional units of S cm^2 mol^{-1} for the molar conductance and cP for the viscosity.

TABLE 3: Static Dielectric Constants ϵ_S of Dilute Solutions of Bu$_4$NBr in CCl$_4$ at 298.15 K and Derived Effective Dipole Moments μ_{eff}

$10^4 x_2$	$10^4 c$ (mol dm^{-3})	ϵ_S	μ_{eff} (D)
0	0	2.228	11
0.102	1.056	2.2293	9.6
0.150	1.55	2.2297	9.0
0.333	3.43	2.2310	8.0
0.501	5.16	2.2320	7.5
1.01	10.4	2.2339	6.3

vibrating tube densimeter, σ is the zero-frequency conductivity (specific conductance) determined by a Wayne−Kerr bridge (model B-905), and η is the viscosity determined by an Ubbelohde viscometer.[20] Table 3 summarizes the results of direct measurements of ϵ_S with the Wayne−Kerr bridge below 0.01 mol dm^{-3}. All data refer to 298.15 K.

III. Discussion

Electrical Conductance. We begin the discussion by a brief consideration of the molar conductance $\Lambda = \sigma/c$ in systems at low T^*. At high dilution Λ is known to show a rapid decrease with increasing salt concentration, because ion association to uncharged pairs drains the concentration of free ions toward zero. Effects beyond pair formation cause Λ to pass a minimum. By comparison with solutions in other apolar solvents such as benzene,[21,22] we estimate the conductance minimum of our system to occur below 10^{-5} mol dm^{-3} with a conductance lower than 10^{-5} S cm^2 mol^{-1}. This is beyond the range in which measurements were feasible with our equipment.

Figure 2 shows the concentration dependence of the molar conductance above $c = 0.1$ mol dm^{-3}. Λ increases with concentration up to a maximum near 1.2 mol dm^{-3}, where it exceeds the hypothetical value of 0.01 S cm^2 mol^{-1} for molten Bu$_4$NBr, estimated by extrapolation of the data of Lind et al.[23] Conductance maxima are found in many systems, provided that the solubility enables sufficiently high salt concentrations.[9,22] In the absence of elaborate conductance theories, the conductance−viscosity product $\Lambda\eta$, often termed "Walden product", is thought to be more indicative of free-ion concentration than Λ itself.[1,24] Figure 2 shows that in concentrated solutions this product increases rapidly with concentration, indicating a substantial concentration of free ions. Moreover, this product does not reflect the conductance maximum, corroborating the interpretation that conductance maxima do not reflect distinct

ionic processes but result from the increasing viscosity of the solutions.

Dielectric Constant. The current knowledge of the behavior of ϵ_S in apolar solvents mainly results from studies at high dilution, e.g., with benzene as a solvent.[21,25] In accordance with such results, the data in Table 3 reflect an increase of ϵ_S with concentration. Because it can be inferred from conductance behavior that in the dilute regime ion pairs are the dominating species, this increase can be well-understood in terms of an increasing polarization, when more and more ion pairs with high dipole moments are added.

As long as the picture of ion pairing is correct, ϵ_S can be described by Kirkwood's theory.[26,27] Specifically, we use here the so-called Oster equation[28,29] for a binary mixture in which the total molar polarization P is given by

$$P = x_1 P_1 + x_2 P_2 = \frac{(\epsilon_S - 1)(2\epsilon_S + 1)}{9\epsilon_S}\frac{(x_1 M_1 + x_2 M_2)}{d} \quad (8)$$

where P_1 and P_2 are the molar polarizations of the solvent and solute, respectively. Moreover, d is the density of the mixture interpolated from data in Table 2, and M_i ($i = 1, 2$) is the molecular mass.

For further evaluation P_1 was assumed to be independent of the concentration and was calculated from the dielectric constant of pure CCl$_4$. P_2 is given by

$$P_2 = P_{\infty,2} + \frac{4\pi}{3}N_A\frac{\mu_{eff}^2}{3k_B T} \quad (9)$$

where μ_{eff} is the effective dipole moment of the solute, N_A is Avogadro's constant, and $P_{\infty,2}$ describes high-frequency contributions of electronic and atomic polarizations to P_2. We set $P_{\infty,2} = 120$ cm^3 mol^{-1}, which corresponds to $\epsilon_\infty = 2.5$ of the pure salt. Because $P_{\infty,2}$ is only a few percent of P_2, this rough estimate is tolerable.

The resulting effective dipole moments are tabulated in Table 3. Extrapolation yields for the dipole moment of Bu$_4$NBr at infinite dilution in CCl$_4$ $\mu_o = 11.0$ D ($1D = 3.335 \times 10^{-30}$ C·m) with an estimated uncertainty of ± 0.5 D, in good agreement with the result of Geddes and Kraus[25] for Bu$_4$NBr in benzene, $\mu_o = 11.6$ D. μ_o is considerably lower than the value of $\mu = 28$ D estimated for two charged hard spheres at a contact distance of $a = 6$ Å. Similar discrepancies are found for other salts as well.[25] Davies and Williams[30] have shown that the agreement between the experimental value and theoretical estimate is better when the polarizability of the ions is taken into account, but this removes only part of the discrepancy. [30]

According to Kirkwood's theory the decrease of μ_{eff} with increasing solute concentration reflects correlations between dipoles which are described by the Kirkwood factor[27,28]

$$g_K = \frac{\mu_{eff}^2}{\mu^2} \quad (10)$$

where μ is the dipole moment in the absence of intermolecular dipolar correlations. With $g_K = 1$ Kirkwood's theory reduces to the Onsager theory[31] of the dielectric constant.

If we set $\mu = \mu_o$, the resulting factors g_K in Figure 3 show a rapid decrease with increasing salt concentration, reflecting strong dipole−dipole interactions even at concentratïons as low as 10^{-4} mol dm^{-3}.[32,33] The observed values of $g_K < 1$ indicate preferred antiparallel orientations of the dipoles. Actually, there are only a few neutral fluids which reflect such strong
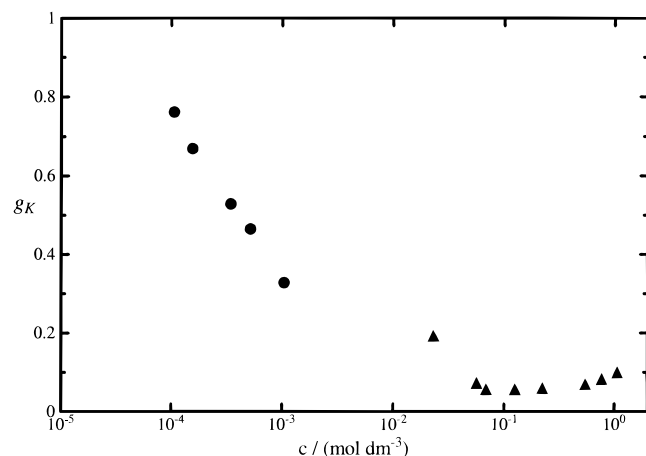
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Figure 3. Kirkwood factors g_K of solutions of Bu$_4$NBr in CCl$_4$ at 298.15 K: circles, values derived from static data in Table 3; triangles, values derived from frequency-dependent dielectric spectra in Table 1.
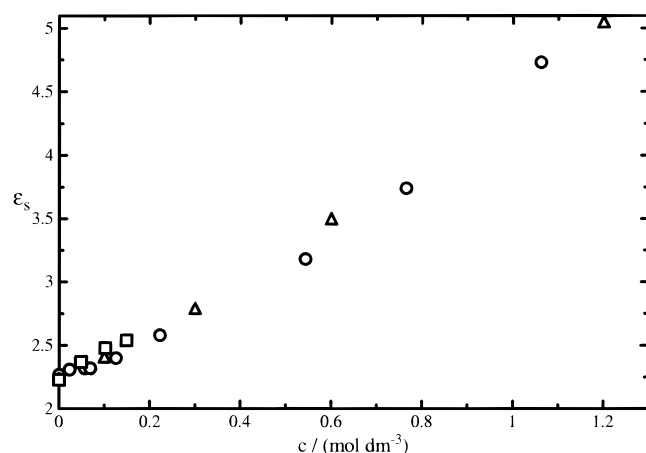

Figure 4. Concentration dependence of the static permittivity ϵ_S in concentrated solutions of Bu$_4$NBr in CCl$_4$ at 298.15 K: circles, data derived from frequency-dependent spectra (Table 1); squares, data measured with a conventional bridge at 2 MHz; triangles, data from ref 17.

interactions.[27] These interactions should probably be accounted for by allowing for the formation of bound quadrupolar tetramers or even higher ionic clusters.

There is little knowledge about the behavior of ϵ_S at high salt concentrations. Such information is, however, crucial when trying to develop more elaborate thermodynamic theories which make allowance for a state-dependent dielectric constant.[14,15] Figure 4 shows that between $c = 0.01$ and 1 mol dm^{-3} ϵ_S increases almost linearly with salt concentration. Note that the estimated uncertainty of these data of $\pm 3\%$ is much larger than in static experiments. Sigvartson et al.[34] observed for tetrabutylammonium perchlorate in solvents of intermediate polarity ($5 < \epsilon_S < 10$) that ϵ_S levels off at concentrations above 0.1 mol dm^{-3} to values between 10 and 15. No such leveling off is found by us. In more polar solvents a large part of the polarization is, however, determined by the dipolar solvent.

In contrast to the situation encountered in dilute solutions, a sound theoretical basis for data analysis at high concentrations is lacking. As discussed below, the dielectric spectra at high salt concentrations seem to indicate processes beyond dipole relaxation. In this case it seems doubtful whether Kirkwood's theory can form the basis of an adequate analysis. If, nevertheless, one calculates the Kirkwood factors, the behavior shown
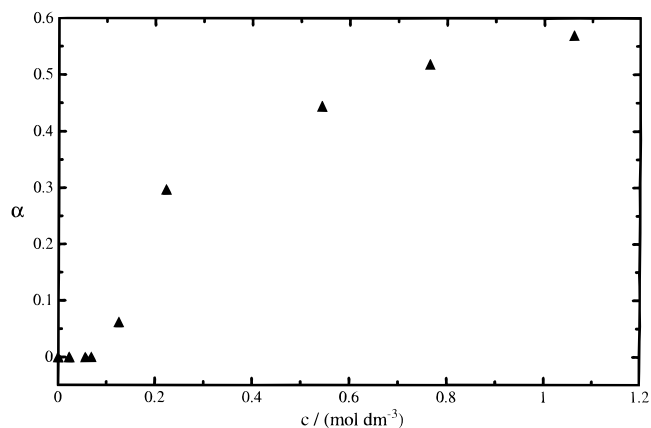

Figure 5. Width parameter α of the Cole−Cole distribution as a function of salt concentration. $\alpha = 0$ corresponds to a Debye-type spectrum.

in Figure 3 is found, which decreases to values near 0.05 and then increases slightly.

Dielectric Spectra. Below about $c = 0.1$ mol dm^{-3} the dielectric spectra reflect Debye behavior, as would be expected for dipole reorientation in a fluid solvent. This picture is supported by an analysis of the magnitude of the relaxation time. Considering the solution at $c = 0.01$ mol dm^{-3} as a representative example, we have $\tau \approx 20$ ps. We have used this figure to extract the microscopic correlation time τ' by using the Powles relation[18,35]

$$\tau = \frac{3\epsilon_S}{2\epsilon_S + \epsilon_\infty} g_K \, \tau' \tag{11}$$

which, in turn, can be compared with the reorientation time of an ellipsoid in a viscous medium. As long as the anisotropy in shape is not extreme, the latter is given by[18,36]

$$\tau' = \frac{3V\eta}{k_B T} \tag{12}$$

where V is the molecular volume. Equations 11 and 12 allow an estimate of V which corresponds to a radius of the equivalent sphere of about 4 Å. Although the deficiencies of the model are well-known, this figure is of the order of magnitude expected for a dipolar ellipsoid.

Above 0.1 mol dm^{-3} a broadening is observed which within experimental uncertainty can be rationalized by the Cole−Cole model of a symmetrical distribution of relaxation times. The observation of a Cole−Cole process is somewhat at variance with results of Cachet et al., who have argued that data for some salts in CCl$_4$[17] and benzene[37] are indicative of more complex spectra. In fact, a glance at their data seems to indicate a bimodal behavior. While part of the high-frequency mode observed by them lies above the frequency coverage of our equipment, according to their figures this mode extends sufficiently to frequencies below 20 GHz to enable reexamination. Our own results lead us to discard the bimodal process. This does, of course, not exclude the existence of a high-frequency process, provided that its wings do not appreciably extend to frequencies below 20 GHz.

The abrupt broadening of the distribution is reflected in the parameter α in Figure 5. This broadening is accompanied by an increase of the mean relaxation time which, to a first approximation, seems to reflect only the moderate increase in viscosity. Broad distributions of relaxation times are well-known for viscous liquids of neutral and ionic liquids in the supercooled

regime near the glass transition, so that the viscosity may differ by many orders of magnitude from those obtained here.[38] The observed behavior of α is unique, because the viscosity remains low and the principal relaxation times in Table 1 remain in the fluid domain, where the usual explanations of broad distributions in systems near the glass transition can be ruled out.

In view of the rapidly increasing conductance, an appealing interpretation may be based on a model suggested by Lestrade et al.[39] These authors have attributed the excess polarization to the response of the ion cloud to the movement of the central ion. Actually, Lestrade's interpretation considers a generalization of the Debye–Falkenhagen theory,[40] originally developed for treating ion cloud relaxation in dilute solutions in high-ϵ_S solvents. Unfortunately, we do not find the bimodal distribution predicted by Lestrade et al. which hinders quantitative theoretical calculations. Nevertheless, the basic physical picture may be correct. A challenge to theory would then be to find a plausible explanation for the spectral broadening. In fact, some hint may come from a quite different direction. Funke[41] has made use of a Debye–Falkenhagen-type theory to explain broad spectral distributions in solid ion conductors. In the latter case, the lattice responds to a hopping motion of a mobile charged defect by cooperative motions in the same way as the ion cloud is expected to respond to a translational displacement of the central ion. Funke's theory gives rise to broad spectral distributions which obviously result from the cooperativity of the process.

A Debye–Falkenhagen-type mechanism seems particularly apt in the light of recent thermodynamic theories of solutions at low T^*. For example, Fisher and Levin[5,13] have developed a thermodynamic theory which accounts for an increase of the free-ion concentration in concentrated solutions which agrees quite well with experimental results at low T^*. Following Debye–Hückel methods, the authors account for the interaction of ion pairs with the screening ionic fluid as a major effect at low T^*. Their approach may be extended to account for shielded dipole–dipole interactions and a state-dependent dielectric constant.[14,15] While the results of the various approaches disagree in detail, they commonly predict a rapid dissociation with increasing salt concentration as the crucial effect determining the solution properties at low T^*.

IV. Conclusions

It is appropriate to open this concluding section by making some remarks on the model character of our system. When defining reduced variables by eqs 1 and 2, one implicitly uses the restricted primitive model (RPM) as a reference system.[1] The RPM pictures the ionic fluid as equally sized charges in a dielectric continuum. To convert the state variables of real systems to reduced variables T^* and ρ^*, one has to select an appropriate value for the distance parameter a and the dielectric permittivity of the medium. The dielectric permittivity is usually chosen to be that of the pure solvent, neglecting the effect of a state-dependent dielectric constant in solution. T^* and ρ^* are also uncertain, because of difficulty in representing real ions as hard spheres with a sufficiently known radius.

With $a = 6$ Å for Bu$_4$NBr and $\epsilon_S = 2.228$ for CCl$_4$, we find $T^* = 0.023$. The most recent Monte Carlo simulations predict a phase instability of the RPM with an upper critical point near $T^* = 0.05$.[42] The absence of an immiscibility in the real system indicates that non-Coulombic interactions may play a considerable role in determining the thermodynamic properties. Despite this deficiency, we believe that our system may mimic the basic features of a Coulombic system. One may, however, note that $T^* = 0.023$ corresponds to conditions at the bottom of the

theoretical coexistence curve rather than to a near-critical temperature. This may imply that the typical effects at low T^* may be exaggerated in comparison with the properties expected for the near-critical regime, on which most theoretical work has been concentrated.

Having these limitations in mind, we single out two features of our study. The first one concerns the concentration dependence of the dielectric constant. ϵ_S increases with salt concentration, but this increase is much lower than expected on grounds of the high dipole moment of the ion pairs. Theories should therefore consider the possibility for formation of quadrupoles and higher clusters. Simulations[43] and theoretical estimates[44] indicate indeed that near the critical point ($\rho^* \approx 0.07$ corresponding to $c \approx 0.3$ mol dm^{-3}) the RPM consists mainly of higher clusters. One might expect that this clustering reduces the number of free ions in comparison with predictions by current analytical theories. Until now such a clustering is not built into analytical theories (see, however, ref 13b).

Fortunately, the comparatively low increase of the static permittivity with salt concentration is advantageous, when replacing the dielectric constant of the medium by that of the pure liquid. For example, at $c = 0.3$ mol dm^{-3} ϵ_S is only about 2.6 compared with $\epsilon_S = 2.23$ in pure CCl$_4$. Noninteracting ion pairs with $\mu = 11$ D would result in $\epsilon_S = 4$. Friedman[11] and Cavell and Knight[12] have suggested that this increase in dielectric constant hinders ion pair formation and causes an increase in free ion concentration, because the pair association constant depends sensitively on ϵ_S. Because a strong antiparallel alignment of the dipoles leads only to a moderate increase of ϵ_S, this effect may be open to question as a distinct mechanism for driving phase separation. We emphasize that such a conclusion may perhaps be somewhat overoptimistic, because our results refer to $T^* = 0.023$ which is only about one-half of the critical temperature.

The second major aspect concerns the change in the spectrum around $c = 0.1$ mol dm^{-1}. According to Figure 5 this effect sets in quite abruptly near 0.1 mol dm^{-3} which corresponds to about one-third of the theoretical critical density. This is also in the range where the Walden product $\Lambda\eta$ begins to increase. If the interpretation of the broadening in terms of a Debye–Falkenhagen-type mechanism is correct, the number of free ions must become notable around this concentration in good agreement with the Fisher–Levin picture[5,13] of dissociation.

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(33) We use here the dipole moment μ_o at infinite dilution in CCl_4 as a reference state for calculating the Kirkwood factor. Of course, one may argue that the dipole moment of the isolated molecule in the gaseous phase may form the proper reference state. Then, all Kirkwood factors have to be corrected by the factor $(11/7.9)^2 = 1.94$. This correction yields $g_K = 1.94$ at infinite dilution in CCl_4 which reflects the contribution of the reaction field of the solvent CCl_4. To eliminate these solute–solvent correlations, it seemed more appropriate to us to base the calculations on μ_o as a reference value. We note that this problem does not occur in theoretical calculations based on charged hard spheres in a dielectric continuum, because the assumption of unpolarizable spheres implies $\epsilon_\infty \approx 1$.

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