Dielectric Relaxation Spectroscopy of Electrolyte Solutions: $ZnCl_2$ in N-Methyl-2-pyrrolidone

U. Brockmann, A. Steffen, and M. Stockhausen

Institut für Physikalische Chemie der Universität Münster

The complex permittivity of the title solution system ($c \leq 1.5$ mol/l) was measured at frequencies ranging up to 72 GHz at 20 °C. Apart from the conductivity contribution there are two distinguishable relaxation regions, which are ascribed to the solvent (at higher frequencies) and to solvated ionic species (at lower frequencies).

Introduction

The dielectric relaxation spectrum of liquid electrolytic solutions is generally related to conceptually distinguishable dynamic processes such as translational motion of charged entities (causing conductivity) and reorientational motion of dipolar entities (solvent molecules and, in a broad sense, ion pair species). Examples which unequivocally allow for a distinction of those contributions, however, are scarce, in particular with highly polar solvents since these lead normally to high conductivity, so that a possible ion pair contribution to the total permittivity is swamped by the conductivity contribution. Therefore it seems worth reporting on a particular system exhibiting a clearly discernible absorption contribution which is likely to originate in ionic species, namely $ZnCl_2$ dissolved in N-methylpyrrolidone (NMP). Aqueous solutions of that salt have already been subject of a dielectric relaxation investigation [1]. The present solvent is known to show a simple dielectric relaxation behaviour (nearly of Debye type and, in particular, without any indication of self association effects [2]) and should therefore be advantageous in interpreting the results.

Results

We have measured the frequency dependent total complex permittivity of moderately and highly concentrated solutions (salt concentration $c \leq 1.5$ mol/l) between 5 MHz and 72 GHz at 20 °C. Two typical absorption spectra representing the total imaginary part $\varepsilon''_{tot}(\omega)$ of the permittivity (i.e., including the conductivity contribution) are displayed in Figure 1. The conductivity is about an order of magnitude smaller than with comparable NMP solutions of various other salts, and as a result of that the development of an absorption band in the region of some 100 MHz is in evidence. As Fig. 1 shows, one observes at certain concentrations an $\varepsilon''_{tot}(\omega)$ plateau extending over a broad frequency range. When the salt concentration is changed this feature behaves qualitatively as though two overlapping absorption bands (in a distance of
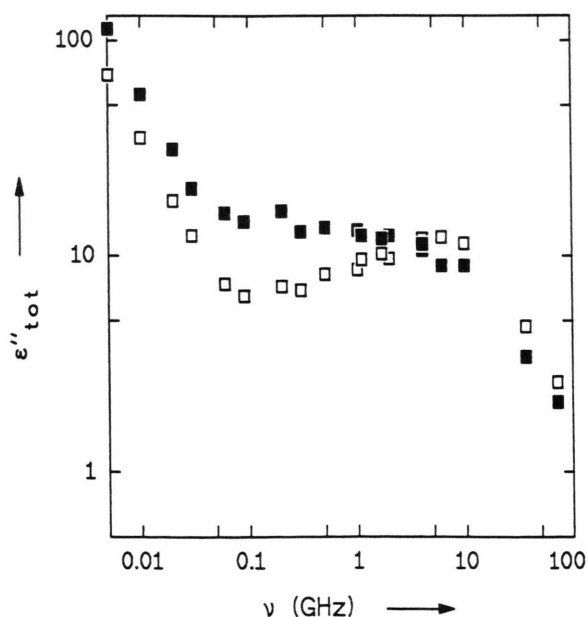

Fig. 1. Total dielectric loss ε''_{tot} against frequency v (double log plot) for NMP solutions with $ZnCl_2$ concentrations of $c = 0.5$ (open symbols) and 1.0 mol/l (full symbols).
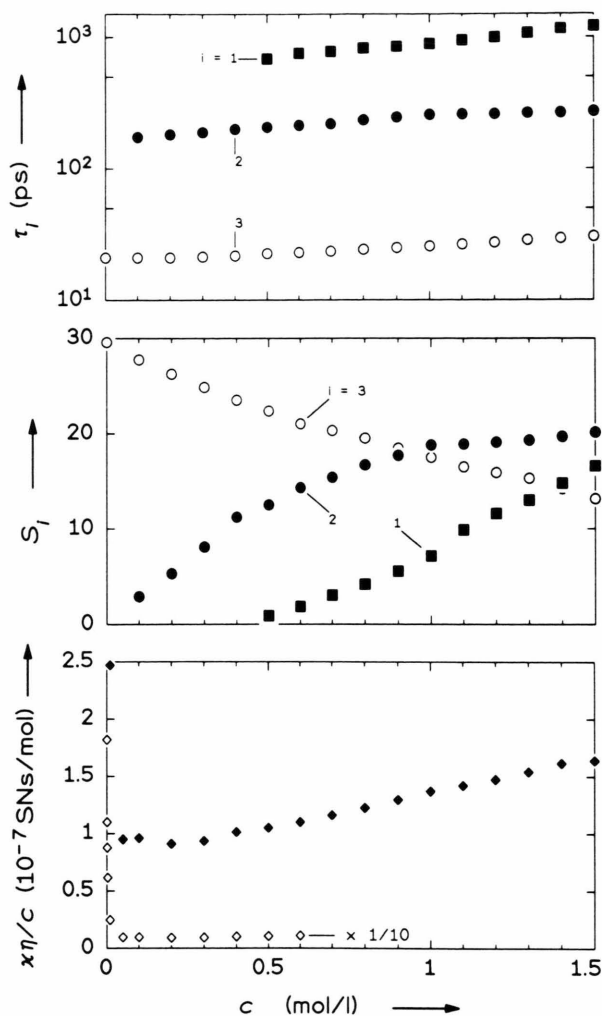
Fig. 2. Relaxation parameters τ_i (log scale) and S_i, and conductivity $\varkappa$ (included in the Walden product $\varkappa\eta/c$) against salt concentration c.

about their resolution limit) are altered in their intensity ratio.

A formal description of the results was obtained by fitting a conductivity term plus a minimum number of Debye type relaxation terms to the experimental data:

$$\varepsilon''_{\text{tot}}(\omega) = \frac{\varkappa}{\varepsilon_0\,\omega} + \sum_i S_i \frac{\tau_i\,\omega}{1 + \tau_i^2\,\omega^2}\,.$$

The conductivities $\varkappa$ obtained from the fitting procedure agree well with the values measured conventionally in the kHz region, which indicates the absence of dipolar absorption processes in the lower frequency region. Up to three Debye type spectral components

C_i are required for fitting the relaxation contribution (a further but very weak high frequency term may be disregarded here). The relaxation parameters τ_i (relaxation time) and S_i (relaxation strength) are represented graphically in Figure 2. In addition, this figure shows the conductivity given as a Walden type product, $\varkappa\eta/c$, where η is the viscosity of the solution and c is the salt concentration.

The relaxation parameters corroborate the qualitative assessment given above. Because of their intermediate position the spectral components C_1 and C_2 are somewhat less certain than the high frequency component C_3; therefore they may be regarded as a homogeneous region and may be replaced by one correspondingly broadened component. Nonetheless the well defined component C_3, which is on the frequency scale about an order of magnitude apart from C_2, has to be considered as a separate contribution.
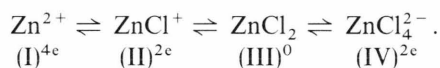
Discussion

In an attempt to explain the relaxation part of the spectrum we shall first of all presuppose that it is caused by the tumbling motion of distinct polar entities which are long-lived in comparison to the τ_i values found, with that disregarding possible exchange effects. Such an assumption is borne out by results of previous dielectric studies on NMP mixture systems with nonelectrolytes, which concern not only the solvent but also associated species involving NMP molecules. In the present case it is obvious that C_3 is attributable to NMP, essentially to unaffected solvent since τ_3 changes with the salt concentration to merely the extent as usually found on variation of viscosity. The above mentioned dielectric properties of NMP allow to reckon with an appropriate proportionality $S_{\text{NMP}} \sim c_{\text{NMP}}$ for the unaffected solvent. The decrease of S_3 on increasing c is too marked to be explainable by dilution or even by the kinetic depolarization effect. It can actually be accounted for only by a "disappearance" of a noticeable part of NMP from spectral component C_3, giving cause for the inference that "disappeared" NMP is now contributing to C_1 and/or C_2.

The two components C_1 and C_2 are undoubtedly related to the salt ZnCl$_2$ in some way. Note that $\sum S_i$ increases with increasing salt content, which in view of the properties of NMP gives clear evidence that polar species are provided by the solute. The question remaining is merely whether solvent and solute contri-

butions to the spectrum are separable. In that respect two possibilities of the qualitative assignment of C_1 and C_2 may briefly be discussed.

(i) The solvent which has "disappeared" from C_3 may be affected by the salt such that it is slowed down in its tumbling motion but not firmly bound to any ionic species, as it is similarly known for polymeric solutes [3, 4]. The approximate constancy of the sum $S_2 + S_3$ suggests an according interpretation of C_2. The relaxation times $\tau_2 \approx 170 \ldots 270$ ps, however, are rather long for such a motion when compared to the results on polymer solutions. One may further argue that this interpretation can at the most apply to a part of the "disappeared" solvent, since otherwise C_1 would be left as a component to be assigned to isolated ("naked") ionic species, which is unlikely to be an adequate picture.

(ii) Both C_1 and C_2 may be attributable to ionic species involving solvent molecules, i.e. in general solvated species. From the cation's point of view, at least the following ionic compositions (which have been proposed also for ZnCl$_2$ in some other aprotic solvents [5–7]) may be taken into consideration:

$$\text{Zn}^{2+} \rightleftharpoons \text{ZnCl}^+ \rightleftharpoons \text{ZnCl}_2 \rightleftharpoons \text{ZnCl}_4^{2-} .$$
$$\text{(I)}^{4\text{e}} \qquad \text{(II)}^{2\text{e}} \qquad \text{(III)}^0 \qquad \text{(IV)}^{2\text{e}}$$

In the lower row, the number of charges (per ZnCl$_2$) contributing to $\varkappa$ is given as superscript. From the exceptionally low conductivity it follows that (III) must be present to a considerable degree. Consequently the slight increase of $\varkappa\eta/c$ with increasing c (Fig. 2) may be indicative of the formation of (IV). Species (IV) may be dielectrically inactive on ground of symmetry, so the spectral components under consideration, C_1

and C_2, should be related to species of kind (II) and (III). This would require a polar configuration of (III), e.g. nonsymmetric octahedral or tetrahedral. A tetrahedral coordination has previously been taken into consideration for Zn species corresponding to (II) and (III) [8, 9]. Alternatively one may suppose that there is only one particular ionic composition resulting in polar entities which, however, might possibly develop subspecies distinguished by the involvement of solvent molecules (e.g. solvent shared contact and solvent separated ion pairs).

Although it seems tempting to regard the c dependence of S_1 and S_2 (Fig. 2) as reflection of an equilibrium of ionic species, we desist from any detailed assignment since this would be conjecture for several reasons. As mentioned before, the formally obtained two spectral components C_1 and C_2 need not necessarily correspond to just two distinct kinds of relaxators. The list of ionic compositions might be incomplete as well. Furthermore the assessment of S_i values of ionic complexes is generally problematic [10]. Anyhow, the τ_i values exhibited by the presumed ionic species allow by comparison with relaxation times of molecular solutions [11] for the conclusion that these complexes are rather compact in size, their diameter being probably less than about twice that of an NMP molecule. This is in accord with the picture that relatively long-lived solvated entities of the above-mentioned types, though possibly indistinguishable by dielectric spectroscopy, are responsible for C_1 and C_2. Thus at least the general distinction between the lower and higher frequency absorption region as due to ionic species and solvent, respectively, is substantiated after all.

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