Dielectric Relaxation Study of $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, and $Mg(NO_3)_2$ Solutions in Water/DMSO Mixtures

A. Galstian and M. Stockhausen[a]

Department of Chemistry, Yerevan State University, 375049 Yerevan (Armenia)
[a] Institut für Physikalische Chemie der Universität Münster, D-48149 Münster (Germany)

Z. Naturforsch. **53a**, 989–992 (1998); received November 19, 1998

Dielectric spectra have been measured for the title systems up to 72 GHz at 20 °C with salt concentrations ≤1 mol/l and DMSO mole fractions of the mixed solvent in the 0.3 to 0.6 range. Results can be described by a superposition of two Debye terms (at lower frequencies) plus one Cole-Davidson term (at higher frequencies). The discussion is particularly focused on the lowest frequency term, which is related to ionic species. These are likely to consist in nonsymmetrically solvated cations rather than ion pair complexes. While Cu, Ni and Mg nitrates behave similarly, the Zn salt shows some differences which possibly are due to a change of the coordination number with increasing salt content.

Introduction

The properties of salt solutions in the mixed solvent water/dimethylsulfoxide (DMSO) are of interest from a scientific as well as a practical point of view [1–6]. Dielectric spectroscopy provides a means of gathering information on microdynamical and structural circumstances in complex liquid systems of that kind. In a preceding paper [7] we described and discussed the dynamic dielectric properties of zinc halides in water/DMSO. In continuation of that work, the present communication deals with nitrates of Zn^{2+} and of three further cations (Cu^{2+}, Ni^{2+}, Mg^{2+}) in order to see how the dielectric spectra depend on the nature of anion and cation, and to gain dynamical and structural information concerning the polar constituents of the solutions which besides the solvent molecules may consist in polar species involving ions.

Experimental

The dielectric loss spectrum $\varepsilon''_{\text{tot}}(\omega)$ was measured over the frequency range between some ten MHz and 72 GHz at 20 °C using various apparatus. The (static) conductivity κ was determined in the kHz range with an impedance bridge. Also, the viscosity η was measured with a capillary viscometer.

Chemicals from Fluka were used as obtained. The salts contain hydration water as follows: $Zn(NO_3)_2 \cdot 6\,H_2O$, $Cu(NO_3)_2 \cdot 3\,H_2O$, $Ni(NO_3)_2 \cdot 6\,H_2O$, and $Mg(NO_3)_2 \cdot 6\,H_2O$.

Since the binary water/DMSO solvent mixture shows peculiarities around $x_{\text{DMSO}} = 0.3$, indicating hetero-interactions [7], the water/DMSO ratio for the ternary salt solutions was chosen in that range. By x_{DMSO} we denote the actual solvent composition as already corrected for water introduced with the hydrated salt. Salt contents were $c_s \leq 1.0$ mol/l.

Results

The dielectric loss spectrum obtained experimentally, that is $\varepsilon''_{\text{tot}}(\omega)$, contains the conductivity contribution

$$\varepsilon''_c(\omega) = \frac{\kappa}{\varepsilon_0\,\omega}, \tag{1}$$

where ε_0 is the permittivity of empty space. The relaxational contribution, which is of primary interest in the present context, is

$$\varepsilon''(\omega) = \varepsilon''_{\text{tot}}(\omega) - \varepsilon''_c(\omega). \tag{2}$$

In [7], $\varepsilon''(\omega)$ was described by a sum of up to four Debye type spectral components C_i ($i = 1, \dots, 4$ in the order of increasing frequency). For the sake of comparability we adopt this scheme also for the present systems, indexing the spectral components by corresponding numbers although C_1 appears to be insignificant in the case of the nitrates studied here which exhibit a higher conductivity than the zinc halide solutions. Moreover, the fits for the present systems are improved by using a high frequency component C_4 of Cole-Davidson (CD) rather than Debye type. Consequently, results are described by relaxation times τ_i, relaxation strengths S_i ($i = 2, \dots, 4$)

Reprint requests to Prof. M. Stockhausen; Fax: (0251) 8323441.

0932-0784 / 98 / 1200-0989 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

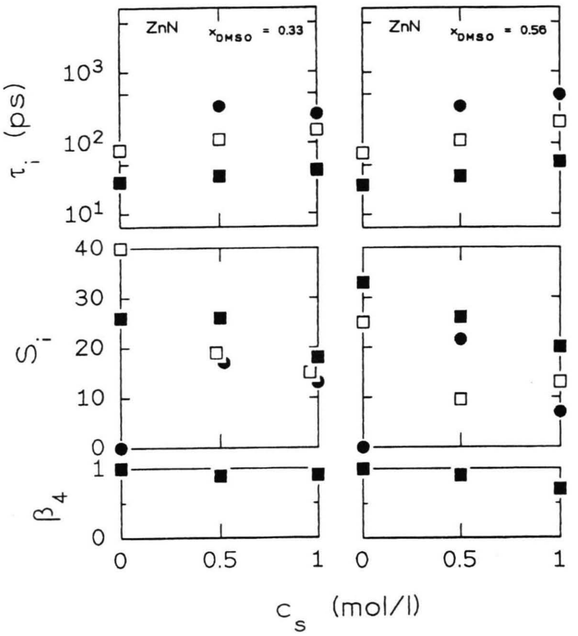

Fig. 1. Relaxation parameters τ_i, S_i, and β_4 for $Zn(NO_3)_2$ solutions against salt concentration c_s. Symbols for spectral components: ● C_2, □ C_3, ■ C_4. – Left: Solvent composition $x_{DMSO} = 0.33$. – Right: $x_{DMSO} = 0.56$.

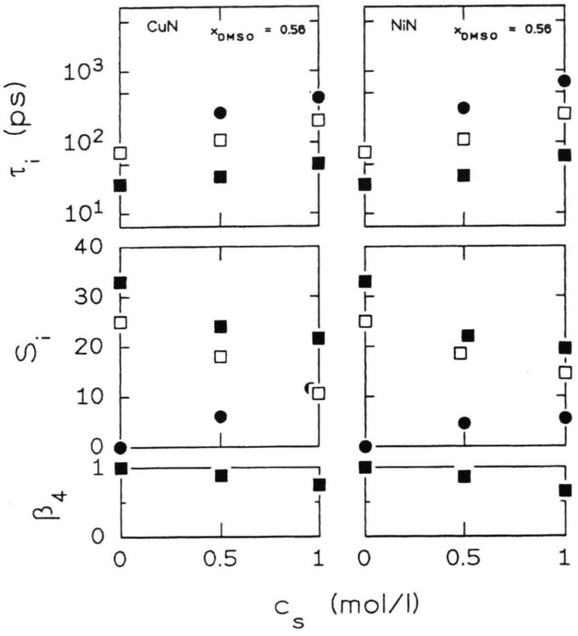

Fig. 2. As Fig. 1, but for $Cu(NO_3)_2$ and $Ni(NO_3)_2$ solutions. – Left: $Cu(NO_3)_2$, $x_{DMSO} = 0.56$. – Right: $Ni(NO_3)_2$ $x_{DMSO} = 0.56$.

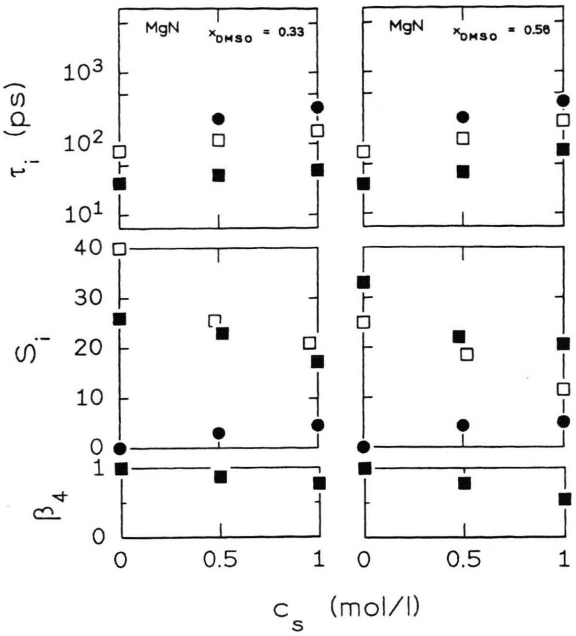

Fig. 3. As Fig. 1, but for $Mg(NO_3)_2$ solutions. – Left: $x_{DMSO} = 0.33$. – Right: $x_{DMSO} = 0.56$.

and the CD skewness parameter β_4 (≤ 1, where $\beta_4 = 1$ means Debye type).

The parameters τ_i, S_i and β_4 for solutions of the four nitrates in water/DMSO are given graphically in Figs. 1 to 3.

Discussion

The formal description of the spectra by three spectral components does not necessarily mean that these components should originate in physically distinguishable relaxation processes, nevertheless it is tempting to interprete them in this sense. By comparison with salt-free water/DMSO mixtures it was shown in [7] that the higher frequency components C_3 and C_4 are likely to be related to the mixed solvent not only for these binary systems but also in case of ternary salt/water/DMSO systems. Component C_3, which in effect describes a broadening of the solvent relaxation spectrum towards lower frequencies, is indicative of solvent-solvent hetero-interactions which are most intense for mixture ratios around $x_{DMSO} \approx 0.3$. The lower frequency relaxation contributions, on the other hand, appear only in the presence of salt and are doubtless related to relaxation processes involving ions. The following discussion will be focused on these contributions and the differences found in comparison to $ZnCl_2$ and $ZnBr_2$ solutions [7].

As mentioned before, a low frequency (C_1) spectral component as found for the halide solutions, which is ascribable to ion-ion interactions, is not significant for the present nitrates. Concerning C_2, there are some indications that it is mainly caused by ion-molecule species such as cations with nonsymmetric, thus polar, mixed solvation shells rather than by ion-ion species such as ion-pairs involving solvent molecules. Other than with zinc halide solutions [7], the static permittivity is decreased by the addition of salt. Furthermore, the Walden type product $\kappa\eta/(zc_s)$ for the solutions studied here is in the 0.05...0.08 $Scm^2\ mol^{-1}$ P as range, that is about an order of magnitude larger than with zinc halides, and is roughly as to be expected for complete dissociation. It can therefore be assumed that C_2 is caused by cations with mixed solvation, M^{2+} $(DMSO)_x(H_2O)_{m-x}$.

The question as to what kind of relaxation mechanism might be effective can scarcely by answered from only dielectric data. There are two limiting possibilities to be taken into account, that is the tumbling motion of long-lived species and, on the other hand, the re-arrangement and exchange kinetics of the solvation shell in the case of short-lived species. Regarding for the moment the first possibility, one can roughly estimate the effective radius r_{eff} of tumbling entities from the relaxation time τ_2 and the solution viscosity η by comparison with data for quasi-rigid polar molecules [8]. We find that $r_{eff} \approx 0.50$ (± 0.05) nm for all systems studied. This is not inconsistent with the size of a mixed solvate complex. Therefore the second solvation shell need not be taken into consideration, at least not if the assumption of long-lived entities should be tenable. The alternative process, exchange of molecules in the solvation shell, may play a secondary role. Exchange times for the hydration shell of the ions considered here are longer than τ_2 by at least an order of magnitude, but it cannot be excluded that they become shorter in the case of mixed water/DMSO solvation.

The solutions of $Zn(NO_3)_2$ (Fig. 1) differ markedly in their dielectric behaviour from the zinc halides and from the other nitrates studied (Figures 2, 3). While the relaxation times τ_i (with the exception of τ_2 in case of $x_{DMSO} = 0.33$ in Fig. 1) depend monotonously on the salt concentration c_s, increasing as a function of solution viscosity as for all the other systems, the relaxation strengths S_i of $Zn(NO_3)_2$ solutions show striking features, in particular a maximum of S_2. This may be due to competing ion-molecule and molecule-molecule interactions which according to proton NMR results [9] may be pictured as follows. At low c_s the cation Zn^{2+} is mainly solvated by DMSO, but on increasing c_s the number x of DMSO molecules in the complex Zn^{2+} $(DMSO)_x(H_2O)_{m-x}$ is decreased while the number of water molecules is increased, possibly accompanied by a change of the coordination number m (as found with ions of lanthanoids [10]). This is probably promoted by the fact that the interaction of NO_3^- ions with DMSO is stronger than with H_2O [9], which may be due to the interaction between nitrogen of the nitrate ion and sulfur of the DMSO molecule. For Zn^{2+}, complexes with coordination numbers 4, 5 and 6 are known [11]. Since with increasing c_s the number of available 'free' solvent molecules is reduced, the mean coordination number m may be gradually reduced to a lower value, perhaps from 6 to 4.

The peculiariaties of Zn^{2+} in comparison to the other ions studied are probably due to the fact that this ion has a filled *d*-orbital. For Cu^{2+}, Ni^{2+}, and Mg^{2+} (Figs. 2, 3), the relaxation strength S_2 increases monotonously with the salt concentration c_s. Its intensity decreases, however, over the series of ions given, and at the same time the CD parameter β_4 decreases, too. Qualitatively this could be ascribed to a reduced tendency towards mixed solvation and an increased fraction of 'free' solvent molecules, either water or DMSO, which exhibit short relaxation times so that C_4 appears broadened towards its high frequency side. It may be noted in that context that the acceptor numbers of the ions Zn^{2+}, Cu^{2+}, Ni^{2+}, and Mg^{2+} decrease in that order [12], in accordance with the dielectric findings.

Acknowledgements

A. G. thanks the DAAD (Deutscher Akademischer Austauschdienst) for a scholarship which made it possible for him to work at the Institute for Physical Chemistry in Münster, Germany.

[1] H. H. Füldner, D. H. Devia, and H. Strehlow, Ber. Bunsenges. Phys. Chem. **82**, 499 (1978).

[2] S. A. Markarian et al., Fiziol. Biokhim. Rastenii **24**, 169 (1992).

[3] F. V. Deviatov, V. F. Safina, L. G. Lazareva, and J. I. Salnikov, Zh. Neorg. Khim. **38**, 1085 (1993). – A. F. Borina, ibid. **38**, 1749 (1993).

[4] S. A. Markarian, K. R. Grigorian, and R. S. Arutiunian, Zh. Fiz. Khim. **69**, 990 (1995).

[5] S. A. Markarian, E. R. Sarukhanian, and E. A. Kazoian, Visokomolek. Soed. B **37**, 163 (1995).

[6] S. A. Markarian and A. S. Galstian, Zh. Neorg. Khim. **42**, 510 (1997).

[7] A. Galstian and M. Stockhausen, Z. Naturforsch. **53a,** 783 (1998).

[8] G. Turky, G. Wilke, U. Witt, A. Ghoneim, and M. Stockhausen, Proc. 3rd Conf. Dielectric and Related Phenomena, Zakopane 1994.

[9] A. Galstian, Dissertation 1997, Library of the Institute of Chemical Physics, Yerevan (Armenia).

[10] F. V. Deviatov. V. F. Safina, and J. I. Salnikov, Isv. Vuzov. Khim. Khim. Tekhn. **33**, 59 (1990).

[11] A. F. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, London 1972, p. 503.

[12] Y. Marcus, Ion Properties, Marcel Dekker, New York 1997, p. 194.