Bromide Ion Quadrupole Relaxation in Non-aqueous Solution

BJÖRN LINDMAN

Division of Physical Chemistry 2, Lund Institute of Technology, Chemical Center,
S-220 07 Lund, Sweden

The ^{79}Br quadrupole relaxation of the bromide ion was studied as a function of counterion and concentration in dimethyl sulfoxide and methanol and in water-dioxane mixtures. Whereas alkali and halide ion quadrupole relaxation is generally observed to be rapid in non-aqueous environments, ^{79}Br relaxation in dilute dimethyl sulfoxide solutions was found to be slower than in aqueous solution. The extrapolated infinite dilution ^{79}Br$^-$ relaxation rate in dimethyl sulfoxide was found to be in good agreement with that predicted by a theory of Hertz assuming an electrostatic origin of the time-modulated electric field gradients causing relaxation.

Nuclear magnetic resonance has in many different ways been fruitfully applied to elucidate molecular interactions and microdynamic properties of electrolyte solutions.[1-4] Studies based on static or dynamic characteristics of the resonance signal from the solvent's nuclei have, in a number of cases, given quite detailed information on many aspects of solvent-solvent and ion-solvent interactions, such as solvation numbers, life-times of ion-solvent complexes and the effects of ions on solvent-solvent interactions. The NMR signals from the ions in the solution contain complementary information on ion-solvent interactions as well as information on ion-ion interactions. Many simple ions do possess nuclei with manageable NMR sensitivities, but progress in the field has been made more difficult by problems of accounting quantitatively for both shielding and relaxation effects.

Most monoatomic ions have nuclei with electric quadrupole moments and the interactions of these with electric field gradients generally dominate nuclear magnetic relaxation in diamagnetic systems. A quantitative

rationalization of an ions's quadrupole relaxation is of great significance in connection with attempts to understand several aspects of electrolyte solutions. However, as regards the origin of the field gradients, the time-modulation of which gives relaxation, there has been considerable controversy. While the early "electrostatic" approach of Hertz[5] and Valiev[6,7] related the field gradients to point charges and dipoles, an alternative model, based on overlap effects, was advanced by Deverell.[8] Whereas Deverell's model is difficult to test quantitatively, Hertz has with a recently improved version[9,10] of his electrostatic theory been able to account[11-13] for ion-ion and ion-solvent contributions to relaxation in a large number of aqueous systems.*

While several systematic studies of ion relaxation in aqueous solution have been reported, the information on non-aqueous or mixed solvent systems is very limited. Halide ion quadrupole relaxation rates have been reported for methanol,[14,15] dimethyl sulfoxide,[14] nitromethane,[16] and for mixtures of acetonitrile,[17] methanol,[15,18] and acetone[18] with water. However, in general, these data do not permit a separation of the relaxation rates into contributions from ion-solvent and ion-ion interactions. Recently, Melendres and Hertz[19] presented the first analysis using the electrostatic theory of ion relaxation rates in non-aqueous solution. An interesting result of theirs is that, in contrast to aqueous solutions, the methanolic solutions show (using the data of Ref. 15) a considerable orientation of the molecules in the first solva-

---

* Further support for the "electrostatic" origin of the field gradients will be given in a forthcoming review article together with S. Forsén.

tion sphere of Cl^- and Br^- ions.

The approach of Hertz [9,10] appears to be fruitful and its further application to other systems is expected to be helpful in the elucidation of ion-solvent and ion-ion interactions in non-aqueous environments. The present study, concerned with $^{79}Br^-$ relaxation in methanol and dimethyl sulfoxide as well as in dioxane-water mixtures, lends further support to the relevance of the electrostatic approach and gives some new aspects on the variation of the relaxation rate with concentration. The NMR experiments were performed at $26 \pm 2\,°C$ essentially as in our previous ^{79}Br NMR investiga-

Fig. 1. $^{79}Br^-$ transverse relaxation rates in non-aqueous and mixed solvent systems as a function of electrolyte concentration. Systems studied were
1, NaBr in dimethyl sulfoxide (DMSO); 2, KBr in dimethyl sulfoxide; 3, NH$_4$Br in dimethyl sulfoxide; 4, (C$_4$H$_9$)$_4$NBr in dimethyl sulfoxide; 5, NaBr in a mixture of dioxane (20 % by weight) and water; 6, KBr in a mixture of dioxane (20 % by weight) and water; 7, (C$_4$H$_9$)$_4$NBr in a mixture of dioxane (20 % by weight) and water; 8, KBr in a mixture of dioxane (40 % by weight) and water; 9, NaBr in methanol.

tions.[14,20,21] The experimental concentration dependences for $1/T_2$ of ^{79}Br are given in Fig. 1 for NaBr, KBr, NH$_4$Br and Bu$_4$NBr in dimethyl sulfoxide, for NaBr in methanol and for NaBr, KBr and Bu$_4$NBr in dioxane-water mixed solvent. The value obtained by extrapolation to infinite dilution in methanol, $1/T_{20} \simeq 14\,700$ s^{-1}, agrees closely with that derived by Melendres and Hertz [19] from the ^{81}Br data of Hall et al.[15] for LiBr in methanol. For dimethyl sulfoxide solutions, the concentration dependence of Br relaxation is much greater than for water or methanol solutions, thus making the estimation of $1/T_{20}$ quite difficult. With KBr, Bu$_4$NBr and NaBr the concentration dependence of the relaxation is approximately linear and in all these cases a value of $1/T_{20} = 1050$ s^{-1} is obtained by linear extrapolation to zero concentration. Since it has been emphasized recently by Hertz et al.[12] that instrumental broadening may be important in the present type of measurements, attempts were made by reducing field modulation amplitude and frequency and by employing flux stabilizer and field homogeneity coils to obtain an improved value of $1/T_{20}$ in dimethyl sulfoxide. The value then obtained was close to that given above but must, in view of the marked concentration dependence of relaxation, still be considered as rather approximative. This is, however, not critical for the present discussion.

It is interesting to note that, while in all cases considered by Melendres and Hertz [19] the alkali and halide ion quadrupole relaxation rates were found to be greater in non-aqueous environment than in water, we find the $^{79}Br^-$ relaxation rate in dimethyl sulfoxide to be smaller than in water ($1/T_{10} = 1500$ s^{-1} according to Hertz et al.[12] and $1/T_{20} = 1650$ s^{-1} according to our own line width measurements). The implications of this for Br$^-$ ion solvation in dimethyl sulfoxide will now be examined using Hertz' theory [9] and following the procedure of Melendres and Hertz.[19] These authors consider three cases, characterized by different degrees of solvent orientation around the relaxing ion, and give explicit formulae for the infinite dilution relaxation rates. Their "fully random distribution model", which assumes a random orientation and distribution of solvent point dipoles, predicts $(T_1 = T_2$, *i.e.* an extreme narrowing situation, is assumed)
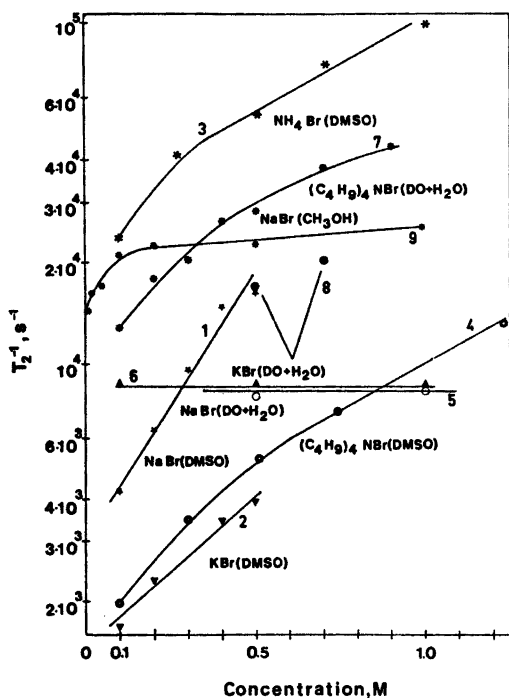
$$\frac{1}{T_{20}} = \frac{24\pi^3}{5} \times \frac{2I+3}{I^2(2I-1)} \left[\frac{PeQ(1+\gamma\infty)}{h}\right]^2 \times$$

$$\frac{m^2 c_{solv} \tau_{solv}}{r_0^5} \quad\quad\quad (1)$$

where I is the spin quantum number; P the polarization factor; eQ the nuclear quadrupole moment; $(1 + \gamma\infty)$ the Sternheimer antishielding factor; m is the electric dipole moment of the solvent molecule; c_{solv} the solvent concentration; τ_{solv} is the rotational correlation time of the solvent; r_0 the distance of closest approach between the relaxing nucleus and the solvent point dipoles. For P and $1 + \gamma\infty$ the same values were used as in Ref. 19, for m the gas phase value was used and c_{solv} was calculated from the density.[22] τ_{solv} was taken to be 4.5×10^{-12}s (*cf.* Refs. 2, 23 and 24), a value which is close to that calculated from the Debye equation with the Gierer-Wirtz microviscosity factor.[25] If r_0 is taken as the sum of the solvent molecular radius (calculated from molecular volume, assuming hexagonal closest packing), and the Br⁻ ionic radius (assumed to be 1.95 Å) one obtains from eqn. (1) $1/T_{20} = 750$ s⁻¹. It can thus be inferred that Hertz' electrostatic theory of ion quadrupole relaxation assuming random solvent distribution and orientation gives a good rationalization of the experimental findings. (Probably the above procedure overestimates r_0; a slightly smaller value would improve agreement between theory and experiment but in view of the considerable uncertainty in some of the quantities in eqn. (1), and in the experimental $1/T_{20}$, more detailed considerations are not presently justified.)

Melendres and Hertz [19] also consider two models characterized by the presence of a distinct first solvation sphere. For their "non-oriented solvation" model we obtain a calculated relaxation rate of $1/T_{20} = 2000$ s⁻¹ and for the "fully oriented solvation" model we obtain, assuming random lateral distribution,* $1/T_{20} = 3600$ s⁻¹. In the calculations we have used the same r_0 values as above and assumed the solva-

* One difficulty in this analysis is that the fully random distribution model may predict the same relaxation rate as the fully oriented solvation model with some lateral order. Information from other types of studies which does not seem presently available is required to provide a safe distinction between the two possibilities.

tion number to be 6. (A more realistic r_0 value may lead to markedly greater calculated relaxation rates.) It can be seen that the two models assuming a distinct solvation sphere predict much higher values of $1/T_{20}$ than given by experiment. On the other hand, the much higher value of $1/T_{20}$ for Br⁻ in methanol is, as shown by Melendres and Hertz,[19] best described by the "fully oriented solvation" model, which involves a distinct solvation sphere of radially oriented solvent dipoles. Surveying temperature dependence studies of 0.4 M KBr, NaBr, NH₄Br and Bu₄NBr solutions in dimethyl sulfoxide were performed to elucidate these problems further. The Arrhenius' activation energies of Br⁻ relaxation, which were found to be $11 - 12$ kJ/mol for KBr, NaBr, NH₄Br and somewhat higher for Bu₄NBr, are considerably smaller than the activation energy of viscosity (16.7 kJ/mol [22]), *i.e.* the same relation as for aqueous solutions.

The discussion of the infinite dilution relaxation rate of Br⁻ in dimethyl sulfoxide supports the applicability of Hertz' electrostatic theory of ion quadrupole relaxation. Furthermore, according to our analysis, data are consistent with a bromide ion solvation in dimethyl sulfoxide which does not involve a distinct solvation sphere. This is the same as deduced for water [9] but in contrast to the findings with methanol as solvent.[19] A weak bromide ion solvation in dimethyl sulfoxide correlates well with what Schläfer and Schaffernicht [26] deduced for the chloride ion from conductivity data. These authors refer this observation to the low accessibility of the positive part of the solvent dipole. A weak halide ion solvation in dimethyl sulfoxide has also been inferred recently by Gopal and Jha.[27] By investigating further solvents in the same way and correlating the deduced solvation characteristics with solvent molecular properties a more detailed understanding of the variation in halide ion solvation between different solvents can probably be provided.

While the ion-solvent contribution to an ion's quadrupole relaxation is now fairly well understood, an interpretation of the ion-ion contribution is much more difficult.[10] The data given in Fig. 1 show some interesting features, such as the very strong variation of the ⁷⁹Br⁻ relaxation with cation in dimethyl sulfoxide,

but a detailed discussion of the variable concentration results has to await experimental studies of further systems as well as of the effect of electrolyte on solvent mobility. It appears, however, that the magnitude of the relaxation rate alterations is within a range which can be explained by ion-pair formation,[19] but it is not clear why the ion-pair contribution to Br⁻ relaxation should vary with the cation in the way indicated. (Another possible interpretation would be in terms of a perturbation by the cation of a symmetrical solvation sphere involving lateral order and thus quenching effects.) The observations for the dioxane-water mixed solvent system resemble those of aqueous systems with a weak concentration dependence for alkali halides but a very strong one for tetraalkylammonium halides.[14,20,21] It is interesting to note that the strong effect of non-polar groups on Br⁻ relaxation is evident even in the presence of a considerable amount of dioxane. Thus, complete elimination of Br⁻ ions from the surface of the nonpolar solute is not effected by dioxane.

Note added in proof. The author was recently informed about similar studies in progress in Prof. Hertz' laboratory. Prof. Hertz and Dr. Weingärtner (personal communication) have in agreement with the present findings observed Br⁻ and I⁻ quadrupole relaxation at low concentrations to proceed more slowly in dimethyl sulfoxide than in water. Hertz and Weingärtner have also studied halide ion quadrupole relaxation in several other solvents.

REFERENCES

1. Hertz, H. G. In Falkenhagen H., Ed., *Theorie der Elektrolyte*, S. Hirzel Verlag, Leipzig 1971, p. 479.
2. Hertz, H. G. *Progr. Nucl. Magn. Resonance Spectrosc.* 3 (1967) 157.
3. Hertz, H. G. In Franks, F., Ed., *Water. A Comprehensive Treatise*, Plenum Press, New York 1973, Vol. 3, p. 301.
4. Deverell, C. *Progr. Nucl. Magn. Resonance Spectrosc.* 4 (1969) 235.
5. Hertz, H. G. *Z. Electrochem. Ber. Bunsenges. Phys. Chem.* 65 (1961) 20.
6. Valiev, K. A. *Sov. Phys. JETP 11* (1960) 883.
7. Valiev, K. A. *Sov. Phys. JETP 10* (1960) 77.
8. Deverell, C. *Mol. Phys. 16* (1969) 491.
9. Hertz H. G. *Ber. Bunsenges. Phys. Chem. 77* (1973) 531.
10. Hertz, H. G. *Ber. Bunsenges. Phys. Chem. 77* (1973) 688.
11. Hertz, H. G., Holz, M., Keller, G., Versmold, H. and Yoon, C. *Ber. Bunsenges. Phys. Chem. 78* (1974) 493.
12. Hertz, H. G., Holz, M., Klute, R., Stalidis, G. and Versmold, H. *Ber. Bunsenges. Phys. Chem. 78* (1974) 24.
13. Hertz, H. G. and Holz, M. *J. Phys. Chem. 78* (1974) 1002.
14. Lindman, B., Forsén, S. and Forslind, E. *J. Phys. Chem. 72* (1968) 2805.
15. Hall, C., Haller, G. L. and Richards, R. E. *Mol. Phys. 16* (1969) 377.
16. Gentzler, R. E., Stengle, T. R. and Langford, C. H. *Chem. Commun.* (1970) 1257.
17. Stengle, T. R., Pan, Y.-C. E. and Langford, C. H. *J. Amer. Chem. Soc. 94* (1972) 9037.
18. Richards, R. E. and Yorke, B. A. *Mol. Phys. 6* (1963) 289.
19. Melendres, C. A. and Hertz, H. G. *J. Chem. Phys. 61* (1974) 4156.
20. Lindman, B., Wennerström, H. and Forsén, S. *J. Phys. Chem. 74* (1970) 754.
21. Wennerström, H., Lindman, B. and Forsén, S. *J. Phys. Chem. 75* (1971) 2936.
22. Lindberg, J. J. *Finska Kemistsamf. Medd. 71* (1962) 77.
23. Zeidler, M. D. *Ber. Bunsenges. Phys. Chem. 69* (1965) 659.
24. Chaughule, R. S. and Gupta L. C. *Proc. Indian Acad. Sci. Sect. A 76* (1972) 153.
25. Gierer, A. and Wirtz, K. *Z. Naturforsch. 8a* (1953) 532.
26. Schläfer, H. L. and Schaffernicht, W. *Angew. Chem. 72* (1960) 618.
27. Gopal, R. and Jha, J. S. *J. Phys. Chem. 78* (1974) 2405.