Structure and Dynamics of Electrolyte Solutions. A NMR Relaxation Approach

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1 Introduction

To understand the properties of electrolytes in solvent media it is important to examine the solute–solvent (solvation) interactions or, in the case of solvent mixtures, the enrichment of one of the components of the mixture in the solvation sphere of the solute (preferential or selective solvation). Numerous theoretical approaches have been applied to the study of solvation[1] and a large number of experimental techniques have also been used.[2] Of the latter, the best results have been obtained using spectroscopic methods. In recent years NMR spectroscopy has been very successful. In fact, it is possible to monitor the behaviour of the individual components of the solution by observing separately the properties of either the nuclei of dissolved electrolyte or the nuclei residing in solvent molecules. However, NMR relaxation methods provide information on both the structure and dynamics of solutions.

2 Theoretical Principles of Nuclear Magnetic Relaxation

Around 1960 it was realized that nuclear magnetic relaxation allowed microscopic properties of electrolyte solutions to be studied. Until that time NMR studies had been based almost exclusively on the determination of chemical shifts. NMR relaxation experiments observe the decay of the longitudinal or transversal components of the nuclear magnetization towards equilibrium values following the application of a perturbating radiofrequency pulse. The approach towards the equilibrium is different for the components parallel and perpendicular to the external magnetic field, and is characterized by relaxation times, T_1 and T_2, respectively. Here we are interested in the longitudinal (spin–lattice) relaxation, as characterized by T_1.

The advantage of relaxation studies stems from the fact that generally the relaxation rate, $1/T_1$, obeys the relation

$$\frac{1}{T_1} = A \cdot \frac{E_1^2}{\hbar^2} \cdot \tau_c \tag{1}$$

where E_1 and τ_c represent the energy of interaction of the particular relaxation process and a molecular correlation time, respectively; $\hbar$ is Planck's constant divided by 2π. The energy E_1 is linked to the structural properties of the solution, while τ_c is linked to the dynamics. Therefore by determining the relaxation time, and with the knowledge of E_1, we obtain information on the dynamics of the solutions and, *vice versa*, with the knowledge of τ_c we obtain information on the structure of the solutions.

Antonio Sacco was born in Foggia in 1939. He received his laurea degree in Chemistry from the University of Bari. He began his academic career as an assistant in Physical Chemistry and lecturer in Spectroscopy at the University of Bari, where since 1980 he has been Associate Professor of Spectroscopy. His principal research interests lie in the investigation of the structure and microdynamics of pure liquids, binary mixtures, and electrolyte solutions by NMR spectroscopy.

Another advantage derives from the use of relaxation phenomenon: it is possible to separate inter- and intramolecular contributions. The most important relaxation mechanisms involve the magnetic dipole–dipole (DD) and nuclear electric quadrupole–electric field gradients (QF) interactions. In both cases, the relaxation rate is the sum of intra- and intermolecular contributions:

$$(1/T_1)_{\mathrm{tot}} = (1/T_1)_{\mathrm{intra}} + (1/T_1)_{\mathrm{inter}} \tag{2}$$

A knowledge of the two contributions leads not only to the identification of the interactions between ion–solvent, ion–ion, and solvent–solvent but also probes the interactions within the solvent molecules. In the case of dipolar relaxation, the separation is directly obtained using the method of isotopic dilution which singles out interactions between nuclei at specific molecular sites.[3] In the case of quadrupolar interaction the relaxation is either purely intramolecular, if the nucleus resides in a molecule, or purely intermolecular, if the nucleus resides in a monoatomic ion or noble gas species.

2.1 Dipole–Dipole Relaxation (DD)

Two types of dipole–dipole magnetic interactions are effective in NMR relaxation in solution: (i) electronic dipole–nuclear dipole and (ii) nuclear dipole–nuclear dipole. The former are of major importance where unpaired electron spins are present in solution: *e.g.*, in the presence of dissolved oxygen or paramagnetic transition metal ions. In the cases considered here, simple diamagnetic ions are involved with complete electronic structure and therefore this effect is absent. Therefore, in cases where the relaxation in solution is dominated by nuclear dipole–nuclear dipole interaction, the following equations apply for the spin–lattice relaxation rate $1/T_1$ for two like spins (*e.g.* protons):

$$\frac{1}{T_1} = \frac{3}{2}\gamma^4\hbar^2 I(I+1)[J(\omega) + J(2\omega)] \tag{3}$$

with $\omega = 2\pi\nu$ where ν is the resonance frequency of the particular nucleus, γ its magnetogyric ratio, I the nuclear spin, and $J(\omega)$ are the spectral densities at frequencies ω and 2ω. The spectral density is the Fourier transform of the autocorrelation function which describes motion of the internuclear vector r. Let us now consider an intramolecular relaxation process, where both nuclei belong to the same molecule. Then, the correlation function is often assumed to decay exponentially with a single correlation time τ_c, which describes the molecular reorientation. With this assumption the familiar equation for interacting spins of the same type is obtained:

$$\left(\frac{1}{T_1}\right)_{\mathrm{intra}} = \frac{2}{5}\gamma^4\hbar^2\frac{I(I+1)}{r^6}\left[\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+4\omega^2\tau_c^2}\right] \tag{4}$$

Moreover, for fluids of not too high viscosity, the correlation time is of the order of picoseconds, while for protons ν is typically of the order of 100 MHz, so that $\omega\tau_c \ll 1$. In this case, denoted as an 'extreme-narrowing' regime, equation 4 simplifies to

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = 2\gamma^4\hbar^2\frac{I(I+1)}{r^6}.\tau_c \qquad (5)$$

On the other hand, if the interacting nuclei belong to different molecules, the situation is more complicated, because the internuclear distance also changes with time due to self-diffusion of the molecules.[3] In this case, assuming again the extreme-narrowing assumption to hold, the intermolecular relaxation rate between two protons is written in a proper approximation as[3]

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \text{const}.c_H.\tau_c\int_a^{\infty}\frac{1}{r^6}g_{HH}(r)r^2\text{d}r \qquad (6)$$

where c_H is the proton concentration and g_{HH} is the radial distribution function, which is the probability of finding a proton at a distance r from another proton selected at random, and 'a' is the closest distance of approach. In this case the correlation time τ_c is to a good approximation given by

$$\tau_c = \frac{a^2}{3D} \qquad (7)$$

where D is the self-diffusion coefficient of the fluid (or in mixtures the mean self-diffusion coefficient of the spin-carrying species). As D is often known, or can be measured by the NMR spin-echo technique (see below), information can be obtained on g_{HH}, *i.e.* on the structure of the solution.[3]

This method is particularly suitable when combined with the so-called isotopic dilution technique. The constant in equation 6 contains the product of the squares of the magneticogyric ratios of the interacting spins I and S, $\gamma_I^2\gamma_S^2$. If we replace the interacting proton S by a deuteron with a substantially smaller magnetogyric ratio, we can 'switch off' the respective interaction. In this way, by site-specific isotopic substitutions, one obtains separate informations on site–site distribution functions, the combination of which then yields information on mutual molecular orientations. Evidently, such experiments are not limited to protons as interacting nuclei, but can *e.g.* be performed with heteronuclear interactions such as ^{19}F–^{1}H or ^{7}Li–^{1}H as well.

2.2 Quadrupole Relaxation of Ionic Nuclei in Pure Solvents

A nucleus endowed with an electric quadrupole moment eQ may interact with external electric field gradients, causing the nucleus to relax. In the limit of extreme narrowing ($\omega\tau_c \ll 1$) the relaxation rate is given by:

$$\frac{1}{T_1} = \frac{3}{8}\frac{2I+3}{I^2(2I+1)}\left(\frac{eQ}{\hbar}\right)^2\int_0^{\infty}\langle V_{zz}(0).V_{zz}(t)\rangle\text{d}t \qquad (8)$$

where $\langle V_{zz}(0).V_{zz}(t)\rangle$ is the time correlation function of the fluctuation of the electric field gradient at the nucleus, V_{zz} being a diagonal component of the electric field gradient tensor in the laboratory frame. The brackets $\langle\ldots\rangle$ denote the ensemble average. No experimental method is, however, capable of yielding $\langle\ldots.\rangle$ directly in the isotropic liquid phase. If we assume that the field gradient time correlation function decays exponentially with a characteristic single value, τ_c, we have:

$$\frac{1}{T_1} = A\langle V_{zz}^2(0)\rangle\tau_c \qquad (9)$$

where A is a constant for a given nucleus.

We limit discussion to the quadrupolar relaxation of nuclei in monoatomic ions, where the field gradients causing relaxation are of purely intermolecular origin. Examples are alkali metal nuclei (as ^{23}Na$^+$ or ^{87}Rb$^+$) or halide nuclei (as ^{35}Cl$^-$ or ^{81}Br$^-$). Various theories have been formulated in order to interpret experimental relaxation data. The best results have been obtained by the 'electrostatic theory'.[4] According to this theory, the electric field gradients necessary for the relaxation of a quadrupolar nucleus are generated principally by dipoles of the solvent molecules and by monopoles of the counter ions surrounding the relaxing ionic nucleus. Experimentally, the separation of the ion–solvent interaction is achieved by measuring the ionic relaxation rates as a function of the salt concentration, followed by extrapolation to infinite dilution of all ionic species.[4]

The field gradient acting at the ionic nucleus results from the following factors: (i) The dipole moments m of the solvent molecules cause relaxation. The resulting field gradient is proportional to m/r_0^4, where r_0 is the closest distance of approach between the ion and the solvent molecule. Hence, the resulting contribution to the relaxation rate depends on r_0^{-8}, which makes quadrupolar relaxation a very short-range probe for *local* structure and dynamics of ions. (ii) There is a distortion of the spherical electronic cloud around the ionic nucleus caused by polarization due to the perturbing field of the dipoles. This distortion can be appropriately taken into account by the so-called Sternheimer anti-shielding factor, which enters into the constant A in equation 9. (iii) There is a further 'electronic' contribution due to the distortion of the spherical electronic cloud by collision with the solvent molecules which appears however to play an insignificant role,[4] and is thus neglected in the formula given below. Neglecting minor effects, the final formula of the relaxation rate of a quadrupolar nucleus according to Hertz's theory is given by:

$$\frac{1}{T_1} = k.\frac{m^2n_c}{r_0^8}.\tau_c.\Lambda \qquad (10)$$

where n_c is the solvation number of the ion.

Moreover, the relaxation rate is very sensitive to the arrangement of the solvent molecules around the nucleus. In fact, the geometry of the solvation shell plays a major role in nuclear relaxation: *e.g.*, in a perfect arrangement of tetrahedral or octahedral symmetry of the solvent molecules the mean-square field gradient would vanish, and hence, the nuclear relaxation would be infinitely slow. This effect is called 'field gradient quenching', and is taken into account in Hertz's theory by the parameter Λ, which assumes values ranging between 0 and 1. $\Lambda = 1$ means the total absence of quenching (complete asymmetry), while perfect symmetry is described by $\Lambda = 0$. Obviously, for intermediate situations of symmetry we shall have all the values included between 0 and 1.

2.3 Quadrupole Relaxation of Ionic Nuclei in Mixed Solvents

For mixed solvents further complications emerge. In fact, analogous to what was said in the case of ions in pure solvents, we ought now to take into account the dipolar moments of the two solvents (m_1 and m_2), two distances (r_{01} and r_{02}), and two reorientational correlation times (τ_{c1} and τ_{c2}). Then, the generalization of equation 10 leads to the following expression for the relaxation rates of ions dissolved in mixed solvents as a function of the molar fractions x_1 and $x_2 = 1 - x_1$ of the two components of the mixture:[5]

$$\begin{aligned}\left(\frac{1}{T_1}\right)(x_1) = {} & \left(\frac{1}{T_1}\right)_1^p\frac{\tau_{c1}(x_1)}{\tau_{c1}^p}\frac{k(x_1)}{k_1^p}x_{l1} \\ & + \left(\frac{1}{T_1}\right)_2^p\frac{\tau_{c2}(x_1)}{\tau_{c2}^p}\frac{k(x_1)}{k_2^p}(1 - x_{l1}) + \Lambda^*(x_1)\end{aligned} \qquad (11)$$

In order to use this expression it is necessary to know the reorientational correlation times of solvent molecules in the mixtures $\tau_{ci}(x_1)$ and in the corresponding pure solvents τ_{ci}^p ($i = 1,2$). These may be obtained by means of subsidiary measurements of QF intramolecular relaxation rates of nuclei such ^{2}H and ^{14}N which may be present in the solvent molecules.[6] The

k coefficients which represent the ratio between the reorientational correlation times of the solvent molecules in the first coordination sphere of the ions and those in the bulk, may be obtained by means of the so-called B' NMR coefficients,[7] as described below Of fundamental importance in equation 11 are the two quantities x_{i1} and Λ^* The former represents the molar fraction of solvent 1 in the ionic solvation sphere so that if $x_{i1} = x_1$ (molar fraction of solvent 1 in the bulk) there will be no preferential solvation, while for $x_{i1} \neq x_1$ there is preferential solvation $\Lambda^*(x_1)$ takes account of possible non-additivity in total symmetry quenching effects [5] in simple terms it describes asymmetry effects due to the presence of two different components

2.4 Self-diffusion Coefficients

So far we have only considered relaxation processes However, a further fundamental quantity to be considered is the self-diffusion coefficient Self-diffusion coefficients can be measured very accurately by using NMR techniques

If a spin-system is perturbed by a radiofrequency (r f) pulse, perpendicular components of the magnetization are produced These decay either with the time constant T_2 or due to magnetic field inhomogenities, whichever process is faster The latter decay is however reversible, so that the relevant component of the magnetization can be restored This gives rise to the so-called spin-echo,[8] which may be generated by a second restoring pulse at time τ after the first perturbing pulse If such echoes are produced, their amplitude A decays as a function of the time τ between the r f pulses with the spin–spin relaxation time T_2

In the presence of large magnetic field inhomogenities, a second irreversible process occurs due to the self-diffusion of the molecules The latter effect can be magnified by producing a well-defined artificial linear magnetic field gradient, G, superimposed on the static magnetic field This gradient can be applied at certain times between the r f pulses, as suggested by Stejskal and Tanner [9] The pulse sequence used by Stejskal and Tanner is shown in Figure 1 In the presence of the two pulsed field gradients, the attenuation of the echo amplitude is given by the following ratio

$$A(G) = A(0)\exp\ -(\gamma\ G\ \delta)^2(\Delta - \delta/3)\,D \tag{12}$$

In equation 12 $A(0)$ is the amplitude of the echo observed without the field gradient, Δ and δ are the parameters of the experiment, as defined in Figure 1 Thus, if G, Δ, and δ are known, a measurement of the echo amplitude with and without application of the gradient pulses enables calculation of D

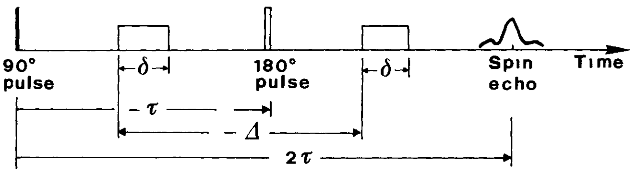

Figure 1 The time sequence of pulses for pulsed gradient spin-echo diffusion measurements

3 Electrolytes in Pure Solvents

The following discussion will be devoted to a method for obtaining information on microdynamical processes in solution, and adapted on a broad basis in our recent work At the end of this section we briefly consider some other recent work dealing with pure electrolytes solutions

Hertz *et al* [7] published a fundamental paper concerning the study of microdynamics of aqueous electrolyte solutions using nuclear magnetic relaxation and self-diffusion data They introduced, in analogy to viscosity B-coefficients, NMR B'-coefficients and showed that these coefficients contain information about the reorientational behaviour of solvent molecules in the first coordination sphere of ions Self-diffusion data were used in a similar way to study the influence of the dissolved ions on the translational behaviour of solvent molecules

The viscosity B-coefficient obtained by means of the Jones–Dole equation

$$\frac{\eta}{\eta_0} = 1 + Bc + Cc^2 + \tag{13}$$

provides information on the properties of electrolytes in solution In analogy, Hertz *et al* [7] introduced the following equation for the relative relaxation rate of solvent nuclei

$$\left(\frac{1}{T_1}\right)\Big/\left(\frac{1}{T_1}\right)_{c\ \ 0} = 1 + B'c + C'c^2 + \tag{14}$$

The NMR B'-coefficients were used to yield a microdynamical model of the electrolyte solution characterized by certain correlation times of solvent molecules We note that, as in the case of viscosities, the measured B'-coefficients may be separated into single-ion contributions Then, Hertz and co-workers show that from the B'-coefficients it is possible to estimate the factor $k = \tau_c/\tau_c^0$ which represents the ratio between the reorientational or internal correlation times in the solvation sphere and the correlation time in the bulk solvent

$$k = \frac{\tau_c}{\tau_c^0} = 1 + B'\ \frac{55\ 5}{n_c} \tag{15}$$

where n_c is the hydration number of the ion The results obtained for aqueous solutions indicated that typical structure-breaking ions show correlation times in their hydration spheres which are smaller than those of pure water In other words, the liquid within the hydration spheres of these ions is more fluid than in pure water

Subsequently, Engel and Hertz[10] extended those measurements and data analysis to non-aqueous solutions, including methanol, ethanol, acetone, dimethyl sulfoxide (DMSO), formamide (FA), *N*-methyl formamide (NMF), ethylene glycol, and glycerol Except for solvents with two or more OH-groups, giving rise to extensive hydrogen-bonding, only positive values for B'-coefficients were found Again, there is the problem of subdividing these experimental quantities into single-ion contributions This can only be done using somewhat arbitrary assumptions based on plausible arguments rather than rigorous methods The resulting anion sequence is $I^- < Br^- < Cl^-$, while that for the cations is $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$

Nearly all single-ion values are positive Exceptions are the largest ions considered, Cs^+ and I^- in glycol and additionally Rb^+ and Br^- in glycerol, where $B' < 0$ are found

So far, the measurements have been concerned with the total proton relaxation rate in organic solvents, which according to equation 2 consists of an intra- as well as an inter-molecular contribution Considering solutions in DMSO as representative examples, we have shown that the separate determination of these two contributions is possible [11] In detail, we first measured the total proton relaxation rates After subdivision into single ion values a first important result was the observation that $B'(Na^+) \approx B'(K^+)$ This is surprising, because in other dipolar aprotic solvents the B'-coefficients (*e g* the viscosity B-coefficients) for alkali metal ions decrease as the ionic radius increases Therefore $B'(Na^+) > B'(K^+)$ is expected On the other hand, these results confirm the viscosity measurements in DMSO by Feakins *et al*,[12] where an even slightly higher $B^+(K^+)$ compared with $B^+(Na^+)$ was found DMSO is not the first solvent where the relative position of Na^+ and K^+ has reversed, this pattern has also been observed for the corresponding B-coefficients in NMF [13]

Now let us consider the application of equation 2 in more detail If the solvent nuclei relax by dipolar interaction, as in the case of the DMSO protons, the total relaxation rate $(1/T_1)$ has an intra- and an inter-molecular contribution. The correlation time for the intramolecular contribution is the reorientational correlation time of the vector connecting the interacting protons in the solvent molecule. On the other hand, the correlation time for the intermolecular contribution is proportional to D^{-1}, the inverse self-diffusion coefficient of the solvent molecules.[7,14] Thus $(1/T_1)_{\text{intra}}$ is connected with the rotational and $(1/T_1)_{\text{inter}}$ with the translational motion of the solvent molecules. If we are able to separate $1/T_1$ into the two contributions, we can define in analogy to equation 14 new coefficients by:

$$\left(\frac{1}{T_1}\right)_{\text{intra}} \Bigg/ \left(\frac{1}{T_1}\right)_{\text{intra},c=0} = 1 + B'_{\text{intra}}c + \dots \qquad (16)$$

and

$$\left(\frac{1}{T_1}\right)_{\text{inter}} \Bigg/ \left(\frac{1}{T_1}\right)_{\text{inter},c=0} = 1 + B'_{\text{inter}}c + \dots \qquad (17)$$

These coefficients B'_{intra} and B'_{inter} reflect the influence of the dissolved salt on the rotational and translational motion of the solvent respectively. However, there is another measurable quantity, namely the self-diffusion coefficient of the solvent molecule, which leads to the definition of B_{D} coefficients of the reciprocal self-diffusion coefficients by:[7]

$$\left(\frac{1}{D}\right) \Bigg/ \left(\frac{1}{D}\right)_{c=0} = 1 + B_D c + \dots \qquad (18)$$

Clearly, the two coefficients B_{D} and B'_{inter}, both representing the influence that the dissolved salts exert on the translational properties of the DMSO molecules, must be the same, *i.e.* $B'_{\text{inter}} = B_{\text{D}}$. Then the intermolecular contribution at any salt concentration can be calculated:

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \left(\frac{1}{T_1}\right)_{\text{inter},c=0} \cdot \frac{D_{c=0}}{D} \qquad (19)$$

In our calculations for DMSO we use the value $(1/T_1)_{\text{intra},c=0} = 0.17\ \text{s}^{-1}$,[15] obtained by the isotopic dilution method. Hence we obtain $(1/T_1)_{\text{inter},c=0} = 0.15\ \text{s}^{-1}$. With the measured D values and equation 19 we obtain the results shown in Table 1.

Table 1 B_{D} and B'_{intra} coefficients in DMSO at 25 °C

Salt	$B_{\text{D}}(= B'_{\text{inter}})$	B'_{intra}
NaBr	0.178(± 0.006)	0.178 ± (0.009)
KBr	0.174(± 0.003)	0.180 ± (0.005)
NaI	0.156(± 0.003)	0.150 ± (0.005)
KI	0.153(± 0.003)	0.155 ± (0.005)
RbI	0.140(± 0.004)	0.140 ± (0.009)
CsI	0.134(± 0.005)	0.130 ± (0.008)

Values in parentheses are standard errors.

For DMSO, $B' = B'_{\text{intra}} = B_{\text{D}}$ holds for all the salts investigated, which means that rotational and translational motion of the solvent DMSO is affected to the same extent by addition of a salt.

Moreover, in molecules with internal flexibility, the intramolecular relaxation rate does not only reflect molecular overall reorientation, but also internal rotations in the solvent molecules. This fact has been used by Ansari and Hertz[16] to monitor the influence of ion–solvent interactions on the internal dynamics of solvent molecules, using ethanol as the representative example. For these purposes, they determined the B' coefficients of all non-equivalent protons in the ethanol molecule as a function of the concentration of added lithium halides. Applying this procedure they found in the case of ethanol: $B'(\text{CH}_2) > B'(\text{OH}) > B'(\text{CH}_3)$.

Hitherto, we were interested only in dipole–dipole relaxation of nuclei residing in solvent molecules. It is, however, worthwhile to mention the possibility of monitoring dipole relaxation of solute nuclei, and of discussing the information gained from studies of this type. As is seen from equation 6, the relevant dipole–dipole energy depends on the distance between the interacting spins. Thus, it is possible to obtain precise information on the structure of solvation around an ion by measuring the interactions of the solute nucleus with well-defined interaction partners, for example at specific sites in solvent molecules. For this purpose it is convenient to apply the so-called isotopic substitution technique, which we use to single out interaction between specific molecule sites by deuteration of the remaining parts of the molecule. In other words we 'switch on and off' the DD (dipole–dipole) interactions of the solute nuclei with the interacting partners.

Hertz and Müller[17] obtained information on the orientation of water molecules in the first hydration sphere of fluoride ions by comparing the ^{19}F–^{1}H interactions with the ^{19}F–^{17}O interactions, obtained from ^{19}F relaxation-time measurements in H_2O, D_2O, and $D_2{}^{17}O$. Surprisingly they found that the most favourable configuration of the two possibilities in Figure 2 corresponds to the 'symmetrical' arrangement shown in (a). This result differs from what has been found in quantum mechanical, Monte Carlo, and molecular dynamics computations. On the other hand, the same technique applied to ^{7}Li relaxation in LiCl aqueous solutions[18] gives results in complete agreement with theoretical predictions. Hence, there is no obvious reason why the experimental results for F$^-$ should be incorrect.

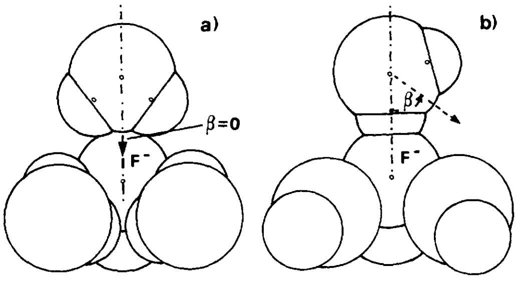

Figure 2 Two possible orientations of the water molecules in the hydration sphere of the F$^-$ ion. (a) Symmetrical arrangement; (b) 'H-bonded' arrangement of water molecules.
(Reproduced with permission from reference 17.)

Finally, we draw attention to other important studies of electrolyte solutions in pure solvents, and above all in water, for illustrating the type of information that can be gained from magnetic relaxation experiments. Van der Maarel *et al.* studied proton, deuteron, and oxygen-17 relaxation rates of water molecules in solutions of alkali metal,[19] magnesium,[19] and zinc[20] salts. The nuclear quadrupolar coupling constant (NQCC) of ^{2}H and the O–H distance in water were calculated. When salts are added, these quantities are remarkably changed relative to their values in pure water. Above all, there are indications from ^{2}H and ^{17}O relaxation for anisotropic reorientation of water molecules in the solvation spheres of cations.

With respect to the relaxation of nuclei residing in ions, more extensive and systematic investigations have been done. Most of this work has dealt with ionic nuclei of the alkali metal group. We consider here some illustrative examples using ^{7}Li relaxation.

All alkali metal nuclei posses quadrupole moments and therefore they relax predominantly by the quadrupolar mechanism. A notable exception is ^{7}Li, where the quadrupole moment is low and the DD mechanism can compare with the quadrupole interaction. Different authors[18,21] have attempted to separate these contributions by investigating ^{7}Li relaxation as a function of the H_2O/D_2O ratio. While early work was limited to high salt concentrations in the molar range, we have extended these studies towards low concentrations, close to the Debye–Hückel regime.[22] Indeed we found that at very dilute concentration of LiCl salt the relaxation rate exhibits a $\sqrt{c}$ law, which can be interpreted in terms of Debye–Hückel ion–ion distribution. As already mentioned above, Mazitov *et al.*,[18] have determined the orientation of water molecules in the hydration sphere of LiCl in ^{7}Li by means of ^{7}Li relaxation.

4 Electrolytes in Binary Mixtures

Perhaps the most important problem in studying ion–solvent interactions in binary mixtures is the preferential solvation of ions; various techniques have been used to look at this. In the present context we make use of D_2O–H_2O dynamical isotopic effects on the magnetic relaxation by quadrupole interaction of ionic nuclei.[23] The method until recently was used for studying only mixtures containing water as one of the components, but has now been generalized to treat phenomena in binary organic mixtures.

As we have seen in Section 2.3, the general equation for the quadrupolar relaxation rate of the ionic nucleus in binary mixtures, *i.e.* equation 11, contains two unknown quantities x_{i1} and Λ^*. A first approach assumes $x_{i1} = x_1$ and puts $\Lambda^*(x_1) = 0$. This implies that preferential solvation and any field gradient quenching effects are absent. Surprisingly, as can be observed in Figures 3 and 4, this model yields good agreement between the experimental and predicted relaxation rates for Na^+ in methanol–water[5] and Na^+ in FA- and NMF–water,[24] which means that preferential solvation effects are largely absent in these systems.

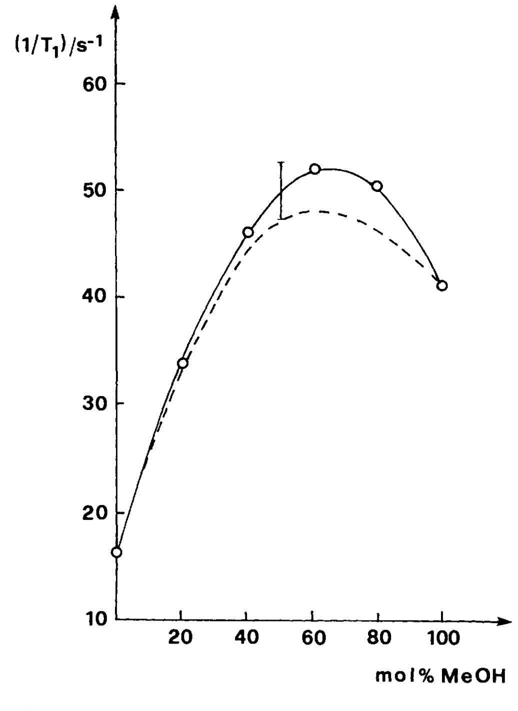

Figure 3 $^{23}Na^+$ relaxation rates extrapolated to zero salt concentration in water–methanol(MeOH) mixtures (○) as a function of mol% MeOH. Dashed line, values calculated from equation 11 assuming $x_{i1} = x_1$ and $\Lambda^* = 0$.
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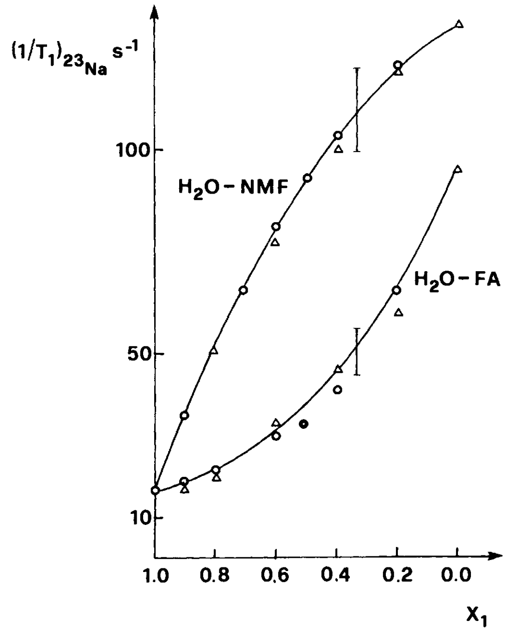

Figure 4 $^{23}Na^+$ relaxation rates extrapolated to zero salt concentration in water–FA and water–NMF mixtures as a function of x_1, the mole fraction of water. Δ, experimental values. ○, values calculated from equation 11 assuming $x_{i1} = x_1$ and $\Lambda^*(x_1) = 0$.
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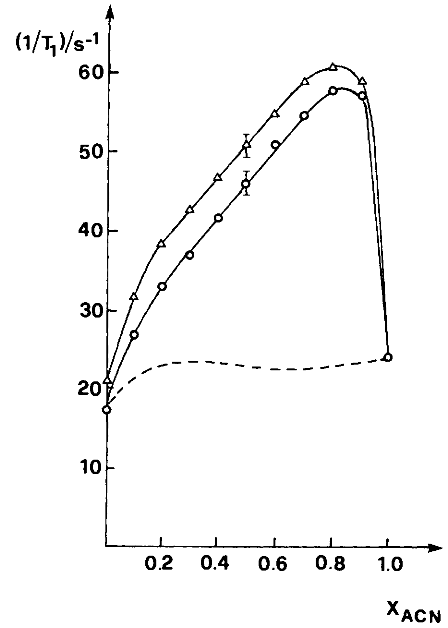

Figure 5 $^{23}Na^+$ relaxation rates for 1 m NaI in D_2O–ACN (Δ) and H_2O–ACN (○) mixtures as a function of the mole fraction of ACN, x_{ACN}. The dashed line represents the 'expected' relaxation rate curve according to equation 11 with $x_{i1} = x_1$ and $\Lambda^*(x_1) = 0$.
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When the investigations were extended to Na^+ and Cs^+ in water–acetonitrile (ACN),[25] and Na^+ in water–hexamethylphosphorous triamide (HMPT) mixtures,[6] we observed dramatic differences between measured and predicted relaxation rates (Figures 5 and 6). It is intriguing to attribute these discrepancies to selective solvation and associated field gradient quenching. To obtain independent information on x_{i1} and $\Lambda^*(x_1)$ we could apply, as mentioned before, measurements of the H_2O–D_2O isotopic effect on the relaxation rates of ionic nuclei in the binary aqueous mixtures. In detail, separate measurements of $1/T_1$ of the ionic nucleus were made in mixtures of organic solvent with H_2O, and subsequently with D_2O, which produced two sets of relaxation rates which determined the two unknown quantities x_{i1} and $\Lambda^*(x_{i1})$ as a function of the macroscopic mole fraction x_1. The results obtained in this way are displayed in Figure 7 for the systems Na^+ and Cs^+ in water–ACN and Na^+ in water–HMPT.

As is seen, in the case of ACN–H_2O mixtures both ions are preferentially solvated by water. In fact the local mole fraction of water, x_{i1}, in the solvation sphere of ions is higher than the mole fraction x_1 in the bulk. In the case of Na^+ dissolved in

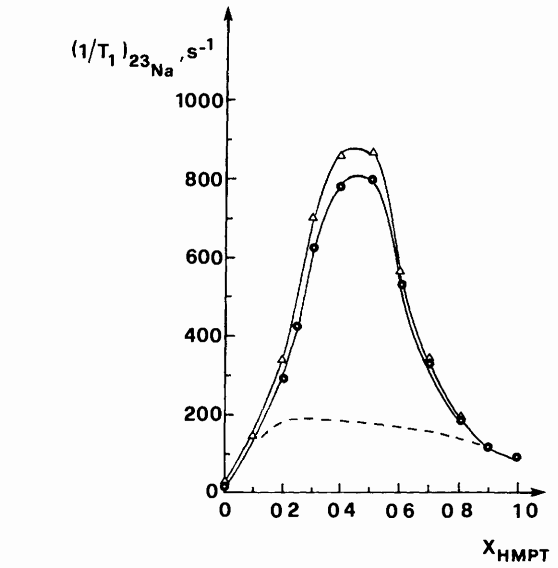

Figure 6 $^{23}Na^+$ relaxation rates of 0 4 m NaBr in D_2O–HMPT (Δ) and H_2O–HMPT (○) mixtures as a function of the mole fraction of HMPT, x_{HMPT} All other details as in Figure 5
(From reference 6)

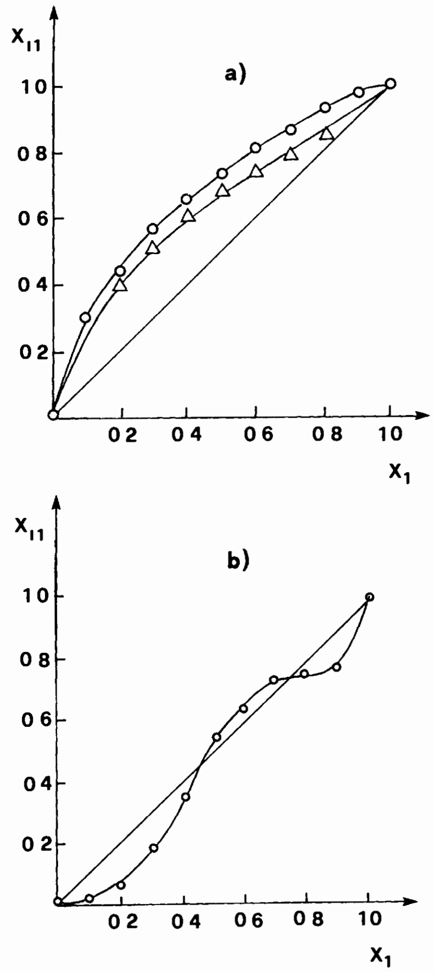

Figure 7 Local mole fraction x_{i1} of water in the solvation sphere of Na^+ (○) and Rb^+ (Δ) plotted against x_1, the macroscopic mole fraction of water in water–ACN (a) and water-HMPT (b) mixtures The straight line corresponds to the case of non-preferential solvation
(Reproduced with permission from references 6 and 25)

$HMPT–H_2O$, our result indicates that in the HMPT-rich region selective solvation by HMPT occurs The preference for HMPT is as expected from its high donor number and low acceptor number [26] Also, the Gibbs energy of transfer from water to HMPT[27] $\Delta G^0_{tr}(Na^+) = -39$ kJ mol [1] indicates preferential solvation by HMPT Therefore, it was surprising that in the range $0\,5 < x_1 < 0\,7$ no preferential solvation or even small preference for water was found It is, however, not the first time that a change in the selectivity has been observed For DMF–water and DMSO–water such a change has been established[24] and ascribed to structural peculiarities in the binary solvent system

An analogous investigation has been performed by us for Na^+ and Cs^+ in water–dimethylacetamide (DMA) mixtures [28] As seen in Figure 8, the microscopic mole fractions x_{i1} for Na^+ and Cs^+ given as a function of the macroscopic mole fractions clearly reveal preferential solvation of these cations in water–DMA mixtures In the range $1 > x_1 > 0\,7$ we observed weak preferential hydration Below these concentrations a change in the selectivity occurs, and for $0\,7 > x_1 > 0$ we observed marked preferential solvation by DMA Interestingly, this change in selectivity occurs near the mole fraction, where the reorientational correlation time of water has its maximum, as also found for cations in DMF–water, DMSO–water, and HMPT–water These maxima in reorientational correlation times appear to be characteristic for organic co-solvents with more than one hydrophobic methyl group

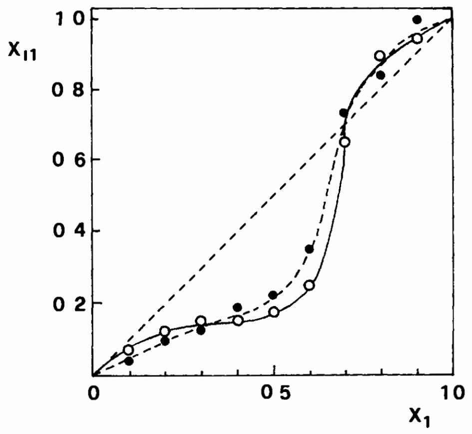

Figure 8 Local mole fraction x_{i1} of water in the solvation sphere of Na^+ (●) and Cs^+ (○) plotted against x_1, the macroscopic mole fraction of water in water DMA mixtures The straight line corresponds to the case of non-preferential solvation
(From reference 28)

Until recently the application of this technique had been limited to systems containing water as one of the components, because it had been assumed that the relatively large $H_2O–D_2O$ dynamic isotopic effect of 23% at 25 °C was the only effect which could be exploited However, in recent separate studies on the isotope effects of non-aqueous solvents we found that in several cases there were surprisingly high effects as well, *e g* about 12% in methanol/methanol-d_4 and DMF/DMF-d_7 [29 30] We thought, therefore, that with a high measuring accuracy it would also be possible to use the method of the dynamic solvent isotope effect to study electrolytes in binary *non-aqueous* mixtures Moreover, another important advantage turns out to result from the fact that in suitable cases *both* components of the solvent mixture may show dynamic isotope effects sufficiently high for direct observation Then it is possible to check the reliability of the method immediately by comparing the two independent sets of results obtained

In order to confirm this possibility we have studied the system NaI in methanol + DMF [31] The relaxation experiments for obtaining the local mole fractions (x_{i1}) of methanol in the solvation sphere of Na^+ have covered the following solvent mixtures $CH_3OH + DMF$, $CD_3OD + DMF$, and $CH_3OH + DMF\text{-}d_7$ The results for x_{i1} of CH_3OH obtained from the data for $CH_3OH + DMF$ and $CD_3OD + DMF$ are reported in Figure 9 The local mole fraction of methanol around Na^+ is always lower than the macroscopic value, which leads to the conclusion that in the whole composition range Na^+ is preferentially solvated by DMF Subsequently, we performed 'inverse' experiments in mixtures of $DMF + CH_3OH$ and $DMF\text{-}d_7 + CH_3OH$ These yielded the local mole fractions x_{i2} of DMF As can be seen from Figure 10, in the whole composition range, x_{i2} is higher than its macroscopic analogue x_2, once more confirming preferential solvation by DMF Two entirely independent sets of experiments have thus led to the same conclusions

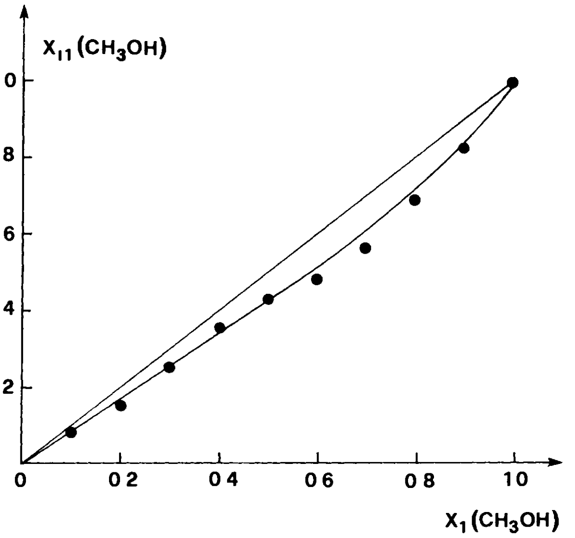

Figure 9 Local mole fraction x_{i1} of CH_3OH in the solvation sphere of Na^+ as a function of x_1, the macroscopic mole fraction of CH_3OH (From reference 31)

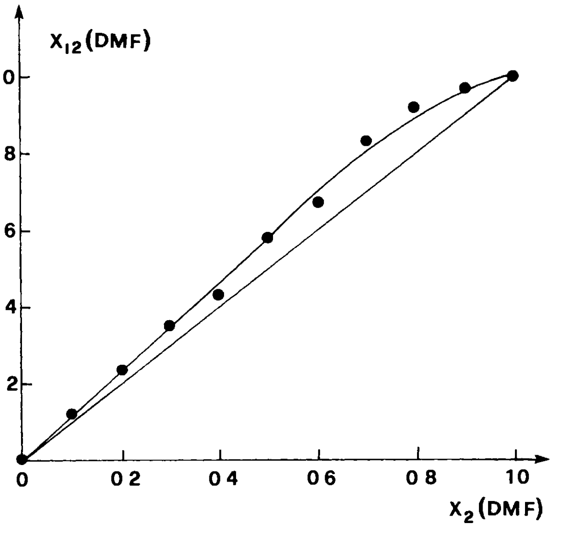

Figure 10 Local mole fraction x_{i2} of DMF in the solvation sphere of Na^+ as a function of x_2, the macroscopic mole fraction of DMF (From reference 31)

Table 2 Local mole fraction values in function of mole fraction of methanol in methanol–DMF mixtures

$x_1(CH_3OH)$	$x_{i1}(CH_3OH)$	$x_{i2}(DMF)$	$(x_{i1} + x_{i2})$
1	1	0	1
0 9	0 83	0 12	0 95
0 8	0 71	0 23	0 94
0 7	0 60	0 35	0 95
0 6	0 52	0 47	0 99
0 5	0 42	0 58	1 00
0 4	0 34	0 69	1 03
0 3	0 25	0 79	1 04
0 2	0 16	0 89	1 05
0 1	0 08	0 96	1 04
0	0	1	1

In more quantitative terms, the values for x_{i1} and x_{i2} can be used to check the consistency of the results (and the quality of the method) by noting that $x_{i1} + x_{i2} = 1$ must be valid In Table 2 we report the resulting numerical values of x_{i1} and x_{i2} as a function of composition, taken from the smoothed curves in Figures 9 and 10 In a separate column of Table 2 the sum $(x_{i1} + x_{i2})$ is shown the experimental values of $(x_{i1} + x_{i2})$ agree within 5% with the theoretical value of unity The remaining small deviations are explained by the experimental error and by certain approximations of minor importance entering in the equations The results show convincingly that this method provides a powerful tool for investigating preferential solvation of relatively weakly solvated monovalent ions like Na^+ In fact, comparatively strong dynamic isotope effects now found in various organic solvents open the possibility of quantitative investigations in a great number of non-aqueous binary mixtures

Finally, in the context of selective solvation studies, we briefly review other relaxation methods Finter and Hertz[32] studied preferential ion solvation in aqueous mixtures of FA and NMF Their method was based upon a separation of the dipole–dipole contributions of ionic nuclei to the relaxation rate of the formyl or amide protons of FA, and of formyl, amide, and methyl protons of NMF, respectively They showed that over the complete composition range of NaI in aqueous mixtures of FA, preferential solvation of Na^+ by FA occurs, while I^- is preferentially hydrated [32] The observed effects were termed 'heteroselectivity', because the cation and anion prefer different components of the binary mixture According to these authors, heteroselectivity occurs more often than homo-selectivity In the case of NaI dissolved in water + NMF,[13] analogous results were obtained, but were subject to larger uncertainty

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