

## NMR AND SOLVATION OF IONS IN NON-AQUEOUS SOLVENTS

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**Abstract** - Solvation of ions as a microscopic property is understood to be given by certain time independent and time dependent probability functions which describe the structure and internal dynamics around the ions in a heap of mass points representing ions and solvent species in the liquid state. It is shown in an abbreviated and simple form in which way the three macroscopic observables  $\omega$ ,  $T_1$ ,  $T_2$  characterizing one of the nuclear magnetizations of the solution give a partial and truncated picture of the microscopic object of interest here. Interpretation of chemical shift data very often is rendered more difficult by the fact that the local microscopic magnetic field is determined by the electron density, for the nuclear magnetic relaxation data this is the case to a much lesser degree. Literature references referring to non-aqueous solutions are given as examples for the basic relations outlined where for reasons of room detailed discussion is not possible.

Figure 1 shows the object of our interest in the simplest form, we have a binary mixture of a salt with a non-aqueous solvent, here methanol. In fact, the solute should have cations and anions, for simplicity we have only shown the cationic species  $Me^{\nu+}$ ,  $\nu = 1, 2, 3$ . Obviously, the solvent splits into bulk and "solvation liquid". The solvation liquid surrounds the solute species, and, as may be seen from Fig. 1 all  $Me^{\nu+} - O$  distances are equal and all nearest neighbour  $O - O$  distances are also equal. Thus here the solvation may be described with a "chemical language" as  $Me(H_2O)_n^{\nu+}$  where, for instance,  $n = 6$  if the picture is completed to a three dimensional one.

In Fig. 2 we have again a binary mixture electrolyte - methanol. Now the splitting of the solvent in bulk and solvation liquid becomes more ambiguous. Still, in some way one can say that the solvation liquid surrounds the cations, however the two distances mentioned above are distributed over fairly wide ranges. In Fig. 2 we have shown cationic species with diffuse solvation spheres, for the anions we have to imagine such type of solvation in almost all cases. Now the chemical, stoichiometric language to characterize solvation becomes meaningless and we have to take recourse to a configurational description. Our object in the microscopic sense is a heap of mass points, the atoms, or atomic nuclei, each mass point represents a certain element. And now we wish to describe the system in terms of geometrical properties of this heap of mass points. The tool to do this is a suitable set of pair distribution functions. Fig. 3 shows a schematic representation; the pair distribution function  $p(r)$  gives the probability density of finding an atom at position  $\vec{r}$  relative to the position of another atom or ion. In fact, we could also have included in Figs. 1 and 2 the electrons as another type of mass points, the number of electrons around a given solute nucleus would define the ionic species, however we shall not make explicit structural statements about the electron distribution.

So the primary aim of our investigation of the solvation of ions should be the presentation of a set of cation - atom and anion - atom distribution functions. Of course, the different atoms in a binary mixture are members of the same solvent molecule. The solvent molecule connects a certain set of ion - atom distribution functions to give an ion - molecule distribution function, however this combination of atomic pair distribution functions sometimes is not an easy task because the solvent molecules are flexible, i.e.

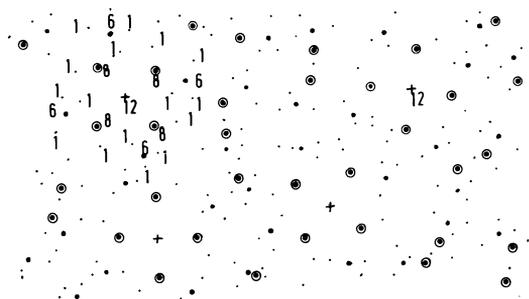


Fig. 1

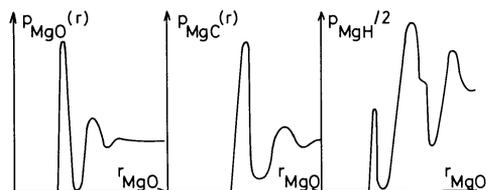


Fig. 1.  $Mg^{2+}X_2$  dissolved in methanol, represented as a heap of mass points. Numbers give location of atoms in periodic table.

Fig. 2.  $Na^+X$  dissolved in methanol as a system with weak solvation, again represented as a heap of mass points.

Fig. 3. Three atomic pair distribution functions describing the heap of mass points Fig. 1.

they do not represent a rigid body. As will be shown below, NMR methods can supply structural information in the strict sense only in a partial or truncated form. Full pair distribution functions cannot be obtained.

Usually, when one speaks of ionic solvation, the desire is to have other informations apart from a set of simple time-independent ion - atom or ion - molecule pair distribution functions. We list the various topics to describe ionic solvation in a wider sense which can be investigated by NMR methods in the following way: (1) absolute translational motion as studied by self-diffusion coefficients of solute and solvent particles, (2) relative translational motion of solvent molecules with respect to the ions. These are the solvent exchange processes, (3) absolute rotational motion of particles, mostly solvent molecules, but in principle also molecular ions, (4) relative rotational motion of solvent molecules or parts of these molecules relative to axes given by the solvation complex.

All these informations have to be derived from the behaviour of the one or more (partial) nuclear magnetizations of the solution system which are arising in the presence of a static magnetic field  $H_0$ . Under suitable perturbations the magnetization considered performs a precessional motion around the direction of the static magnetic field with the Larmor frequency  $\nu = \omega/2\pi$ , where  $\omega = \gamma H_0$ , after the times  $T_2$  and  $T_1$  the deviations from the equilibrium values of the transverse and longitudinal components, respectively, essentially have disappeared.  $\gamma$  is the gyromagnetic ratio. The number of nuclei with vanishing magnetic moment which cannot be replaced by suitable magnetic isotopes is comparatively small, so the amount of structural and dynamic information which can be obtained from the study of the respective nuclear magnetization with its three parameters  $\omega$ ,  $T_1$  and  $T_2$  is enormously great. In the following it will be attempted to give a brief outline of the interconnection between the three observables  $\omega$ ,  $T_1$ ,  $T_2$  and the pertinent geometric and dynamic features of the heap of mass-points which represents an electrolyte solution. The example quoted as literature references will refer to non-aqueous systems (sometimes with admixture of water).

#### SOLVATION STRUCTURE AND EXCHANGE RATES FROM CHEMICAL SHIFT MEASUREMENTS

Let us begin with the evaluation of the chemical shift, i.e. the resonance frequency  $\nu$  of the solution relative to that in a certain standard environment. Here the situation is of particular interest in which for a given solvent nucleus two resonance frequencies occur. One partial magnetization being defined by the resonance frequency  $\nu_s$  corresponds to the solvation sphere of the cations, the other partial magnetization  $\nu_b$  has to be assigned to the "bulk", i.e. to all the remaining solvent nuclei including the solvation spheres of the anions. Let the total intensity of the signal stemming from the former magnetization and that of the bulk solvent molecules be  $J_s$  and  $J_b$ , respectively. Then the first coordination number  $n_c$  of the cation in question is given by the relation

$$\frac{J_s}{J_b} = \frac{n_c C_s^*}{C_i^* - C_s^* n_c} \quad (1)$$

where  $c_s^*$  and  $c_1^*$  are the solute and solvent concentrations in the molality scale. The  $J_i$  ( $i = s, b$ ) are the integrals over the spectral intensity  $g(\nu)$

$$J_s = \int_{\nu_0}^{\nu^*} g(\nu) d\nu \quad (2)$$

$$J_b = \int_{\nu^*}^{\nu_\infty} g(\nu) d\nu \quad (3)$$

with  $g(\nu_0) = g(\nu_\infty) = 0$ . It may be seen that  $n_c$  can only be obtained without arbitrariness if there is a  $\nu^*$  for which  $g(\nu^*) = 0$  with  $\nu_0 < \nu^* < \nu_\infty$ . Let us set  $g(\nu) = g_s(\nu)$  in the frequency range  $\nu_0 < \nu < \nu^*$  and  $g(\nu) = g_b(\nu)$  in the remaining range.  $g_s(\nu)$  is connected with the ion-solvent atom pair distribution function  $p(r)$ , the quantity which is the aim of our structural investigation:

$$g_s(\nu) = \int_0^{r^*} f_s(\nu, r) p(r) dr \quad (4)$$

where the limit of integration  $r = r^*$  is the location of the first relative minimum of  $p(r)$  which defines the first coordination sphere

$$n_c = 4\pi \int_0^{r^*} p(r) r^2 dr = \int_0^{r^*} p(r) dr \quad (5)$$

The local signal function  $f_s(\nu, r)$  is determined by the electronic and nuclear distribution around the solvent nucleus in question. The electronic distribution determines the position of the maximum of  $f_s(\nu, r)$ , the nuclear distribution and dynamics may alone determine the shape (width) of  $f_s(\nu, r)$ . Likewise for the bulk we have

$$g_b(\nu) = \int_{r^*}^{\nu} f_b(\nu, r) p(r) dr \quad (6)$$

where  $f_b(\nu, r)$  ( $= f(\nu, r)$  for  $r > r^*$ ) does not depend on  $r$  and  $p(r) = \text{const.} = c' = N/V$ .  $N$  is the number of particles and  $V$  is the volume of the system. Usually the behaviours of  $p(r)$  and  $f(\nu, r)$  are correlated: If  $p(r)$  is very sharp, i.e. practically a  $\delta$ -function, then the maxima of the functions  $f_s(\nu, r)$  and  $f_b(\nu, r)$  with respect to  $\nu$  are widely separated. Then there is a  $r^*$  value such that  $p(r^*) = 0$  and  $n_c$  appears to be well-defined. This condition is often fulfilled for polyvalent cations like  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , however, for univalent cations and anions it is never fulfilled. So there are many examples in the literature where  $n_c$  has been determined by analysis of the solvent spectra with separated solvation and bulk signals. In most cases the first coordination number was found to be six (Ref. 1 - 13).

Let us now consider the cases where  $p(r)$  is not practically a  $\delta$ -function. This means that even at the minimum position  $r^*$  of  $p(r)$  we have  $p(r) = p(r^*) \neq 0$ . From the static description we transcribe this statement to a dynamic one. We say: the fact that  $p(r^*) \neq 0$  must also mean that  $\mathcal{P}(r_0, r^*, t) \neq 0$ , where  $r_0$  is the position of the maximum of  $p(r)$ .  $\mathcal{P}(r_0, r, t)$  is the propagator describing the solvent motion relative to the ionic species considered, it gives the probability density of finding the solvent atom at  $r$  at time  $t$  if we know that it was at  $r = r_0$  at  $t = 0$ . Of course, the total function  $\mathcal{P}(r_0, r, t)$  would be difficult to obtain, however, we may form a suitable space integral of  $\mathcal{P}(r_0, r, t)$  in order to get partial information. Thus we write

$$1 - e^{-t/\tau} = \int_{r^{**}}^{\infty} \mathcal{P}(r_0, r, t) dr \quad (7)$$

which defines the residence time  $\tau$  of the solvent molecule (or atom) in the first coordination sphere in terms of the propagator for the relative

translational motion. In this situation one obtains an additional broadening of the two lines forming the spectral intensity  $g(\nu)$ , thus we have now  $g(\nu, \tau)$ . The latter quantity is given by the solution of a set of coupled Bloch-equations, these are differential equations for the partial magnetizations which involve the relaxation and exchange process (Ref. 14). It is hoped that the relaxation and exchange process contribute independently to  $g(\nu, \tau)$  which essentially means that the distance  $r^{**}$  occurring in eq.(7) is the same as the distance  $r^*$  where  $p(r)$  has its minimum. First solvation sphere exchange rates for a number of divalent and trivalent cations dissolved in various solvents have been determined in this way (Ref. 3,12,13,15 - 28).

Of course, this method can only work if the life time broadening of the spectral line is of the order of the frequency separation  $\Delta\nu$  between the solvation and bulk line, i.e. we must require  $1/\tau \lesssim \Delta\nu$ . If  $1/\tau \gg \Delta\nu$ , then  $g(\nu)$  again becomes independent from  $\tau$  and the spectrum only consists of one line representing the mean value of the chemical shift in the solvation sphere ( $\Delta\nu^+$ ) and the bulk ( $\Delta\nu_b^+$ ). Let the maximum of  $g(\nu)$  occur at  $\nu'$ . Then, if  $\nu_0'$  is any reference frequency, we have for  $\Delta\nu = \nu' - \nu_0'$  (see eq.(5)).

$$\Delta\nu' = \frac{n_s}{n_1} \int_0^{r^*} \Delta\nu(r) p(r) d\vec{r} + \left(1 - \frac{n_s}{n_1} \int_0^{r^*} p(r) d\vec{r}\right) \Delta\nu_b' \quad (8)$$

$$= \frac{c_s^* M_1}{1000} \int_0^{r^*} p(r) d\vec{r} \cdot \Delta\nu^+ + \left(1 - \frac{c_s^* M_1}{1000} \int_0^{r^*} p(r) d\vec{r}\right) \Delta\nu_b^+ \quad (9)$$

$n_s$  and  $n_1$  are the numbers of moles of the solute and solvent, respectively,  $c_s^*$  is the solute concentration in the molality scale. In eq.(8) the chemical shift  $\Delta\nu(r)$  is a function of the electron distribution  $\rho_e(r)$ ,  $\Delta\nu' = \Delta\nu'(\rho_e(r))$ , and the electron distribution in turn is determined by the relative configurations of the nuclei.  $g(\nu)$  can be described by only one width parameter  $T_2$ , mostly  $T_2 = T_1$ . Now qualitative structural information is obtainable when the chemical shift  $\Delta\nu^+$  in the solvation sphere can be interpreted, e.g. in terms of rupture of hydrogen bonds of the solvent, polarization of the solvent molecule etc. (Ref. 29- 31). The extension of eq.(8) to incorporate also an anionic solvation contribution is straightforward.

If the solvent is itself a mixture of two non-electrolytes, components 1 and 2, say, then in eqs. (2) and (3) or (8) and (9)  $g(\nu)$  or the chemical shift  $\Delta\nu_i'$ ,  $i = 1, 2$  can be measured for both components. Now, considering the fast exchange case, we introduce the respective ion-solvent atom pair correlation function  $g_i(r)$  by the relation

$$p_i(r) = c_i' g_i(r) \quad i = 1, 2$$

where  $c_i'$  is the number density of component  $i$ . Then eq.(9) reads

$$\Delta\nu_i' = c_s N_0 \int_0^{r^*} g_i(r) d\vec{r} \cdot \Delta\nu_i^+ + \left(1 - c_s N_0 \int_0^{r^*} g_i(r) d\vec{r}\right) \Delta\nu_{i,b}^+ \quad (10)$$

where  $N_0$  is Avogadro's number.

For the two pure solvents we have the first coordination number of the ion

$$n_{co}^{(i)} = c_{io}' \int_0^{r^*} g_i(r) d\vec{r} \quad i = 1, 2$$

Usually one assumes that  $n_{co}^{(1)} = n_{co}^{(2)}$ , then eq.(10) can be used to study preferential solvation: If for  $x_i < 1$  ( $x_i =$  mole fraction of solvent  $i$ )

$$\int_0^{r^*} g_i(r) d\vec{r} > \frac{n_{co}^{(i)}}{c_{io}'}$$

then the cation is preferentially solvated by component  $i$ , if

$$\int_0^{r^*} g_i(r) d\vec{r} = \frac{n_{co}^{(i)}}{c_{io}'}$$

( $c'_{i0}$  = number density in pure solvent  $i$ ) over the entire composition range, preferential solvation is absent. Since in eq.(10)

$$n_{ci}^{(ion)} = c_s N_0 \int_0^{r^*} g_i(r) dr^{\rightarrow}$$

is the first coordination number of the solvent molecule  $i$  with respect to the ion in question, we can also say: If preferential solvation is absent, then  $n_{ci}^{(ion)}$  is only dependent on  $c_s$ , but it is independent on the solvent composition. Furthermore, in eq.(10) the first term on the right-hand side may be written (e.g. for component 1)

$$c_s N_0 \Delta v_1^+ \int_0^{r^*} g_1(r) dr^{\rightarrow} = c_s N_0 \left\{ \sum_{j=0}^{n_{c0}^{(1)}} \int_0^{r_1^*} p^{(j)}(r_1, r_1^{(2)}, \dots, r_j^{(2)}) \Delta v_1^+(r, r_1^{(2)}, \dots, r_j^{(2)}) dr^{\rightarrow} \prod dr_j^{(2)} \right\} \quad (11)$$

where  $p^{(j)}(r, r_1^{(2)}, \dots, r_j^{(2)})$  is the occurrence probability of a solvation complex with  $n_{c0}^{(1)} - j$  molecules 1 and  $j$  molecules 2 with positions  $r_1^{(2)}, \dots, r_j^{(2)}$ . In eq.(11) the orientational degree of freedom of the molecules should be included, however is neglected. For the linear expression (10) to be valid it must be required that  $\Delta v_1^+(r, r_1^{(2)}, \dots, r_j^{(2)})$  does not depend on the number and position of the  $j$  molecules 2.

The situation is different when the chemical shift  $\Delta v_n^+$  of the ionic nucleus is studied. Then of course  $\Delta v_n^+(r_1^{(1)}, r_2^{(1)}, \dots, r_k^{(1)}, r_1^{(2)}, r_2^{(2)}, \dots, r_{n-k}^{(2)})$

must depend on the relative number of 1- and 2-molecules in the first solvation sphere. The chemical shift is given as

$$\Delta v_n^+ = \sum_{\substack{k, \ell \\ k+\ell=n_c}} \int_0^{r_1^{(1)*} \dots r_\ell^{(2)*}} p_{k\ell}(r_1^{(1)}, \dots, r_k^{(1)}, r_1^{(2)}, \dots, r_\ell^{(2)}) \Delta v_n^+(r_1^{(1)}, \dots, r_\ell^{(2)}) \prod_{k, \ell} dr^{\rightarrow (1)} dr^{\rightarrow (2)} \quad (12)$$

where  $p_{k\ell}(r_1^{(1)}, \dots, r_\ell^{(2)})$  is the occurrence probability for the set of coordinates  $r_1^{(1)}, \dots, r_k^{(1)}, r_1^{(2)}, \dots, r_\ell^{(2)}$ .

For the practical application it is assumed that  $\Delta v_n^+(r_1^{(1)}, \dots)$  depends linearly on the relative amount of 1 and 2 molecules in the solvation sphere. If this requirement is fulfilled, then eq.(12) can be used to study preferential solvation. In the absence of preferential solvation  $\Delta v_n^+$  is a linear function of  $x_1$ , non-linearity is taken as an indication for selective solvation. The nucleus whose resonance is studied, passes through all the environments  $r_1^{(1)}, \dots, r_k^{(1)}, r_1^{(2)}, \dots, r_\ell^{(2)}$  appearing as arguments in eq. (12). If the residence time in the various distinct environments is long compared with the inverse difference of the chemical shifts  $\Delta v_n^+(r_1^{(1)}, \dots)$  assigned to these environments, then the spectrum is again split to give a set of separate resonance lines. We quote a number of literature references, where this method has been applied (Ref. 12, 32 - 45) in some cases the second solvent component is water.

In all the expressions of this section the concept of the first coordination number  $n_c$  occurs as an integral over the atomic or molecular distribution function.  $n_c$  can also be defined by suitable sets of "thermodynamic" or "chemical" stability constants (Ref. 46, 47). By these stability constants the distances  $r^*$  occurring as the upper limits of these integrals is implicitly defined. This is the problem of correspondence between the chemical and the configurational language.

## NUCLEAR MAGNETIC RELAXATION TIMES

In diamagnetic solutions the relaxation times  $T_1$  and  $T_2$  are equal in most cases (Ref. 48) and even if  $T_1 \neq T_2$  very few experimental data pertinent to our subject are available, so in the following the transverse relaxation time  $T_2$  does not require a separate discussion.

The longitudinal relaxation time  $T_1$  is the macroscopic kinetic parameter which describes the approach of the z-component (z-direction of the static magnetic field) of the nuclear magnetization  $m_z$  towards equilibrium ( $m_z^0$ ) if by suitable experimental techniques this equilibrium magnetization has been disturbed. We have

$$\frac{dm_z}{dt} = \frac{1}{T_1} (m_z^0 - m_z) \quad (13)$$

The bridge between the macroscopic relaxation rate  $1/T_1$  and the microscopic structure and dynamics of the electrolyte solution is given by the basic relation

$$\frac{1}{T_1} = K \gamma(\omega) \quad (14)$$

where the factor of proportionality  $K$  contains nuclear quantities like the spins  $I$  or  $S$  and gyromagnetic ratios  $\gamma_I, \gamma_S$  (Ref. 48).  $\gamma(\omega)$  is the spectral density of the interaction of the nuclear magnets with their surroundings which causes the spin system to exchange energy with the remainder of the system, the so-called lattice. For our purpose two kinds of interaction are of importance. (1) The magnetic dipole-dipole interaction, it involves only the magnetic moments of the nuclei in the system and (2) the electric quadrupole interaction. Here the interaction of the nuclear electric quadrupole moment with the electric field gradient produced by the nuclei and electrons are effective. Let us begin with the simpler case of the magnetic dipole-dipole interaction.

The spectral density is given by the relation

$$\gamma(\omega) = \int_{-\infty}^{+\infty} G(t) e^{-i\omega t} dt \quad (15)$$

i.e. it is the Fourier transform of  $G(t)$ , the suitably normalized time correlation function of the magnetic dipole-dipole interaction,  $\omega$ , the resonance frequency, is of the order of  $10^8 \text{ s}^{-1}$ ,  $G(t)$  in most cases decays towards zero after a time of the order  $10^{-11} \text{ s}$ , so in this situation of greatest practical importance, the Fourier transform degenerates to a time integral over  $G(t)$ . We write  $G(t)$  in a form which is suitable for our objective (Ref. 49, 50):

$$G(t) = \int p(r_0) \frac{Y_2^{(m)}(0)}{r_0^3} \frac{Y_2^{*(m)}(t)}{r^3} P(\vec{r}_0, \vec{r}, t) d\vec{r}_0 d\vec{r} \quad (16)$$

The integrand in eq.(16) is built up of the following three parts:  $p(r_0)$  is the pair distribution function of the atoms which carry the magnetically interacting nuclei. According to the purpose of the present article, here eq.(16) is applied to the situation that one of the pair partners is the ion whose solvation we are studying.  $Y_2^{(m)}(t)$  is the spherical harmonic of second degree, it is a function of the orientation of the vector connecting the two magnetic nuclei. The correlation function does not depend on the order ( $m$ ) of the spherical harmonic.  $r_0$  and  $r$  are the internuclear separations at  $t = 0$  and  $t = t$ , respectively, so  $Y_2(t)/r^3$  essentially represents the magnetic dipole-dipole interaction. The occurrence of  $r$  in this expression offers the possibility to "measure" the distance in the liquid as will be seen shortly. The important feature of eq.(16) is that it does not contain the electron density.  $P(\vec{r}_0, \vec{r}, t)$  characterizes the relative motion of the two interacting nuclei (see eq.(7)). The practical physical content of eq.(16)

is as follows: If we can make any reasonable prediction of the motional part  $\bar{P}(\vec{r}_0, \vec{r}, t)$ , then from the experimental knowledge of  $1/T_1$  via eqs. (14) - (16) information about  $p(r_0)$  can be obtained. Or, alternatively, if  $p(r_0)$  is sufficiently well known, the motional properties of the solution can be studied. We shall first turn to the discussion of the former case. In a simplifying way we may consider only the rotational contribution to  $\bar{P}(\vec{r}_0, \vec{r}, t)$ , then eq. (16) takes the form (Ref. 49):

$$G(t) = \int \frac{p(r_0)}{r_0^6} c(\vec{r}_0) \cdot e^{-t/\tau_c^*} \quad (17)$$

where  $\tau_c^*$  is the effective rotational correlation time of the dipole-dipole interaction. Appropriate further reduction of this formula and combination with eqs. (14) and (15) ( $\omega = 0$ ) yields the result (Ref. 49):

$$\frac{1}{T_1} = \frac{4}{3} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{n_c}{\epsilon} \tau_c^* + \Delta \quad (18)$$

where  $\Delta$  is the contribution from the region of the solution outside the first coordination sphere.  $a$  is the closest distance of approach between the two interacting nuclei, that is, in eq. (12)  $p(r_0) = 0$  for  $r_0 < a$ . In the sense of the microdynamic structure  $\tau_c^*$  is the rotational correlation time of the vector connecting the two interacting nuclei, which in many cases is the same as the rotational correlation time of the solvation complex (Ref. 51).

Let us now treat two examples. In the first example the relaxing ionic nucleus was  $^{19}\text{F}$  in  $\text{F}^-$  and two solvents have been used to apply this method: methanol and formamide (Ref. 52). Then the interacting solvent nucleus may be  $^1\text{H}$  of  $\text{HOCD}_3$  or it may be the representative proton spin of  $\text{CH}_3\text{OD}$ . Measurements of the  $^{19}\text{F}$  relaxation rate in these two isotopically labelled methanols yielded the two distances of closest approach as given in Fig. 4. In the same way the  $^{19}\text{F}$  relaxation rates caused by  $\text{HCOND}_2$  and by  $\text{DCONH}_2$  have been measured yielding the first coordination sphere configuration shown in Fig. 5 (Ref. 52). The number of possible applications of this method is not great because the relaxing nucleus in the centre of the solvation complex has to have a spin  $I = 1/2$  and the atom must not have too many electrons because otherwise other relaxation mechanisms become dominant.  $^{19}\text{F}$  is almost the only favourable case. The other example is given by  $^7\text{Li}$  which has  $I = 3/2$ , thus it relaxes by quadrupole interaction, however very often the quadrupolar contribution is so small that the magnetic dipole-dipole interaction as a partial cause of relaxation can be identified by isotopic substitution and the relaxation rate evaluated in the sense as described above. Fig. 6 gives an example, namely  $\text{Li}^+$  solvated by formic acid (Ref. 53). Here the solvent molecule is flexible, thus, as was mentioned in the introduction, the derivation of the solvent molecule orientation from the atomic model pair distribution functions is not a priori unique. Quantum mechanical calculations yield the result that the trans-conformation with respect to the protons is the stable one (Ref. 54) and thus Fig. 6a gives the correct ion solvent configuration.

As has already been mentioned above, most of the ionic nuclei have an electric quadrupole moment. Then eq. (14) appears in a generalized form (Ref. 55,56):

$$\begin{aligned} G(t) &= \int p(r_1^0, r_2^0, \dots, \theta_1^0, \theta_2^0, \dots) \left( \sum \frac{X_i(-Q_i^0, \theta_i^0)}{(r_i^0)^4} \right) \left( \sum \frac{X_i(-Q_i, \theta_i)}{r_i^4} \right) \\ &\quad \times \bar{P}(r_1^0, r_2^0, \dots, \theta_1^0, \theta_2^0, \dots, r_1, r_2, \dots, \theta_1, \theta_2, \dots, t) d\vec{r}_1^0 \dots d\theta_s \end{aligned} \quad (19)$$

The sources of the electric field gradient are the electric dipole moments of the solvent molecules surrounding the ion, whose nuclear magnetic relaxation is studied; the distance dependence of this interaction is  $\sim r^{-4}$ . Apart from a constant factor, the Sternheimer or antishielding factor (Ref. 57),

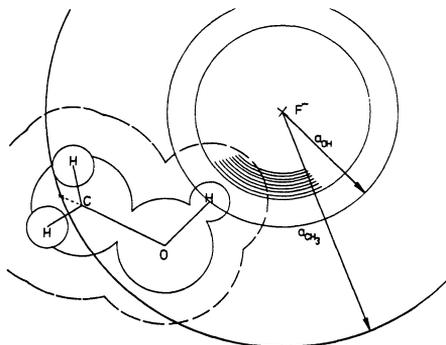


Fig. 4

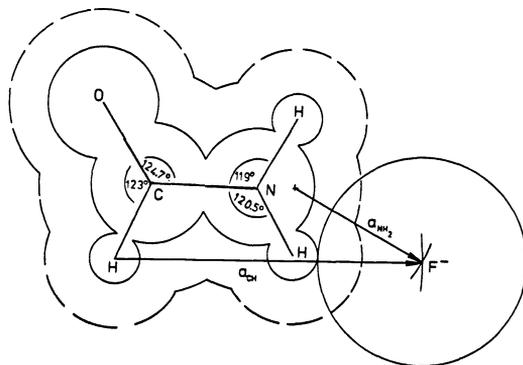


Fig. 5

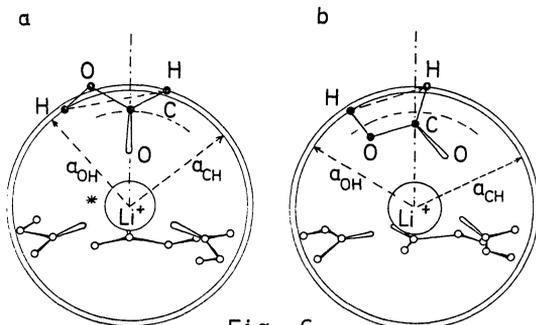


Fig. 6

Fig. 4. Orientation of methanol molecule in solvation sphere of  $F^-$  (Ref. 52).

Fig. 5. Orientation of formamide molecule in solvation sphere of  $F^-$  (Ref. 52).

Fig. 6. a) Solvation structure for  $Li^+$  in formic acid. b) rejected possibility due to improper conformation of acid molecule (Ref. 53).

the electron distribution does not enter explicitly in this expression, it occurs only implicitly through the location of the point dipoles in the molecules. Other approaches which make use of the electron density more explicitly have also been reported in the literature (Ref. 61 - 63). The structural part of  $G(t)$  is given by the many-body distribution function  $p(r_i^0, \dots, \theta_i^0, \dots)$  which incorporates also the orientation  $\theta_i^0$  of the dipole moments. The interaction term contains functions  $X_i$  of the dipole orientation and of the orientation  $\Omega_i$  of the dipole location relative to the centre. Likewise the propagator  $P(r_i^0, \dots, \theta_i^0, t)$  determines the motion of the molecules building up the solvation complex and the reorientational motion of the dipole moments. The remarkable feature of eq. (19) is given by the fact that symmetric configurations with certain  $r_i^0, \dots$  and  $\theta_i^0, \dots$  values may occur with high probability  $p(r_i^0, \dots, \theta_i^0, \dots)$  for which the interaction  $\sum X_i/r_i^4$  virtually vanishes. In this event the quadrupolar contribution to the relaxation rate - eqs. (14) and (15) remain valid - is strongly quenched (F.O.S. model (Ref. 56, 64)). This situation is found for strongly solvated cations (Ref. 56). In the case of more weakly solvated ions, the variables  $r_i^0, \dots, \theta_i^0, \dots$  may form a wide range of different configurations for which  $p(r_i^0, \dots, \theta_i^0, \dots)$  has appreciable and more or less equal values. This has the consequence that we have also a marked reduction of the relaxation rate, however now caused by disorder, not by order. Finally connected with the comparatively great amount of disorder in the first solvation sphere a rapid approach of the motional propagator to orientational uniformity takes place, which also causes a reduction of the quadrupolar relaxation rate (F.R.D. model, (Ref. 56, 64)). The solvation of  $Li^+$ ,  $Na^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  in simple alcohols and amides, in formic acid,  $(CH_3)_2CO$ ,  $CH_3CN$ , and DMSO has been studied along these lines (Ref. 56). Order and motion in the solvation sphere can be correlated with the ionic standard entropies.

#### ABSOLUTE TRANSLATIONAL AND ROTATIONAL MOTION

In those cases where the relaxation time  $T_2$  ( $= T_1$ ) is sufficiently long the self-diffusion coefficients of the ion ( $D_c$  or  $D_a$ ) and the solvent molecule,  $D$ , can also be measured by the NMR method (Ref. 65, 51). Then the following relation which is the analog of eq. (9) is of particular interest (Ref. 50, 66 - 68):

$$D = \frac{c_s^* M_1}{1000} n_c^+ D^+ + \left(1 - \frac{c_s^* M_1}{1000} n_c^+\right) D_0 \quad (20)$$

$D^+$  and  $D_0$  are local self-diffusion coefficients of the solvent molecule in the cationic solvation sphere and in the bulk plus anionic surroundings, respectively. At sufficiently high concentrations  $c_s^*$  the second term should vanish and thus  $D^+$  can be compared with the cation self-diffusion coefficient  $D_c$ . When strong or weak solvation exists, then one should find  $D_c = D^+$  or  $D_c < D^+$ , respectively. For aqueous systems the corresponding measurements have been performed (Ref. 68 - 71), however not yet for non-aqueous solvents, although results should be interesting. In eq.(20) the D's can be replaced by the rotational correlation times (Ref. 66,67):

$$\tau_c = \frac{c_s^* M_1}{1000} (n_c^+ \tau_c^+ + n_c^- \tau_c^-) + (1 - \frac{c_s^* M_1}{1000} (n_c^+ + n_c^-)) \tau_c^0 \quad (21)$$

the  $\tau_c$ 's are the time constants determining the local propagator  $P(\vec{r}_0, \Omega, t)$  which occurs in eqs.(16) and (19) when these relations are reformulated to refer to the intramolecular contribution to the relaxation rate only. In non-aqueous solvents  $\tau_c^+ > \tau_c^0$ , i.e. rotational motion in the solvation sphere is slower than in the bulk (Ref. 72, 73). For the anions we have  $\tau_c^- \approx \tau_c^0$ , only two cases are known where definitely  $\tau_c^-$  (or  $\tau_c^+$ )  $< \tau_c^0$ , these solvents are ethylene glycol and glycerol (Ref. 71). In water there are many ions for which  $\tau_c^+, \tau_c^- < \tau_c^0$ , these are the so-called structure breaking ions.

#### RELATIVE TRANSLATIONAL AND ROTATIONAL MOTION

Relative translational motion of the solvent molecule with respect to the ion has already been discussed in conjunction with eq.(7). Rotational motion in the solvation sphere relative to axes given by the geometry of the complex may occur when the orientational forces are comparatively weak. This situation has been treated for a number of quadrupolar ionic nuclei in organic solvents as mentioned in section "Nuclear Magnetic Relaxation Times" (Ref.56). Another type of relative rotational motion appears and has been studied when the solvent molecules have methyl or ethyl groups which are able to rotate more or less freely. The difference of these internal motions in the bulk and in the solvation sphere have been investigated for  $Li^+$  (Ref. 74),  $Ca^{2+}$  and  $Mg^{2+}$  salts in methanol and ethanol (Ref. 75).

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