Dielectric Absorption and ESR Results on the Relaxation of some Manganese Complexes in Organic Solvents *

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The limiting models — rotational or fluctuational process — for electron spin relaxation of Mn^{2+} in solution are discussed by comparison with dielectric correlation times. Free (solvated) ions presumably relax by the fluctuational, ionic complexes with static zfs by the rotational process. The latter conclusion requires the spectral density function to be more flat than the Debye function.

The ESR linewidth of ^6S transition metal ions in solution is governed by stochastic modulation of zero field splitting (zfs), represented by D and E in the spin Hamiltonian [1]. The parameters D and E are due to axial and rhombic distortions of the electric ligand field symmetry, respectively, and are expected to vanish for cubic symmetry. Since there is no other interaction process contributing significantly to the linewidth (at least at room temperature), ^6S ions are sensitive probes to the dynamical processes in their neighbourhood causing relaxation by certain spectral components of the fluctuating ligand field. The limiting cases are: a) Stochastic modulation of zfs by rotational tumbling of a complex exhibiting static zfs, that means a complex of distorted ligand field symmetry which is quasi rigid for times in the order of T_2 (typically 100 ps); b) stochastic modulation of zfs by transient fluctuations in the ligand shell, while mean zfs is vanishing. These mechanisms, referred to as rotational and fluctuational process, respectively, are not distinguishable from ESR results alone, since no differences in lineshape are expected, whatever the relaxation process will be. By variation of parameters such as temperature or viscosity, it was attempted to get information on the dominating process. Especially with the Mn^{2+} ion in dilute solution, many results fit to the assumption of the rotational process [2–6], although, looking on the presumed symmetry of a hexasolvated ion, the fluctuational process should be preferred. A decision on the dominating process, if possible at all, is not yet reached. To further elucidate its nature, dielectric absorption results may be helpful, since dielectric relaxation is mostly due to rotational processes. Thus, in the following, correlation times as derived from ESR spectra will be compared with rotational correlation times as evaluated or estimated from dielectric measurements. Furthermore, conclusions will be drawn not only from results on solvate complexes but also from ionic complexes, using both ends of the conductivity range to get as unambiguous conditions as possible.

Solvate Complexes

On sufficient dilution, the ESR spectra of manganous salts dissolved in organic solvents in some cases are merely due to free ions, meaning ions not involved in complexes with counterions but only in solvate complexes, with assumed coordination number 6. Spectra of several solutions show slight deviations from the expected shape, indicating additional species, yet are mainly due to free ions [6]. Altogether, 11 solvents as given in Fig. 1 have been used to derive free ion ESR linewidths. If the hyperfine lines are not completely resolved, the linewidth may be calculated with sufficient accuracy from the degrees of meandering and of sloping [6]. All measurements are made at room temperature.

From X and Q band linewidths, the zfs parameter $\Delta = (\frac{2}{3} D^2 + 2 E^2)^{1/2}$ and the correlation time τ_{XQ} are derived, using the results of Redfield theory calculations [1, 7] and presupposing a Deby spectral density function

$$J_1(\omega) = \frac{\tau_{XQ}}{1 + \omega^2 \tau_{XQ}^2} . \qquad (1)$$

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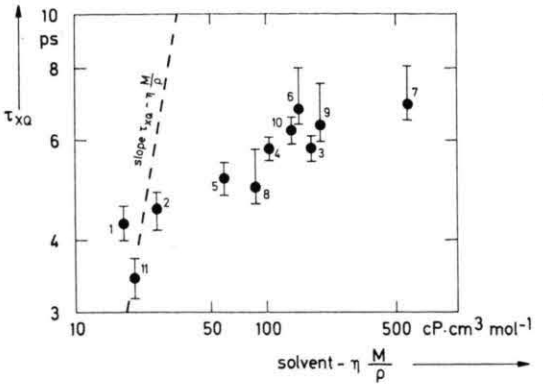

Fig. 1. Apparent correlation times τ_{XQ} of free Mn^{2+} ions vs. mole volume × viscosity. Solvents: 1 water, 2 methanol, 3 formamide, 4 methylformamide, 5 dimethylformamide, 6 diethylformamide, 7 ethylacetamide, 8 dimethylacetamide, 9 diethylacetamide, 10 dimethylsulfoxide, 11 acetonitrile.

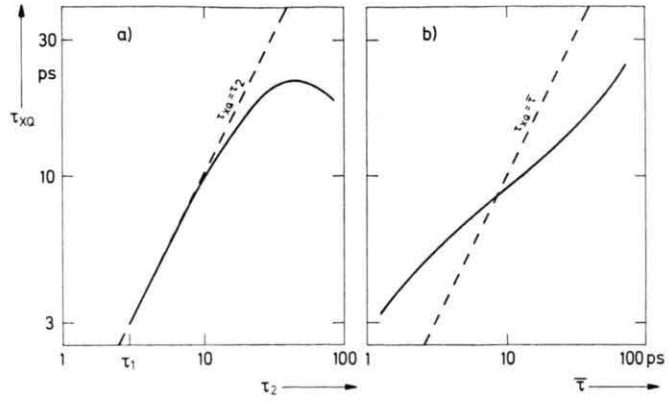

Fig. 2. Relation between apparent τ_{XQ} and model correlation times. a) according to Eq. (4), τ_1 (e. g. fluctuational) fixed, τ_2 (e. g. rotational) variable, $w_2/w_1 = 10$. b) according to Eq. (5), $p = 3$.

Previous work [6] has already shown that the X band linewidths of free ions depend on the solvent viscosity in a nonlinear manner. Now, similar results are obtained for the correlation time τ_{XQ}:

$$\tau_{XQ} \approx k \eta^{\varkappa}, \qquad (2)$$

here with $\varkappa \approx 0.5$ (η: solvent viscosity; k is solvent independent). Obviously, Eq. (2) is an approximation, and the results might also be fitted to another nonlinear relation. Figure 1 shows τ_{XQ} vs. $\eta M/\varrho$ instead of η, but this does not cause a qualitative modification of the plot, except of giving now a logarithmic slope of about 0.2.

Assuming the rotational process as predominant, Eq. (2) means that the Debye relation sometimes used,

$$\tau_{rot} = \frac{4 \pi r_{eff}^3}{3 k T} \eta, \qquad (3)$$

does not hold. This is also found by other methods investigating rotational motions, e. g. of polar molecules [8, 9] or of free radicals [10]. Nevertheless, it can not be concluded from the observed nonlinear dependence that the rotational model might be favoured. The results as given in form of Eq. (2) merely indicate that relaxation may be described as an activated process whose activation enthalpy differs by a factor $\varkappa$ from the activation enthalpy of viscous flow. Likewise one may easily develope suitable fluctuation models. Supposing the fluctuations to be caused by molecular collisions, the quantity given in the abscissa of Fig. 1 may serve as a simple model correlation time [11].

It is well known that the rotational correlation time increases in any way with increasing complex radius r_{eff}. Since the assumption of a quasi rigid complex is inherent in the rotational model, a r_{eff} dependence of τ_{XQ} is expected in addition to the η dependence. The solvent molecules used differ in diameter by a factor up to 2.2, resulting in hexasolvated complexes of different radii. Nevertheless, the results, given in Fig. 1 for these Mn^{2+} complexes, do not at all exhibit a marked dependence on the complex radius, but are rather similar to the results on $FeCl_4^-$ [12], which is a complex of solvent independent radius.

Finally, the absolute values of τ_{XQ} should be compared with rotational correlation times τ_{rot} to be derived from dielectric results. Since solvate complexes are expected to be dielectrically ineffective, τ_{rot} will be *estimated* from the radius of a hexasolvated complex and from solvent viscosity, using an empirical relation for dielectric correlation times τ_D [8] instead of Eq. (3), and taking $\tau_{rot} = \tau_D/3$. The estimated values agree with those observed if r_{eff} is not too large, as in solvents of moderate molecular size, but they are orders of magnitude longer than observed if r_{eff} becomes larger. Only if complete hydration is assumed, estimated and observed correlation times appear to agree, but with the possible traces of water in the solvents this is not very likely, as known from measurements in water solvent mixtures [6]. Thus, although the rotational model describes to some extent the relaxation in solvents such as water, methanol or acetonitrile, its

applicability seems to be somewhat accidental. In general the dominating relaxation process of free Mn^{2+} ions should be described by the fluctuational model. This conclusion is further supported by the simultaneous observation of fluctuation induced magnetic *and* dielectric relaxation in manganese acetylacetonate [13] with a correlation time of about 5 ps, which is in the region of the τ_{XQ} values mentioned above.

Ionic Complexes

Less uncertainty on the dominating relaxation process should be expected from complexes exhibiting static zfs, e. g. complexes including counterions, or, in a general sense, ion pairs. Since they may have a permanent electric moment, immediate comparison of measured magnetic and dielectric correlation times will be possible. Ion pair species are common in manganous salt solutions. For a straightforward evaluation, however, one definite species, as found in solutions of very weak conductivity, must be selected.

As an appropriate example, the complex formed by manganous nitrate in dioxane may be considered. From its dielectric absorption spectrum [13], it may be approximately described as consisting of two nitrate ions in *trans* position, some water and further dioxane molecules around the manganese ion in the first (at most second) coordination sphere. This complex is stable for times longer than the dielectric correlation time, that is longer than 300 ps. Structural details are of no further interest since, considering the relaxation problem, only any definite complex is needed.

From the ESR spectra of this complex, a correlation time $\tau_{XQ} = 18$ ps is obtained. Since the theory may not be strictly valid in this region, this value may be somewhat uncertain but will be of the right order. The zfs parameter ($\Delta = 600$ Oe) is markedly greater than for free ions ($\Delta = 175$ to 225 Oe. increasing with increasing solvent molecule size), once more indicating static zfs.

From dielectric absorption, on the other hand, a rotational correlation time $\tau_{rot} = 105$ ps is obtained [13]. Thus, by comparison with τ_{XQ}, the rotational process seems to be unlikely for magnetic relaxation.

However, it must be emphasized that the magnetic results are based on measurements at only two frequencies, which is the minimum to derive a correlation time at all. Therefore, one only gets an apparent correlation time called τ_{XQ}, presupposing the Debye spectral density according to Eq. (1). Now, if the two limiting relaxation processes would, for example, work together via the same interaction, the spectral density in the fast exchange limit would be

$$J_2(\omega) = \sum_{1,2} w_i \frac{\tau_i}{1+\omega^2 \tau_i^2}, \qquad (4)$$

with the weights $w_1 + w_2 = 1$. This somewhat peculiar assumption is nothing but a purely formal way to construct a flattened spectral density function. For a rotational process, there is strong evidence of such a flattening from the dielectric results, since these must be described in terms of a correlation time distribution. Adopting from there the more realistic Fröhlich distribution function [14], the spectral density would be

$$J_3(\omega) = \frac{1}{\omega p} \arctan\left(\frac{2\omega\bar{\tau}}{1+\omega^2\bar{\tau}^2} \sinh\frac{p}{2}\right) \qquad (5)$$

instead of Equation (1). This distribution is rectangular on a logarithmic time scale between the correlation times τ_1 and τ_2, the distribution parameter being $p = \ln(\tau_2/\tau_1)$, while $\bar{\tau} = (\tau_1\tau_2)^{1/2}$. Equation (5) is advantageous in being compatible to the picture of relaxation as an activated process. More complicated distribution functions often show no alterations of experimental relevance [15]. Appropriate stochastic time functions may be constructed using the pulse model [16].

The consequence of a flattened spectral density is a shift of the apparent τ_{XQ} from the "real" τ towards the picosecond range, that is the range inspected by the two ESR frequencies. Both, Eq. (4) as well as Eq. (5),, may be fitted to give agreement between τ_{rot} and τ_{XQ}. Demonstrative examples are shown in Fig. 2 from a simplified calculation, assuming the ESR linewidth as solely proportional to $J(\omega)$. Consequently, the ionic complex relaxation conceivably may be dominated by the rotational process, provided the spectral density function is flattened in any way. For further information on its shape, however, ESR measurements at more frequencies are required.

Returning to free ions, the assumption of a flattened spectral density will give a somewhat larger $\varkappa$ value, but the conclusions drawn in favour of the fluctuational process, as generally dominating in this case, will not be affected.

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