Electron Spin Resonance of Manganese Nitrate in Diethylacetamide-Water Solution

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At small water concentrations, ESR spectra at room temperature exhibit distinguishable contributions which are ascribed to the following ionic species: (I) a small fraction of residual manganese ions with mixed amide-water solvation, (II) amide solvated ions (having altered hyperfine splitting and *g*-factor due to nitrate in an outer coordination sphere, so that they may be considered loose ion pairs), (III) tight ion pair species. Presumably, (II) and (III) are not well defined "chemical" species but constituents of fluctuating aggregations.

Introduction

Electron spin resonance (ESR) spectra of manganese salts in various organic solvents show comparatively seldom the well known six line spectrum of the Mn^{2+} ion in a form which is simple enough to be attributed to one certain ionic species. Due to additional species or else complicated relaxation processes, one often finds broad background signals [1]. Investigation of these spectral features can contribute to our knowledge of the structure and dynamics of electrolytic solutions. Unfortunately, broad background signals mostly elude detailed discussion since they are too weak to be well separable from the main signal. In this paper we examine an example showing an exceptionally intense "background" signal, in the hope of obtaining information about its origin. The system in question is tetrahydrated manganese nitrate, $Mn(NO_3)_2 \cdot 4\,H_2O$, dissolved in N,N-diethylacetamide (DEA).

From preliminary results it was known that the ESR spectral features of this system depend on the water content of the solution. Therefore the water concentration will be chosen as main experimental parameter. In this connection it should be mentioned that amide-water mixtures, in general, show remarkable nonlinear variations of several properties with composition, e. g. of the viscosity [2] and of the dielectric constant [3]. Solutions of electrolytes in those mixed solvents have properties such as conductivity which reflect to a certain extent the solvent properties [4]. In our special case, the apparent ESR linewidth of Mn^{2+} in DEA-water mixtures behaves in quite an analogous manner (Figure 1). However, the linewidth maximum, as with other solvent mixtures, is not completely explainable as the result of the viscosity maximum of the solvent. Like the corresponding conductivity effect [4], it further may reflect the diversity of mixed solvation states [5]. Nevertheless, in the range of the linewidth maximum and on the water rich side the spectrum is "normal" so far as a detectable background signal is lacking. It is not this region we want to consider in the following, but the "anomalous" spectral shape associated with a broad back-

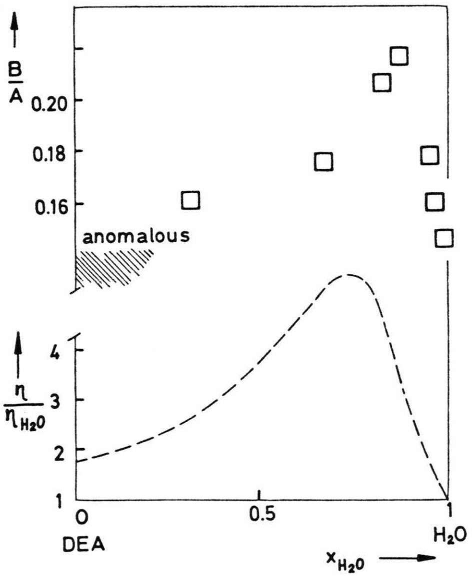

Fig. 1. Apparent Q band linewidths B (relative to hyperfine splitting A) of 1.0×10^{-2} mol/l manganese nitrate in DEA-water mixtures (room temperature). — Relative viscosity η/η_{H_2O} of the mixed solvent (20 °C).

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ground signal, which is observed in the DEA rich region only.

Experimental

Manganese nitrate (Merck) was used without further purification after partial drying by different methods, the choice of which did not influence the ESR results. Diethylacetamide (Merck-Schuchardt) was purified by vacuum distillation. Solutions were prepared under dry air or nitrogen in a glove box, where ESR sample tubes could be filled and sealed, too.

Freshly prepared solutions were used. Moreover, we made sure that storage in dark bottles for a few days had no effect on the ESR results.

The water content of each solution was determined by Karl Fischer titration.

ESR spectra were taken at X and Q band by means of several spectrometers. At Q band, with a few exceptions, a Bruker B-ER 420 Q was employed. For calibration purposes, we used the free radical Bis-diphenylene-phenyl-allyl (BDPA) [6]. At Q band, it is advisably used as internal standard. Those solutions, however, were regarded further only when comparison with radical free solutions indicated that the spectra were not influenced by ion-radical interactions to any considerable degree.

All measurements were made at room temperature.

Results

X band spectra, at low water concentrations, consist of a weak sextett superimposed on a structureless, broad line centered at $g \approx 2$. This is the otherwise so called background which in the present example gives the main contribution to the signal. The broad line is slightly asymmetric, the high field side having the steeper slopes. The low field wing extends in almost linear manner to about half the resonance field. This overall lineshape cannot be described in terms of discrete, though overlapping, hyperfine lines of any simple (e. g. Lorentzian) shape. It is noteworthy that the overall shape (in case that no more than roughly the hydrate water of the salt is present) is practically independent of the salt concentration from the lowest measurable one (some 10^{-2} mol/l) up to about 0.7 mol/l, whereby the intensity increases proportional to the salt concentration. The total intensity, as obtained after double integration, was compared with that of other salts in the same or in several other solvents, indicating that within an experimental error of about 20 percent the complete spin population is observed. A quantitative quotation of all these features seems to be somewhat uncertain, so we retain X band spectra for occasional comparison with Q band spectra, while detailed results will be given in particular for the latter.

Q band spectra of dilute manganese nitrate solutions (meaning concentrations below 0.1 mol/l) show a structure which obviously results from the superposition of two, more or less resolved sextetts. Figure 2 gives a representative example. These spectra can satisfactorily be simulated (Fig. 2) at all investigated water concentrations by assuming two spectral components (I) and (II) as follows. Each component is a sextett of equidistant Lorentzian lines (hyperfine splitting A_i), having equal intensities and equal widths B_i. (The expected differences of individual hyperfine lines may be concealed owing to the relatively broad lines involved.) The relative intensities of the two components are described by coefficients C_i as proportional to the respective spin population and to the concentration of a corresponding i-th species. The last simulation parameter is the distance δ of the spectral centers. From several independent simulation runs it was seen that $\Delta A/A_i$, B_i/A_i and δ/A_i may be reproduced within 5 percent or even better, while $C_i/\Sigma C_i$ is less

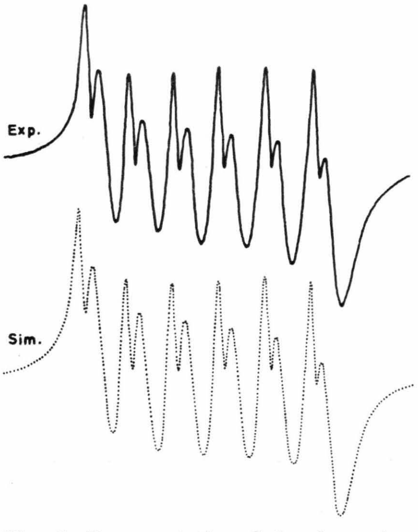

Fig. 2. Representative Q band spectrum of manganese nitrate in DEA; $c_{\mathrm{Mn}} = 1.0 \times 10^{-2}$ mol/l, $c_{\mathrm{H2O}} = 0.3$ mol/l. — Experimental (above) and simulated spectrum (below).

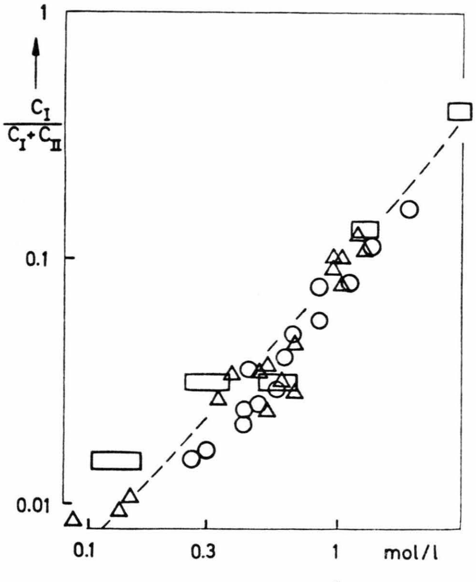

Fig. 3. Relative intensity of Q band spectral component (I) versus water concentration, according to simulation of experimental spectra. Salt concentrations c_{Mn}: □ 1.0×10^{-2} (water content only from preparation by weight), △ 1.4×10^{-2}, ○ 6.3×10^{-2} mol/l. Dashed line: Theoretical curve, see Eqs. (2), (3) and text.

reliable, having an uncertainty in the 20 to 40 percent range. In the following, Q band results will be given in terms of these parameters.

Figure 3 shows the spectral parameters C_i in the form of $C_I/\Sigma C_i$, as dependent on water concentration c_{H_2O}, for different salt concentrations c_{Mn}. The linewidths B_i depend on c_{Mn} but are independent of c_{H_2O} (however, a slight increase with increasing water content is possible within simulation uncertainties). The remaining parameters, A_i and δ, are practically constant in any instance, and so are the g-factors. The values of the parameters not yet given in Fig. 3 are:

$$\begin{array}{rlrlr} A_I = & 9.4\,\mathrm{mT}, & A_{II} = & 9.1\,\mathrm{mT}, & \\ B_I/A_I = & 0.12, & B_{II}/A_{II} = & 0.57, & (1.0) \\ & 0.13, & & 0.59, & (1.4) \\ & 0.17, & & 0.61, & (6.3) \\ & 0.21, & & 0.61, & (7.9) \\ g_I = & 2.002, & g_{II} = & 1.998. & \end{array}$$

(In parentheses, the respective salt concentration c_{Mn} is given in units of 10^{-2} mol/l.)

For the total intensity contained in the two Q band components together we have got only a rough estimate, according to which a fraction in the 50 to 60 percent range is missing at a salt concentration $c_{Mn} \approx 1 \times 10^{-2}$ mol/l in case of low water content. (This value is substantiated by comparison with manganese perchlorate spectra as mentioned in the discussion section.) The missing percentage increases with increasing salt concentration. Thus we have to assume a third component (III) with even broader lines, so that it is not displayed in the spectra considered here. However, respective broad wings are indicated in the (less resolved) spectra of higher concentrated solutions [1].

Discussion

The aim of the following considerations is to conclude from the observed ESR features on structures and, possibly, dynamics in the vicinity of the probing manganese ion. As well known, this undertaking may in general encounter several difficulties, which nevertheless should be briefly recalled.

First it may be a problem to decide if a somewhat complex spectrum is due to one uniform kind of relaxing structure, or if it is the superposition of spectra from different kinds. Whenever the decision seems to be straightforward since the spectrum is of simple (say Lorentzian) shape, another question may arise. The spectrum may be due to one distinct structure with long lifetime, which then can be called a complex or “chemical” species. On the other hand, it may as well result by time averaging from chemically non-equivalent, rapidly exchanging structures, thus comprising different transient species. The chemical exchange process, in this case, appears equivalent to the physical relaxation mechanisms operating without that. Since averaging times are to be compared to the respective transversal relaxation times, it may happen that at Q and X band apparently different species are observed.

Furthermore, by consideration of the concentration dependence of spectral parameters (as in the following), one recognizes exclusively those constituents of a complex which are not only concentration dependent but do moreover affect the parameters in question. Therefore, species deduced from mere ESR results should in general be considered virtual species, representing the pith but not always the whole of a complex.

Q Band Nitrate Spectra

The two superimposed spectral components of these spectra are reasonably ascribed to two distinct species. A third species, though "unseen" in dilute solutions, is to be taken into account. These presupposed complexes will now be discussed with respect to their water dependent equilibrium, making in particular use of the intensity parameters C_i.

Beforehand a remark upon the concentration dependence of the linewidths, since this is not material to the following considerations. The increase with salt concentration, though clearly different for both species, is roughly in the order of average dipole broadening as usually found. A possible slight increase with water concentration would be attributable to the viscosity increase.

The spectrum of species (I) resembles that of manganese ions in other solvents, where they exist with pure or mixed solvation, but in any case without complexation to counterions. Therefore it is reasonable to consider species (I) as such a "free" ion. One gets a hint on the composition of its (probably mixed) solvation shell by regarding the excess linewidth over the whole mixture range of Figure 1 [5]. Another hint is given by the Walden product which, decreasing while going towards the DEA rich side, reaches a shoulder or (in case of lower salt concentrations than those used for the ESR measurements) even a plateau before the region of anomalous ESR. From both considerations it becomes likely that the solvation shell of species (I) contains already a majority of DEA molecules, together with less or even no water molecules.

Concerning the remaining two species we have to reckon with the nitrate ion, since spectral features as in the present case are not observed with other salts. Species (II) may contain the NO_3^- ion besides solvate molecules of both kinds. With respect to nitrate, the third species must succeed to the second, since its intensity increases with increasing salt concentration. For simplicity it is anticipated as water free. Thus we have to consider a minimal set of three species in equilibrium:

$$\begin{array}{cccccc} & MN_mL_i & \rightleftharpoons & MN_nL_jH_a & \rightleftharpoons & ML_kH_b\,, \\ \text{DEA} & (\text{III}) & & (\text{II}) & & (\text{I}) \quad H_2O\,, \end{array} \qquad (1)$$

where $M = Mn^{2+}$, $N = NO_3^-$, $L = \text{DEA}$, $H = H_2O$. Here, species (I) may represent the last member of a series of free ions in mixed solvation states, which all are presupposed to exhibit regular spectra. Those subsequent species are neglected for the moment since they will not contribute any distinctive spectral feature and will, moreover, represent only a minor fraction in the case of small water concentrations.

The stoichiometric coefficients of (1), except the L-coefficients, can be obtained from the concentration dependence of relative intensities C_i shown in Figure 3. With that we should go into some detail to give evidence that the coefficients in conclusion are unambiguous if only integer numbers are allowed.

The experimental results of Fig. 3 are sufficiently accurate to establish a linear relationship (as contrasted with a conceivable quadratic or higher power one) in the range of small water concentrations. This finding, in the first instance, allows for estimation of the water coefficients a and b.

The experimental $C_\text{I}/(C_\text{I}+C_\text{II})$ is to be compared to the theoretical concentration ratio $c_\text{I}/(c_\text{I}+c_\text{II})$. The limiting behaviour of the latter is paralleled by that of the fractional concentration $x_\text{I} = c_\text{I}/(c_\text{I}+c_\text{II}+c_\text{III})$, which may be regarded for a first view since it is more easily assessable. The dependence of x_I on water concentration, in the limit of small water content, is unaffected by the choice of coefficients n and m but depends on the water coefficients a and b only. A linear relationship occurs for $a = 0$, $b = 1$, whereas higher power laws are obtained for all other a, b combinations. Thus, species (I) still contains solvate water. Species (II) and (III), on the other hand, are the complexes to be expected in water free DEA solution.

To obtain now information about the number of involved nitrate ions (n and m), it is inevitable to pay regard to the influence of salt concentration. With respect to this, the possible n, m combinations are to be arranged in two groups, according as $n = 0$ or $n = 1$. In each group one may give prominence to the case $m = n + 1$ which corresponds to a one ion step in complex formation. Having regard to the adequate concentration ratio $c_\text{I}/(c_\text{I}+c_\text{II})$ instead of x_I, we first consider the $n = 1$ case. This is the case coming forcibly into mind since such anomalous ESR features as component (II) are only observed in the presence of nitrate.

In the $n = 1$, $m = 2$ case, x_I as well as $c_\text{I}/(c_\text{I}+c_\text{II})$ decrease with increasing salt concentration, which, in contrast, is not evident from the experimental results (Figure 3). Other than the x_I reduction, the reduction of $c_\text{I}/(c_\text{I}+c_\text{II})$ is the less pronounced the more substantial the fractional concentration x_III is.

If the expected decrease should be concealed in Fig. 3 owing to errors, we must take into account higher uncertainties than those quoted before. If so, the results (within their limited range of salt concentration) could just be consistent with the above coefficients, provided that $x_{III} > 0.5$. To come to a decision, we have investigated a few solutions of higher concentrations, which again give points within the scatter of Figure 3. Thus, $C_I/(C_I + C_{II})$ is practically independent of salt concentration. This finding rules out the nitrate coefficients under consideration as well as all other combinations with $n = 1$.

In the $n = 0$, $m = 1$ case, on the other hand, $c_I/(c_I + c_{II})$ becomes almost independent of the salt concentration, provided that the stability constant of (III) is not too small. Consequently, these coefficients can be consistent with all results. The same will hold for $n = 0$, $m = 2$. A decision in favour of one or the other composition of the anyhow "unseen" species is not needed. Conductivity data, however, do not force the assumption of an uncharged species (III), so we adhere to $n = 0$, $m = 1$ (not excluding the possibility of a subsequent uncharged species in addition).

The remaining solvent coefficients i, j and k cannot be deduced from ESR results in the same manner. Since optical absorption exhibits the bands typical for hexacoordinated manganese, they may be chosen accordingly. Thus we arrive at the equilibrium

$$\underset{\text{(III)}}{MNL_5} \rightleftharpoons \underset{\text{(II)}}{ML_6} \rightleftharpoons \underset{\text{(I)}}{ML_5H}\,, \tag{2}$$

with that bounding the virtual complexes by the first coordination sphere.

A quantitative example may illustrate the applicability of this model to the description of Q band intensity results as presented in Figure 3. For this purpose we assume species (I) to comprise an additional solvation state and consider, instead of (I) in Eq. (2), now:

$$\underbrace{\underset{\text{(Ia)}}{ML_5H} \rightleftharpoons \underset{\text{(Ib)}}{ML_4H_2}}_{\text{(I)}}\,. \tag{3}$$

For individual stability constants $K_{Ia} = 0.25$ and $K_{II} = 2$, the theoretical $c_I/(c_I + c_{II})$ curve (holding good for any investigated salt concentration) is given in Figure 3. Those K values are arbitrary to a certain degree. Provided that $K_{III} \gtrsim 10$, the curve is not influenced by that value, which can be chosen as $K_{III} = 800$ to yield $x_{III} = 0.58$ to 0.50 (within the c_{H_2O} range of Fig. 3) for $c_{Mn} \approx 1 \times 10^{-2}$ mol/l, that is roughly the value found experimentally.

In view of the possibility that fast exchange might occur, one should also allow for non-integer coefficients. This could be relevant to species (II). However, assuming a MN_xL_6 species we find that $x < 0.1$ to 0.2 is required for consistency with experimental results.

We resume that Q band spectra can be interpreted in terms of virtual species exhibiting a well defined stoichiometry. One might hope to obtain more information about their structure and dynamics by comparison of Q with X band spectra, supposing that they are recognizable at X band as well.

X Band Nitrate Spectra

Electron spin relaxation of Mn^{2+} in solution is believed to be generally governed by fluctuations of the zero field splitting (Zfs) tensor, as described by the correlation time τ as dynamical parameter, and by the mean Zfs parameter $\Delta^2 = (2/3)D^2 + 2E^2$ as geometrical parameter. Both parameters can in principle be obtained from comparison of X and Q band spectra. Their estimation should be possible even in the present case of broad X band lines by considering the latter in the aspect of slow motion peculiarities. Slow motion spectra tend to become asymmetric with increasing τ and increasing Δ^2 [7], and beginning asymmetry, as discernible in the present case, indicates that $\tau D^2 \approx \omega$ [8]. Furthermore, E may be considered according to the tendency of asymmetry [8, 9]. The Q band linewidth, on the other hand, gives a second relation to τ and Δ^2 from fast motion theory [10] which is applicable in that case. Thus, an estimate of the characteristic parameters τ and Δ^2 of any relaxing species should be accomplishable.

A treatment along these lines needs a clear discrimination of related spectral components. In view of the intensity results mentioned above, the broad part of the X band spectrum is expected to comprise Q band components (II) and (III). However, its corresponding decomposition is by no means self-evident. More so, if one regards merely the broad X band line it seems questionable wether it must necessarily be ascribed to different kinds of relaxing species at all. In the following, we shall briefly discuss the broad line from different points of view, as due to one, or two, or two exchanging species.

Put the case that the total intensity measurements at X as well as Q band are extraordinarily erroneous, then the broad X band line could possible stem from one species only, e. g. from (II), while (III) could again be "unseen". One estimates then parameters $\tau \approx 100$ ps and $|\Delta| \approx 100$ mT for species (II). Those values can scarcely be due to a purely solvated ion species, as presupposed. Comparable correlation times in other solutions are without exception shorter than 10 ps [11]. After all, this one species case may be disregarded.

Returning to the supposition that both Q band species contribute to the broad line, one may first consider a superposition of two components with different but roughly invariable shapes. Attempts failed to apportion experimental spectra into those components in a manner consistent with the Q band intensity ratios, which is not surprising in view of the concentration independent features. On the other hand, any constant intensity ratio would be agreeable, but then we cannot adhere to the stoichiometry of Eq. (2) but have to consider instead of (II) a modified species ($\mathrm{II}_{\mathrm{mod}}$) containing nitrate to the same amount as species (III), though in a different state, thus in an outer coordination sphere. This would mean that at X band, in contrast to Q band, we observe virtual species bounded by the second coordination sphere at least.

As a consequence of demanding the concentration ratio of both species to be roughly invariable, those species with the same MN gross composition should be the vast majority among all "enlarged" complexes. This in turn requires that the X band bounds of the virtual species are such as to enclose most probably a nitrate. Accepting this hypothesis for the moment, we have to assume that nitrate in an outer coordination sphere is fluctuating rapidly enough to appear as quasi free at Q band. For this the characteristic time is in the order of $T_2(\mathrm{II}, \mathrm{Q}) \approx 1$ ns.

We have referred before to the finding that the broad line shows no significant dependence of its shape on salt concentration. This is in contrast to the usual solution behaviour where dipole broadening becomes effective at concentrations as used here. From a general point of view this observation means that, within the sample volume, there exist domaines enclosing a certain number of spins, which yield an invariable spectrum due to inner domain relaxation processes, while apart from this the domains are relaxing independently from each other.

Though an unambiguous interpretation of X band spectra is missing so far, we get altogether evidence that we do not observe as small virtual species as at Q band, but some sort of outer sphere interaction with nitrate, bringing about enlarged virtual species. Furthermore, domains or aggregations are presumable, including spins in the form of species ($\mathrm{II}_{\mathrm{mod}}$) and (III).

Finally, exchange between both species e. g. by in-out fluctuation of nitrate may be considered, which possibly leads to a uniform spectrum. An appropriate mechanism should work via different *g*-factors of both species, which could account for exchange effects observable at the lower X band but not yet at the higher Q band frequency. The characteristic times are in the order of $1/\Delta\omega$. Taking, for example, the regular spin only value for the (unknown) *g*-factor of (III), this gives about 10 ns at X band, which would be compatible with the fluctuation time of nitrate in the outer region as estimated before. A more quantitative consideration, however, should imply detailed knowledge of species (III) spectral parameters.

Perchlorate Spectra for Comparison

In substantiation of the "anomalous" character of these findings, we make reference to the only salt exhibiting a comparatively "regular" spectrum in DEA (resembling, as standard example, spectra of aqueous solutions), that is manganese perchlorate. In the classification scheme of Ref. [5], its X band spectrum is a sextett of type B (Fig. 3 therein), meaning that the hyperfine lines must formally be described by broader than Lorentzian wings. Nevertheless the spectrum may be attributed for the most part to "free" ions.

The Q band spectrum is a well resolved sextett which only on accurate examination reveals that the hyperfine lines are again of non-Lorentzian shape. Now X as well as Q band spectra can consistently be simulated by assuming a superposition of two spectral components, in such a way covering the total intensity. The respective Q band linewidths are very close to those of components (I) and (II) of the nitrate, and the two species distinguishable in perchlorate solution seem to be of the same kind as considered for the nitrate solution, viz. solvate complexes (I) $= ML_5H$ and (II) $= ML_6$, while an ion pair species is negligible. Using the fast motion theory of linewidths [10], one gets the following (only roughly estimated) parameters: $\tau_I \approx 6$ ps, $|\Delta_I| \approx 20$ mT, and $\tau_{II} \approx 3$ ps, $|\Delta_{II}| \approx 40$ mT. The values for (I) are similar to those found in other solvents [11] and can be ascribed to fluctuations in the solvate shell as dominating relaxation process rather than to a rotational motion. It is remarkable that the values for (II) indicate a faster and more serious distortion of this pure DEA solvate complex.

So far, the perchlorate results support the model developed for the nitrate solutions. As differences the following facts are to be mentioned. First: Though for components (II) of nitrate and of perchlorate the linewidths at Q band are found similar, at X band a nitrate component corresponding to perchlorate cannot be ascertained. Second: The (I) – (II) equilibrium is different for comparable nitrate and perchlorate solutions, species (II) being preferred in the nitrate case. Third: Both perchlorate species have equal splittings, $A_I = A_{II}$, and equal g-factors, $g_I = g_{II}$, while these quantities are different for both species in the nitrate case.

The first and second item become explainable if nitrate species (II) (in contrast to the corresponding perchlorate species) should in fact be a loose ion pair. This may be demonstrated for the first item. As mentioned before, the nitrate must be supposed to fluctuate sufficiently fast in the outer coordination region. In view of the similarity of Q band linewidths, it must additionally be supposed to have only minor influence on the Q band linewidth but, on the other hand, appreciable influence on the X band linewidth. This may happen under the following circumstances. Assume that the presence of nitrate does not affect the Zfs parameter Δ^2 (since mainly due to the first coordination shell), but influences the correlation time τ of solvate fluctuations (which are supposed to be the dominating relaxation mechanism). Since the dynamical factor in the linewidth expression reaches a maximum for $\tau \approx 1/\omega$, the attachment of nitrate will have little influence on the Q band linewidth if by accident $\tau \approx 1/\omega(Q) \approx 4 \ldots 5$ ps. This condition is approximately met by the value $\tau_{II} \approx 3$ ps as estimated before. An increase of τ_{II} due to nitrate would nevertheless be observable at X band by a substantial linewidth increase.

Concluding Remarks

Concerning the third item, let us consider once more the Q band features of species (II). If one accepts its initial description as DEA solvated manganese ion and gives fullest consideration to the A and g alterations as observed with nitrate in contrast to perchlorate, then these alterations must again be described as an outer coordination sphere ion pair effect. Generally spoken, A and g are due to an appreciable extent not only to nearest but also to further neighbours of the manganese ion in solution.

Looking for similar examples one notices that anomalous parameters A and g are observed only exceptionally with electrolytic solutions. There is a first group of examples, tetrahalogeno complexes with normal g but substantially reduced hyperfine splitting, $A \approx 8.0$ mT [12 – 15]. A second group comprises several complexes with nitrogen containing ligands. They mostly show normal g, and a less pronounced but obvious reduction of hyperfine splitting, $A \approx 9.2$ mT [12, 13, 16]. Among these, there is an example with decreased g (≈ 1.998) in addition, which was ascribed to $Mn(NCS)_2(MeOH)_4$ [13]. These A and g values are similar to the present findings.

With respect to the structure of complexes in solution, small alterations of g may be not very significant since they may be caused by their dynamics as well [7]. Alterations of A, on the other hand, seem to be more informative, since from solid state examples it is known that A is correlated to certain complex properties. Decreasing A is generally assumed to indicate increasing covalency [17], the highest ionic character corresponding to about $A \approx 10$ mT [18]. Furthermore, A tends to decrease with decreasing ligand distances [19].

Those examples, however, are not appropriate to the present problem as far as they reflect essentially the influence of nearest neighbours. We feel that A and g values as found here for species (II) at Q band, might be altered by changes in the surrounding solution without affecting the possibility of discriminating that special species again. On the other hand, for the investigated nitrate solutions we could make use of constant A and g values at all salt concentrations. In return, this may be taken as hint on the formation of certain aggregations, which moreover would allow to understand the A and g alterations as cooperative effects.

To complete the microscopic picture one may imagine that a hexasolvated manganese ion, presumably from reasons as the size of the DEA molecules, is rather an unstable, intensely fluctuating configuration, as indicated by the perchlorate results. In the presence of nitrate a specific interaction occurs which is leading to loose, fluctuating ion pairs (as concluded from X band results as well) and further to contact ion pairs, whereby the interaction is likely to promote the formation of aggregations.

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