

Magnetization Measurements on Iron (III) Solutions for Detecting Oligomer Formation

F. Rodríguez, M. Moreno, and J. C. Gómez Sal

Departamento de Optica y Estructura de la Materia. Facultad de Ciencias, Universidad de Santander, Santander, Spain

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By measuring the magnetization at low temperatures (near 1 K) and intense magnetic fields (≥ 100 KG), information about oligomer formation in ferric salts solutions can be obtained. It is shown that, under rather general conditions, the magnetic moment per ferric ion of a given ferric solution measured in the saturation regime should be equal to 5β if all the complexes involved in the solution are high-spin monomers. Moreover, if the solution is mainly composed by monomeric species and antiferromagnetic dimers, the relative concentration of monomeric and dimeric species can easily be determined. This technique has been applied to solutions of Cl_3Fe and $(\text{NO}_3)_3\text{Fe} \cdot 9\text{H}_2\text{O}$ in isopropanol as solvent containing about 0.4 M of water. In the first case the present measurements are consistent with the existence of dihydroxo ferric dimers suggested by previous Mössbauer and Optical Absorption data. The relative concentration of these dimers increases from 25% to 50% when the water content increases from 0.4 M to ~ 10 M. In the second case it is confirmed that the solution is mainly composed by oligomers, the relative concentration of monomeric species being less than 30%.

Introduction

Iron (III) solutions can form a large variety of species whose nature and concentration depend on temperature, pH, additives etc. [1–5]. Thus non-aqueous solutions of Fe^{3+} salts are strongly affected by adding water [6, 7]. A similar situation is encountered in the case of non-aqueous solutions of salts containing Al^{3+} and Be^{2+} [8, 9].

Some Iron (III) solutions are of special interest because they are useful etchants for revealing dislocations in ionic crystals [10, 11].

The characterization of a liquid solution is much more difficult than that of a pure crystal, and so several complementary techniques are needed for reaching reasonable conclusions about the nature and concentration of the involved species.

An important point to be ascertained in the case of Iron (III) solutions is the formation of dimers and oligomers. Traditionally, susceptibility measurements at or near room temperature have been used for this purpose [3, 4].

In fact if all ferric species present in a real solution were high-spin monomers having their first

excited state far enough from the ground state the susceptibility in the “high temperature” region should be practically equal to that corresponding to free Fe^{3+} ions. This is mainly because for high-spin ferric monomers the g factor is equal to $g_0 = 2.0023$ to less than 5%. In view of this, the deviations of the experimental susceptibility, $\chi(T)$, with respect to such a behaviour should be ascribed to the presence of dimers (or oligomers).

Besides its sensitivity this technique has some inconvenients. In this way if measurements are performed at room temperature the magnetic susceptibility of a dimer could be that of a monomer provided the high-temperature approximation be right for describing the dimer. In practice it means that if we have a dimer formed by two $S = 5/2$ ferric complexes coupled through the effective exchange interaction

$$J \mathbf{S}_1 \cdot \mathbf{S}_2, \quad (1)$$

its susceptibility at room temperature behaves like that of a monomer if J/K is lower than about 15 K.

Even if this situation does not occur and J/K lies between 20 and 100 K the interpretation of the room temperature susceptibility may be not simple unless we know the concentration of monomeric species by other methods, mainly because a dimer even with antiferromagnetic coupling gives a non negligible magnetic response at room temperature.

Reprint requests to Dr. M. Moreno, Departamento de Optica y Estructura de la Materia, Facultad de Ciencias, Universidad de Santander, Santander/Spain.

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Furthermore the interpretation of the $\chi(T)$ curve in the 273 K–373 K range can still be more difficult because the concentration of the involved species may undergo significant changes upon warming.

Owing to these reasons the interpretation of the susceptibility data of Iron (III) solutions containing dihydroxo dimers has been rather controversial. In this way Mulay and Selwood [3] assume that these species at room temperature are diamagnetic while other authors [4, 12] conclude that they behave as free monomers but having $S = 3/2$. The last conclusion is in fact very hard to believe in view of the results on several crystalline compounds containing dihydroxo dimers [13–15]. In fact these data reveal that the dihydroxo dimers can be understood as two ferric ions with $S = 5/2$ coupled antiferromagnetically through the exchange interaction (1) with J values lying between 14 and 25 cm⁻¹. On the other hand crystalline ferric compounds with $S = 3/2$ for the ground state are indeed very scarce [16] because they need the existence of a strong axial distortion which splits the two e_g levels of Fe³⁺ to a large extent.

The main goal of this paper is to show that the inconvenients of the susceptibility measurements at room temperature for obtaining a reliable information about the presence of antiferromagnetic dimers (or more complex oligomers) in Iron (III) solutions can be largely overcome by performing magnetization measurements with intense fields at low temperatures (near 1 K) which allow one to detect a “saturation regime”. The theoretical arguments on which this idea is founded are given in the next section while in the applications section two examples of the usefulness of such measurement are reported.

Theoretical

Let us assume that a given ferric solution is composed by several high-spin monomers in which only the ground state having $S = 5/2$ is responsible of the magnetic properties. Taking as a guide the case of a monomer with axial symmetry its corresponding spin-hamiltonian can be written as

$$\mathcal{H} = g_{\parallel} S_z H_z + g_{\perp} (S_x H_x + S_y H_y) + D (S_z^2 - 1/3 S(S+1)) + \dots, \quad (2)$$

where besides the Zeeman term an axial zero field splitting (ZFS) term has been written while other

smaller terms such as the rhombic ZFS term $E(S_x^2 - S_y^2)$, the cubic spin term or the hyperfine interaction have not been explicitly included.

As regards the experimental values of the g -tensor corresponding to monomeric ferric complexes it is found that both g_{\parallel} and g_{\perp} are very close to $g_0 = 2.0023$. This situation comes from the perfect quenching of the orbital angular momentum L for the free Fe³⁺ ion which anyway is slightly overcome in the case of ferric complexes due to configuration mixing with excited charge transfer states having $S = 5/2$ [17].

In this sense for instance the very covalent [FeCl₄]⁻ and [FeBr₄]⁻ complexes have a g -factor $g_{\parallel} = g_{\perp} = g$ whose value is 2.019 and 2.05, respectively [17]. Concerning the value of the D constant characteristic of the ZFS term it has been experimentally observed that for ferric complexes it is usually smaller than 5 cm⁻¹, lying typically in the range 0.05–2 cm⁻¹.

Owing to these values we come to the conclusion that if we apply strong magnetic fields, for which $g\beta H \gg D$, to a ferric monomer the magnetic moment per ferric ion in the saturation regime must be equal to 5β . This value of course is just that expected for a free Fe³⁺ ion.

Therefore, if it is experimentally found that the magnetic moment per ferric ion of a given solution is different from 5β it would prove that ferric oligomers are formed.

From this we can also derive a useful consequence for the analysis of chemical reactions induced by the variation of parameters such as pH, temperature or the addition of external ions. Let us assume that a ferric solution is formed initially by a set of high-spin ferric monomers. If in the course of the reaction only ferric monomers are formed then the magnetic moment per ferric ion should remain unchanged. Thus, if a variation of the magnetic moment per ferric ion in the saturation regime is observed we can conclude that oligomers have been formed in the course of the reaction.

The preent idea is valid under the following conditions:

1) All the monomers involved in a given solution must be high-spin monomers having $S = 5/2$ and with its first excited state lying at least 20 cm⁻¹ above the ground state. In practice Iron (III) complexes with ligands such as H₂O, OH⁻, oxygen, halides, etc. ... give rise to high-spin monomers. In

the case of O_h systems this can be easily understood taking into account the condition

$$10 D q \cong 28 B \quad (3)$$

which determines the crossing of ${}^6A_{1g}$ and ${}^2T_{2g}$ state [18] and using the values of $10 D q$ and the reduced Racah parameter B estimated by Jørgensen [19].

Anyway a low-spin situation is sometimes found for ferric complexes with ligands containing nitrogen.

2) If H_M denotes the maximum magnetic field attainable, then

$$g \beta H_M \gg D \quad (4)$$

in order to ensure that the magnetic moment of a monomer measured in the saturation regime is that of a free Fe^{3+} ion. If $D \lesssim 1 \text{ cm}^{-1}$, (4) is well fulfilled using magnetic fields $H_M \gtrsim 100 \text{ KG}$.

3) Of course for well detecting the "saturation plateau" the condition

$$KT \ll g \beta H_M \quad (5)$$

is necessary.

The advantages of the present technique with respect to susceptibility measurements at or near room temperature are mainly the following:

1) The sensitivity can be increased by a factor of about 10^3 , which allows one to study much more diluted solutions.

2) Antiferromagnetic dimers of Iron (III) with J values lower than about 500 cm^{-1} give a non negligible contribution to the susceptibility at room temperature, and in the case of $J \lesssim 15 \text{ cm}^{-1}$ the susceptibility per ferric ion at room temperature should be the same as that of a monomer. By contrast, measuring the magnetization at around 1 K, dimers with $J \gtrsim 3 \text{ cm}^{-1}$ should be *silent*.

Therefore in a given Iron (III) solution composed by monomers and antiferromagnetic dimers the present technique could be worthwhile for measuring in a very simple way the relative concentration of both monomeric and dimeric species provided the effective exchange constant J of dimers be higher than $\sim 3 \text{ cm}^{-1}$ if we work at a temperature near 1 K.

By contrast if in such experimental conditions the dimer exhibits ferromagnetic instead of antiferromagnetic coupling it should give a magnetic moment per ferric ion equal to that of a monomer. In such a case one could distinguish, however, a

dimer from a monomer looking at the behaviour of the magnetization curve at lower fields. It must be pointed out however that all Iron (III) dimers up to now studied in a crystalline compound exhibit an antiferromagnetic coupling [13–15].

It is worthwhile remarking here that Mössbauer spectroscopy is a useful technique for analysing Iron (III) solutions [1, 20, 21] and, in particular, for detecting the formation of oligomers. However by means of that technique it is not simple to say anything about the size of the oligomer or, in other words, whether it is a dimer or a trimer etc. ... As regards this problem the magnetization measurements may have some advantages over Mössbauer spectroscopy. In this way for instance a trimer involving an odd number of electrons cannot be magnetically silent as it happens for a dimer with antiferromagnetic coupling.

Experimental Section

The solutions studied in the present work were prepared using Merk products. Magnetization measurements were performed at the Service National de Champs Intenses (S.N.C.I.) at Grenoble (France), in fields up to 150 KG, the temperature range being 1.9–10 K. All the studied solutions were checked spectrophotometrically.

Applications

The first application is devoted to study a 0.2 M Cl_3Fe solution in isopropanol containing 0.4 M H_2O .

Previous results obtained through Optical Absorption (O.A) and EPR spectroscopy at room temperature indicate that about 55% of the ferric ions introduced as $FeCl_3$ give rise to $[FeCl_4]^-$ complexes in the solution [7, 22]. These complexes, however, are destroyed by a further addition of water, and so its concentration is negligible when the water concentration is higher than about 10 M. Optical Absorption data also reveal the formation of a complex containing two chlorines as ligands and whose concentration is favoured by addition of water [22]. We shall denote this complex as $FeCl_2L_4$ where L is likely to be H_2O or perhaps OH^- . The existence of complexes of this kind has been suggested in aqueous solutions of $FeCl_3$ [21, 23]. Finally the acid character of the solution as well as the O.A. data

[6, 7] strongly suggest the formation of Iron (III) complexes containing OH^- as ligands whose concentration is raised by a further addition of water. Moreover Mössbauer spectroscopy data on this solution are consistent with the formation of dihydroxo bridged ferric dimers in it [7]. It is worth recalling here that if enough Cl^- ions are added to the present solution all ferric ions are in the form of $[\text{FeCl}_4]^-$ complexes. This situation, which has been noticed for solutions of FeCl_3 in several non-aqueous solvents [24, 25], is achieved by adding HCl to a concentration higher than 1 M.

As regards the results obtained by means of the present technique they can be seen on Figure 1.

The first remarkable result is obtained when comparing Figs. 1a and 1b. In the latter case all ferric ions are in the form of $[\text{FeCl}_4]^-$ complexes and the experimental magnetic moment per ferric ion measured in the saturation regime is indeed equal to 5β . Moreover the experimental curve obtained at 4.2 K can be well fitted to a Brillouin function $B_{5/2}$. For this solution we have also carried out measurements at 1.95 K, 6 K and 10 K, and in every case the experimental magnetization fits well with a Brillouin function $B_{5/2}$.

Nevertheless the magnetic moment for ferric ion measured in the saturation regime for Fig. 1a is only 75% of that corresponding to Fig. 1b. This fact, which indicates that in the solution there are Iron (III) complexes which are not monomers, can of course be related to the presence of dihydroxo ferric

dimers in the solution as suggested by previous results, in particular Mössbauer data [7]. The present results can be easily understood assuming that the relative concentration of Iron (III) monomers in the solution is 75% while the remainder corresponds to silent dimers. It is worth recalling here that *all* ferric dimers up to now studied in a crystalline phase are antiferromagnetic with J values lying between 14 and 200 cm^{-1} [13–15]. The present results suggest that the dimer which is in the solution has a J value higher than 15 cm^{-1} .

The relative concentration of monomeric species (75%) determined in this experiment is in fact higher than that corresponding to $[\text{FeCl}_4]^-$ complexes (55%) derived from EPR data at room temperature [7, 22].

Therefore the present measurements would indicate that about 20% of the ferric ions give rise to monomeric species others than $[\text{FeCl}_4]^-$. In view of the O.A. data we can assign them reasonably to FeCl_2L_4 complexes.

The results shown by Fig. 1c can be understood assuming that upon further addition of water the concentration of dimers increases, and so when $[\text{H}_2\text{O}] \cong 10\text{ M}$ the dimer concentration is about 50%. Nevertheless in this situation there are still 50% of monomeric species. As pointed out before the O.A. and EPR results at RT indicate that in the present situation the concentration of $[\text{FeCl}_4]^-$ species (which dominate when $[\text{H}_2\text{O}] = 0.4\text{ M}$) is negligible and suggest that the main Iron (III) species present in the solution are the FeCl_2L_4 complex and ferric complexes with OH^- as ligands [6, 7, 22]. The magnetization measurements reported on Fig. 1c are consistent with this view and indicate that the relative concentration of dihydroxo dimers increases from 25% for $[\text{H}_2\text{O}] = 0.4\text{ M}$ to 50% for $\text{H}_2\text{O} \cong 10\text{ M}$. Furthermore, though the total concentration of monomers decreases when H_2O is raised from 0.4 M to 10 M, Fig. 1c is consistent with an increase of FeCl_2L_4 species in such a process if we take into account the destruction of $[\text{FeCl}_4]^-$ complexes due to water addition [6, 7].

Due to the possible existence of a significant ZFS term in the spin-hamiltonian which describes a ferric monomer the full magnetization curve has not to follow necessarily a Brillouin function $B_{5/2}$. Anyway, the best Brillouin function which fits the experimental magnetization curves reported on Figs. 1a and 1c is a Brillouin function $B_{5/2}$.

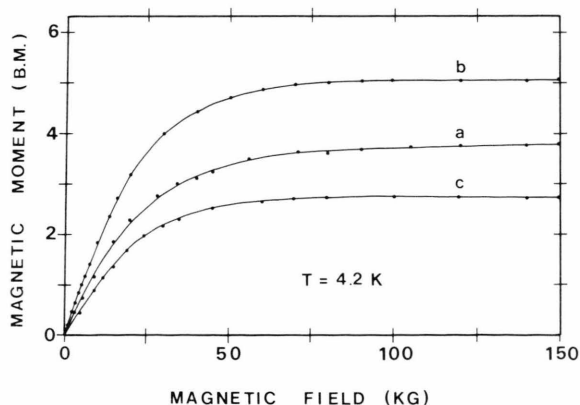


Fig. 1. Magnetic moment per ferric ion at 4.2 K vs. applied magnetic field. a) For a frozen solution 0.2 M Cl_3Fe in isopropanol containing 0.4 M of H_2O . b) For the solution described in a) to which 1 M of HCl has been added. c) For the solution described in a) but whose water concentration has been raised to 10 M.

The second example given in this section concerns the study of a 0.3 M solution of $(\text{NO}_3)_3\text{Fe} \cdot 9\text{H}_2\text{O}$ in isopropanol, the total concentration of water present in the solution being 3 M.

This solution has been chosen for the following reason. In the preceding example it has been seen that the two main monomeric species detected involve Cl^- ions arising from chlorine ions introduced in the solution as Cl_3Fe . Therefore, if we form an Iron (III) solution by means of a salt whose anion is a bad ligand for complex formation this could increase in principle the amount of dihydroxo dimers.

The O.A. spectrum of this solution [22] looks very similar to that of a $(\text{ClO}_4)_3\text{Fe}$ solution in water with a $\text{pH} \cong 2.5$ [3] and is in fact consistent with the formation of complexes involving OH^- as ligands. Anyway, if enough ClH is added to the solution the O.A. data reveal [22] that all ferric ions are in the form of $[\text{FeCl}_4]^-$ complexes as well.

The results concerning the present technique are shown on Figure 2.

In particular Fig. 2b shows that when the HCl concentration is 1.3 M the magnetic moment per ferric ion in the saturation regime is in fact 5β . This is consistent with the mentioned O.A. data in the sense that when $[\text{HCl}] \gtrsim 1 \text{ M}$ all ferric ions are in the form of $[\text{FeCl}_4]^-$ complexes.

However if we compare Fig. 2a with Fig. 2b we notice a dramatic decrease of the magnetic moment. In fact the magnetic moment at saturation in the

case of Fig. 2a is only 30% of that of Figure 2b. Therefore we can conclude that a significant fraction of Iron (III) oligomers is indeed present in the solution corresponding to Figure 2a.

Moreover, if we assume that only monomers and antiferromagnetic dimers are present in the solution of Fig. 2a the present data would indicate that the relative concentration of dimers is now about 75%. It is worth noting here that this figure, which is in fact much larger than that obtained for the solution of Fig. 1a, is very close to the relative concentration of dihydroxo dimers in $\sim 4 \cdot 10^{-2} \text{ M}$ aqueous solutions of $(\text{ClO}_4)_3\text{Fe}$ for a $\text{pH} \cong 2.5$ derived by Milburn and Vosburgh [26]. This fact outlines the ability of water (or of OH^- ions produced by the hydrolysis) for replacing the isopropanol as ligand of Fe^{3+} [7]. This feature has also been noticed for solutions of Al^{3+} and Be^{2+} in non-aqueous solvents [8, 9].

Anyway, the results shown on Fig. 2 clearly illustrate the ability of $(\text{NO}_3)_3\text{Fe} \cdot 9\text{H}_2\text{O}$ solutions for giving rise to ferric oligomers. It must be recalled here that Spiro *et al.* [27] succeeded in forming oligomers of about 70 Å in size using aqueous solutions of $(\text{NO}_3)_3\text{Fe}$.

In conclusion, magnetization measurements performed at low temperatures and using strong magnetic fields can provide us with a good information about the presence of oligomers in a given ferric solution. In particular of oligomers are silent this kind of measurements can be very fruitful for measuring the relative concentration of monomeric and polymeric species of Iron (III) present in the solution.

In the case of antiferromagnetic dimers they would become silent at $T \cong 1 \text{ K}$ for J values higher than about 3 cm^{-1} . For cases in which the effective coupling, J , is in fact much smaller than this figure but higher than about 0.05 cm^{-1} , good information about dimerization can be reached by performing susceptibility measurements down to 50 mK. A good example on the usefulness of this kind of measurements for cases involving very weak dimerization has been recently reported [28].

Further work along this line is now in progress.

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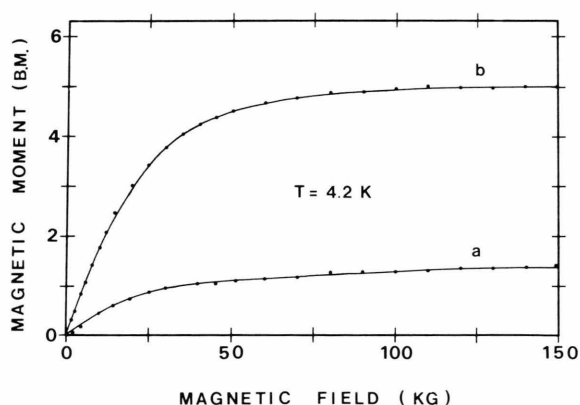


Fig. 2. Magnetic moment per ferric ion at 4.2 K vs. applied magnetic field. a) For a 0.3 M solution of $(\text{NO}_3)_3\text{Fe} \cdot 9\text{H}_2\text{O}$ in isopropanol. The total water concentration of the solution is $\sim 3 \text{ M}$. b) For the solution described in a) to 1.2 M of HCl has been added.

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