A Study of the Relationship Between the Spin Relaxation and Certain Chemical Properties of Paramagnetic Iron(III) Salt Solutions by Mössbauer Spectroscopy

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The paramagnetic spin-relaxation phenomenon in iron salt solutions was studied by the method of Mössbauer spectroscopy. It has been found that the nature of the chemical bonding between iron and its ligand sphere (bonding conditions) influences the magnitude of the internal magnetic field pertaining to the $m_I = \pm 3/2 \longrightarrow \pm 1/2$ transition of the Kramers doublet $S_z = \pm 5/2$, and by increasing the asymmetry of the 3*d* electron orbital the frequency of spin–lattice relaxation, *i.e.* relaxation time. The method provides information on the number of solvated and complex species of iron present in the solution under investigation, as well as on the relative quantities of the components. The experiments have shown that the study of paramagnetic spin relaxation will provide manifold information on the chemical structure of the investigated systems.

In some of our earlier communications[1-7] we have assumed that rapidly frozen solutions (cooled at a rate of 15 K s^{-1}) preserve the chemical structure they had in the liquid state, thus the structure of complex compounds and ions and the states of hydrolysis, hydration, and solvation remain essentially unchanged during rapid freezing. This assumption was strongly suggested by the fact that after a threshold rate (10 K s^{-1}) the Mössbauer parameters were already independent of the rate of freezing.[8] Recent d.t.a. tests carried out by Ruby *et al.*[9] also prove that in the course of rapid freezing, vitreous ice, a ' solidified solution ', is formed.

Consequently, from the results of the Mössbauer spectroscopic tests of frozen solutions, conclusions can be drawn with respect to the structure of the solution.

Here we present the study of the paramagnetic spin relaxation phenomenon in some frozen iron(III) salt solutions (4·2 K) by means of the Mössbauer spectroscopic method and shall draw from the results certain conclusions concerning the chemical properties of these solutions. The magnitude of the hyperfine splitting serves as a measure for the covalency of the iron ion in the frozen solution. We use the disappearance of the hyperfine splitting, which depends on pH change and the other chemical alterations, as an indication of dimerization and polymerization.

Paramagnetic Spin Relaxation.—Mössbauer spectroscopy allows a more thorough investigation of the hyperfine magnetic interactions between paramagnetic systems, and these problems have recently been studied by a number of authors.[10-14]

The source of the energy necessary for paramagnetic relaxation can be: (i) energy transmission originated from the ' turning ' of another spin; $(S_{1+}S_{2-})$, the so-called spin–spin relaxation (SSR); (ii) liberation of a phonon from the crystal lattice surrounding the paramagnetic ion or atom, called spin lattice relaxation (SLR).

If the average times are given the symbols τ_{SSR} and τ_{SLR}, respectively, then the time of spin relaxation (SR) will be

$$\tau_{SR} = \frac{1}{1/\tau_{SSR} + 1/\tau_{SLR}} \qquad (1)$$

where τ_{SSR} is independent of the temperature, while τ_{SLR} is temperature dependent (*cf.* ref. 15).

If the average life-time of the excited Mössbauer atom is τ_M and τ_{SR} is not less than the reciprocal frequency of the so-called Larmor precession of the magnetic momentum of the atomic nucleus

$$\tau_{SR}, \tau_M > \omega_L^{-1} \qquad (2)$$

then the Mössbauer atomic nucleus ' senses ' a magnetic field, hence the Mössbauer spectrum will show a Zeeman splitting.

The realization of the criterion implicit in inequality (2) may be promoted by increasing τ_{SR} or decreasing ω_L^{-1}. It follows from equation (1) that the increase of both τ_{SSR} and τ_{SLR} will result in the increase of τ_{SR}. The value of τ_{SSR} may be increased by increasing the distance between the paramagnetic atoms or ions (dilution), since in this way the probability, *i.e.* the frequency, of spin–spin interaction decreases.

The increase of τ_{SLR} can be realized by reducing the

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temperature. It should be pointed out here that SLR, which is the interaction between lattice oscillations and the spin system, is manifest through the orbital momentum. Consequently, in the case of Fe^{3+} ions which possess a spherically symmetrical $3d^5$ external shell configuration ($^6S_{5/2}$ basic term and $L = 0$), a slow SLR is *ab ovo* to be expected.

To the description of the various interactions within the paramagnetic field the ' spin-Hamiltonian-operator ' technique, frequently used in the study of electron-spin resonance (ESR), can be applied.

$$\bar{H}_s = \bar{H}_Z + \bar{H}_{CF} + \bar{H}_{mhf} + \bar{H}_Q \tag{3}$$

where $\bar{H}_s$ is the sum of the most important interactions and the other operators represent in order: the Zeeman, the crystal field, the magnetic hyperfine, and the electric hyperfine interactions. The various interactions can be described in the following manner:

$$\bar{H}_Z = \beta HgS \tag{4}$$

$$\bar{H}_{CF} = D[S_z^2 - (1/3)S(S + 1)] + E(S_x^2 - S_y^2) \tag{5}$$

$$\bar{H}_{mhf} = A_zS_zI_z + A_xS_xI_x + A_yS_yI_y \tag{6}$$

$$\bar{H}_Q = P(I_z^2 - (1/3)I(I + 1)) + 1/3P'(I_x^2 - I_y^2) \tag{7}$$

where H is the external magnetic field, D and E are crystal field parameters, A_z, A_x, and A_y are the main components of hyperfine magnetic interaction depending on the crystal field parameters of the Hamiltonian operator, P and P' are H operator parameters describing electric quadrupole interaction (*e.g.* in the case of iron $P = 1/4e^2qQ$).

TABLE 1

Position of lines

$S_z = \pm 1/2$

$7/4A - 13/4A^* - P + \delta$
$7/4A - 1/4A^* (1 + 4R) + \delta$
$-1/4A - 13/4A^* - P + \delta$
$-1/4A - 1/4A^* (1 + 4R) + \delta$
$-5/4A - 1/4A^* (1 + 4R) + \delta$
$7/4A - 1/4A^* (1 - 4R) + \delta$
$-1/4A + 3/4A^* + P + \delta$
$-1/4A - 1/4A^* (1 - 4R) + \delta$
$-1/4A + 11/4A^* - P + \delta$
$-5/4A - 1/4A^* (1 - 4R) + \delta$
$-5/4A + 11/4A^* - P + \delta$

$S_z = \pm 3/2$

$\pm 3/4(A - 3A^*) + P + \delta$
$\pm 3/4(A - A^*) - P + \delta$
$\pm 3/4(A - A^*) - P + \delta$

$S_z = \pm 5/2$

$\pm 5/4(A - 3A^*) + P + \delta$
$\pm 5/4(A - A^*) - P + \delta$
$\pm 5/4(A + A^*) - P + \delta$

$R = \sqrt{7 - P/A^* - P^2/A^{*2}}$, $A^*/A = -0{\cdot}571$

The ratio $\lambda = E/D$ is used to describe the absolute magnitude of the crystal field[11] which in the case of most hitherto investigated systems does not exceed the value of 1/3. Thus, according to experience $0 < \lambda < 1/3$.

In the vitreous systems (rapidly frozen solutions) investigated by us $\lambda \sim 0$ and the hyperfine interactions (HFI) can be considered isotropic. Thus for the case $H = 0$ the following Hamiltonian operator is obtained from equations (3)—(7) to describe the energy levels of the nucleus ^{57}Fe.

$$\bar{H} = A[I_zS_z + 1/2(S_+I_- + S_-I_+)] + P[I_z^2 - 1/3I(I + 1)] \tag{8}$$

The eigenvalues of $\bar{H}$ can be calculated from equation (8) taking into account the three Kramers doublets ($S_z = +5/2$; $\pm 3/2$; $\pm 1/2$) and the nuclear spin $I = 1/2$ and $I = 3/2$ of the ground state and the excited state respectively. The positions of the Mössbauer lines which result from these energy levels are given in Table 1 for ^{57}Fe. This description is only an approximation, because no mixed states of the different Kramers doublets are considered.

EXPERIMENTAL

The solutions were prepared from metallic iron containing 90% of ^{57}Fe. (The Fe_2O_3 obtained from Oak Ridge was reduced in a H_2 atmosphere.) The pH was adjusted with $NaHCO_3$; using a pH titrimeter or a precision pH paper. It was determined with an accuracy of ±0·1 pH.

The reagents were analytical grade Merck preparations.

The solutions were placed in Teflon sample holders provided with Mylar windows. The length of the path of the gamma-ray in the solution was 1·5 mm. The sample holders with the solutions were immersed in the cryostat directly into liquid helium.

The 10 mCi, $^{57}Co(Pt)$ radiation source was kept at room temperature. The device moving the radiation source was controlled by a sine signal. The pulses were detected by means of a 0·2 mm thick NaI scintillator and a ' Laben ' type 400 channel analyzer in multi-scaler operation.

For the determination and evaluation of the γ-resonance spectra a computer type IBM 360/91 was used. In the course of measurements two identical spectra were recorded, so that as the first step in computer evaluation these spectra had to be united. The assignment and decomposition of the single spectra lines were performed by means of the Lorentz functions and the conventional least square method. Because of the complicated shape of the relaxation spectra only lines, used in Table 2 were fitted.

The number of pulses collected in each channel varied between 10^6 and 2×10^6.

Magnetic susceptibility measurements were carried out with the Foner-type vibrational magnetometer.

The sensitivity of the measuring equipment was $\pm 10^{-9}$ c.g.s.u., $\left(\pm 10^{-15} \frac{Wb}{A\,.\,m}\right)$ while in the solutions under investigation the susceptibility value, corrected by a value accounting for the glass tank, varied between 0·6 and $1{\cdot}5 \times 10^{-7}$ c.g.s.u. $\left(10^{-13} \frac{Wb}{A\,.\,m}\right)$.

RESULTS AND DISCUSSION

Influence of the Cation and Anion Concentration.—The most important parameters of the Mössbauer spectra of the investigated solutions at liquid helium temperature (4·2 K) are summarized in Table 2. $H_{5/2}$ Is the internal magnetic field pertaining to the $S_z = 5/2$ Kramers doublet.

From the experimental results conclusions can be drawn with respect to the correlation between the average distance of the iron(III) ions [iron(III) concentration] and τ_{SSR}. Figures 1 and 2 illustrate the Mössbauer spectra of iron(III) solutions of different concentrations in the presence of Cl^- and ClO_4^- anions. The pH of all solutions is <0. It was found for both series of solutions that a slight hyperfine magnetic structure is apparent on the spectra even in the case of the highest, 0·5 and 1 mol kg^{-1} of iron(III), concentrations. This hyperfine magnetic structure can be assigned to $\tau_{SSR} \sim 2 \times 10^{-9}$. In the case of a concentration of 1 mol kg^{-1} of iron(III) the average Fe–Fe distance is 11·6 Å. (When the concentration is 0·05 mol kg^{-1} of iron(III) the Fe–Fe distance is 31·7 Å.)

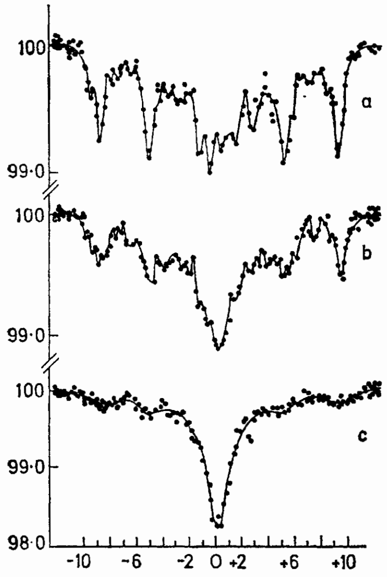

FIGURE 1 Mössbauer spectra of frozen solutions of $FeCl_3$ at 4·2 K. The concentration is varied: (a) $0{\cdot}05FeCl_3 + 2HCl$; (b) $0{\cdot}2FeCl_3 + 2HCl$; (c) $0{\cdot}5FeCl_3 + 1HCl$; (concentrations in mol kg^{-1} H_2O)

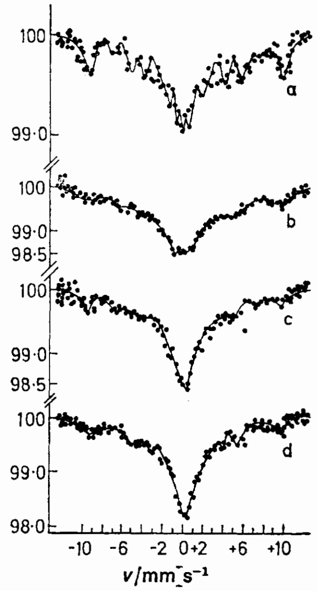

FIGURE 2 Mössbauer spectra of frozen solutions of $Fe(ClO_4)_3$ at 4·2 K. The concentration is varied: (a) $0{\cdot}01Fe(ClO_4)_3 + 2HClO_4$; (b) $0{\cdot}05Fe(ClO_4)_3 + 2HClO_4$; (c) $0{\cdot}5Fe(ClO_4)_3 + 1HClO_4$; (d) $1{\cdot}0Fe(ClO_4)_3 + 0{\cdot}5HClO_4$; (concentrations in mol kg^{-1} H_2O)

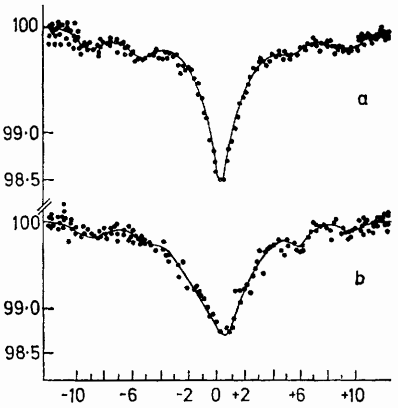

FIGURE 3 Mössbauer spectra of frozen solutions of $FeCl_3$ and $Fe(ClO_4)_3$ at 4·2 K (a) $0{\cdot}2FeCl_3$; (b) $0{\cdot}2\ Fe(ClO_4)_3$ (concentrations in mol kg^{-1} H_2O)

Investigation of the effect of anion concentration shows that a reduction in anion concentration (Figure 3) results in an increase in the frequency of relaxation. This observation indicates that an increase in the quantity of diamagnetic anions between the iron(III) ions inhibits (shields) the interactions which may raise the frequency of relaxation. The mechanisms of this phenomenon is not yet clear.

It should be noted that a similar phenomenon was observed when the experiments were carried out at the temperature of liquid nitrogen.[16]

Covalence Effects.—In Table 2 the substances are arranged with decreasing $H_{5/2}$. One immediately realizes, that the value of $H_{5/2}$ is related to the degree of covalence of the chemical bond between the iron(III) in the solution and the internal ligand sphere of the latter. This may be explained by the direction of the polarization of the ' bond ' electron-pairs in the first internal ligand sphere which is opposite to the direction of the $3d^5$ electrons of iron(III) with a high spin-number, so that the bond electron-pairs can have a shielding effect on the latter. In this way the polarizing effect of the $3d^5$ electrons on the *s* electrons and consequently the Fermi-contact interaction too, will be lower.

The experiments have shown that the utilization of relaxation phenomena for the study of chemical bonds is an extremely sensitive method. For instance, in the case of such anions as NO_3^- and ClO_4^- it is difficult to distinguish by any other method the ligand spheres of iron (according to the literature in the case of both anions a hexa-aquo-complex is present), while the present method of investigation indicates a difference ($\Delta H_{5/2}$) one order higher than the experimental error for both anions. This result is in good agreement with the results of some of our earlier Mössbauer spectroscopic tests.[6] It should be mentioned here that the results of the present method are not equivalent to saying that iron(III) when in solution in the presence of any of the two anions cannot be present in the hexa-aquo-complex form, since the difference in $H_{5/2}$ may be due to the composition of the second ligand sphere. Also in the case of the SO_4^{2-} anion from the value $H_{5/2} = 560$ kOe the conclusion can be drawn that the sulphate anion participates in the structure of the internal ligand sphere of iron.

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[16] A. S. R. Platshinda, M. Komor, and A. Vértes, *J. Radioanalyt. Chem.*, 1972, **10**, 89.

Figure 4 shows an iron (edta) complex. In the solution of pH 4 the lines $\pm 5/4\,(A - 3A^*) + P + \delta$ are doubled; $(H_{5/2})_{\mathrm{I}} = 540$ kOe and $(H_{5/2})_{\mathrm{II}} = 460$ kOe). The internal magnetic field of 460 kOe indicates a strong covalence effect. Certain authors concluded from X-ray diffraction [17] and Mössbauer measurements [18] that in the $\mathrm{NaFe(OH)_2}$–e.d.t.a.–$n\mathrm{H_2O}$ complex iron(III) has a co-ordination number of seven, so that the possibility of the iron having a co-ordination number of seven in solution, too, cannot be dismissed. In this case probably $(H_{5/2})_{\mathrm{II}}$ is assigned to the complex with a co-ordination number of seven, and $(H_{5/2})_{\mathrm{I}}$ to the complex with a co-ordination number of six. This assumption is supported by the fact that in case of pH < 3 only the lines of the latter complex are present, while in the solution with a pH value of 4 the ratio of the two complexes is 14·6 : 11·5 (in the more acidic solution the number of non-co-ordinated acetate groups is greater).

The Mössbauer spectrum of the solution containing thiocyanate is shown in Figure 5. The spectrum is the superposition of the lines of the three different complexes [$\mathrm{Fe(SCN)}_x$, $x = 1$, 2, or 3] in the solution, a fact which makes the decomposition of the spectrum extremely difficult.

From the low $H_{5/2}$ value (540 kOe) one sees that the Fe–SCN bond is relatively highly covalent.

One can summarize the experimental results by giving a series of anions in which $\mathrm{Fe^{3+}}$ is bound more and more covalently in going from the left to the right. This series is: $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, $\mathrm{SO_4^{2-}}$ $\mathrm{Cl^-}$, NTA, $\mathrm{SCN^-}$, $\mathrm{CH_3COO^-}$, and e.d.t.a.

TABLE 2

Summary of the experiments on frozen aqueous solutions at 4·2 K

No.	Composition of solution/mol kg^{-1}	$H_{5/2}$ kOe	Isomer shift mm s^{-1} δ	Quadrupole Splitting $2P$ mm s^{-1}	$\pm 5/4(A - 3A^*) + P + \delta$ Area of Pair of Lines in % of total area
1	$0{\cdot}05\mathrm{Fe(ClO_4)_3} + 2\mathrm{HClO_4}$	582 ± 8·0			
2	$0{\cdot}05\mathrm{Fe(ClO_4)_3} + 2(\mathrm{NaClO_4} + \mathrm{HClO_4})$; pH = 0·5	578 ± 0·5	0·165 ± 0·01	0·02 ± 0·01	19·3 ± 1·7
3	$0{\cdot}05\mathrm{Fe(ClO_4)_3} + 2(\mathrm{NaClO_4} + \mathrm{HClO_4})$; pH 1				3·24 ± 0·64, 19·15 ± 1·70
4	$0{\cdot}05\mathrm{Fe(ClO_4)_3} + 2\mathrm{NaClO_4} + \mathrm{HClO_4})$; pH = 2	583 ± 0·6	0·155 ± 0·016	0·05 ± 0·02	20·5 ± 3·0
5	$0{\cdot}05\mathrm{Fe(ClO_4)_3} + 2(\mathrm{NaClO_4} + \mathrm{HClO_4})$; pH = 2·3	582 ± 1·5	0·17 ± 0·02		18·1 ± 2·4
6	$0{\cdot}01\mathrm{Fe(ClO_4)_3} + 2\mathrm{HClO_4}$	586 ± 4·3			9·1 ± 3·1
7	$0{\cdot}2\mathrm{Fe(ClO_4)_3}$				6·0 ± 3·8
8	$0{\cdot}5\mathrm{Fe(ClO_4)_3} + 1\mathrm{HClO_4}$	583 ± 6·0			6·5 ± 3·0
9	$1\mathrm{Fe(ClO_4)_3} + 0{\cdot}5\mathrm{HClO_4}$				3·1 ± 1·7
10	0·3% $\mathrm{Fe^{III}}$ + 65% $\mathrm{HNO_3}$	569 ± 1·4	0·18 ± 0·01	0·00 ± 0·01	27·6 ± 1·1
11	0·3% $\mathrm{Fe^{III}}$ + 30% $\mathrm{HNO_3}$	570 ± 1·5	0·175 ± 0·003	0·022 ± 0·003	22·1 ± 1·6
12	$0{\cdot}05\mathrm{Fe(NO_3)_3} + 2\mathrm{HNO_3}$	568 ± 2·1	0·155 ± 0·02	0·03 ± 0·02	21·3 ± 3·0
13	$0{\cdot}05\mathrm{Fe(NO_3)} + 2(\mathrm{NaNO_3} + \mathrm{HNO_3})$; pH = 1	569 ± 0·9	0·14 ± 0·02	0·04 ± 0·02	20·4 ± 1·1
14	$0{\cdot}05\mathrm{Fe(NO_3)_3} + 2(\mathrm{NaNO_3} + \mathrm{HNO_3})$; pH = 2	567 ± 1·3	0·145 ± 0·04	0·05 ± 0·04	17·7 ± 2·5
15	$0{\cdot}025\mathrm{Fe_2(SO_4)_3} + 1\mathrm{H_2SO_4}$	561 ± 1·2	0·135 ± 0·017	0·03 ± 0·02	19·8 ± 3·0
16	$0{\cdot}025\mathrm{Fe_2(SO_4)_3} + 1(\mathrm{Na_2SO_4} + \mathrm{H_2SO_4})$; pH = 1	561 ± 1·6	0·135 ± 0·02	0·03 ± 0·025	13·0 ± 3·0
17	$0{\cdot}025\mathrm{Fe_2(SO_4)_3} + 1(\mathrm{Na_2SO_4} + \mathrm{H_2SO_4})$; pH = 2	558 ± 4·9			11·4 ± 4·0
18	$0{\cdot}025\mathrm{Fe_2(SO_4)_3} + 1(\mathrm{Na_2SO_4} + \mathrm{H_2SO_4})$; pH = 2·4		0·147 ± 0·02		1·3 ± 1·1
19	$0{\cdot}05\mathrm{FeCl_3} + 2\mathrm{HCl}$	549 ± 1·4	0·22 ± 0·05	0·10 ± 0·05	17·5 ± 2·4
20	$0{\cdot}05\mathrm{FeCl_3} + 2(\mathrm{NaCl} + \mathrm{HCl})$; pH = 1	548 ± 1·2			16·1 ± 2·6
21	$0{\cdot}05\mathrm{FeCl_3} + 2(\mathrm{NaCl} + \mathrm{HCl})$; pH = 2				11·4 ± 2·1, 5·04 ± 1·7
22	$0{\cdot}2\mathrm{FeCl_3} + 2\mathrm{HCl}$				14·2 ± 3·2
23	$0{\cdot}2\mathrm{FeCl_3}$		0·20 ± 0·02		1·83 ± 1·7
24	$0{\cdot}5\mathrm{FeCl_3} + 1\mathrm{HCl}$				10·1 ± 3·4
25	$1\mathrm{FeCl_3} + 0{\cdot}5\mathrm{HCl}$				2·5 ± 1·8
26	$0{\cdot}02\mathrm{Fe(ClO_4)_3} + 0{\cdot}06\mathrm{NTA} + 1\mathrm{NaClO_4}$; pH = 4	546 ± 0·3	0·13 ± 0·01	1·43 ± 0·017	11·2 ± 2·2
27	$0{\cdot}02\mathrm{Fe(ClO_4)_3} + 0{\cdot}06\mathrm{NTA} + 1\mathrm{NaClO_4}$; pH = 2·5	553 ± 1·75	0·15 ± 0·03	0·036 ± 0·03	21·7 ± 3·2
28	$0{\cdot}02\mathrm{Fe(ClO_4)_3} + 0{\cdot}06\mathrm{NTA} + 1(\mathrm{NaClO_4} + \mathrm{HClO_4})$ pH = 1	557 ± 1·1			27·86 ± 3·0
29	$0{\cdot}05\mathrm{Fe(ClO_4)_3} + 1{\cdot}8\mathrm{HClO_4} + 0{\cdot}17\mathrm{KSCN}$	542 ± 3			
30	0·02% $\mathrm{Fe^{III}}$ + 96% $\mathrm{CH_3CO_2H}$		0·194 ± 0·008	0·58 ± 0·05	
31	0·2% $\mathrm{Fe^{III}}$ + 65% $\mathrm{CH_3CO_2H}$	500 ± 15			
32	0·2% $\mathrm{Fe^{III}}$ + 40% $\mathrm{CH_3CO_2H}$	540 ± 15			
33	0·02 $\mathrm{Fe(ClO_4)_3}$ + 0·05 edta + 1 $\mathrm{NaClO_4}$; pH = 4	540 ± 2 463 ± 4			14·6 ± 1·6 11·5 ± 2·3
34	0·02 $\mathrm{Fe(ClO_4)_3}$ + 0·05 edta + 1 $\mathrm{NaClO_4}$; pH = 3	540 ± 1·8			21·4 ± 2·4

pH-*Dependence of Dimerization and Polymerization.*—As we have seen the paramagnetic hyperfine splitting decreases, if the distance between the iron ions increases. If one has mainly to take into account SSR processes, the splitting can totally collapse if the iron atoms come very close together. This is the case if dimerization or polymerization takes place in the solution. Usually only a part of the ions participate in these processes,

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[17] M. O. Lind and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 34.

[18] I. I. Spijkerman, L. H. Hall, and I. L. Lambert, *J. Amer. Chem. Soc.*, 1968, **90**, 2039.

depending on chemical conditions such as pH-value. For that reason the spectra consist of two parts, one which shows non-magnetic splitting and one which is a superposition of magnetically split lines belonging to the electronic spin $S_z = \pm 5/2, \pm 3/2$, and $\pm 1/2$. For many reasons an exact decomposition of the two parts is not an easy undertaking and it was not tried in this publication. But even without an exact calculation some conclusions can be drawn with respect to the degree of dimerization and polymerization.

Figure 6 shows the Mössbauer spectra of $FeCl_3$ solutions at different pH.

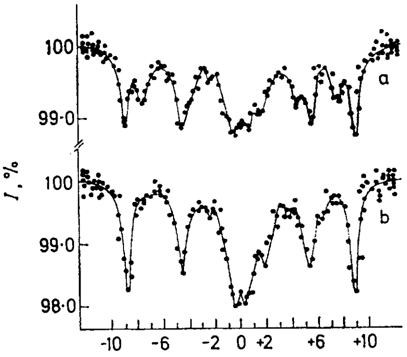

FIGURE 4 Mössbauer spectra of frozen solutions of edta at 4·2 K. The pH is varied, (a) pH 4·0; (b) pH 3·0

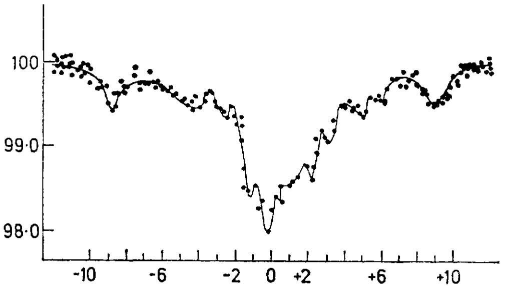

FIGURE 5 Mössbauer spectrum of KSCN solution at 4·2 K 0·05Fe$(ClO_4)_3$ + 1·8$KClO_4$ + 0·17KSCN (concentration mol kg^{-1} H_2O)

It can be ascertained that an increase in pH results in the increased intensity of the spectral centre in the following area-percentage proportions:

(for identical rate intervals)

pH < 0	49·2%
pH $= 1$	55·5%
pH $= 2$	58·6%

This increase of the area is related to the fact that the number of Fe–OH bonds increases with increasing pH values and the formed complex ions containing also ‘ OH ’ and ‘ Cl ’ bonds may lead to dimerization. We have demonstrated on the basis of electron exchange studies in an earlier paper [6] that Cl^- will remain in the internal ligand sphere of iron even when the pH is increased. Our present work, on the other hand, seems to indicate that this condition does not prevent a dimerization through the OH or Cl bridges.

The outer lines of the spectra can be assigned to the lines pertaining to $S_z = \pm 5/2$ alone ($\pm 3{\cdot}391A + P + \delta$). The internal magnetic field, $H_{5/2} \sim 550$ kOe, which can be calculated from the position of these lines seems to indicate that in the case of solutions containing 2·12 mol kg^{-1} of Cl^- anion irrespective of the pH, one chlorine is co-ordinated to the bulk (>60%) of the iron. Two pairs of lines of lower intensity having a lower or higher internal magnetic field respectively are superimposed on the pair of lines $H_{5/2} = 550$ kOe (see Figure 6). These pairs of lines can be identified with the ions $[FeCl_2(H_2O)_4]^+$ and $[Fe(H_2O)_6]^{3+}$, respectively. For solutions with pH = 2 the decomposition of the two extreme pairs of lines will furnish the area-percentages: 11·4 ± 2·1% and 5·0 ± 1·7%. This percentage ratio is proportional to the quantities of the ions $[FeCl(H_2O)_5]^{2+}$ and $[FeCl_2(H_2O)_4]^+$.

Figure 7 shows the spectra of solutions containing 1·075 mol kg^{-1} of SO_4^{2-} anion. On the spectrum pertaining to pH < 0 the appearance of all three Kramers doublets is quite clearly visible.

As the pH increases, more and more of the iron in solution loses its hyperfine magnetic structure (HMS) which indicates the formation of hydroxide bonds and dimerization (we have demonstrated in one of our earlier papers [4] on the basis of electron exchange studies for sulphate too that in the case when OH groups are formed, *i.e.* dimerization takes place, the sulphate will still be present in the internal co-ordination sphere of iron). From the decomposition of spectra the following values are obtained for the quantities of complex iron ions having no HMS in solutions of different pH values:

pH < 0	0%
pH $= 1{\cdot}0$	50 ± 12%
pH $= 2{\cdot}0$	65 ± 8%
pH $= 2{\cdot}4$	98·7 ± 6%

The Mössbauer spectra of solutions containing NO_3^- anion are shown in Figure 8. According to the literature in solutions of low pH values containing NO_3^- and ClO_4^-, iron(III) is always present in the hexa-aquo-complex form.

It appears from the measured spectra that in the case of nitrate solutions the population of the $S_z = \pm 5/2$ level is greater than that of the other two doublets. It follows from the intensity of the lines $[\pm 5/4(A - 3A^*) + P + \delta]$ (compare Table 1) that the level $S_z = \pm 5/2$ is populated by more than 50% of the total quantity or iron. On the basis of the Boltzmann statistics it follows from this that of the three different Kramers doublets the lowest energy level belongs to $S_z = 5/2$. In case of the spectrum pertaining to pH = 2·0 the area ratio of the quadrupole pair of lines ($2P = 0{\cdot}43 \pm 0{\cdot}03$ mm s^{-1}) having no hyperfine magnetic structure is: $21{\cdot}8 \pm 5{\cdot}6\%$. This pair of lines can in all probability be identified with the complex ion $[Fe_2(OH)_2(H_2O)_8]^{4+}$.

The Mössbauer spectra of perchlorate solutions are shown in Figure 9. Compared to the solution series discussed so far a new fact arises, namely a sudden rise in relaxation frequency $\tau_{SR} \sim 5 \times 10^{-9}$ s at pH < 0. A broadening of the external lines indicates that we are dealing here not with the superposition of a new line without hyperfine magnetic structure, as is the case *e.g.* at pH 2.

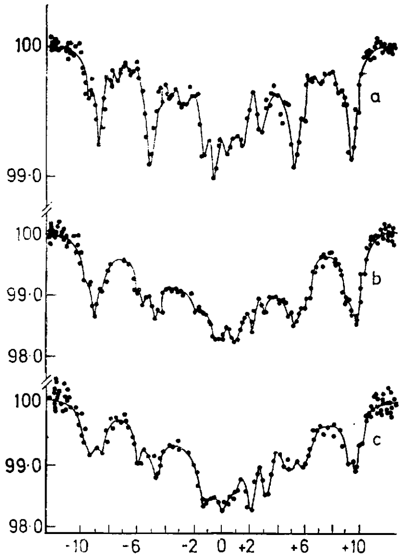

FIGURE 6 Mössbauer spectra of frozen solutions of $FeCl_3$ at 4·2 K. The pH is varied, (a) pH < 0; (b) pH 1·0; (c) pH 2·0

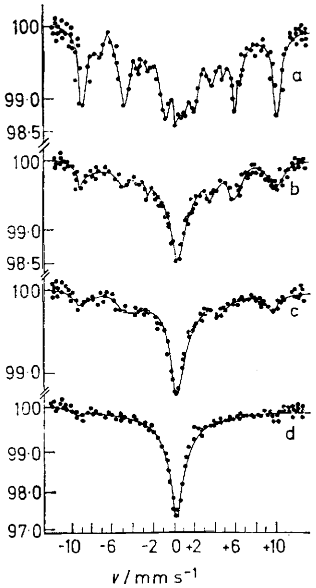

FIGURE 7 Mössbauer spectra of frozen solutions of $Fe_2(SO_4)_3$ at 4·2 K. The pH is varied, (a) pH < 0; (b) pH 1·0; (c) pH 2·0; (d) pH 2·4

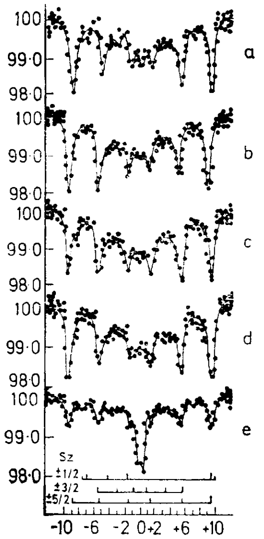

FIGURE 8 Mössbauer spectra of frozen solutions of $Fe(NO_3)_3$ at 4·2 K. The pH is varied, (a) 65% HNO_3; (b) 30% HNO_3; (c) 11·2% HNO_3; (d) pH 1·0; (c) pH 2·0. The intensity of lines pertaining to the various Kramers doublets are plotted with the assumption that the population and τ_R values of the doublets are equal. This assumption is, however, not valid for practical conditions

The intensity of the line pertaining to the dimer[19] is in a solution of pH 2; $60 \pm 15\%$ and in a solution of pH 2·3: $67 \pm 14\%$. (We wish to add here that the quantity of dimer can be determined more accurately from the measurement of electron exchange.[20])

Figure 10 shows the Mössbauer spectra of some CH_3CO_2H–H_2O–Fe systems.

The values of δ point to an iron oxidation level of Fe^{III}. Almost the entire quantity (more than 90%) of iron dissolved in 96% acetic acid furnishes a quadrupole pair of lines, thus lacks HMS. The comparatively extensively quadrupole splitting ($2P = 0{\cdot}58$ mm s^{-1}) indicates that the iron solvate has a mixed ligand. Since iron was dissolved in acetic acid in the presence of oxygen, this result, namely the lack of HMS, supports our earlier assumption[3] that when iron is dissolved in concentrated acetic acid in the presence of oxygen, after dissolution polymer formation will start in the solution.

In systems containing 35 or 60% of H_2O a considerable part of the iron in the solution will have a form possessing a hyperfine magnetic structure. This obviously indicates that in the last two cases the water molecules also participate in the formation of the internal ligand sphere of iron and will hinder polymerization. The short relaxation time ($\tau_{SR} \sim 2 \times 10^{-9}$ s) which follows from the relatively small internal magnetic field ($H_{5/2} \sim 500$ kOe) and from the shape of the spectrum indicates that the presence of large quantities of water is unable to displace from the internal ligand the acetate or OH groups representing a greater covalent bond.

Iron–acetate bonds will be formed in a similar manner when the solution contains ethylenediaminetetra-acetic acid or nitrilotriacetic acid (NTA).

The Mössbauer spectra of NTA solutions of differing pH values are presented in Figure 11. For pH 4 the spectrum can be decomposed into a quadrupole pair of lines and a spectrum component showing Zeeman splitting.

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[19] L. N. Mulay and P. W. Selwood, *J. Amer. Chem. Soc.*, 1955, **77**, 2693.

[20] M. Komor, A. Vértes, J. Dézsi, and J. Ruff, *Acta Chim. Acad. Sci. Hung.*, 1970, **66**, 285.

In this solution the lack of a hyperfine magnetic structure may be due either to dimerization (polymerization) or to an electron structure of low spin. To clarify this problem the magnetic susceptibility of an aqueous solution containing $FeCl_3$ (0·33) and NTA (0·68 mol kg^{-1}) was measured at pH 4 and in a temperature interval between 95 and 259 K. (The concentration could not be as low as that used for Mössbauer measurements, since in the case of such very low concentrations the error of susceptibility measurements is too high.) The experimental results followed the Curie–Weiss law and $i = 30 \pm 5°$. A value of $2·8 \pm 0·2$ B.M. was obtained for 'spin only.'*

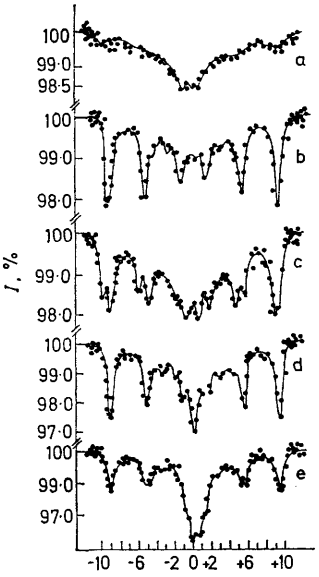

FIGURE 9 Mössbauer spectra of frozen solutions of $Fe(ClO_4)_3$ at 4·2 K. The pH is varied, (a) pH < 0; (b) pH 0·5; (c) pH 1·0; (d) pH 2·0; (e) pH 2·3

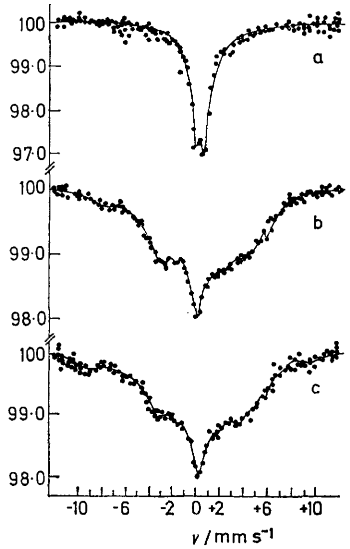

FIGURE 10 Mössbauer spectra of frozen solutions of the system $CH_3CO_2H–H_2O–Fe$ at 4·2 K. The concentration of CH_3CO_2H is varied, (a) 96%; (b) 65%; (c) 40% CH_3CO_2H

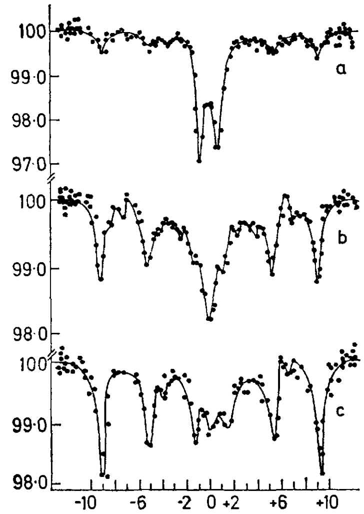

FIGURE 11 Mössbauer spectra of frozen solutions of NTA at 4·2 K. The pH is varied, (a) pH 4·0; (b) pH 2·5; (c) pH 1

This value indicates an electron structure with a low number of spins which, however, does not unambiguously exclude the possibility of dimerization (polymerization), since even in the polynuclear iron(III)–acetate complex with a high number of spins similar 'spin only' values have been found,[21] because in the dimer (or polymer) the spin of some iron atoms may have an opposite orientation. The relatively high Weiss constant also points to an antiferromagnetic interaction and therefore when these experimental results are evaluated together it appears that the quadrupole pair of lines can be identified with a polynuclear complex ion.

The value of $H_{5/2}$ gradually increases with decreasing pH values (see Table 2) indicating a decrease in the number of acetate bonds. The great quadrupole splitting pertaining to the complex without HMS ($2P = 1·43 \pm 0·02$ mm s^{-1}) shows that the internal ligand sphere, that is the electron structure of iron is highly asymmetric. From the decomposition of the spectra the following values are obtained at different pH values for the component without HMS:

pH = 1·0	68·9 ± 4·5%
pH = 2·5	58·5 ± 14%
pH = 1·0	0%

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[21] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37; W. M. Reiff, G. J. Long, and W. A. Baker, *J. Amer. Chem. Soc.*, 1968, **90**, 6347.