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The Mössbauer Spectra of the Iron - Sodium Metaphosphate Systems

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The Mössbauer spectra of three iron - sodium metaphosphate systems have been studied. The bonding characteristics of the iron atom with the phosphates have been discussed from the results of the Mössbauer spectra. The data for the fused iron oxide - sodium metaphosphate system suggest that the bonding of the iron atom with the phosphates is considerably ionic and the arrangements of metaphosphates in these systems are at random and in a tangle. Some informations on the structure of the $Fe_2(OH)(PO_3)_5$ system were described.

It was shown in a previous paper[1] that the Mössbauer effect was observed even for the iron atoms bound in an amorphous substance, and it may permit us to study the chemical structure of iron compounds in an amorphous state.

In the present study, the Mössbauer spectra of two systems, Fe_2O_3- and Fe_3O_4-sodium metaphosphate, have been measured in order to understand the bonding characteristics between the iron and phosphates. Furthermore, several compounds having empirical formula of $Fe_2(OH)(PO_3)_5$ were prepared by the reaction of iron(III) with metaphosphate ions in solution,[2] and the Mössbauer spectra of these compounds were measured.

The bond character between the iron and phosphates has been discussed by using the isomer shift and the quadrupole splitting data.

Experimental

Apparatus and Procedure. The apparatus and procedure for the Mössbauer spectroscopy were virtually identical with those described in a previous paper.[1] As a source of radiation was used ^{57}Co diffused into metallic copper. All the samples were finely pulverized and then used for the measurement. The isomer shifts were expressed in mm/sec with reference to the stainless steel. All the measurements were performed at room temperature.

The magnetic susceptibilities of the Fe_2O_3-$NaPO_3$ system were measured according to the Gouy method.

Fe_2O_3-$NaPO_3$ System. Sodium metaphosphate was prepared by the thermal dehydration of monosodium dihydrogen orthophosphate dihydrate followed by quenching the melt. The sodium metaphosphate was mixed with various amounts of Fe_2O_3 in a platinum crucible so that P/Fe ratios reached to 5, 7, 10, 15 and 20, respectively. The mixtures were melted in the air at 1200°C for two hours and then quenched quickly to glass by compressing it between two flat copper blocks. The products were all of brownish glasses.

Fe_3O_4-$NaPO_3$ System. Mixtures of sodium metaphosphate and Fe_3O_4 having the P/Fe ratios, 3, 5, 7, 10 and 15, were fused in graphite crucibles at 1100°C for two hours in a stream of nitrogen in order to prevent iron(II) in Fe_3O_4 from oxidation and then cooled them quickly to glass. The products were of brownish glasses without exception.

$Fe_2(OH)(PO_3)_5$ System. To 40 m*l* of 0.5 M ferric chloride solution 50 m*l* of 1 M (as $NaPO_3$) sodium metaphosphate solution was added. After the fine white precipitate had settled, the mother liquor was filtered off. The precipitate was washed only once with water and then with dioxane until the washing liquid was free from sodium and chloride ions. Sodium metaphosphates with various average chain lengths were prepared

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[1] Y. Takashima and S. Ohashi, This Bulletin, **38**, 1684 (1965).

[2] M. K. McElroy, J. F. Hazel and W. M. McNabb, *J. Inorg. Nucl. Chem.*, **27**, 859 (1965).

by the thermal dehydration of the mixtures of disodium hydrogen orthophosphate and sodium dihydrogen orthophosphate. The average chain lengths ($\bar{n}$) of the sodium metaphosphates used was determined by pH titration method[3] to be 9, 25, 38, 104 and 150, respectively.

Results and Discussion

Fe_2O_3-$NaPO_3$. Table 1 shows results obtained in the Mössbauer and magnetic susceptibility measurements. The Mössbauer spectrum of the sample having the P/Fe ratio of 5 is shown in Fig. 1 as an example.

TABLE 1. ISOMER SHIFT, QUADRUPOLE SPLITTING AND MAGNETIC MOMENT OF Fe_2O_3-$NaPO_3$ SYSTEM

Sample	Isomer shift mm/sec	Quadrupole splitting $\frac{1}{2}e^2qQ$ mm/sec	Magnetic moment B. M.
Fe_2O_3[4]	0.47	0.24	2.1
P/Fe= 5	0.46	0.34	4.0
P/Fe= 7	0.47	0.34	
P/Fe=10	0.49	0.36	4.1
P/Fe=15	0.48	0.44	4.1
P/Fe=20	0.46	0.52	3.7

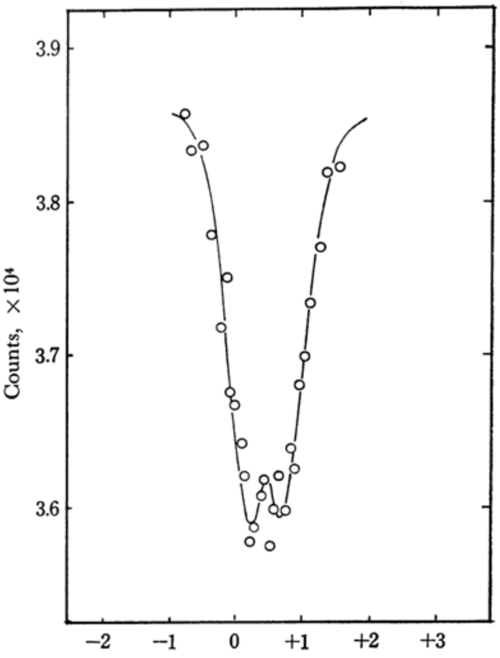

Fig. 1. Mössbauer spectrum of Fe_2O_3-$NaPO_3$ system (P/Fe=5).

The spectra of this system have double absorption peaks which are interpreted as the quadrupole splitting of iron(III). Since the isomer shifts of this system were essentially constant and nearly equal to that of Fe_2O_3 itself, it was not able to decide whether the new bonding between the iron atom and the phosphates was formed or not. But, the iron atoms are considered to be bound to the phosphates from the results of magnetic susceptibility, because the iron atoms in this system have the different magnetic moments from that of Fe_2O_3.

The quadrupole splitting gradually increases with increasing P/Fe ratio. This fact was not successfully interpreted. It is conceivable that

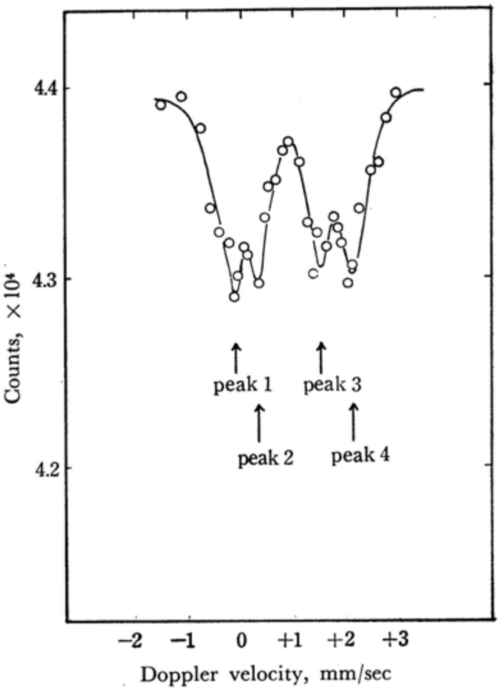

Fig. 2. Mössbauer spectrum of Fe_3O_4-$NaPO_3$ system (P/Fe=3).

TABLE 2. ISOMER SHIFT AND QUADRUPOLE SPLITTING OF Fe_3O_4-$NaPO_3$ SYSTEM

	Fe(III)	Fe(II)	
Sample	Isomer shift mm/sec	Isomer shift mm/sec	Quadrupole splitting $\frac{1}{2}e^2qQ$ mm/sec
Fe_3O_4[5]	0.46, 0.87	0.87	~0
P/Fe= 3	0.35	1.27	2.76
P/Fe= 5	0.37	1.62	3.16
P/Fe= 7	0.45	1.44	2.94
P/Fe=10	0.44	1.49	2.98
P/Fe=15	0.48	1.60	3.20

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[3] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954).

[4] O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters*, **4**, 412 (1960).

[5] A. Ito, K. Ôno and Y. Ishikawa, *J. Phys. Soc. Japan*, **18**, 465 (1963).

the chain length of metaphosphate increases with increasing P/Fe ratio, and this causes the irregularity of the chain arrangement and the entanglement of the long chain molecule to increase. However, these molecular architecture will not always explain the reason, why the strong electric field gradient was developed at the site of the iron nucleus.

The observed isomer shifts of this system were comparable to those of iron orthophosphate tetrahydrate and iron pyrophosphate nonahydrate.1) In view of this fact, it seems that the nature of chemical bonding between iron and phosphate in this system is analogous to those of the compounds described above.

Fe_3O_4-$NaPO_3$. Table 2 shows results obtained in the Mössbauer measurements. The Mössbauer spectrum of the sample having the P/Fe ratio of 3 is shown in Fig. 2. Since two kinds of iron, bivalent and trivalent, are included in this system, the absorption peak intensity of each sample is weaker than that of the Fe_2O_3-$NaPO_3$ system so far as the same amounts of iron are compared. Therefore, the error accompanied with the determination of the isomer shift and quadrupole splitting should be relatively large.

Four peaks are expediently named 1, 2, 3 and 4 towards the right in Fig. 2. Analysis of the peculiar spectrum is quite difficult, because there appear to be many possible explanations to account for the absorption peaks. We tentatively interpreted this spectrum for the best as follows; the second peak is due to iron(III), the first and the fourth peaks are the doublet of iron(II), the third peak is one part of the doublet of the other kind of iron(II) and the other part of it superimposes in 1 or 2, but it is not evident why two kinds of iron(II) are contained in this system. Moreover, iron(III) in this system may be considered to have the similar splitted peaks to iron(III) in the Fe_2O_3-$NaPO_3$ system. But we could not observe any splitting due to iron(III) taking into account of error.

If our conception is true, then all the values of the isomer shift and quadrupole splitting of this system differed clearly from those of Fe_3O_4. In view of this fact, it is obvious that the bonding of the iron atom with the phosphates is formed in the Fe_3O_4-$NaPO_3$ system.

The isomer shift values of iron(III) are similar to those of the Fe_2O_3-$NaPO_3$ system. This fact means that the iron(III) state in this system is the same with that in the Fe_2O_3-$NaPO_3$ system.

We are not in a position to discuss the variety of the quadrupole splitting observed in this system because of the large error. The values of the quadrupole splitting of this system, however, differed distinctly from those of Fe_3O_4. From this fact it can be concluded that iron atoms in Fe_3O_4 do not merely disperse in the glass, but combine with the phosphates.

The isomer shift value of iron(II) in the glass, roughly 1.3—1.6 mm/sec, is characteristic of typical ionic bivalent irons. Thus its bonding must be considerably ionic.

In view of the fact that the quadrupole splitting is larger than that of Fe_3O_4, it seems reasonable to assume that the electric field gradient at the iron nucleus arises from the bonding with metaphosphates in addition to the iron atom itself.

$Fe_2(OH)(PO_3)_5$ System. Five sorts of $Fe_2(OH)(PO_3)_5$ were prepared from ferric chloride and the sodium metaphosphates with various average chain lengths. The nature and structure of these compounds were not completely understood. In the present work, the Mössbauer spectra of a series of these compounds were measured. All the spectra obtained showed single absorption peaks. The isomer shifts and the relative intensities of the absorption peaks are given in Table 3. It should be noticed that the isomer shifts are fairly constant ranging from 0.48 to 0.53, and the values are characteristic of typical ionic trivalent irons. Going into details, however, these values are a little larger than those for ferric chloride and the Fe_2O_3-sodium metaphosphate system, but rather close to those for ferric sulfate or ferric pyrophosphate. This fact means that there is close resemblance in the electronic structures between iron(III) in $Fe_2(OH)(PO_3)_5$ and those of ferric sulfate or ferric pyrophosphate. Therefore we may be able to postulate that $Fe_2(OH)(PO_3)_5$ have the iron coordinated with six oxygen atoms on adjacent phosphate chains, since both ferric sulfate and ferric pyrophosphate have the iron coordinated with six oxygen atoms. The iron in ferric chloride6) is also surrounded by six chlorine atoms arranged at the corners of a more or less regular octahedron. A little discrepancy of the isomer shifts between $Fe_2(OH)(PO_3)_5$ and ferric chloride could be ascribed to the difference of the electronegativities of the relevant atoms (*i. e.* O=3.5, Cl=3.0).

TABLE 3. ISOMER SHIFT, QUADRUPOLE SPLITTING AND RELATIVE INTENSITY OF THE ABSORPTION PEAK OF $Fe_2(OH)(PO_3)_5$ SYSTEM

Average chain lengths of sodium metaphosphate $\bar{n}$	Isomer shift mm/sec	Relative intensity
9	0.53	1.00
25	0.53	0.90
38	0.53	0.83
104	0.48	0.82
150	0.51	0.74

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6) J. N. Murrell, S. F. A. Kettle and J. M. Tedder "Valence Theory," John Wiley & Sons., New York, N. Y. (1965), p. 203.

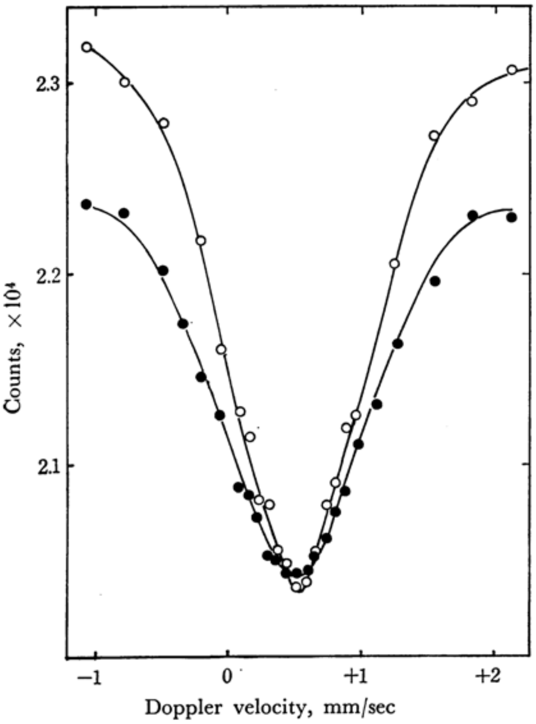

Fig. 3. Mössbauer spectra of $Fe_2(OH)(PO_3)_5$ system.
○: $\bar{n}=9$ ●: $\bar{n}=150$

The next point we were interested in was the intensity and shape of the absorption peak of these compounds. It has been observed from the spectra that the compounds having the shorter chain metaphosphate showed the more intense and sharp absorption. Figure 3 shows the two spectra obtained from $Fe_2(OH)(PO_3)_5$ made from sodium metaphosphate with different chain lengths, *i. e.*, 9 and 150. The latter spectrum exhibits considerably more line broadening than the former spectrum. This broad line seems most reasonably interpreted as a spectrum composed of various components with different values of the quadrupole splitting.

Such a variation in the quadrupole splitting can be attributed to a number of chemical species arising from the partial disruption of the long phosphate chain by means of iron atoms during the course of the preparation.

It is difficult to make a exact explanation on the absorption intensity variation of the $Fe_2(OH)(PO_3)_5$ system with respect to the average chain length of the metaphosphates. However, since the intensity of the absorption is the measure of binding strength, our findings support the view that there is a distinguishable recoil probability in the iron atoms bound in the series of compounds, though they are all chemically analogous. The observed decrease of the intensity with increasing chain length of the compounds must be associated in part with the bonding strength between the iron atoms and phosphate tetrahedra, *i. e.*, the iron atoms are less strongly bound in the compound with longer chain length.

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