2724 © *1994 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***67**, 2724—2730(1994)* [Vol. 67, No. 10

Studies on the Interaction between Iron(III) and Glycerol or Related Polyols over a Wide pH Range

Yasuyoshi Mori and Hiroshi Yokoi*
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432

(Received May 9, 1994)

The interaction between iron(III) and glycerol or related polyols was studied in some detail over a pH range of 1 to 13 mainly by spectrophotometric and NMR measurements. At acidic pH, there appeared a new absorption band at 350 nm in the difference spectra of iron(III) before and after the addition of glycerol, showing that iron(III) and glycerol form a 1 : 1 complex. Although the ^{13}C NMR relaxation rates for all of the carbon atoms of glycerol and 1,3-propanediol were markedly affected by the addition of iron(III), the rate for C-2 of 1,4-butanediol remained unchanged. These facts indicate that either 1,2- or 1,3-diol, as didentate ligand, coordinates to a hydrolyzed iron(III) ion at acidic pH. In all of the present systems of iron(III) and polyols, iron(III) hydroxide-like precipitates resulted at around neutral pH. The polyols were removed in some quantities from solutions by adsorption on the precipitates; the removability depended on their molecular structures. In these polyols, only glycerol, which has three neighboring OH groups, formed soluble complexes at pH >9 if $R>20$. Accordingly, three neighboring OH groups seemed to be essential in the formation of soluble complexes at alkaline pH. In conclusion, the interaction between iron(III) and polyols are severely dependent upon the molecular structures of the polyols.

Polyols have long been known to interact with many kinds of metal ions in aqueous solution.[1—3] In particular, numerous studies have been conducted concerning iron(III)–saccharide systems, because of their biological and chemical importance. The ability of saccharides and related compounds to form soluble complexes with iron(III) in neutral or alkaline solutions has been studied in order to elucidate the absorption and transportation of iron(III) ions in living organism.[4] In practice, dextran–iron(III) complexes (Imferon) have been used for treating iron-deficient anemia.[5] On the other hand, the weak interaction between iron(III) and saccharide at acidic pH was suggested to play an essential role in the photochemically-induced oxidation and selective C–C bond cleavage of monosaccharide.[6]

Some water-soluble polymers, for example poly (vinyl alcohol) (PVA) and dextran, inhibit the formation of iron(III) hydroxide precipitates even when aqueous mixtures of these polymers and iron(III) are neutralized.[5,7] This fact indicates that these polymers can form water-soluble polymer complexes with iron(III). It has recently been revealed that iron(III) ions exist as hydroxide-like clusters in the PVA complexes.[7] However, there is only a small amount of information concerning the detailed structures of these polymer complexes. 1,2,3-Propanetriol (glycerol) and related polyols are monomeric constituents of these polymers. Studies of the interaction between iron(III) and the polyols are also of importance for elucidating more detailed structures of these polymer complexes. The purpose of this study was to investigate the interaction between glycerol or related polyols and iron(III) over a wide pH range in some detail mainly by spectroscopic techniques. We previously reported a similar study in which the main experiments were magnetic susceptibility measurements.[8]

Experimental

Materials and Preparation of Sample Solutions. The polyols used here and $Fe(ClO_4)_3\cdot 6H_2O$ (Kanto Chemicals) were of the highest grade, and were used as received.

Sample solutions for the magnetic susceptibility, ESR, and spectrophotometric measurements were prepared by mixing aqueous solutions of iron(III) perchlorate and each polyol at various molar ratios (R=[polyol]/[iron(III)]), followed by adjusting the pH with NaOH or HCl solutions without any buffer. Sample solutions for NMR measurements were prepared by using D_2O (Matheson, 99.9 atom% D) as the solvent and NaOD or DCl (Aldrich, 99 atom% D) as reagents for pD adjustment. pD was determined by adding a factor of 0.4 to the usual pH-meter reading.[9]

Magnetic Susceptibility, ESR, and Spectrophotometric Measurements. Magnetic susceptibility measurements for aqueous solutions at room temperature were carried out by the Gouy method[10] in order to obtain experimental plots of the effective magnetic moment (μ_{eff}/B.M.) against the pH. The ESR spectra of aqueous iron(III) solutions with glycerol (pH>9) were recorded at the temperature of liquid nitrogen with a JEOL JES-FE1XG ESR spectrometer; attention was paid only to the characteristic signal observed at $g\simeq 4.3$. The assignment of this signal has been reported in the literature.[8] All of the ESR signal intensities were expressed in relative values with respect to that of the iron(III)–glycerol system at pH 13.0.

The absorption spectra were recorded at room temperature on a Hitachi U-2000 spectrophotometer, using 10 mm quartz cells.

NMR Measurements. All of the ^{13}C NMR spectra were taken on a JEOL EX-90 NMR spectrometer operating at a fixed magnetic field of 2.1 T (22.4 MHz) with complete noise decoupling of the protons. A D_2O solution of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP) (Aldrich, 99 atom% D) was used as an external standard. The longitudinal relaxation times (T_1) for the ^{13}C NMR signals were determined at 25±0.1°C by the inversion-recovery method[11] at 8 different pulse intervals. The accuracy of the determined T_1 values is ±2%. The paramagnetic contributions to the relaxation rate ($1/T_{1P}$) were calculated using

$$1/T_{1P} = 1/T_1 - 1/T_1^0,$$

where $1/T_1$ and $1/T_1^0$ represent the relaxation rates in the presence and absence of iron(III), respectively. Here, $1/T_{1P}$ is quantitatively correlated with both the distance between the magnetic nuclei and iron(III) and the concentration of complexing polyols, as is expressed in the Solomon–Bloembergen equation.[12] The shorter is the distance between iron(III) and polyol, or the higher is the concentration of complexing polyol becomes, the larger $1/T_{1P}$ becomes.

Adsorption Measurements of Polyols on Precipitated Iron(III) Hydroxide. The removability of polyols from aqueous solutions by adsorption on precipitated iron(III) hydroxide was determined by ^{13}C NMR measurements. Mixtures of the D_2O solutions of iron(III) and polyols were neutralized to pD 7.0 to form precipitates. The ^{13}C NMR spectra of the supernatants were measured in a quantitative way with a long repetition time (15 s) and short pulse width (6 μs) in order to abolish the effect of NOE.[13]

Results and Discussion

Magnetic Susceptibility Measurements in an Acidic pH Range. Figure 1 shows the pH dependence of μ_{eff} for iron(III) solutions containing glycerol or related polyols. The solid curve in the figure denotes the case of a solution of iron(III) alone. The μ_{eff} values observed at around pH 1 (ca. 5.9 B.M.) were close to the spin-only theoretical value for high-spin iron(III). This fact indicates that almost all of the iron(III) ions exist as hexaaquairon(III) ions in this pH range, whether polyols are present or absent. Then, μ_{eff} fell to ca. 3.8 B.M. with increasing pH. This drop in μ_{eff} was due to an antiferromagnetic interaction between high-spin iron(III) ions,[14] indicating the formation of oxo- and hydroxo-bridged polynuclear complexes, as previously reported.[8]

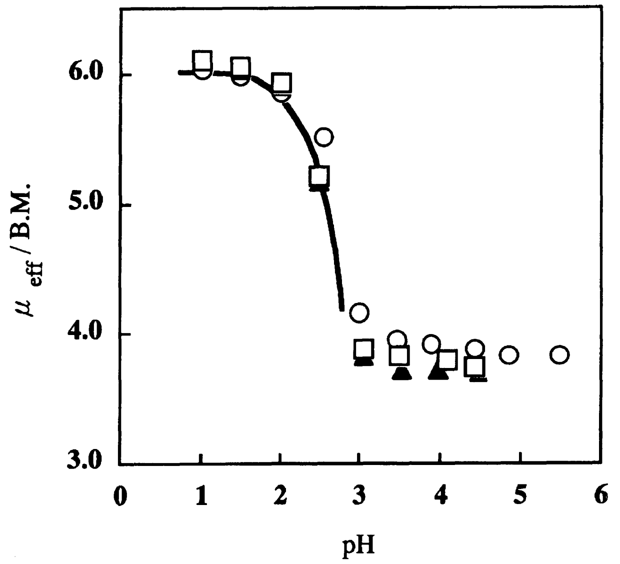

Fig. 1. Plots of μ_{eff} against pH for the aqueous solutions of iron(III) with glycerol (○), ethylene glycol (▲), 1,3-propanediol (□), and iron(III) alone (—) ([iron(III)] = 1.0×10^{-2} mol dm^{-3}; $R = 100$; at room temperature). See text as to the solid line in the figure.

At pH < 3, the polyol–iron(III) system was almost identical in μ_{eff} to those of iron(III) alone. This means that the interaction between iron(III) and polyols at acidic pH is extremely weak. This is also evidenced below regarding spectrophotometric and NMR measurements.

Absorption Spectral Study of Weak Interaction in a Low pH Region. Figure 2 shows the difference spectra of iron(III) before and after the addition of glycerol over the pH range 1 to 2.5, indicating the appearance of an absorption band at 350 nm. This band may be assigned to a ligand-metal charge-transfer (LMCT) band in the iron(III)–glycerol complex, as is the case with the iron(III)–D-fructose complex.[6] Thus, the appearance of this band is an unambiguous indication for the existence of an interaction between them at acidic pH. If the molar absorption coefficient of the band for the iron(III)–glycerol complex is assumed to be of the same order as that for $FeOH^{2+}$ (ca. 2000 mol^{-1} cm^{-1}),[15] it is estimated that only about 0.1% of the glycerol added forms complexes with iron(III) at pH 2.5, suggesting that the interaction is extremely weak.

The absorbance at 350 nm increased remarkably with increasing pH. This result indicates that glycerol has a tendency to interact with the first hydrolytic product, $FeOH^{2+}$, which is one of the dominant species at around pH 2.[15,16] On the other hand, an obscure band observed at pH 1.0 may be due to the formation of an outer-sphere complex of glycerol with hexaaquairon(III) ion, since it has been reported that secondary alcohol can form an outer-sphere complex through hydrogen bonding between the OH group of alcohol and one of the coordinated waters of the hexaaquairon(III) ion.[17]

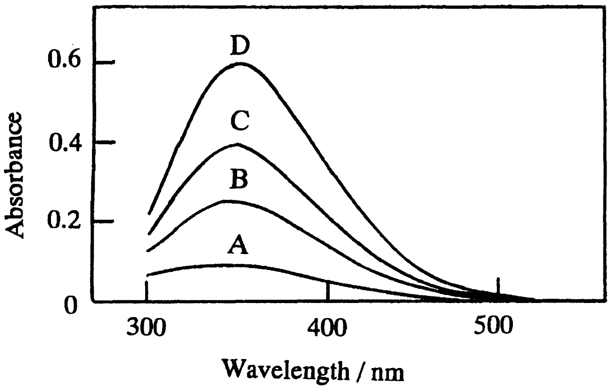

Fig. 2. Difference spectra of the aqueous iron(III) solutions before and after addition of glycerol ([iron(III)] = 2.0×10^{-3} mol dm^{-3}; $R = 500$; at room temperature): A, pH 1.0; B, pH 1.5; C, pH 1.75; D, pH 2.0.

Figure 3 shows the difference spectra of iron(III) before and after the addition of related polyols. The 1,2-ethanediol (ethylene glycol) and 1,3-propanediol system gave new absorption bands at almost the same wavelength as glycerol, although their absorbances were much smaller than that of glycerol. On the other hand, 1,4-butanediol showed only a very weak absorption band, as did ethanol. The relative ability of the polyols to interact with iron(III) was found to be: glycerol> 1,3-propanediol≈ethylene glycol>1,4−butanediol. 1,2- and 1,3-Diol structures are suitable for the interaction, while 1,4-butanediol is characteristic of the formation of an outer-sphere complex with iron(III), as well as monoalcohols.[17] It is now clear that the molecular structures of the polyols are quite important for the interaction.

Plots of the absorbance at 350 nm against R for the iron(III)–polyol systems are shown in Fig. 4, demonstrating that the absorbance is proportional to the concentration of polyol in any system. Thus, the complex formation depends on the first order of the polyol concentration. In a relatively low iron(III) concentration, almost all iron(III) ions exist as hydrated or hydrolyzed monomeric species at pH$\leq$2.[16] Consequently, it is reasonably concluded that polyols and iron(III) form 1 : 1 complexes at around pH 2.

The absorbance at 350 nm for the glycerol system was about twice as large as those for the ethylene glycol and 1,3-propanediol systems. Glycerol has both 1,2- and 1,3-diol structures. Thus, the number of chances for glycerol to interact with iron(III) is twice as many as those for ethylene glycol and 1,3-propanediol. From this experimental fact, it is reasonably considered that glycerol coordinates to iron(III) in either the 1,2- or 1,3-diol form; glycerol is not a tridentate ligand at acidic pH.

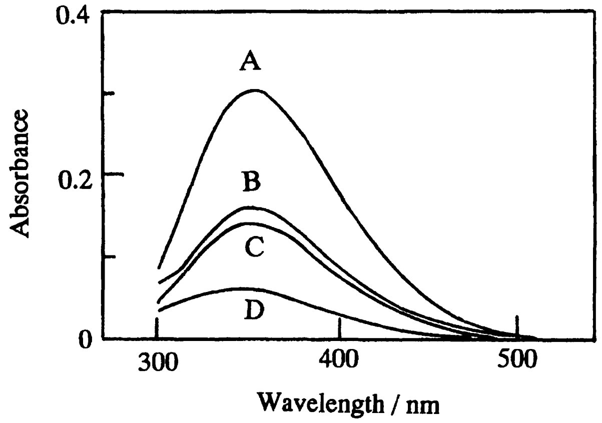

Fig. 3. Difference spectra of the aqueous iron(III) solutions before and after the addition of related polyols ([iron(III)]=2.0×10^{-3} mol dm^{-3}; R=250; pH 2.0; at room temperature): A, glycerol; B, 1.3-propanediol; C, ethylene glycol; D, 1,4-butanediol.

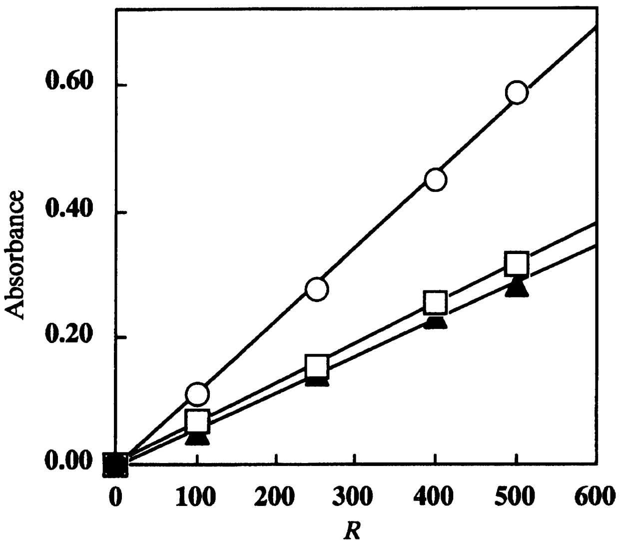

Fig. 4. Plots of absorbance at 350 nm against R for the iron(III)–polyol systems ([iron(III)]=2.0×10^{-3} mol dm^{-3}; pH 2.0; at room temperature): ○, glycerol; ▲, ethylene glycol; □, 1,3-propanediol.

NMR Investigation of Weak Interaction at Acidic pH. Figure 5 shows the ^{13}C NMR spectra for the glycerol–iron(III) system at acidic pD. A remarkable reduction in the intensities of both signals was observed with increasing pD. This reduction was caused by a paramagnetic effect of iron(III) on the glycerol. All of the carbon atoms in every glycerol molecule are clearly in the state of interaction with paramagnetic iron(III) ions at around pD 2. The interaction was quantitatively investigated by NMR re-

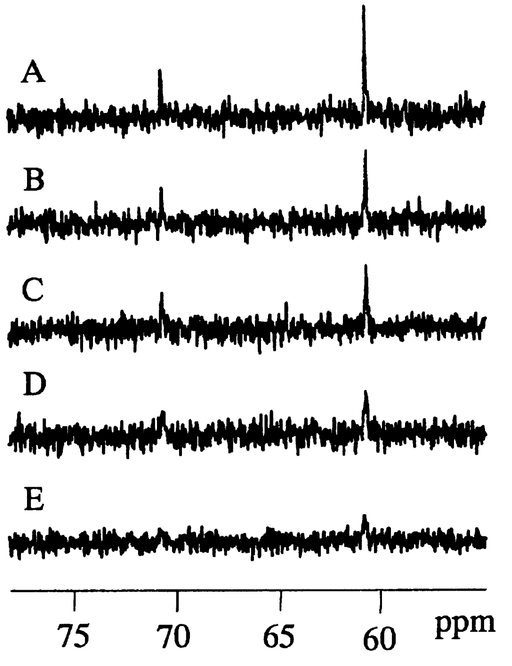

Fig. 5. pH dependence of ^{13}C NMR spectra for the glycerol–iron(III) system ([iron(III)]=1.0×10^{-2} mol dm^{-3}; R=50; at room temperature): A, pD 1.0; B, pD 1.75; C, pD 2.25; D, pD 2.5.

laxation-time measurements, as described below.

Figure 6A, and B show the pD dependence of $1/T_{1p}$ for various polyol–iron(III) systems. Glycerol, ethylene glycol, and 1,3-propanediol increased in $1/T_{1p}$ with increasing pD, whereas 2-propanol decreased (Fig. 6A). This result indicates that the former three polyols interact with iron(III) at acidic pH.

The values of $1/T_{1p}$ for glycerol were about twice as large as those for ethylene glycol and 1,3-propanediol. This result indicates that glycerol interacts with iron(III) in either the 1,2- or 1,3-diol form, as already mentioned above. This is further supported by the fact that the $1/T_{1p}$ values of 1,2,4-butanetriol were almost identical to those of glycerol (Fig. 6B). Therefore, three neighboring OH groups in glycerol are not always of structural importance in a strong interaction with iron(III).

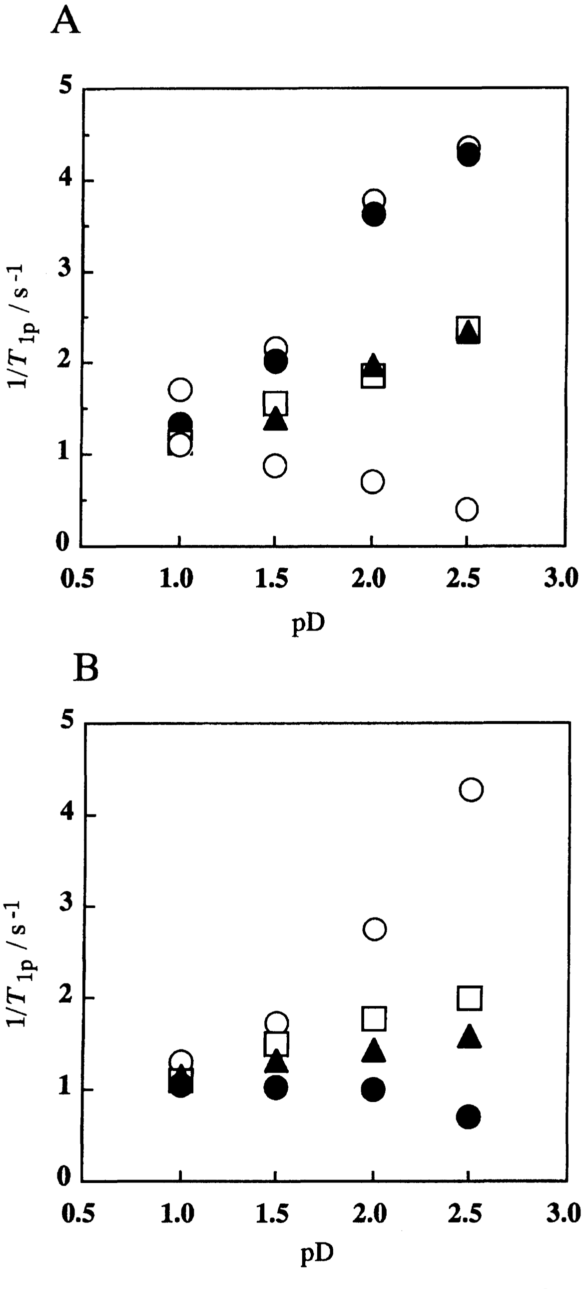

Fig. 6. pD dependence of the paramagnetic contribution of iron(III) to $1/T_1$ for the ^{13}C NMR of various polyols ([iron(III)]=1.0×10^{-2} mol dm^{-3}; R=50; 25±0.1°C). (A): ○, C-1 of glycerol; ●, C-2 of glycerol; ▲, ethylene glycol; □, C-1 of 1,3-propanediol; ○, C-2 of 2-propanol (B): ○, C-2 of 1,2,4-butanediol; □, C-2 of 1,3-propanediol; ▲, C-2 of 2-methyl-1,3-propanediol; ●, C-2 of 1,4-butanediol.

Interestingly, the CH_2 group of 1,3-propanediol increased in $1/T_{1p}$ along with increasing pD, in spite of no OH groups (Fig. 6B). However, the CH_2 group of 1,4-butanediol slightly decreased in $1/T_{1p}$ with increasing pH. These facts strongly suggest that 1,3-diol as a didentate ligand coordinates to iron(III) to form stable six-membered chelate ring. The CH_2 group of 1,3-propanediol in the chelate ring was sufficiently close to iron(III) to suffer a paramagnetic effect of iron(III). On the other hand, the CH_2 group of 1,4-butanediol is apart from iron(III), since it can form only an outer-sphere complex. This is also supported by the smaller values of $1/T_{1p}$ for the CH group of 2-methyl-1,3-propanediol than those for the CH_2 of 1,3-propanediol (Fig. 6B). The methyl group of the former diol may give an inhibitory effect on chelate formation. Furthermore, the CH_2 group for ethylene glycol has almost the same $1/T_{1p}$ value as that for 1,3-butanediol. It is reasonably considered that ethylene glycol coordinates as a didentate ligand to form a five-membered chelate ring.

It has been revealed that polyols can not coordinate to metal ions at acidic pH, due to their low acidity.[2] However, the rate of the substitution reaction for the hydrolytic product, $[Fe(OH)(H_2O)_5]^{2+}$, is much higher than that for $Fe(H_2O)_6^{3+}$, owing to the effects of electron donation from the OH^- ion to the iron(III).[18] Such an activated water molecule in $[Fe(OH)(H_2O)_5]^{2+}$ must be substituted by polyols which have structures suitable for the formation of five- and six-membered chelate rings. This is considered to be a reason why the interaction is enhanced along with an increase in pH from 1 to 2.5.

Interaction in a Neutral or High pH Region. Iron(III) hydroxide-like precipitates are formed when aqueous mixture of iron(III) and polyols are neutralized to pH>3. Polyol are removed in varying portions from their aqueous solution by adsorption on the precipitates according to their molecular structure, as well as saccharide.[19] The removability of the polyols is summarized in Table 1, which shows the following order of removability: glycerol>1,3-propanediol≈ethylene glycol>1,4-butanediol. Interestingly, this order is the same as that of the ability to interact with iron(III) at acidic pH. These facts indicate that the polyols are adsorbed on iron(III) hydroxide precipitates through a weak interaction between the OH groups of polyols and the surface of the precipitates, and that the interaction is selective about the structures of polyols.

Figure 7 shows the precipitation area on a pH–R

Table 1. Removability of Polyols from Aqueous Solutions by Adsorption on Precipitated Iron(III) Hydroxides (R=50; [polyol]=0.5 mol dm^{-3}; pD 7.0)

Polyol	Removability/%
Glycerol	5.9
1,3-Propanediol	2.8
Ethylene glycol	2.7
1,4-Butanediol	0.7
2-Propanol	0

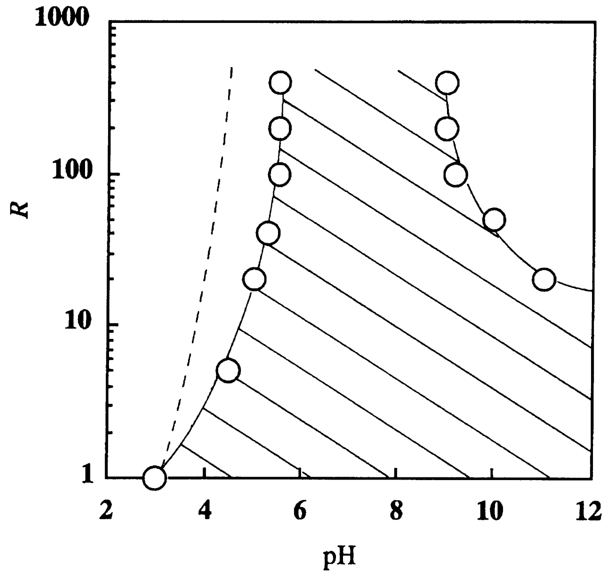

Fig. 7. Precipitation area (shaded) in a pH–R graph for the glycerol–iron(III) system ([iron(III)]=1.0×10^{-2} mol dm^{-3}). The dotted line expresses a boundary on the right-hand side of which precipitation occurs in the cases of ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1-methoxy-2,3-propanediol.

graph for the glycerol–iron(III) system. The precipitation area was determined by visually judging whether or not precipitation or turbidity formation occurred under every condition of pH and R. The shaded area in the figure shows the region of precipitation, and the dotted line expresses a boundary on the right-hand side of which precipitation occurs in the cases of ethylene glycol, 1,3-propanediol, 1,2,4-butanetriol, and 1-methoxy-2,3-propanediol. At around neutral pH, precipitation was observed in all of the systems. For all of the polyols, except for glycerol, the precipitates once produced were never redissolved at pH>5, even at a large R value of 500. On the other hand, only glycerol formed soluble complexes at pH>9 if R>20. From this result, it is reasonably concluded that three neighboring OH groups in polyols are essential for the reproduction of soluble complexes at alkaline pH. This is consistent in outline with the results so far reported,[2,3] although the experimental conditions and procedures are not exactly the same. Emphasis has previously been placed to the necessity of 1,2-[2] or 1,3-diol structure[3] in the reproduction of soluble complexes at alkaline pH.

The above-mentioned soluble complexes formed at alkaline pH were characterized by magnetic susceptibility and ESR measurements. Figure 8 shows the pH dependences of μ_{eff} and the ESR signal intensity at $g \simeq 4.3$ for the iron(III)–glycerol system at pH>9. Plots of μ_{eff} against the pH were quite similar in tendency to those of the ESR signal intensity. Relatively small values of μ_{eff} and weak ESR signal intensities were obtained at around pH 10, indicating that some kind of water-soluble polynuclear complexes of iron(III) are formed in the alkaline pH range.

Both μ_{eff} and the ESR signal intensity at $g \simeq 4.3$ increased with increasing pH, as is the case with monosaccharide.[8] This is undoubtedly caused by the formation of mononuclear high-spin iron(III) complexes, as previously reported.[8] These facts suggest that three neighboring OH groups are essential for the formation of mononuclear complexes. Accordingly, glycerol as a tridentate ligand coordinates to the iron(III) ion at a high-pH region. This is further supported by the fact that PVA can not form mononuclear complexes, even if pH>12.[7,20]

It is well-known that ethylene glycol and PVA deprotonate upon the formation of copper(II) complexes at strongly alkaline pH.[21] It is of great interest to see whether or not such deprotonation occurs in the case of iron(III); however, there is no unambiguous experimental evidence for it at present, although deprotonation is supported to be true. This is an important subject for further study.

Conclusion

The structural requirements for the interaction of

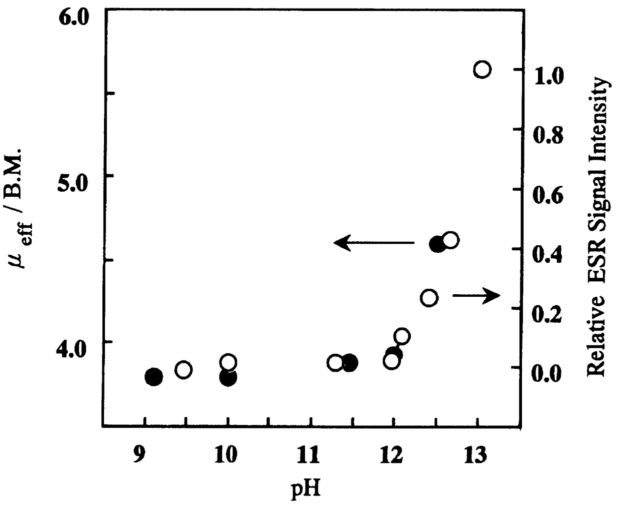

Fig. 8. Plots of μ_{eff} (●) and relative ESR signal ($g \simeq 4.3$) intensity (○) against pH for the iron(III)–glycerol system ([iron(III)]=1.0×10^{-2} mol dm^{-3}; R=100).

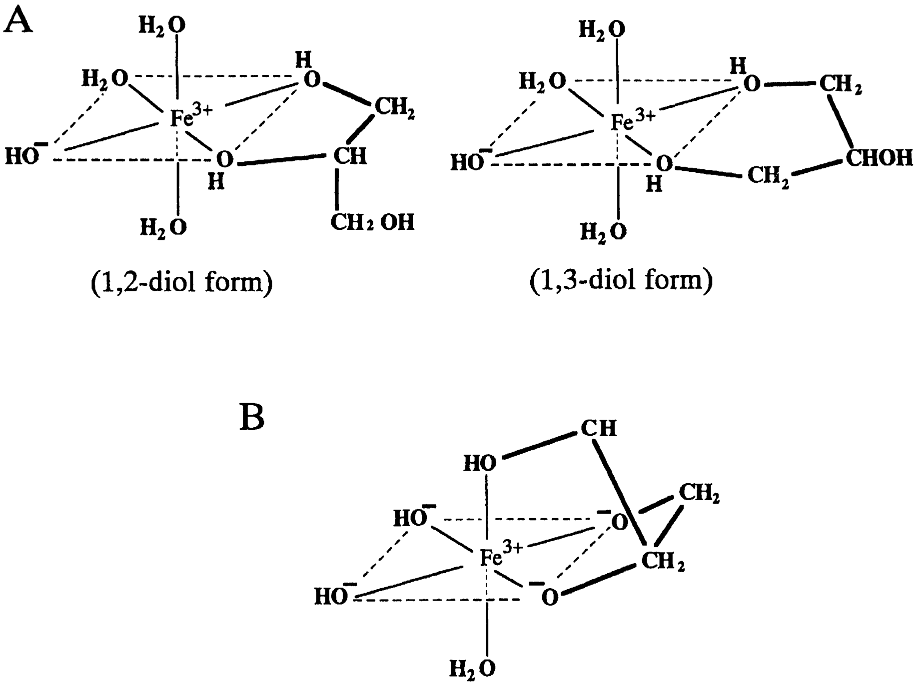

Fig. 9. Possible structures of iron(III) complexes with glycerol in acidic (A) and alkaline solution (B).

polyols with iron(III) in acidic solution are different from those in an alkaline solution. At acidic pH, it has been revealed that either 1,2- or 1,3-diol as a didentate ligand coordinates to the first hydrolytic product of iron(III) ion, $FeOH^{2+}$. Glycerol has a marked ability to interact with iron(III), because it has both 1,2- and 1,3-diol structures. Such three neighboring OH groups as in glycerol have no substantial significance in the interaction, while they are essential for the formation of both soluble polynuclear and mononuclear complexes at alkaline pH. Glycerol must destroy iron(III) hydroxide-like clusters formed in order to form mononuclear complexes at strongly alkaline pH. Therefore, glycerol may be a tridentate and fairly strong chelating ligand, although unambiguous evidence supporting the deprotonation of glycerol in the chelation has not yet been obtained. The possible structures of iron(III) complexes with glycerol in acidic and alkaline solutions were estimated, as shown in Fig. 9, with reference to the literature concerning sugar complexes.[4,22] In an alkaline solution, neighboring OH groups in glycerol may deprotonate upon complex formation, as is the case with the copper(II)–ethylene glycol complex formed at pH>13.[21] Furthermore, it is an important suggestion for depicting the structure (B) that the complex formation of $[Fe(OH)_4]^-$ with four deprotonations has been predicted in a strongly alkaline solution of iron(III) by pH titration.[7,15]

It has been revealed that molecular-recognition is achieved between polyols and iron(III) hydroxide-like precipitates, since the adsorption of polyols on the precipitates is dependent upon the polyol structures. This type of molecular-recognition interaction is very suggestive in considering some aspects of the mechanism in biomineralizaton.[23]

PVA and dextran are polymers mainly comprising 1,3- and 1,2-diol structures, respectively. The PVA–iron(III) complex has been estimated to differ in structure from that of the dextran–iron(III) one.[5,7,20] For example, dextran forms a mononuclear complex with iron(III) to some extent at pH>12, but PVA does not.[20] The above-mentioned structural requirements for the interaction of polyols with iron(III) are of great importance in elucidating the nature and structure of these polymer complexes.

Thanks are given to Mr. H. Matsumura for his assistance in the experimental work.

References

1) R. Aasa, B. Makmström, P. Saltman, and T. Vänngård, *Biochim. Biophys. Acta*, **88**, 430 (1964); R. N. Pandey and W. M. Smith, *Can. J. Chem.*, **50**, 194 (1972); H. A. Tajmir-Riari and T. Theophanides, *Can. J. Chem.*, **63**, 2065 (1985); E. J. Bourne, F. Searle, and H. Weigel, *Carbohydr. Res.*, **16**, 185 (1971); D. M. Templeton and B. Sarkar, *Biochem. J.*, **230**, 35 (1985).

2) H. W. Rich, K. Hegetschweiler, H. M. Streit, I. Erni, and W. Schneider, *Inorg. Chim. Acta*, **187**, 9 (1991).

3) P. S. Davis and D. J. Deller, *Nature*, **212**, 404 (1966).

4) P. Saltman, *J. Chem. Educ.*, **42**, 682 (1965).

5) J. S. G. Cox and R. E. King, *Nature*, **207**, 1202 (1965); J. S. G. Cox, G. R. Kennedy, J. King, P. R. Marshall, and D. Rutherford, *J. Pharm. Pharmacol.*, **24**, 513 (1972).

6) K. Araki and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **59**, 229 (1986); K. Araki and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **59**, 3661 (1986).

7) H. Yokoi, "Kobunshi Sakutai (Dynamic Interactions and Electronic Processes of Macromolecular Complexes)," ed by E. Tsuchida, Japan Scientific Society Press, Tokyo (1991), p. 181; Y. Mori, H. Yokoi, and Y. Fujise, *Macromolecules*, to be published.

8) H. Yokoi, Y. Mori, T. Mitani, and S. Kawata, *Bull. Chem. Soc. Jpn.*, **65**, 1898 (1992).

9) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

10) P. L. Martin and A. Whitley, *J. Chem. Soc.*, **1958**, 1934.

11) G. C. Levy and I. R. Peat, *J. Magn. Reson.*, **18**, 500 (1975).

12) I. Solomon, *Rhys. Rev.*, **99**, 559 (1955); I. Bertini and C. Luchinat, "NMR of Paramagnetic Molecules in Biological Systems," ed by A. B. P. Lever and H. B. Gray, The Benjamin/Cummings Publishing Company, California (1986), p. 47.

13) D. Shaw, "Fourier Transform N. M. R. Spectroscopy," Elsevier Scientific Publishing Company, New York (1976), p. 257.

14) D. F. Harvey, C. A. Christmas, J. K. McCusker, and P. M. Hagen, *Angew. Chem., Int. Ed. Engl.*, **5**, 30 (1991); J. Kürti, M. A. Mostafa, L. Korecz, L. Nagy, and K. Burger, *J. Radioanal. Nucl. Chem. Lett.*, **118**, 437 (1987); M. Kiyama and T. Takada, *Bull. Chem. Soc. Jpn.*, **46**, 1680 (1973).

15) C. F. Base, Jr., and R. E. Mesmer, "The Hydrolysis of Cations," Jhon Wiley & Sons, New York (1976), p. 226.

16) C. M. Flynn, Jr., *Chem. Rev.*, **84**, 31 (1984); G. H. Khoe, P. L. Brown, R. N. Sylva, and R. G. Robins, *J. Chem. Soc., Dalton Trans.*, **1986**, 1901.

17) J. H. Carey and C. H. Langford, *Can. J. Chem.*, **53**, 2436 (1975).

18) S. Funahashi, S. Adachi, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **46**, 479 (1973).

19) H. Yokoi, T. Tsutsui, Y. Mori, and T. Mitani, *Chem. Lett.*, **1991**, 2231.

20) Y. Mori and H. Yokoi, in preparation.

21) H. Yokoi and A. Kadowaki, *Nippon Kagaku Kaishi*, **1988**, 209, and references cited therein.

22) W. Schneider, *Chimia*, **42**, 9 (1988); S. J. Angyal, G. S. Bethell, and R. J. Beveridge, *Carbohydr. Res.*, **73**, 9 (1979).

23) S. Mann, *Nature*, **332**, 119 (1988); D. D. Archbald and S. Mann, *Nature*, **364**, 430 (1993); S. Mann, D. D. Archbald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum, and N. J. Reeves, *Science*, **261**, 1286 (1993); L. Addadi and S. Weiner, *Angew. Chem., Int. Ed. Engl.*, **31**, 153 (1992).