CHEMISTRY LETTERS, pp. 281-284, 1994.

Complex Formation between Iron(III) and Tartaric and Citric Acids in a Wide pH Range 1 to 13 as Studied by Magnetic Susceptibility Measurements

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Computer simulation analysis of the experimental plots of effective magnetic moment against pH for aqueous solutions of iron(III) and either L-tartaric acid or citric acid at different concentration ratios has first given the whole aspect of complex formation in a wide pH range 1 to 13 at room temperature. Formation of various kinds of poly- and mono-nuclear complexes has been elucidated in these solutions.

Tartaric and citric acids are complex ligands bearing both of one or more hydroxyl and carboxyl groups. They have numerous uses in analytical chemistry as masking reagents, in solvent-extraction chemistry as complex-forming agents1) and in many other fields as solubilizing and peptizing agents for various substances . Alkaline iron(III) tartarate solution is utilized as a cellulose solvent,2) and tartaric acid is also used in preparing modified nickel catalysts for asymmetric syntheses,3) as in optical resolution. It is needless to say that citric acid is intrinsically important in biological systems. Iron(III) complexes with tartaric and citric acids have been studied by many investigators.4 - 7) All of these studies, however, were carried out at acid pH; besides, their results were somewhat diverse. The pH region above 6 is rather interesting and important in these complex systems. At any way, the whole aspect of the complex formation still remains unclear. In this study, the complex formation of iron(III) with tartaric and citric acids in a wide pH range 1 to 13 has been investigated by a new method based on magnetic susceptibility measurements and their analyses; this method will be hereinafter called magnetic susceptibility titration for convenience. The usefulness of this method for investigating this sort of complex formation for paramagnetic metal ions which easily hydrolyze and polymerize in aqueous solutions in complicated ways has also been emphasized

The source of iron(III) was $Fe(ClO_4)_3 \cdot 6H_2O$. Tartaric acid was of the L form. All reagents were of reagent grade or higher and used without further purification. All sample solutions contained 10.0 mM iron(III) (1M = 1mol / dm^{-3}), 0.25M $NaClO_4$, and tartaric or citric acid at R = 1, 3, and 5, where R =[tartaric or citric acid] / [iron(III)]. The pH adjustment was done with NaOH and $HClO_4$ without any buffer, being accompanied by an inevitable degree of error in pH. Magnetic susceptibility measurements for sample solutions at room temperature were carried out by the Gouy method to obtain plots of effective magnetic moment, μ_{eff}, against pH in the pH range 1 to 13.8) On the other hand, fraction diagrams of iron(III) complex species as a function of pH were calculated by using a computer program,9) on the

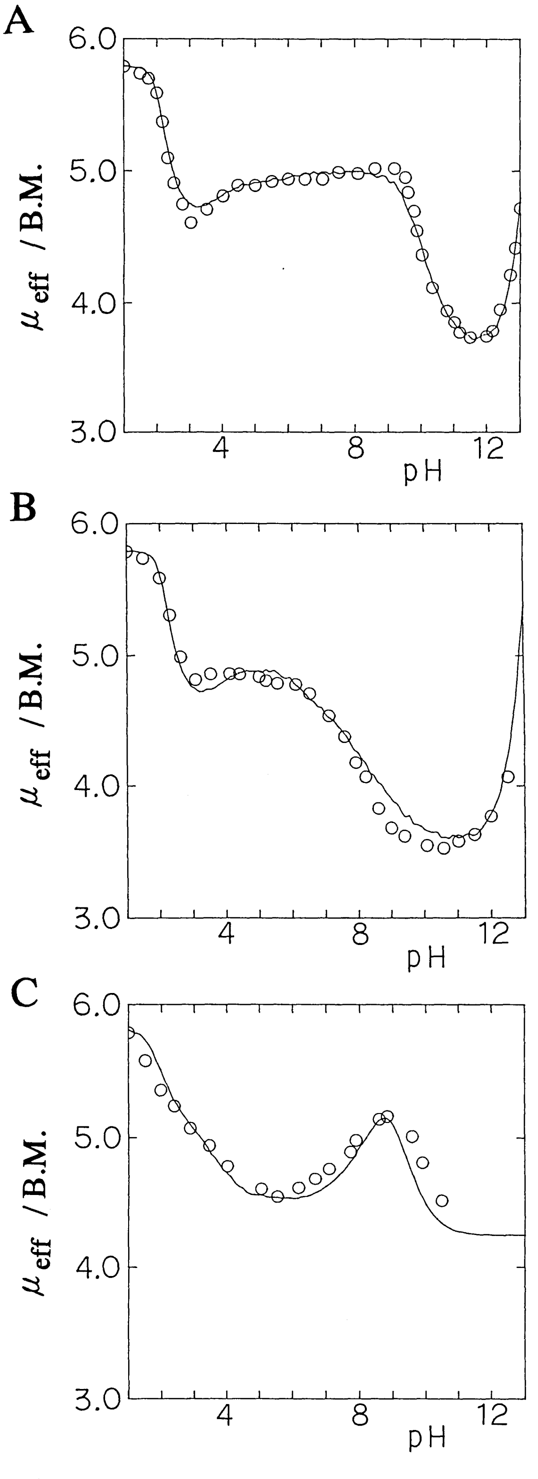

Fig.1. Experimental plots (○) of μ_{eff} against pH and their simulations (—) for the iron(III)-tartaric acid system(A, R =3; B, R =1) and for the iron(III)-citric acid system (C, R =3).

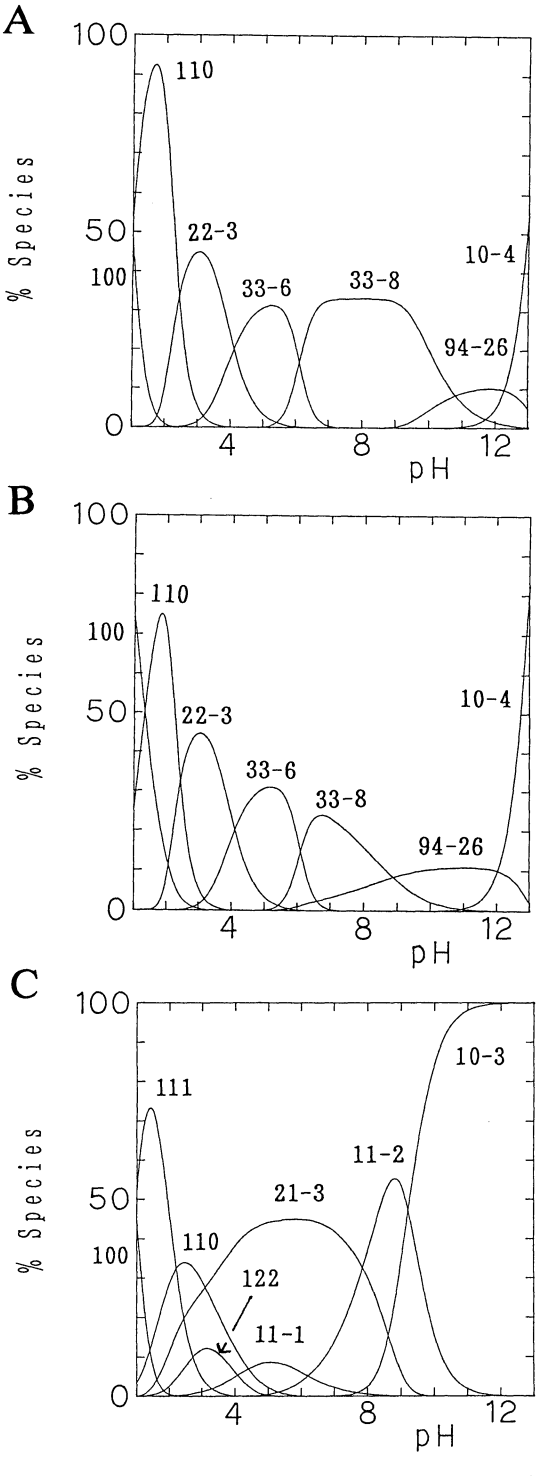

Fig.2. Fraction diagrams of the iron(III)-tartaric acid and iron(III)-citric acid systems (A,B, and C correspond to those in Fig.1) Each of three successive numbers in the figures expresses the p, q, and r values of $Fe_pL_qH_r$ respectively.

assumption of several possible sets of FepLqHr and its β_{pqr} value in the following equations, where tartaric and citric acids are expressed as H_2L and H_3L respectively.

$$p\mathrm{Fe} + q\mathrm{L} + r\mathrm{H} \rightleftharpoons \mathrm{Fe}_p\mathrm{L}_q\mathrm{H}_r \qquad \beta_{pqr} = [\mathrm{Fe}_p\mathrm{L}_q\mathrm{H}_r] / [\mathrm{Fe}]^p[\mathrm{L}]^q[\mathrm{H}]^r$$

In this assumption, data on FepLqHr and β_{pqr} so far obtained especially by the pH titration method were taken into consideration as much as possible. Finally, experimental plots of μ_{eff} against pH over the whole pH range were computer-simulated by assigning each FepLqHr complex to a possible $\mu_{eff,pqr}$ value, where $(\mu_{eff,obsd})^2 = \Sigma f_{pqr}(\mu_{eff,pqr})^2$ was used at every pH value, f_{pqr} being a molar fraction of the corresponding complex. The computer simulation was similarly attempted by using the same parameter values for the other plots obtained at different *R* values. The selected parameter values were concluded to be reliable, if fitting of computer simulation curves to experimental plots was always satisfactory for all sample solutions at different *R* values, although the fitting was done only visually at the present stage of this work. The present method for analyzing the experimental plots of μ_{eff} against pH will soon be reported in full detail elsewhere. Iron(III) ions at $\mathrm{pH} \simeq 1$ exist as mononuclear hydrated ones and have a μ_{eff} value close to the spin-only value of high-spin iron(III) of 5.92 B.M. Iron(III) ions generally have a smaller μ_{eff} value as they form polynuclear complexes at $\mathrm{pH} \gtrsim 2$ by hydrolysis and polymerization.10) Most mononuclear iron(III) complexes besides the above-mentioned hydrated ones are similar in μ_{eff} to the hydrated ones. However, $Fe_1L_0H_{-3}$ in the iron(III)-citric acid system was exceptionally assumed to have a smaller μ_{eff} value, because this complex was considered to be essentially the same as clusterized and precipitated iron(III) hydroxide.1,11) $Fe_1L_0H_{-3}$ is regarded as a solubilized form of $Fe_n(OH)_{3n}$, where n is not so large. Mononuclear high-spin iron(III) complexes usually show characteristic ESR spectra with intense absorptions at $g \simeq 4.2$.10) In the present work, therefore, solution ESR spectra at 77 K were recorded in order to check variations of the mononuclear complexes in quantity.

Table 1. Data on $Fe_pL_qH_r$, β, and μ_{eff}

System	p	q	r	log β	μ_{eff} / B.M.
Iron(III)-tartaric acid	1	0	0	0.0	5.80
	1	1	0	6.4 (6.23) a)	5.80
	2	2	-3	8.0 (8.75) a)	4.70
	3	3	-6	7.2 (9.55) a)	4.95
	3	3	-8	-5.0	5.00
	9	4	-26	-38.5	3.60
	1	0	-4	-21.3	5.80
Iron(III)-citric acid	1	0	0	0.0	5.83
	1	1	1	12.6 (12.38) b)	5.83
	1	1	0	10.4 (11.21) b)	5.83
	1	1	-1	6.0 (8.60) b)	5.83
	1	1	-2	-0.2	5.83
	1	2	2	22.0	5.83
	2	1	-3	8.3	4.40
	1	0	-3	-11.0	4.25 c)

a) Ref.5. b) Ref.7. c) See text as to this small value.

Some of the experimental plots of μ_{eff} against pH obtained for the iron(III)-tartaric acid and -citric acid systems are shown in Fig.1, together with computer simulation curves calculated with the parameter values listed in Table 1. Fitting of the simulation curves to the experimental plots has been satisfactory for all sample solutions at different R values, as exemplified by the results shown in Figs. 1A and B corresponding to $R = 3$ and 1 respectively. This fact indicates that the results of Table 1 are almost valid, although there may be a little room for further refinement. Fraction diagrams of the complex species formed in these solutions have been calculated by using the results of Table 1, as shown in Fig. 2. Support for the appearance of a mononuclear complex around pH 9 in the iron(III)-citric acid system, as shown in Fig. 2C, has been furnished by ESR measurements.

In conclusion, an outline of complex formation between iron(III) and tartaric and citric acids in the pH range 1 to 13 can be depicted by Table 1. The results of $\mathrm{Fe_pL_qH_r}$ and β_{pqr} obtained here are in substantial agreement with those in the literatures, as shown in the table. Detailed structural elucidation of the complexes listed here is the subject for a future study. The magnetic susceptibility titration method developed in this work is now being applied to many other complex formation systems of iron(III). However, it is also necessary to improve extensively the method for analyzing the experimental plots of μ_{eff} against pH. This method may be a most useful and powerful technique for investigating complex formation for such paramagnetic ions as iron(III) in which complex formation is very complicated owing to easy hydrolysis and polymerization.

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(Received October 22, 1993)