

# Complexing properties of bivalent and trivalent iron in the system citric acid—iron(II) perchlorate—iron(III) perchlorate—water

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The system Fe(III)—Fe(II)—aqueous solution of citric acid was investigated at ionic strength  $I = 3 \text{ mol dm}^{-3}$  in the presence of perchlorate and sodium ions by the method of redox potential. The composition of predominating complexes was determined by graphical analysis. The stability constants were calculated as parameters of redox potential by means of a computer by using the method of least squares. The method of statistical optimization was used for solving the intricate nonlinear functional relationship. The conditions of origination and existence of individual complexes have been characterized by distribution curves. Thus, it has been shown that the complexes of trivalent iron of the composition  $\text{FeAH}_2^+$ ,  $\text{FeA}_2\text{H}_4^-$ , and  $\text{FeA}_3\text{H}_6^-$  as well as complexes of bivalent iron of the composition  $\text{FeAH}^-$  and  $\text{FeAH}_2$  exist in the investigated system.

Методом окислительно-восстановительного потенциала была изучена система Fe(III)—Fe(II)—водный раствор лимонной кислоты при ионной силе  $I = 3 \text{ моль дм}^{-3}$  в присутствии перхлоратных и натриевых ионов. Состав преобладающих комплексов был определен графическим анализом. Константы устойчивости были рассчитаны на ЭВМ методом наименьших квадратов как параметры окислительно-восстановительного потенциала. Для решения сложной нелинейной функциональной зависимости был использован метод статистической оптимализации. Условия образования и существования отдельных комплексов охарактеризованы кривыми распределения. Было доказано, что в изучаемой системе существуют комплексы трехвалентного железа состава  $\text{FeAH}_2^+$ ,  $\text{FeA}_2\text{H}_4^-$ ,  $\text{FeA}_3\text{H}_6^-$  и комплексы двухвалентного железа состава  $\text{FeAH}^-$  и  $\text{FeAH}_2$ .

Recently, the interest in the field of physical chemistry of solutions was concentrated on the study of complexing equilibria in complicated systems

containing mixed, polynuclear and protonized complexes. The investigated system belongs into the group of these systems.

The methods for studying the complexing properties of citric acid in the presence of iron(II) and iron(III) ions are diverse and the data given by different authors are frequently incomplete and contradictory [1—4]. Some authors assume solely the transformation of fully deprotonized complex compounds [5, 6]. On the other hand, *Koreychuk* [7] evidenced the presence of complex compounds of trivalent iron which also contained protonized ligands of citric acid. *Bertin* [8] determined only mononuclear complexes. Besides mononuclear complexes, *Vaňura* and *Kuča* [9] also determined binuclear complexes and hydroxo complexes. The acquirement of reliable information about this complicated system demands the possibly most precise measurements and a rigorous mathematical processing of the measured values.

For the study of the above system we used a variant of potentiometric method, i.e. the method of redox potential [10] which enabled us to elucidate the character of arising complexes with sufficient accuracy.

The general equation of redox potential is [11]

$$E = E^0 + \vartheta \log \frac{C^0}{C^R} - \vartheta \log \left\{ \sum_{q=1}^Q \sum_{x=0}^X \sum_{y=0}^Y \sum_{k=0}^K q (\beta_{qxyk}^0)^{1/q} \cdot \omega_{qxyk}^{q-1/q} C_a^{x/q} \cdot \frac{(B_{as})^{x/q} [H^+]^{(k-y)/q}}{\left( \sum_{s=0}^b [H^+]^{b-s} B_{as} \right)^{x/q}} \right\} + \vartheta \log \left\{ \sum_{p=1}^P \sum_{u=0}^U \sum_{v=0}^V \sum_{l=0}^L p (\beta_{puvl}^R)^{1/p} \varrho^{(p-1)/p} C_a^{u/p} \cdot \frac{(B_{as})^{u/p} [H^+]^{(l-v)/p}}{\left( \sum_{s=0}^b [H^+]^{b-s} B_{as} \right)^{u/p}} \right\} \quad (1)$$

Eqns (2—5) [10] suited for evaluating the experimental results concerning complexing equilibria result from the fundamental eqn (1)

$$\left( \frac{\partial E}{\partial p C^0} \right)_{pC^R, pH, pC_a} = -\frac{\vartheta}{q} \quad (2)$$

$$\left( \frac{\partial E}{\partial p C^R} \right)_{pC^0, pH, pC_a} = \frac{\vartheta}{p} \quad (3)$$

$$\left( \frac{\partial E}{\partial p C_a} \right)_{pC^0, pC^R, pH} = \vartheta \left( \frac{x}{q} - \frac{u}{p} \right) \quad (4)$$

$$\left( \frac{\partial E}{\partial pH} \right)_{pC^0, pC^R, pC_a} = \vartheta \left[ \frac{k-y}{q} - \frac{l-v}{p} + \left( \frac{u}{p} - \frac{x}{q} \right) Z \right] \quad (5)$$

where

$$Z = \frac{\sum_{s=0}^b (b-s)[H^+]^{b-s} B_{as}}{\sum_{s=0}^b [H^+]^{b-s} B_{as}}$$

Eqns (2) and (3) enable us to determine the number of nuclei of the oxidized and reduced form of metal while the number of ligands and protogenic groups in complex may be estimated according to eqns (4) and (5).

### Experimental

The complexing properties were investigated by the method of redox potential in a thermostatted hermetically closed measuring vessel (Metrohm, type EA 876-20-T) at ionic strength  $I=3 \text{ mol dm}^{-3}$  and  $25 \pm 0.1^\circ\text{C}$ . Argon deprived of the rests of oxygen [12] was used as inert atmosphere for measurements.

The equimolar solutions of iron(II) and iron(III) perchlorate used as titrants were kept in inert atmosphere. A glass electrode (Metrohm, type EA 109), platinum electrode (Metrohm EA 240), salt bridge filled with a 3 M solution of sodium nitrate, and a saturated calomel electrode (Radiometer K 401) serving as reference electrode were placed in the measuring vessel. The glass electrode EA 109 was standardized according to Schwabe [13].

Iron(II) perchlorate was synthesized from reactive, powdered anal. grade iron by dissolving it in dilute anal. grade perchloric acid [14]. The concentration of iron(II) perchlorate was determined chromatometrically by differential potentiometric titration [15]. Iron(III) perchlorate was made by dissolving freshly prepared iron(III) hydroxide in dilute anal. grade perchloric acid. The concentration of iron(III) perchlorate was determined with complexone III by differential potentiometric titration. The solutions of citric acid were prepared from anal. grade citric acid monohydrate.

The ionic strength was held constant by means of anal. grade sodium perchlorate (Apolda, GDR). The potentiometric measurements were carried out with a compensation pH-meter pHm 4d, titrigraph SBR 4c (Radiometer, Copenhagen, Denmark), and a potentiograph E 336 A (Metrohm). The error of potentiometric measurements was  $\pm 1 \text{ mV}$ . In accord with the theory of redox potential [10], the composition of predominating complex compounds of trivalent and bivalent iron may be determined by analyzing the dependence of redox potential on particular parameters (pH,  $pC_a$ ,  $pC^0$ ,  $pC^R$ ). For obtaining the required relationships, two solutions, *i.e.* titrated and titrating, which distinguished from each other only by concentration of one component, concentrations of other components being constant, were prepared.

### Results and discussion

The complex compounds of the redox system Fe(III)—Fe(II)—citric acid arise in a solution as a result of complicated interactions which also involve the protolytic reactions of coordinated ligands.

The number of nuclei in a complex of trivalent iron in the investigated system is to be determined from the dependence of redox potential on  $pC^O$  at constant values of  $C^R$ ,  $C_a$ , and pH (eqn (2)) while the number of nuclei in a complex of bivalent iron results from the dependence of redox potential on  $pC^R$  at constant values of  $C^O$ ,  $C_a$ , and pH (eqn (3)). The dependence of redox potential on  $pC^O$  is represented in Fig. 1. It ensues from this figure that this dependence is linear with the slope  $-\vartheta$  in the pH region 0.1—1.0 (plots 1—4), which indicates the existence of mononuclear complexes of trivalent iron. In the pH region 1.5—2.4 the plots assume again the linear character with the slope  $-\vartheta/2$ , which reveals the presence of binuclear complexes. Some mononuclear and binuclear complexes must coexist in the pH region 1.0—1.5. Plots 6 and 7 characterizing solutions with rather high concentrations of trivalent iron within the pH range 2.0—2.4 have the slopes with smaller angles, which is a manifestation of the formation of complexes with higher

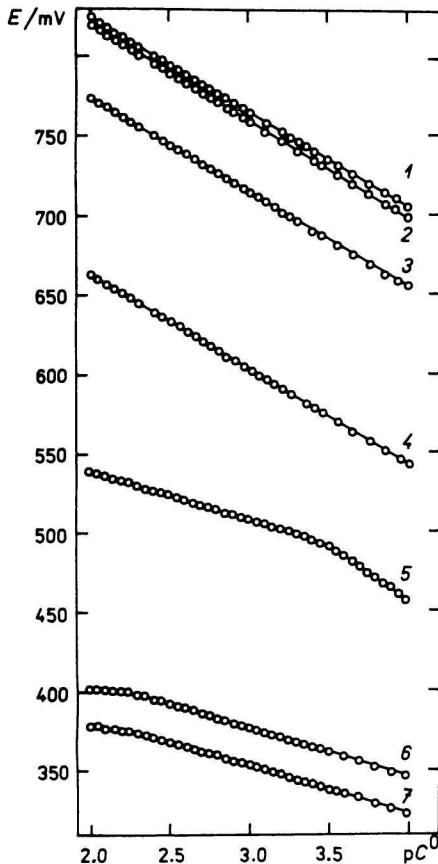


Fig. 1. Redox potential as a function of negative logarithm of the concentration of Fe(III).  
 $C^R = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $C_a = 0.27 \text{ mol dm}^{-3}$ ,  
 $I = 3.0 \text{ mol dm}^{-3}$ .  
 1. pH 0.1; 2. pH 0.2; 3. pH 0.5; 4. pH 1.0;  
 5. pH 1.4; 6. pH 2.0; 7. pH 2.4.

number of nuclei. At very low concentrations of trivalent iron ( $pC^0$  3.5) (plot 5), a tendency to the formation of a linear section with the slope  $-\vartheta$  appears, which suggests the origination only of mononuclear complexes.

The dependence of redox potential on  $pC^R$  in equal pH region (pH 0.1—pH 2.4) has been linear with the slope  $+\vartheta$ , which means according to eqn (3) that the complexes of bivalent iron arise in the investigated system are mononuclear.

The number of the coordinated anions of citric acid may be determined by means of eqn (4) expressing the dependence of redox potential on negative decadic logarithm of the relative concentration of acid. For low pH values and relatively low concentrations of citric acid, some sections parallel to the axis of abscissas appear on the plots, which indicates that an unambiguous bonding of ligands does not yet take place in this region. These sections fade out with increasing pH and entirely disappear at  $pH > 0.8$ . However, linear sections with the slope  $\vartheta$  appear in the pH region 0.5—0.8 while sections with the slope  $3/2\vartheta$  come into existence in the pH region 1.0—2.4. In principle, these values give information about the number of anions of acid bounded in complexes of trivalent iron because the tendency to the formation of complexes with trivalent iron in acidic medium is considerably greater than the tendency to the formation of complexes with bivalent iron. The successive formation of linear sections on the plots with the slopes rising from 0 to  $\vartheta$  and from  $\vartheta$  to  $3/2\vartheta$  indicates successive origination of the complexes of trivalent iron while the slope  $\vartheta$  corresponds to a mononuclear complex containing one anion of citric acid and the slope  $3/2\vartheta$  corresponds to a binuclear complex containing three anions of citric acid.

Information about the number of protogenic groups of complexes is to be obtained from eqn (5) which must be, however, adapted for our system. This modification is based on the fact that mononuclear and binuclear complexes of trivalent iron which coordinate one citrate ion in the first case and three citrate ions in the second case as well as a mononuclear complex of bivalent iron occur in the system. Furthermore, we can assume that no hydroxo complexes ( $y = v = 0$ ) arise in the given pH region and citric acid functions as a tetrabasic acid. If we insert the relative concentration of hydrogen ions into eqn (5), we obtain

$$\left(\frac{\partial E}{\partial pH}\right)_{pC^0, pC^R, pC_a} = \vartheta \left[ \frac{k}{q} - 1 + \left(\frac{u}{p} - \frac{x}{q}\right) \cdot \frac{4[H^+]^4 + 3[H^+]^3 B_{a1} + 2[H^+]^2 B_{a2} + [H^+] B_{a3} + B_{a4}}{[H^+]^4 + [H^+]^3 B_{a1} + [H^+]^2 B_{a2} + [H^+] B_{a3} + B_{a4}} \right] \quad (6)$$

If  $B_{a1} \gg B_{a2}, B_{a3}, B_{a4}$  it holds

$$\left(\frac{\partial E}{\partial pH}\right)_{pC^0, pC^R, pC_a} = \vartheta \left[ \frac{k}{q} - 1 + \left(\frac{u}{p} - \frac{x}{q}\right) \frac{4[H^+] + 3B_{a1}}{[H^+] + B_{a1}} \right] \quad (7)$$

For very acid solutions where the formation of a complex with bivalent iron does not manifest itself significantly, we may assume  $[H^+] \gg B_{a1}$ ,  $u = 0$ ,  $l = 0$ . Then eqn (7) is still more simplified and we may write

$$\left(\frac{\partial E}{\partial \text{pH}}\right)_{pC^0, pC^R, pC_a} = \vartheta \left[ \frac{k}{q} - \frac{4x}{q} \right] \quad (8)$$

The graphical representation of the potential  $E$  as a function of pH shows that the slope of individual plots starts from the zero value and reaches the value  $-4\vartheta$  at which it remains in the pH range 1.0–2.0. If the pH value exceeds the limit pH 2.0, the value of slope begins to decrease again. It results from eqn (8) that the binuclear complex  $\text{Fe}_2\text{H}_4\text{A}_3^{2-}$  prevails within the pH range 1.0–2.0 in the investigated system. The complexes existing outside this region are mononuclear complexes of trivalent iron  $\text{FeH}_k\text{A}^{(k-1)+}$  and mononuclear complexes of bivalent iron  $\text{FeH}_l\text{A}^{(l-2)+}$  of variable composition owing to which it has not been possible to determine the number of their protogenic groups by simple analysis of eqn (5).

The existence of predominating complexes in solution is a result of consecutive reactions involving the formation of complexes and protolytic reactions. The formation of binuclear citrate complex of iron(III) may be brought about by a great number of consecutive reactions which are accompanied by origination of mononuclear and binuclear complexes.

The solution of the problem arising from the presence of a set of complex compounds resulting in the formation of predominating complex compounds must be based on the idea of a stepwise process of the formation of complex compounds. But this solution introduces into the general equation of redox potential other unknown parameters (equilibrium constants of consecutive reactions producing complexes). For this reason, we have to process the experimental results by means of computing technique in order to calculate the equilibrium constants of complex-forming reactions and obtain the general image of the presence of complex compounds.

From the mathematical view-point, it is necessary to determine the parameters  $\beta_{qx0k}^0$  and  $\beta_{1101}^R$  from the regressive relationship expressed by the equation

$$E = E^0 - \vartheta \log \left[ K_{101}^0 [H^+]^{-1} + \sum_{q=1}^2 \sum_{x=0}^3 \sum_{k=0}^9 q (\beta_{qx0k}^0)^{1/q} \omega_{qx0k}^{(q-1)/q} \cdot C_a^{x/q} \frac{(B_{as})^{x/q} [H^+]^{k/q}}{\sum_{s=0}^4 [H^+]^{b-s} (B_{as})^{x/q}} \right] + \vartheta \log \left[ 1 + \sum_{l=0}^3 \beta_{1101}^R C_a \frac{B_{as} [H^+]^l}{\sum_{s=0}^4 [H^+]^{b-s} B_{as}} \right] \quad (9)$$

$$E' = E^0 + \vartheta \log \frac{C^0}{C^R}$$

where  $K_{101}^0 = \frac{[\text{FeOH}^{2+}][\text{H}^+]}{[\text{Fe}^{3+}]}$  is the hydrolytic constant of trivalent iron [10].

The stability constants  $\beta_{qxyk}^0$  and  $\beta_{1101}^R$  were calculated as parameters of the equation of redox potential by the method of least squares [16] ensuring the minimum for eqn (10)

$$\begin{aligned}
 U_{\min} = & \sum_{i=1}^N \sum_{j=1}^{M_j} \left\{ E_{ij} - E'_i + \vartheta \log \left[ K_{101}^0 [\text{H}^+]^{-1} + \right. \right. \\
 & \left. \left. + \sum_{q=1}^2 \sum_{x=0}^3 \sum_{k=0}^9 q (\beta_{qx0k}^0)^{\frac{1}{2}} \omega_{qx0k}^{(q-1)/q} \cdot C_a^{x/q} \frac{(B_{as})^{\frac{x}{q}} [\text{H}^+]^{\frac{x}{q}}}{\left( \sum_{s=0}^4 [\text{H}^+]^{b-s} B_{as} \right)^{\frac{x}{q}}} \right] - \right. \\
 & \left. - \vartheta \log \left[ 1 + \sum_{l=0}^3 \beta_{1101}^R C_a \frac{B_{as} [\text{H}^+]^l}{\sum_{s=0}^4 [\text{H}^+]^{b-s} B_{as}} \right] \right\} \quad (10)
 \end{aligned}$$

where  $i=1, 2, \dots, N$  is the number of a series of measurements at a certain concentration of acid  $C_a$  or pH,  $j=1, 2, \dots$ , and  $M_j$  is the number of measurement within one series. All measured values of redox potential were used for calculation.

The program was devised in language Algol-60 and computers BESM-3M and M-222 were used. The calculated stability constants are listed in Table 1.

The image of individual kinds of Fe(II) and Fe(III) complexes as well as conditions of their existence may be obtained from the distribution curves which were constructed on the basis of the percentage of individual forms of complexes by means of the equation

$$\begin{aligned}
 \alpha_{qx0k} &= \frac{q \omega_{qx0k}}{C^0} 100 \\
 \alpha_{1101} &= \frac{\omega_{1101}}{C^R} 100
 \end{aligned} \quad (11)$$

The formation of a Fe(II) complex is due to increasing concentration of the dissociated citric acid  $[\text{H}_3\text{A}^-]$ . It is likely that just these ions get coordinated with bivalent iron to give the  $\text{FeAH}_2$  complex. The  $\text{FeAH}^-$  complex may originate in protolytic dissociation of carboxyl groups of the coordinated ligand. The cause of this deprotonization may consist in polarizing influence of the Fe(II) ions. The percentage of the  $\text{FeAH}^-$  complex increases with pH (Fig. 2).

The criterion determining the assortment of complexes existing in aqueous solutions was the overall error  $\delta$  (%) of the determination of the percentage of

Table 1

Stability constants of the citrate complexes with bivalent and trivalent iron

Composition of complex	Stability constant	Logarithm of stability constant
$\text{FeAH}^-$	$\beta_{1101}^R = \frac{[\text{FeAH}^-]}{[\text{Fe}^{2+}][\text{A}^{4-}][\text{H}^+]}$	$7.7 \pm 0.1$
$\text{FeAH}_2$	$\beta_{1102}^R = \frac{[\text{FeAH}_2]}{[\text{Fe}^{2+}][\text{A}^{4-}][\text{H}^+]^2}$	$8.6 \pm 0.2$
$\text{FeAH}_2^+$	$\beta_{1102}^0 = \frac{[\text{FeAH}_2^+]}{[\text{Fe}^{3+}][\text{A}^{4-}][\text{H}^+]^2}$	$13.20 \pm 0.05$
$\text{FeA}_2\text{H}_4^-$	$\beta_{1204}^0 = \frac{[\text{FeA}_2\text{H}_4^-]}{[\text{Fe}^{3+}][\text{A}^{4-}]^2[\text{H}^+]^4}$	$25.90 \pm 0.05$
$\text{FeA}_3\text{H}_6^-$	$\beta_{1308}^0 = \frac{[\text{FeA}_3\text{H}_6^-]}{[\text{Fe}^{3+}][\text{A}^{4-}]^3[\text{H}^+]^6}$	$39.9 \pm 0.1$
$\text{Fe}_2\text{A}_3\text{H}_6^{2-}$	$\beta_{2304}^0 = \frac{[\text{Fe}_2\text{A}_3\text{H}_6^{2-}]}{[\text{Fe}^{3+}][\text{A}^{4-}]^3[\text{H}^+]^6}$	$41.62 \pm 0.02$

complex  $\alpha_{qx0k}$  or  $\alpha_{1101}$ . *Nikol'skii* [17] has shown that  $\delta$  may be used as a criterion for determining the optimum composition of complexes in solution. The overall error  $\delta$  arising owing to errors of the potentiometric determination of redox potential is

$$\delta/\% = |10^{+(n\tau/\theta)} - 1| 100$$

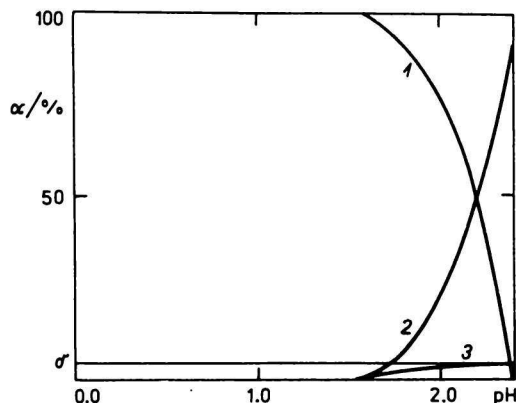


Fig. 2. Distribution curve of the complexes of Fe(II) with citric acid.

$C_a = 0.1 \text{ mol dm}^{-3}$ .

1.  $\text{Fe}^{2+}$ ; 2.  $\text{FeAH}^-$ ; 3.  $\text{FeAH}_2$ .



Provided  $\tau = 1$  mV and  $n = 1$ , the overall error  $\delta = 4\%$ . If the maximum concentration of complex is less than  $\delta$ , the presence of such complex does not significantly influence the course of redox potential.

The distribution curves of individual complexes of trivalent iron with citric acid depend on concentration of this acid and pH (Figs. 3 and 4) and enable us to state that the formation of these complexes is favourably affected by increasing pH and increasing concentration of citric acid. Both these factors give rise to the dissociated particles of citric acid. The formation of the  $\text{FeAH}_2^+$  complex exhibiting a maximum dependent on concentration of citric acid is to be observed at low pH values. The concentration of this complex decreases with increasing pH. Simultaneously with the decrease in its concentration, the concentration of the binuclear complex  $\text{Fe}_2\text{A}_3\text{H}_4^{2-}$  increases and the mononuclear complexes  $\text{FeA}_2\text{H}_4^-$  and  $\text{FeA}_3\text{H}_6^-$

Fig. 3. Distribution curve of the complexes of Fe(III) with citric acid.

- $C_a = 0.1 \text{ mol dm}^{-3}$ .  
 1.  $\text{Fe}^{3+}$ ; 2.  $\text{FeAH}_2^+$ ; 3.  $\text{FeA}_2\text{H}_4^-$ ;  
 4.  $\text{FeA}_3\text{H}_6^-$ ; 5.  $\text{Fe}_2\text{A}_3\text{H}_4^{2-}$ .

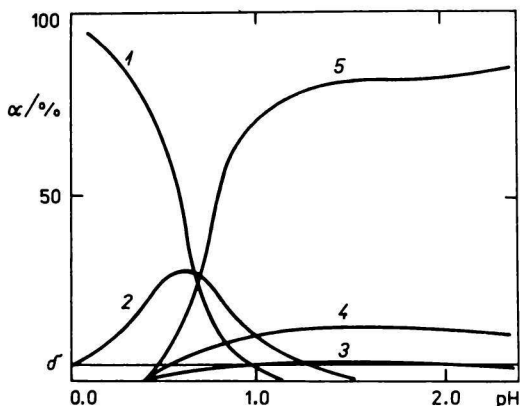
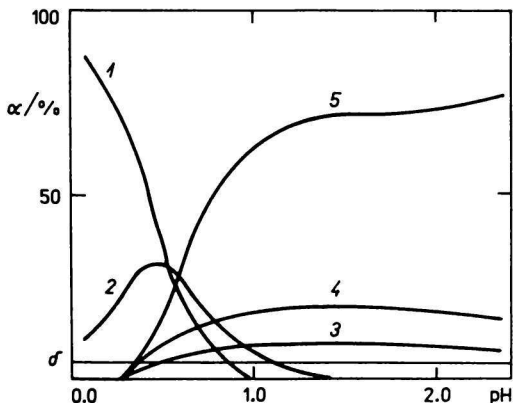
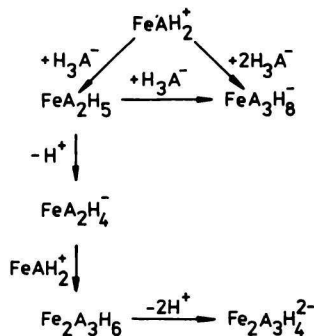


Fig. 4. Distribution curve of the complexes of Fe(III) with citric acid.

- $C_a = 0.05 \text{ mol dm}^{-3}$ .  
 1.  $\text{Fe}^{3+}$ ; 2.  $\text{FeAH}_2^+$ ; 3.  $\text{FeA}_2\text{H}_4^-$ ;  
 4.  $\text{FeA}_3\text{H}_6^-$ ; 5.  $\text{Fe}_2\text{A}_3\text{H}_4^{2-}$ .



come into existence. We may suppose that the complexes  $\text{FeA}_3\text{H}_8^-$  and  $\text{Fe}_2\text{A}_3\text{H}_4^{2-}$  arise from the complexes  $\text{FeAH}_2^+$  and  $\text{FeA}_2\text{H}_4^-$  according to Scheme 1.



Scheme 1

On the basis of experimental results we may assume that mainly the complexes of trivalent iron  $\text{FeAH}_2^+$ ,  $\text{FeA}_2\text{H}_4^-$ ,  $\text{FeA}_3\text{H}_8^-$ , and  $\text{Fe}_2\text{A}_3\text{H}_4^{2-}$  as well as two complexes of bivalent iron  $\text{FeAH}^-$  and  $\text{FeAH}_2$  are present under given conditions in aqueous solution of citric acid.

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## Symbols

$B_{as}$  overall dissociation constant of the  $s$ -th degree on condition that  $B_{a0} = 1$

$B_{as} = \prod_i K_i^a$

$b$  basicity of acid  $\text{H}_b\text{A}$

$C_a$  overall relative concentration of acid  $\text{H}_b\text{A}$

$C^0$  overall concentration of Fe(III) in  $\text{mol dm}^{-3}$  ( $\text{Fe(III)}/3$ )

$C^{\text{R}}$  overall concentration of Fe(II) in  $\text{mol dm}^{-3}$  ( $\text{Fe(II)}/2$ )

$k, l$  number of protogenic groups in a complex of Fe(III) and Fe(II), respectively

$p$  number of nuclei in a complex of bivalent iron

$q$  number of nuclei in a complex of trivalent iron

$\text{p}C^0, \text{p}C^{\text{R}}$ , negative decadic logarithms of the corresponding quantities

$\text{p}C_a$

$s$  degree of protolytic dissociation of the acid

$x, u$  number of the ligands  $\text{A}^{b-}$  in a complex of Fe(III) and Fe(II), respectively

$y, v$	number of the coordinated OH groups without protogenic properties in a complex of Fe(III) or Fe(II), respectively
$\alpha_{qxyk}$	percentage of a $Fe_qH_kA_x(OH)_y$ complex of Fe(III)
$\alpha_{pvul}$	percentage of a $Fe_pH_lA_u(OH)_v$ complex of Fe(II)
$\beta_{qxyk}^0$	stability constant of a $Fe_qH_kA_x(OH)_y$ complex of Fe(III)
$\beta_{pvul}^R$	stability constant of a $Fe_pH_lA_u(OH)_v$ complex of Fe(II)
$\delta$	overall error in %
$\vartheta = \frac{RT}{nF}$	factor in the Nernst equation
$Q_{pvul}$	concentration of a $Fe_pH_lA_u(OH)_v$ complex of Fe(II)
$\omega_{qxyk}$	concentration of a $Fe_qH_kA_x(OH)_y$ complex of Fe(III)
$\tau$	accuracy of potentiometric measurements

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