

Study of heteronuclear complexation in Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system

Mairambu Zhorobekova^{1*}, Altynai Mametova¹, and Farida Miraminzoda²

¹Osh State University, Osh, Kyrgyzstan

²Tajik National University, Dushanbe, Tajikistan

Abstract. Heteronuclear complexation in the Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system at 318 K and ionic strength of 1.0 mol/l was studied by the Clark-Nikolsky oxidation potential method. The formation of complexes of the composition: [FeL(H₂O)₅]²⁺; [FeLOH(H₂O)₄]⁺; [Fe^{III}Mn^{II}L(H₂O)₃]⁴⁺; [Fe^{III}Mn^{II}L(OH)₂(H₂O)₉]²⁺; [FeL(H₂O)₅]⁺; [Fe(L)₂(H₂O)₄]⁰; [Fe(L)(OH)₂(H₂O)₃]⁻, two of which are heteronuclear. The conditions for forming and dominating coordination compounds in an aqueous solution are established.

1 Introduction

Coordination compounds of transition metals are widely used in various fields of science, technology, agricultural industry, medicine, and cosmetology; therefore, they represent great theoretical and practical interests. Research in this direction reveals the mechanism of oxidation and reduction processes in biological systems and can be their models. In addition, complex compounds of Fe, Co, Si, Mn, and Zn with biologically active ligands, including acetic acid, can be the basis of many medicines [1-4]. In this article, the classical Clark-Nikolsky oxidation potential method was used to study heteronuclear complexation in the Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system [5-9].

The oxidation potential method is simple and highly sensitive. Using this method, the processes of mono-, polynuclear, homo- and heteronuclear complexation in systems with Fe(II)-Fe(III); Fe(0)-Fe(II) in aqueous solutions of organic acids have been studied [10-15]. The formation of several coordination compounds is shown, which contain both an organic acid ligand and hydroxyl groups in the internal coordination sphere: [Fe(OH)(H₂O)₅]⁺; [FeHL(H₂O)₅]²⁺; [Fe(HL)(OH)(H₂O)₄]⁺; [Fe(OH)₂(H₂O)₄]⁰; [Fe₂(HL)₂(OH)₂(H₂O)₈]²⁺ and [Fe(HL)₂(H₂O)₄]²⁺.

2 Methodology of the experiment

The potentiometry method determines the EMF in an electrolytic cell, where platinum, glass, auxiliary silver chloride electrodes, inert gas tubes, and a microburet are inserted. EMF measurement is carried out using two galvanic cells:

*Corresponding author: mayram.jorobekova67@bk.ru

Pt test solution/KCl (saturated), AgCl |Ag (I)

Ag|AgCl, (HCl 0,1 n)/ glass | researching solution/KCl (saturated), AgCl|Ag (II)

The first galvanic cell is necessary to measure the EMF of the system, and the second is to determine the pH of the solution in the electrolytic cell. To prevent the oxidation of divalent iron, the working solution is constantly saturated with an inert gas. EMF measurement is carried out using an ionomer [16].

The first working solution is prepared in a 50 ml volumetric flask using an equimolecular mixture of salts (nitrates, perchlorates). The concentration of ferrous and trivalent iron varies between $1 \cdot 10^{-4} \div 1 \cdot 10^{-2}$, and acids - from $1 \cdot 10^{-1}$ to $1 \cdot 10^{-2}$ mol/l [17]. To create a constant ionic strength of the first working solution, nitric (chloric) acids are used. The second working solution contains all the same components as the first, in the same amount. The ionic strength of the solution is adjusted to a constant value using sodium nitrate (perchlorate) and sodium hydroxide. Thus, a higher pH value of the second working solution is achieved. When titrating the first working solution with the second, the pH gradually shifts to an alkaline medium [18]. The first working solution is placed in an electrolytic cell, and an inert gas is passed through it for 15-20 minutes; then, the EMF of the galvanic cells (I) and (II) is measured. Working solutions were prepared according to the experimental dependence of the EMF of the system on the concentration of Fe(III) ions and pH.

The solutions are used to obtain two other solutions with a maximum and minimum concentration of Fe(II) and HL. The general equation of the oxidation potential for the system $M^{Z+} - M^{(Z-c)+}$ - weak aliphatic acid - water, in general, has the form:

$$\varphi = \varphi^0 + \nu \lg C_o / C_r + \nu \lg \sum_1^g \sum_0^x \sum_0^y \cdot q \cdot \beta_{qxy}^{1/q} \cdot Q_{qxy}^{(q-1/q)} \cdot K_a^{x/g} \cdot C_a^{x/g} h^{-(x+y)/q} - \nu \lg \sum_1^p \sum_0^u \sum_0^v \cdot p \cdot \beta_{puv}^{1/p} \cdot P_{puv}^{(p-1/p)} \cdot K_a^{u/p} \cdot C_a^{u/p} h^{-(u+v)/p} \quad (1)$$

where: φ is the oxidation potential of the system; φ^0 is the apparent standard oxidation potential; $\nu = RT/F$; values q, p, b, s, l and k , respectively, the number of oxidized, reduced metal forms, heteroions, coordinated protons, and ligand ions of hydroxyl groups in the complex compound; C_o and S_g are the total concentrations of oxidized and reduced metal forms; C_b is the concentration of the heteroion $Mn(II)$ or $C_0(II)$ β_{qpsl} -constants of formation of the corresponding complexes.

3 Results and Discussion

According to the theory of the method [19], experimental dependences of the EMF (E) of the system on pH were first obtained (Fig. 1).

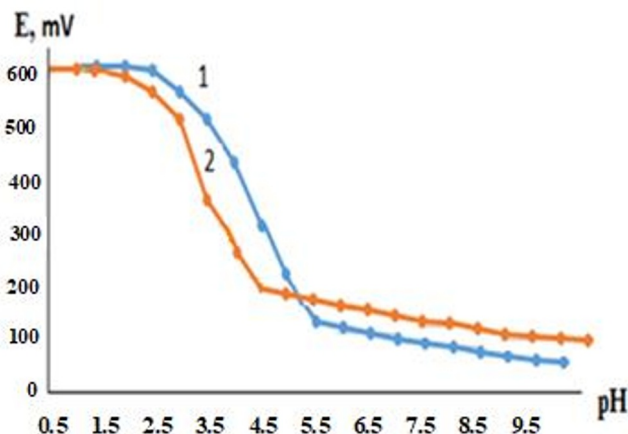


Fig. 1. Dependence of EMF on pH for system: Fe(II)-Fe(III)-CH₃COOH-H₂O (cr.1) Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O (cr.2) at temperature of 318 K and ionic strength of 1.0 solution; $C_{\text{Fe(II)}} = C_{\text{Fe(III)}} = C_{\text{Mn(II)}} = 1 \cdot 10^{-3}$; $C_{\text{HL}} = 1 \cdot 10^{-2}$ mol/l.

It is clear from the above figure that the EMF with an increase in pH to values of 1.3-3.5 remains constant; this indicates the absence of complexation. With a further increase in pH, the EMF decreases according to the Nernst equation, and coordination compounds of Fe(III) are formed in the solution. This process lasts almost to pH 5.0-5.5. In the system, the complexation process proceeds stepwise in a wide pH range from 3.5 to 10.0; then, after pH 10, Fe(III) hydrolysis occurs and forms a brown precipitate. If the Mn heteroion is present in the system, the curves of EMF dependence on pH are shifted to a more acidic region. The experimental data showed that the presence of a heteroion increases the complexing ability of Fe(III). According to the theory of the redoxmetry method, to determine the number of atoms of oxidized and reduced metal forms in the inner coordination sphere, it is necessary to obtain experimental dependence curves $E-pC_0$ (Fig. 2) and $E - pC_r$ (Fig. 3), as well as to analyze their slope.

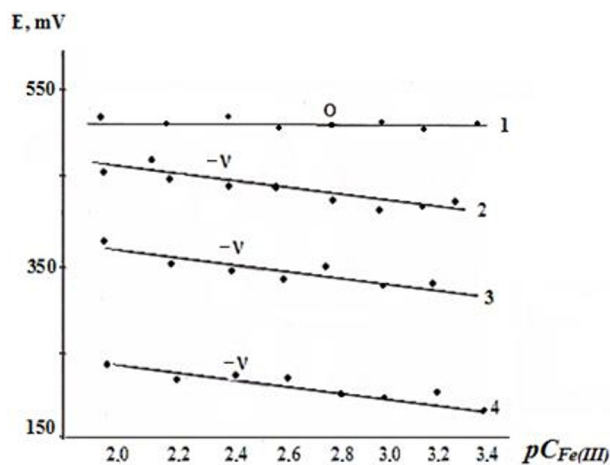


Fig. 2. The dependence of EMF of system Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O from pC_0 at 318 K and ionic strength of solution 0.5; $C_{\text{Fe(II)}} = C_{\text{Fe(III)}} = C_{\text{Mn(II)}} = 1 \cdot 10^{-4}$; $C_{\text{HL}} = 1 \cdot 10^{-3}$ mol/L. Curves relate to pH: 1-2.5; 2-5.0; 3-7.5; 4-9.0.

The first curve refers to pH=2.5. The slope of this curve is 0; therefore, there is no complexation process at the given pH value. At other pH values: 5.0; 7.5; 9.0, the same slopes equal to $-v$ (58 mV) were obtained. This indicates that only one trivalent iron atom is involved in the complexation processes, i.e., mononuclear complexes are formed. With a change in the concentration of divalent iron and a pH above 4.5, curves of the dependence of EMF on pC_r are obtained (Fig. 3) since divalent iron forms coordination compounds above this value. At pH 5.0, the slope of the curves is 0; at these pH values, Fe(II) does not form coordination compounds. A further increase in pH leads to a change in the slope of the experimental curves by a (58 mV), which is associated with the formation of mononuclear Fe(II) complexes.

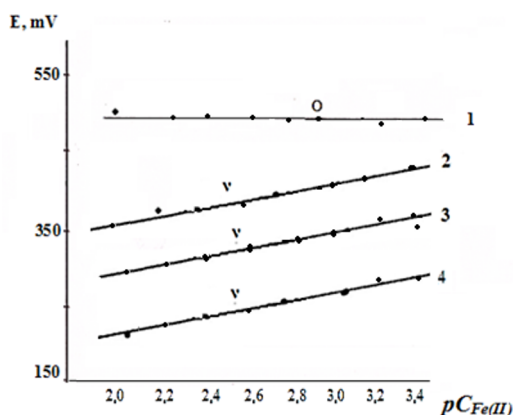


Fig. 3. Dependence of EMF of Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system on pC_r 318 K, and ionic strength of solution is 1.0; $C_{Fe(II)}=C_{Fe(III)}=C_{Mn(II)}=1 \cdot 10^{-4}$; $C_{HL}=1 \cdot 10^{-3}$ mol/l. Curves relate to pH: 1 - 4.5; 2 - 5.5; 3 - 7.5; 4 - 9.5

Experimental curves of the dependence of the EMF of the system on the acetic acid concentration index (pC_L) are obtained (Fig. 4). Slopes v , $2v$, and v are obtained, which indicate the coordination of one, two, and again one ligand to the metal.

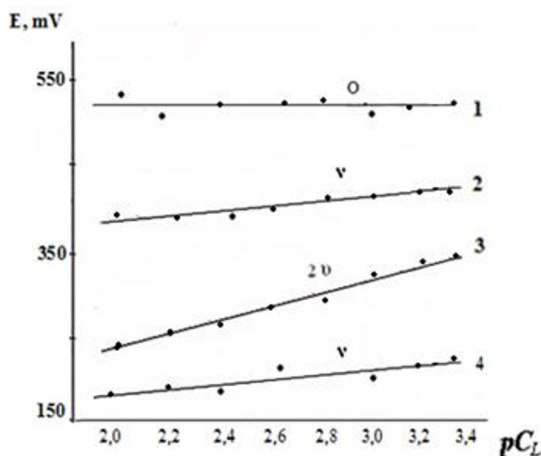


Fig. 4. Dependence of EMF of Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system on pC_L at 318 K, and the ionic strength of solution is 1.0; $C_{Fe(II)}=C_{Fe(III)}=C_{Mn(II)}=1 \cdot 10^{-4}$; $C_{HL}=1 \cdot 10^{-3}$ mol/L. Curves relate to pH: 1-3.0; 2-5.5; 3-7.5; 4-9.5.

A complete analysis of the slopes of all experimental curves allowed us to determine the numerical values of the basic particles: q; p; b; s; l; k. On their basis, a chemical model [20] of the ion equilibria of the studied system was compiled (Table 1).

Table 1. Chemical model of Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system at temperature of 318 K and ionic strength of 1.0 solution; $C_{Fe(II)}=C_{Fe(III)}=C_{Mn(II)}=1 \cdot 10^{-4}$; $C_{HL}=1 \cdot 10^{-3}$ mol/l

№, p/p	Basic particles of the system						Composition of complexes
	g Fe ²⁺	p Fe ³⁺	b Mn ²⁺	s H	l L ⁻	k OH ⁻	
1	0	1	0	0	1	0	[Fe ^{III} L(H ₂ O) ₅] ²⁺
2	0	1	0	0	1	1	[Fe ^{III} LOH(H ₂ O) ₄] ⁺
3	0	1	1	0	1	0	[Fe ^{III} Mn ^{II} L(H ₂ O) ₃] ⁴⁺
4	0	1	1	0	1	2	[Fe ^{III} Mn ^{II} L(OH) ₂ (H ₂ O) ₉] ²⁺
5	1	0	0	0	1	0	[Fe ^{II} L(H ₂ O) ₅] ⁺
6	1	0	0	0	2	0	[Fe ^{II} (L) ₂ (H ₂ O) ₄] ⁰
7	1	0	1	0	1	2	[Fe ^{II} (L)(OH) ₂ (H ₂ O) ₃] ⁻

A joint analysis of all experimental curves and a compiled model showed the formation of the following coordination compounds in the system: [Fe^{III}L(H₂O)₅]²⁺; [Fe^{III}LOH(H₂O)₄]⁺; [Fe^{III}Mn^{II}L(H₂O)₃]⁴⁺; [Fe^{III}Mn^{II}L(OH)₂(H₂O)₉]²⁺; [Fe^{II}L(H₂O)₅]⁺; [Fe^{II}(L)₂(H₂O)₄]⁰; [Fe^{II}(L)(OH)₂(H₂O)₃].

The equations of possible reactions of the formation of complexes of studied system are given in Table 2.

Table 2. Reactions of formation of complex compounds in the Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system at a temperature of 318 K, I=1.0;

$$C_{Fe(II)}=C_{Fe(III)}=C_{Mn(II)}=1 \cdot 10^{-3}; C_{HL}=1 \cdot 10^{-2} \text{ mol/L.}$$

№, p/p	Reactions of formation of coordination compounds
1	[Fe(H ₂ O) ₆] ³⁺ + HL ↔ [Fe ^{III} L(H ₂ O) ₅] ²⁺ + H ₃ O ⁺
2	[FeL(H ₂ O) ₅] ²⁺ + HOH ↔ [Fe ^{III} LOH(H ₂ O) ₄] ⁺ + H ₃ O ⁺ or [Fe(H ₂ O) ₆] ³⁺ + HL + HOH ↔ [Fe ^{III} LOH(H ₂ O) ₄] ⁺ + 2H ₃ O ⁺
3	[Fe(H ₂ O) ₆] ³⁺ + [Mn(H ₂ O) ₆] ³⁺ + HL ↔ [Fe ^{III} Mn ^{II} L(H ₂ O) ₁₁] ⁴⁺ + H ₂ O ⁺ or [FeL(H ₂ O) ₅] ²⁺ + [Mn(H ₂ O) ₆] ³⁺ ↔ [Fe ^{III} Mn ^{II} L(H ₂ O) ₁₁] ⁴⁺
4	[Fe(H ₂ O) ₆] ³⁺ + [Mn(H ₂ O) ₆] ³⁺ + HL + HOH ↔ [Fe ^{III} Mn ^{II} L(OH) ₂ (H ₂ O) ₉] ²⁺ + 3H ₃ O ⁺ or [FeL(H ₂ O) ₅] ²⁺ + [Mn(H ₂ O) ₆] ³⁺ + 2HOH ↔ [Fe ^{III} Mn ^{II} L(OH) ₂ (H ₂ O) ₉] ²⁺ + 2H ₃ O ⁺ или [Fe ^{III} Mn ^{II} L(H ₂ O) ₁₁] ⁴⁺ + 2HOH ↔ [Fe ^{III} Mn ^{II} L(OH) ₂ (H ₂ O) ₉] ²⁺ + 2H ₃ O ⁺
5	[Fe(H ₂ O) ₆] ²⁺ + HL ↔ [Fe ^{II} L(H ₂ O) ₅] ⁺ + H ₃ O ⁺
6	[Fe(H ₂ O) ₆] ²⁺ + HL ↔ [Fe ^{II} (L) ₂ (H ₂ O) ₄] ⁰ + 2H ₃ O ⁺ or [FeL(H ₂ O) ₅] ⁺ + HL ↔ [Fe ^{II} (L) ₂ (H ₂ O) ₄] ⁰ + H ₃ O ⁺
7	[Fe(H ₂ O) ₆] ²⁺ + HL + HOH ↔ [Fe ^{II} (L)OH(H ₂ O) ₄] ⁰ + H ₃ O ⁺ or [Fe(L)OH(H ₂ O) ₄] ⁰ + HOH ↔ [Fe ^{II} L(OH) ₂ (H ₂ O) ₃] ⁻ + H ₃ O ⁺ or [Fe(H ₂ O) ₆] ²⁺ + HL + 2HOH ↔ [Fe ^{II} L(OH) ₂ (H ₂ O) ₃] ⁻ + 3H ₃ O ⁺ or [Fe(L) ₂ (H ₂ O) ₄] ⁰ + 2HOH ↔ [Fe ^{II} L(OH) ₂ (H ₂ O) ₃] ⁻ + HL + H ₃ O ⁺

4 Conclusions

The processes of heteronuclear complexation in the Fe(II)-Fe(III)-Mn(II)-CH₃COOH-H₂O system at 318 K and ionic strength of 1.0 mol/l were studied by the Clark-Nikolsky oxidation potential method. Experimental curves of the system's EMF dependence on the reverse indices of the concentration parameters, pH, pC_o, pC_r, pC_L are obtained. The experimental EMF curve from pH showed that the process of formation of coordination compounds in the studied system occurs in a wide range at pH values above 2 to 10. A complete analysis of the slopes of the obtained curves showed the formation of composition complexes in the system: [Fe^{III}L(H₂O)₅]²⁺; [Fe^{III}LOH(H₂O)₄]⁺; [Fe^{III}Mn^{II}L(H₂O)₃]⁴⁺; [Fe^{III}Mn^{II}L(OH)₂(H₂O)₉]²⁺; [Fe^{II}L(H₂O)₅]⁺; [Fe^{II}(L)₂(H₂O)₄]⁰; [Fe^{II}(L)(OH)₂(H₂O)₃].

It is established that in the studied system, Fe(III) with Mn(II) forms two coordination compounds [Fe^{III}Mn^{II}L(H₂O)₃]⁴⁺; [Fe^{III}Mn^{II}L(OH)₂(H₂O)₉]²⁺, and Fe(II) does not participate in the process of heteronuclear complexation.

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