About the observance of the Nernst equation in acid corrosive media containing oxidative cations¹

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Abstract

Potentiometry on a platinum electrode in the temperature range of $20-95^{\circ}C$ was used to study the redox properties of 2 M H₂SO₄, 2 M HCl, 2 M H₃PO₄, 1 M H₃PO₄ + 1 M H₂SO₄, and 1 M H₃PO₄ + 1 M HCl solutions containing Fe(III) and Fe(II) salts. The redox potentials of systems in the solutions in question are poorly described by the Nernst equation. The observed deviations result from the non-equivalent complexation of potential-determining species, namely Fe(III) and Fe(II) cations, with anions present in a solution due to dissociation of the acids. The active concentrations of Fe(III) and Fe(II) cations in these systems change non-equally, which affects the redox potential of a system. The deviation of a system's redox properties from the Nernst equation is the stronger the higher the complexing ability of the ligands formed from the acid. Among the media studied, the greatest deviation of the redox properties of the Fe(III)/Fe(II) redox couple from the theoretical values is observed in media containing H₃PO₄. The observed effects should be taken into account in the creation and operation of corrosion inhibitors for low-carbon steels in mineral acid solutions containing Fe(III) and Fe(II) salts, since their efficiency considerably depends on the oxidative capability of these environments.

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Introduction

Industrial operation of various aqueous process media that contact metal equipment or products results in contamination of these liquids by soluble corrosion products that can significantly change their process properties and corrosivity. A good example that illustrates

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this situation is given by the contamination of mineral acid solutions with Fe(III) salts where these solutions contact steel structures or items whose surface is often covered with solid corrosion products, including Fe(III) compounds [1]. The presence of Fe(III) cations, which are strong oxidants, in these media not only changes their corrosivity toward steels but also significantly decreases the possibility of efficient inhibitory protection of metals.

The redox potential (*E*) of media containing oxidizing ions is an important parameter characterizing their corrosivity. The higher its value, the greater the corrosivity of the medium toward metals. A quantitative characteristic of aqueous corrosive media under given conditions where the active concentrations of oxidized and reduced forms of potential-determining particles (a_{Ox} and a_{Red}) equal 1 mol/L is provided by the standard electrode potential E^0 . These E^0 potentials corresponding to a temperature of $t=25^{\circ}\text{C}$ are reference values.

The relationship of the redox potential of an aqueous medium containing potentialdetermining particles (Ox and Red) with their concentration for the simplest half-reaction

$$Ox + ze = Red$$

is described by the Nernst equation:

$$E_{\text{Ox/Red}} = E_{\text{Ox/Red}}^0 + \alpha \lg \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

where $E_{\text{Ox/Red}}^0$ is the standard electrode potential of the redox couple; a_{Ox} and a_{Red} are the active concentrations of the oxidant and reductant in the solution; $\alpha = 2.3RT/zF$, where *R* is the universal gas constant, *T* is the absolute temperature, *z* is the number of electrons involved in the redox process, and *F* is the Faraday constant. The use of the Nernst equation in this form, and particularly at high electrolyte concentrations, is difficult because the activity of any type of potential-determining ions in a solution is usually not related to their concentration by a simple relationship. The active concentrations of non-complexed iron cations in a solution can be found using the activity coefficients calculated by the Debye–Hückel equation and the equilibrium constants that characterize complex compounds of Fe. Taking into account the complexity of the system concerned and the uncertainty of its chemical composition, this problem cannot be solved.

From the practical point of view, it is more appropriate to describe the processes that occur in acid solutions containing Fe cations using the real potential of a redox system established in a particular solution at equal starting concentrations of the oxidized and reduced forms of potential-determining ions, without consideration for corrections for complexation, hydrolysis, and other processes [2]. The values of the real and standard redox potentials at equal temperatures coincide if such processes are absent in the system. For the system being studied, its real potential is most convenient for a qualitative interpretation of experimental data related to the complexation of potential-determining ions.

In solutions of mineral acids containing the redox couple of an oxidizer (metal cation) and its reduced form, the values of electrode potentials E^0 at equal analytical concentrations of the oxidized and reduced forms of potential-determining ions can be significantly lower than the reference values, depending on the acid nature [2–5]. This effect is most clearly illustrated by the Fe(III)/Fe(II) and Ce(IV)/Ce(III) redox couples (Table 1).

Acid	$E_{\text{Fe(III)/Fe(II)}}, \text{V}(C_{\text{Acid}} = 1 \text{ N}) [6]$	$E_{\text{Ce(IV)/Ce(III)}}, \text{V}(\text{pH}=1)$ [7]
HClO ₄	0.78	1.70
HNO ₃	0.77	1.61
H_2SO_4	0.68	1.44
HCl	0.67	1.28
H ₃ PO ₄	0.59	_
HF	0.55	_
_	0.770±0.002 [8]	1.72 [9]

Table 1. Stationary potentials $E_{\text{Ox/Red}}$ of a platinum electrode in various acids at a concentration of 1 N ($t = 25^{\circ}$ C) and $C_{\text{Ox}} = C_{\text{Red}}$.

The decrease in the potentials of redox couples $Me^{(x+1)+}/Me^{x+}$ with an increase in the concentrations of acids is believed to result from the non-equivalent complexation of two potential-determining species with the anions present in the solution due to acid dissociation. As a result, the active concentrations of both forms of potential-determining species in the solution do not change equally. On the other hand, the oxidized forms of potential-determining cations should be bound by anions into complex compounds more strongly than their reduced forms [7]. In the case of the Fe(III)/Fe(II) redox couple, the difference in the instability constants of some complex compounds formed by Fe(III) and Fe(II) cations in aqueous media is clearly illustrated by the data given in Table 2.

The decrease in the potential of $Me^{(x+1)+}/Me^{x+}$ couples in acid-containing media is usually explained by a decrease in their oxidative capability that is quantitatively expressed as a decrease in their real redox potentials. This effect is confirmed not only by potentiometric studies but also by cyclic voltammetry data [16–18]. It remains unclear to what extent one should expect the formal observance of the Nernst equation in systems under study if a linear relationship of the system's redox potential *versus* the logarithm of the ratio of active concentrations of potential-determining particles is obeyed.

It appears expedient to use potentiometry on a platinum electrode to study the dependence of the redox potential of the $H_2SO_4-H_2O$, $HCl-H_2O$, $H_3PO_4-H_2O$, $H_2SO_4-H_3PO_4-H_2O$, and $HCl-H_3PO_4-H_2O$ systems containing Fe(III) and Fe(II) salts on the relative content of these cations. Let us specify at once that in our study, we will use their analytical concentrations of the potential-determining species instead of their active concentrations. This approach is not quite strict in theoretical terms, but it will allow us to

obtain important practical information about the oxidative properties of the aqueous systems in question. The potentiometric method was chosen to reach our goal due to the technical simplicity of its implementation and its wide practical application in studies on the complexation processes in aqueous systems containing Fe(III) and Fe(II) cations [19–25]. The data obtained in this study are of great practical significance.

Ligands	р <i>К</i> і1	р <i>К</i> _{і1-2}	р <i>К</i> і1–3	р <i>К</i> і1–4	р <i>К</i> і1–5	р <i>К</i> і1–6	Ref.		
Fe(III)									
SO_{4}^{2-}	4.18	7.4	_	_	_	_	10		
	4.02	5.38	_	_	_	_	11		
HSO_4^-	2.48	_	_	_	_	_	12		
Cl-	1.45	2.10	1.10	-0.85	_	_	10		
	1.52	2.22	_	_	_	_	13		
	1.48	2.13	1.13	_	—	_	14		
$\operatorname{HPO}_{4}^{2-}$	3.5	_	_	9.15	_	_	10		
$H_2PO_4^-$	9.75	_	_	_	_	_	10		
Fe(II)									
SO_4^{2-}	2.30	_	_	_	_	_	10		
	2.25	_	_	_	—	_	11, 12		
Cl ⁻	0.36	0.40	_	_	_	_	10		
$H_2PO_4^-$	1.0	2.7	_	_	_	_	15		

Table 2. The instability constants values (pK_i^*) of Fe(III) and Fe(II) complexes with some inorganic ligands. $t = 20-30^{\circ}$ C.

* $pK_{i1-m} = -lgK_{i1-m}$; $Fe^{x+} + mAn^{y-} = FeAn^{(x-my)+}_{m}$; $K_{i1-m} = \frac{[Fe^{x+}] \cdot [An^{y-}]^m}{[FeAn^{(x-my)+}_{m}]}$, where Fe^{x+} is the iron cation

with charge x+ and An^{y-} is an anion with charge y-.

It is known that the protective effect of steel corrosion inhibitors in acid environments containing Fe(III) salts significantly depends on their oxidative capability [1]. In turn, the oxidative capability of such a corrosion system is determined by the joint presence of Fe(III) and Fe(II) cations in it. To ensure a high protective effect of an inhibitor in a corrosive environment, it has to be understood how the oxidative properties of acid solutions are affected by the variation in the ratio of Fe(III) and Fe(II) salts in them.

Experimental

The solutions were prepared from H_2SO_4 , HCl and H_3PO_4 of "chemically pure" grade and distilled water. Acid solutions containing Fe(III) salts were obtained using the reaction of excess the corresponding acid with Fe(OH)₃ precipitated with NaOH ("chemically pure" grade) from a FeCl₃ solution. The FeCl₃ solution was prepared from "pure" grade FeCl₃·6H₂O. H₂SO₄ solutions containing Fe(II) sulfate were prepared from "chemically pure" grade FeSO₄·7H₂O. Due to the technical difficulties in the preparation of solutions of other acids containing the corresponding Fe(II) salts for potentiometric studies, they were replaced by solutions containing an equivalent concentration of FeSO₄. In this approach, the maximum unaccounted content of SO_4^{2-} did not exceed 4.8% of the total concentration of anions in a solution, which allowed us to neglect this fact in the further discussion.

Potentiometric studies were performed in a temperature-controlled glass electrochemical cell YaSE-2. The accuracy of temperature control in the cell was $\pm 1^{\circ}$ C. A smooth platinum working electrode (1.5 cm²) and a saturated silver chloride reference electrode were used. The potential difference between the working and reference electrodes was determined using a PI-50 potentiostat. The working solutions were deaerated with argon ("chemically pure" grade) for 30 min both before and during the experiment. The potential of the platinum electrode in the working solution was measured in 30 min after the required temperature was established in the cell. In this measurement mode, the potential of the working electrode remained constant for at least the last 20 min. Electrode potentials are reported *versus* the standard hydrogen electrode.

Results and Discussion

The theoretical plot of the potential of a Pt electrode in an aqueous solution containing Fe(III) and Fe(II) cations *versus* the ratio of their concentrations was built from the Nernst equation and the reference characteristics of the Fe(III)/Fe(II) redox couple [26]: $E_{\text{Fe(III)/Fe(II)}}^0$ (25°C) and $dE_{\text{Fe(III)/Fe(II)}}^0 / dT = 0.00119 \text{ V/K}$ (Figure 1). The experimental potentials of a Pt electrode in H₂SO₄, HCl, H₃PO₄, H₂SO₄ + H₃PO₄, and HCl + H₃PO₄ solutions containing Fe(III) and Fe(II) salts are considerably lower due to the formation of complexes of Fe(III) cations with anions of the acids. Other conditions being equal, the maximum potentials of the Pt electrode are characteristic of H₂SO₄ and HCl solutions. They have smaller values in H₂SO₄ + H₃PO₄ and HCl + H₃PO₄ solutions of the Pt electrode in 2 M H₃PO₄. This result is in good agreement with the instability constants of Fe(III) complexes (Table 2). The most stable complexes are characteristic of Fe(III) phosphate complexes, hence the decrease in the Pt electrode is the largest in the presence of these complexes.

In 2 M H₂SO₄ and 2 M HCl containing Fe(III) and Fe(II) salts, the plot of the Pt electrode potential *versus* $lg(C_{Fe(III)} / C_{Fe(II)})$ is close to linear (Figure 1). In both media, the values of the Pt electrode potential characterizing the system at $C_{Fe(III)} = C_{Fe(II)}$ are smaller than the theoretical values. Moreover, a deviation of parameter α from the values determined

by the Nernst equation is observed, although it is closer to theory in 2 M H_2SO_4 than in 2 M HCl (Table 3).

Table 3. Values of the Nernst equation parameters for the Pt electrode in $2 \text{ M H}_2\text{SO}_4$ and 2 M HCl containing 0.10 M Fe(III) + Fe(II).

t, °C	Estimated values		2 M H ₂ SO ₄		2 M HCl	
	E ⁰ _{Fe(III)/Fe(II)}	α	E ⁰ _{Fe(III)/Fe(II)}	α	E ⁰ _{Fe(III)/Fe(II)}	α
20	0.765	0.058	0.675	0.062	0.672	0.055
40	0.789	0.062	0.697	0.066	0.687	0.059
60	0.813	0.066	0.721	0.070	0.703	0.062
80	0.836	0.070	0.746	0.072	0.717	0.063
95	0.854	0.073	0.765	0.073	0.728	0.065

In 2 M H₃PO₄ and acid mixtures containing it, no linear dependence of the Pt electrode potential on $lg(C_{Fe(III)} / C_{Fe(II)})$ is observed (Figure 1). To understand the nature of processes occurring in these systems, it seemed reasonable to compare the experimental data obtained by the potentiometric method with the model based on the Nernst's plot of the system's redox potential versus the logarithm of the ratio of concentrations of Fe cations in the oxidized and reduced forms. In building such model relationships, it will be assumed that they pass through the experimentally determined value of the Pt electrode potential obtained at $C_{\text{Fe(III)}} = C_{\text{Fe(II)}}$ (Figure 2). Comparison of the experimental data with the theoretical relationships shows that at $C_{\text{Fe(III)}} > C_{\text{Fe(III)}}$ the experimental points are close to the theoretical line. In contrast, at $C_{\text{Fe(III)}} < C_{\text{Fe(III)}}$ the experimental points lie in the region of higher potentials in comparison with the theoretical lines, which is particularly evident at $C_{\text{Fe(III)}}/C_{\text{Fe(III)}} = 1:99$. We believe that the nature of this effect primarily lies in the non-equivalent complexation of Fe(III) and Fe(II) cations with phosphate anions. In spite of the weaker stability of Fe(II) complexes with phosphate anions (Table 1), at high $C_{\text{Fe(II)}}$ in H₃PO₄ solutions the major fraction of Fe(II) cations is bound into complexes, which should favor an increase in the E of the system. As it should be expected, the strongest shift of the experimental E values from the theoretical dependence to the positive region is observed in H₃PO₄ solutions rather than in solutions of its mixtures with acids.

In solutions of mineral acids containing Fe(III) and Fe(II) salts, the redox potential of the systems is poorly described by the Nernst equation. The observed deviations are due to the non-equivalent complexation of potential-determining species, namely, Fe(III) and Fe(II) cations, with the anions present in the solution due to dissociation of the acids. In these systems, the active concentrations of Fe(III) and Fe(II) cations change non-equally. The

higher the complexing ability of the ligands formed from the acids, the higher the deviation of the system's redox properties from the Nernst equation.



Figure 1. Potentials of a platinum electrode in argon-deaerated 2 M acid solutions containing an 0.1 M Fe(III) + Fe(II) mixture *versus* the Fe(III)/Fe(II) concentration ratio.



Figure 2. Potentials of a platinum electrode in argon-deaerated 2 M acid solutions (20 and 95°C) containing an 0.1 M Fe(III) + Fe(II) mixture *versus* the Fe(III)/Fe(II) concentration ratio. Experimental data (points) and calculated results (lines).

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This result is interesting not only in theoretical but also in practical respect. We have shown previously [1] that rather a unique property of mixed inhibitors based on triazole derivatives is that they can efficiently hinder the corrosion of low-carbon steels in acid solutions containing Fe(III) salts. It is important that the efficiency of steel protection in these environments by corrosion inhibitors strongly depends on their oxidative capability that should be significantly diminished by the presence of acid anions in the solution that bind Fe(III) into complex compounds. The results of our studies show that, among the anions we studied, the presence of phosphate anions in acid solutions containing Fe(III) salts causes the most efficient binding of Fe(III) into complex compounds. This ensures the strongest decrease in the system's redox potential characterized by $E_{\text{Fe(III)/Fe(II)}}^0$ at $C_{\text{Fe(III)}} = C_{\text{Fe(III)}}$. However, the unequal binding of potential-determining species by phosphate anions into complex compounds results in violation of the Nernst relationship of potential versus the relative content of Fe(III) and Fe(II) cations. The most unexpected result here is the decrease in the effect of lowering the potential of the Fe(III)/Fe(II) redox couple by phosphate anions at low Fe(III) concentrations if the solution has accumulated relatively high concentrations of Fe(II) salts. Undoubtedly, consideration of the possibility of such effects is important in the practice of inhibitory protection in acid media containing Fe(III) salts.

The results of this study show the difficulty in predicting the oxidative properties of acid solutions containing Fe(III) salts. A formal description of the properties of such systems taking the Nernst equation into account can give significant deviations of their E values from the real ones. This problem can be solved more correctly by taking into account all the possible interactions of potential-determining ions with the components of acid solutions. However, this task is extremely complex since the number of these interactions is rather large and is determined to a considerable extent by the composition of the acid medium. From the practical point of view, the simplest solution of this problem involves direct potentiometric measurements of the redox potential of a system in question.

Conclusions

- 1. The redox potential of the Fe(III)/Fe(II) couple in solutions of mineral acids containing Fe(III) and Fe(II) salts is significantly smaller than the theoretical values formally calculated by the Nernst equation based on the reference value of the standard $E_{\text{Fe(III)/Fe(II)}}^0$ potential and its temperature dependence. In 2 M H₂SO₄ and 2 M HCl, the dependence of the systems' potentials on the logarithm of the relative Fe(III) and Fe(II) concentrations is nearly linear. In 2 M H₃PO₄, 1 M H₃PO₄ + 1 M H₂SO₄, and 1 M H₃PO₄ + 1 M HCl, the plots deviate from linearity.
- 2. The reason of the non-observance of the Nernst equation in mineral acid solutions containing Fe(III) and Fe(II) salts lies in the non-equivalent complexation of potential-determining species, namely, Fe(III) and Fe(II) cations, with the solution components.

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