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Short communication

Stability of perchlorate ions in acid medium: Interaction with iron

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1. Introduction

The dissolution mechanism of iron in sulfuric acid and sulfate or chloride containing solutions has been the subject of several studies [1–10]. It is an almost general conclusion that the nature of anions present in the electrolyte solutions affects the dissolution process to a more or less pronounced extent.

In most mechanistic considerations this effect is explained by the role of the specific adsorption of anions. Accepting this view and taking into consideration that the adsorbability of the anions on metals is very different depending on the nature of the anion it is important to study the dissolution process in the presence of anions with very low adsorbability in order to minimize the role of anion adsorption in the dissolution process and, consequently, to obtain experimental data without the interference of anion specific adsorption. According to some very recent views ClO_4^- ion seems to fulfil this requirement [10, 11]. However, it should be taken into consideration that compared to the large amount of work on iron dissolution in H_2SO_4 only a few studies are available concerning the behaviour of iron in $HClO_4$ solutions [10–14].

These investigations are based on the almost general belief that ClO_4^- ions are stable in a very wide potential range at metal–electrolyte interfaces and are resistant to reductive attacks even at low potentials where corrosion, or anodic dissolution of the metals takes place. In the light of new results this belief is hardly acceptable.

In previous communications [15, 16] the problem of the stability of perchlorate ions in acid medium at metal–liquid interfaces was briefly surveyed and as new evidence their interaction with nickel, copper, zinc and aluminium was reported. It was demonstrated that, although the reduction of perchlorate ions at various electrodes is slow, the possible role of this process, first of all the role of Cl^- ion formed in the reduction process, cannot be neglected in most kinetic and mechanistic studies.

It was shown in [15] and [16] that a simple analysis of the solution in contact with the corresponding metal under open circuit conditions can furnish information on the interaction of perchlorate ions with the metals. As almost in all cases where the reduction of perchlorate ions was observed, Cl^- was the main reduction product, the analysis could be restricted to this species.

On the basis of these observations it can be assumed that the iron/perchloric acid system is not an exception. This is supported by experimental evidence published long ago and available in *Gmelins Handbuch der Anorganischen Chemie* [17–19]. The intention of the present short communication is to show that the spontaneous corrosion of iron in the presence of perchloric acid is accompanied by the reduction of perchlorate ions leading to the formation of chloride ions.

2. Experimental details

Similarly to the procedure described in the previous communications [15, 16] the formation of Cl^- ions was followed by potentiometric titration using a silver chloride electrode (detection limit: 2×10^{-5} M Cl^-). Analytical grade chemicals and Aldrich iron chip (99.98%, specific surface area about 2 $cm^2\ g^{-1}$) were used. The measurement of the Cl^- concentration was combined with the determination of the amount of metal consumed, measuring the mass of the metal before and after the corrosion. This procedure enabled us to estimate the grade of conversion of the metal with respect to the anion reduction.

The measurements of the rest potential during the dissolution of iron were carried out in a two compartment cell using a sodium saturated calomel electrode (SSCE) as a reference.

3. Results and discussion

The results of experiments carried out at 25, 35 and 45 °C are presented in Tables 1, 2 and 3, respectively. In each experiment 50 ml solution was used and the

Table 1. Interaction of Fe with ClO_4^- ions (contact time 5 h), $T = 25$ °C

Electrolyte $HClO_4$ /M	$NaClO_4$	*A* Chemical amount corresponding to the mass of dissolved iron/mol	*B* Chemical amount of Cl^- formed during the dissolution of iron/mol	*B*/*A*	Conversion* /%
1	2	1.80×10^{-3}	8.6×10^{-5}	4.77×10^{-2}	19.6
0.1	2.9	5.73×10^{-4}	4.56×10^{-5}	7.96×10^{-2}	31.8
0.1	0.9	4.48×10^{-4}	2.92×10^{-5}	6.52×10^{-2}	26.1
0.5	0	4.48×10^{-4}	2.96×10^{-5}	6.61×10^{-2}	26.4
1	0	1.27×10^{-3}	5.75×10^{-5}	4.53×10^{-2}	18.1

* Percentage of dissolved Fe involved in ClO_4^- reduction (see text).

Table 2. Interaction of Fe with ClO_4^- ions (contact time 5 h), $T = 35$ °C

Electrolyte $HClO_4$ /M	$NaClO_4$	*A* Chemical amount corresponding to the mass of dissolved iron/mol	*B* Chemical amount of Cl^- formed during the dissolution of iron/mol	*B*/*A*	Conversion* /%
1	2	4.98×10^{-3}	1.77×10^{-4}	3.55×10^{-2}	14.2
0.1	2.9	1.25×10^{-3}	1.14×10^{-4}	9.12×10^{-2}	36.3
0.1	0.9	8.77×10^{-4}	5.92×10^{-5}	6.75×10^{-2}	27.0
0.5	0	1.36×10^{-3}	6.31×10^{-5}	4.64×10^{-2}	18.5
1	0	1.95×10^{-3}	7.50×10^{-5}	3.85×10^{-2}	15.4

* Percentage of dissolved Fe involved in ClO_4^- reduction (see text).

Table 3. Interaction of Fe with ClO_4^- ions (contact time 5 h), $T = 45$ °C

Electrolyte $HClO_4$ /M	$NaClO_4$	*A* Chemical amount corresponding to the mass of dissolved iron/mol	*B* Chemical amount of Cl^- formed during the dissolution of iron/mol	*B*/*A*	Conversion* /%
1	2	1.62×10^{-2}	3.84×10^{-4}	2.37×10^{-2}	9.5
0.1	2.9	1.79×10^{-3}	1.79×10^{-4}	1.00×10^{-1}	40
0.1	0.9	9.30×10^{-4}	6.99×10^{-5}	7.52×10^{-2}	30
0.5	0	2.60×10^{-3}	8.47×10^{-5}	3.26×10^{-2}	13
1	0	1.72×10^{-2}	3.20×10^{-4}	1.86×10^{-2}	7.5

* Percentage of dissolved Fe involved in ClO_4^- reduction (see text).

amount of iron was changed from 1.5 to 5.0 g depending on the temperature in order to obtain reliable conditions for the determination of the concentration of Cl^- ions formed.

It follows that two overall processes occur simultaneously:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{1}$$

$$4Fe + ClO_4^- + 8H^+ \rightarrow Cl^- + 4Fe^{2+} + 4H_2O \tag{2}$$

The last column in the Tables (conversion) gives the relative amount of dissolved iron involved in the second reaction (i.e., the efficiency of the dissolution with respect to Reaction 2). These values are very high in comparison with those obtained in the case of Zn, Al and Ni as shown in Table 4. It may be seen from this Table and the previous ones that in the case of iron the ClO_4^- reduction cannot be considered as a negligible side process.

Hydrogen evolution and perchlorate reduction are two parallel cathodic processes linked with the anodic dissolution of Fe.

At a fixed $HClO_4$ concentration the rest potential of the corroding iron remained practically constant (cf. (1) and (2) in Figure 1), evidently the value of the rest potential depends on pH.

It is expected that the rate of hydrogen evolution is directly influenced by the acid concentration, therefore, the decreasing efficiency with respect to ClO_4^- reduction

Table 4. Comparison of conversion values obtained for various metals at 25 °C in 1 M $HClO_4$ (average values) [15, 16]

Metal	Conversion value /%
Ni	~ 1.0
Al	~ 1.4
Zn	~ 1.6
Fe	~ 18.0

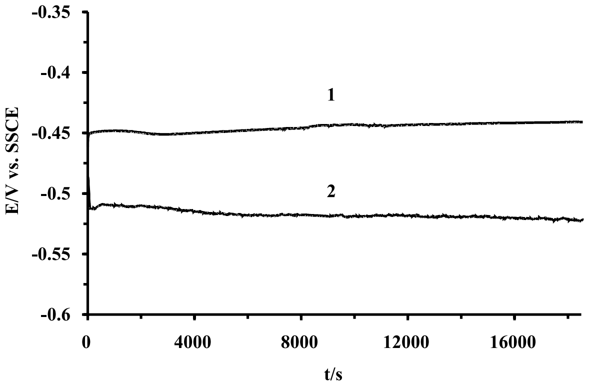

Fig. 1. Rest potential against time curves during dissolution of iron in (1) 1 M $HClO_4$ and (2) 0.1 M $HClO_4$ + 2.9 M $NaClO_4$ solution.

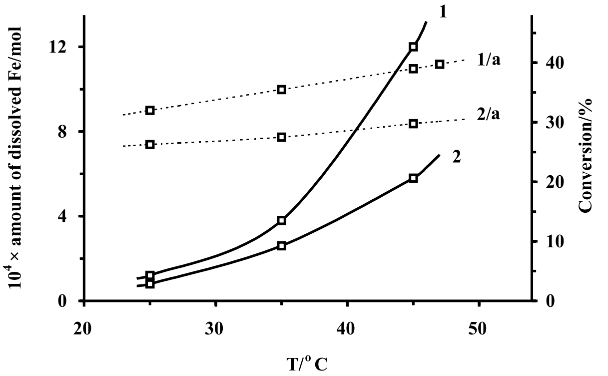

Fig. 2. Amount of Fe dissolved during 5 h from 1 g iron chip (1, 2) and the conversion values (1/a, 2/a) in the presence of 1, 1/a: 0.1 M $HClO_4$ + 2.9 M $NaClO_4$; 2, 2/a: 0.1 M $HClO_4$ + 0.9 M $NaClO_4$.

with increasing acid concentration is reasonable (data in Tables 1, 2 and 3).

However, the picture is very complicated as follows from the temperature dependence of the overall dissolution rate and conversion values. Figure 2 shows the temperature dependence of the overall average dissolution rate and the conversion in the presence of 0.1 M $HClO_4$ while Figure 3 shows the same dependence in the presence of 1 M $HClO_4$. It is of interest that in 0.1 M $HClO_4$ solution despite the significant change in the dissolution rate with temperature there is only a slight increase in the conversion. In contrast to this, in 1 M solution (Figure 3) the conversion decreases and its value is lower than that observed in the case of 0.1 M $HClO_4$.

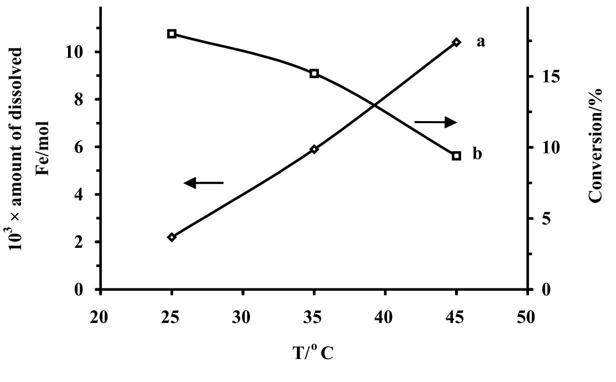

Fig. 3. Amount of Fe dissolved during 5 h from 1 g iron chip (a) and the conversion values (b) in the presence of 1 M $HClO_4$.

It follows from Figure 2 that a significant increase in the ClO_4^- concentration does not exert significant influence on the conversion values.

4. Conclusions

The results provide convincing evidence concerning the spontaneous reduction of ClO_4^- ions at Fe/electrolyte interfaces in acid medium. The rate and extent of the interaction of ClO_4^- ion with iron are commensurable with those of proton discharge leading to the formation of H_2. It follows that the corrosion and anodic dissolution of Fe in perchloric acid cannot be treated in terms of the

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$2H^+ + 2e^- \rightarrow H_2$$

processes without taking into consideration the reduction of ClO_4^- ions. All this means that the whole literature dealing with corrosion or anodic dissolution of iron in perchloric acid or acidic perchlorate media should be revisited and critical analysis of the data is required. This work is in progress.

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References

1. K.E. Heusler, *Z. Electrochem.* **62** (1958) 582.
2. K.E. Heusler and G.H. Cartledge, *J. Electrochem. Soc.* **108** (1961) 731.
3. I. Epelboin, C. Gabrielli, M. Keddam and H. Takenouti, *Electrochim. Acta* **20** (1975) 913.
4. K. Azumi, K. Iokibe, T. Ueno and M. Seo, *Corros. Sci.* **44** (2002) 1329.
5. G. Lendvay-Győrik, L. Mészáros, G. Mészáros and B. Lengyel, *Corros. Sci.* **42** (2000) 79.
6. A.B. Geraldo, O.E. Barcia, O.R. Mattos, F. Huet and B. Tribollet, *Electrochim. Acta* **44** (1998) 455.
7. G. Rocchini, *Corros. Sci.* **39** (1997) 1381.
8. M. Itagaki, R. Oltra, B. Vuillemin, M. Keddam and H. Takenouti, *J. Electrochem. Soc.* **144** (1997) 64.
9. O.E. Barcia, O.R. Mattos, N. Pebere and B. Tribollet, *Electrochim. Acta* **41** (1996) 1385.
10. S.Y. Zhao, S.H. Chen, H.Y. Ma, D.G. Li and F.J. Kong, *J. Appl. Electrochem.* **32** (2002) 231.

11. H.Y. Ma, G.Q. Li, S.C. Chen, S.Y. Zhao and X.L. Cheng, *Corros. Sci.* **44** (2002) 1177.
12. E. Ahlberg and M. Friel, *Electrochim. Acta* **34** (1989) 1523.
13. N.L. Nauyen and K. Nobe, *J. Electrochem. Soc.* **128** (1981) 1932.
14. A. Darwish, F. Hilbert, W.J. Lorenz and H. Rosswang, *Electrochim. Acta* **18** (1973) 421.
15. M. Ujvári, G. Láng and G. Horányi, *J. Appl. Electrochem.* **31** (2001) 1171.
16. M. Ujvári, G. Láng and G. Horányi, *J. Appl. Electrochem.*, **32** (2002) 581.
17. 'Gmelins Handbuch der Anorganischen Chemie', Chlor Ergänzungsband Teil B, Lieferung 2, System Nr. 6 (Verlag Chemie GMBH, Weinheim, 1969), p. 463.
18. A.M. Lecco and V.D. Canić, *Glasnik Hem. Drustva Beograd* **14** (1949) 249/51.
19. V.D. Canić, *Glasnik Hem. Drustva Beograd* **16** (1951) 13/8.