



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 4(1), 2008 [47-49]

Effect of halogen ions on the electrochemical behaviour of lead in hydrochloride medium

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Received: 18th April, 2007 ; Accepted: 23rd April, 2007

ABSTRACT

The effect of the addition of halogen ions on the electrochemical behaviour of lead in 0.3M HCl solution has been investigated by using cyclic voltammetry (CV) technique. For this purpose, $5 \cdot 10^{-2}$ M, 10^{-2} M, $5 \cdot 10^{-1}$ M and 1M KF, KBr and KI solution were used. The results obtained show that the shape of the cyclic voltammograms is not modified in the presence of halogen ions in solution. The examination of the curves illustrates that the anodic current density of lead depends on the type of halogen and on its concentration: At low concentrations, the effect of halogen ions is related to their ionic rays. However, at high concentration, that effect follows the constants of solubility of the salts KF, KBr and KI. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Cyclic voltammetry;
Lead;
Halogens;
Electrochemical.

INTRODUCTION

The electrochemical characteristics of the lead electrode in acid solution depend on the nature and on the composition of this later. In fact, several works focused on the study of the effect of different mediums on the lead and its alloys^[1-7]. When the metal is immersed in acidic solution containing Cl⁻, NO₃⁻ or SO₄²⁻, among the important phenomena that could faced is the interfacial electrochemical reactions that could be attributed to various phenomenon such as the dissolution or the passivation of the metal^[8-11]. Moreover, it's noted that the stimulating effect of a certain anion on the anodic reactions is manifested only when a certain critical

potential has been reached. At this potential, the strength of covalent bond between the surface atoms of the metal and the adsorbed ions equals the covalent bond strength in the corresponding individual compound. Evidently, the different anions must have different values of the critical potentials. Consequently, it could be expected that if at a given potential, several components of the solution are adsorbed, and then all the surface complexes can not pass into solution, but only those with the required chemical bond strength. This probably explains the passivating effect of the halogen ions on the iron dissolution in sulphuric acid^[12].

Therefore, the present paper is devoted to investigate the cyclic voltammetric behaviour of the lead

electrode in hydrochloride solution and the examination of the formed complexes. In fact, this study was undertaken to achieve the following two purposes. Firstly, to integrate our studied on the behaviour of the lead electrode in HCl solution. Secondly, to study the effect of the addition of the halogen ions on the electrochemical characteristics in HCl.

METHODS AND MATERIALS

Electrochemical measurements were recorded with a potentiostat type Amel 550 using a linear sweep generator type Amel 567 at a scan rate of 20mV/min. Before recording each cyclic voltammetry curve, the lead electrode was polarised at -1000mV/SCE for 10 min. We used for all electrochemical tests a conventional three electrodes electrolysis cylindrical Pyrex glass cell. Saturated calomel electrode(SCE) and platinum electrode are used as reference and Auxiliary electrodes, respectively. The working electrode is in form of disc from lead(99.99%) sheet of the surface 0.5 cm². Prior each experiment, the surface of the working electrode was polished with different emery paper up 1000 grade, washed thoroughly with acetone and rinsed with bidistilled water.

The halogen ions are obtained from the salts KF, KBr and KI. All experiments were carried out in 0.3M HCl at 25°C. The solution test was prepared by the dilution of analytical grade 37% HCl with double distilled water. The solution test is also de-aerated by pure nitrogen. Gas pebbling is maintained prior and through the experiments.

RESULTS AND DISCUSSIONS

The electrochemical behaviour of lead in 0.3M HCl solution was studied by cyclic voltammetry. Measurements performed in hydrochloride solution containing different concentrations of halogen ions are presented in figures 1, 2 and 3. The electrochemical parameters derived from these figures are reported in TABLE 1.

From the cyclic voltammograms obtained, one anodic peak and one cathodic peak are observed. It can be seen that the shape of the voltammograms is not influenced although the solution composition varied. In

TABLE 1 : Electrochemical parameters derived from figures 1, 2 and 3

Inhibitor	C (M)	I _{pa} (mA/cm ²)	I _{pc} (mA/cm ²)	E _{pa} (mV/SCE)	E _{pc} (mV/SCE)
Blank	0.3M HCl	29.1	24.7	-343	-510
	5.10 ⁻²	23.5	14.8	-385	-550
Br ⁻	10 ⁻¹	15.4	9.4	-398	-501
	5.10 ⁻¹	10.7	5.5	-409	-500
	1	7.8	2.7	-413	-500
F ⁻	5.10 ⁻²	26.2	21.3	-328	-572
	10 ⁻¹	18.6	18.8	-326	-574
	5.10 ⁻¹	7.4	15.2	-348	-570
	1	2.4	-	-365	-
I ⁻	5.10 ⁻²	10.6	6.77	-387	-430
	10 ⁻¹	8.5	4.1	-391	-436
	5.10 ⁻¹	5.4	-	-391	-
	1	1.9	-	-391	-

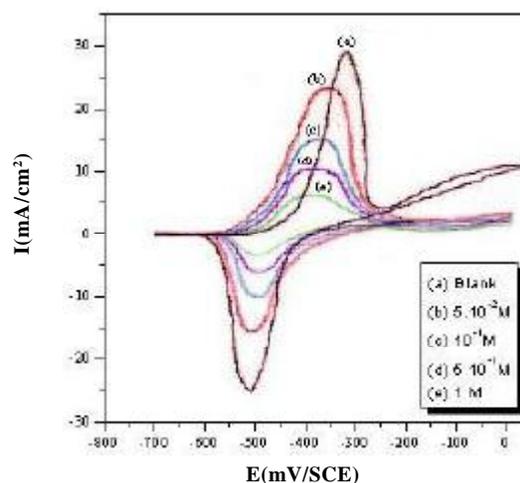


Figure 1 : Cyclic voltammograms for the lead electrode in 0.3M HCl in the presence of Br⁻ at various concentrations.

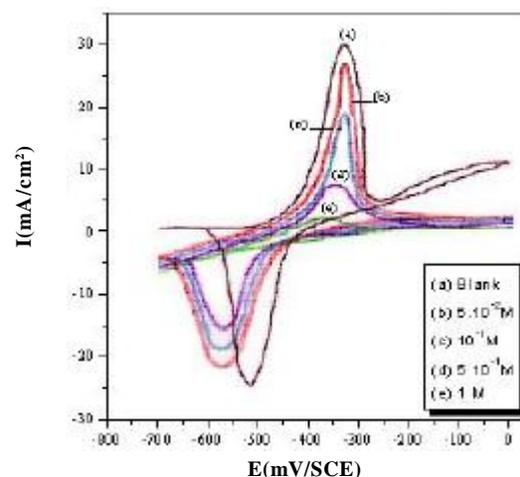


Figure 2 : Cyclic voltammograms for the lead electrode in 0.3M HCl in the presence of F⁻ at various concentrations

fact, the anodic peaks which represent the anodic reaction (oxidation) are characterised by the potential

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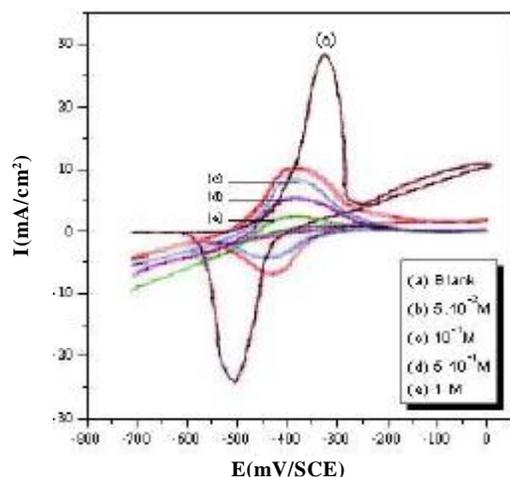


Figure 3 : Cyclic voltammograms for the lead electrode in 0.3M HCl in the presence of I⁻ at various concentrations

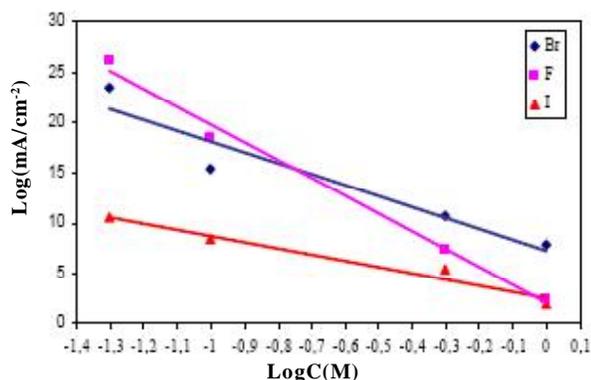


Figure 4 : Evolution of I_{pa} as function of logarithm of the halogens concentration

(E_{pa}) and by the anodic current density (I_{pa}). Also, the cathodic peaks are characterised by the potential (E_{pc}) and by the anodic current density (I_{pc}). These peaks refer to the reactions of the reduction. The same results are found elsewhere^[13].

The examination of the results shows that in the presence of the halogen ions, both anodic and cathodic reactions (I_{pa} and I_{pc}) are reduced. This reduce is more significant with the rise of the halogen ions concentrations. In this subject, two parts can be observed:

***C=10⁻¹M, the currents of the anodic peaks increase following this order: F>Br>I**

This order can be interpreted with the help of the ionic rays; In fact, the ionic rays of the anions increase following the sequence F(1.33Å)>Br(1.96Å)>I(2.2Å)^[14]. The anion that has a big ionic ray occupies a large adsorption surface in comparison with the anion

which has a small ray. This result is in agreement with the literature^[15].

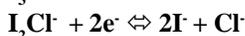
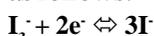
***C=5.10⁻¹M, the currents of the anodic peak I_{pa} increase following this order: Br>F>I**

This order can be explained from the different constants of solubility of salts^[16]. It's around 8.2, 7.6 and 5 respectively for PbI₂, PbF₂ and PbBr₂. For the elevate concentration (1M), the effect of F⁻ ions becomes slightly more important in comparison with I⁻. This phenomenon is bound to the ionic interactions of the ions I⁻ which are more voluminous than F⁻ ions.

Figure 4 shows the variation of the current of anodic peak as function of the halogens concentration. It's clear that the current of the peak decreases linearly with logarithm of the concentration according to the relation (1)^[17]. This dependence is a criteria of inhibition.

$$I_{pa} = a - b \log(C) \quad (1)$$

We noted that the addition of KI in hydrochloride solution accompanied with the appearance of the ions I⁻ that has a brown color which becomes clear from the concentration 10⁻¹M of I⁻ ions. In the presence of I⁻ in the solution, the iodine I gives the complex I₃⁻; However, in the presence of Cl⁻, I forms I₂Cl⁻. The apparent potential $E^\circ(I_2Cl^-/I^-)$ is near to the potential of (I₃⁻/I⁻)^[18]. Therefore, the corresponding reactions are given as follows:



The relation of Nernst related to each reaction are:

$$E_{eq} = E^\circ(I_3^-/I^-) + 0.03 \log[I_3^-] - 0.09 \log[I^-] \quad (2)$$

$$E_{eq} = E^\circ(I_2Cl^-/I^-) + 0.03 \log[I_2Cl^-] - 0.03 \log[Cl^-] - 0.06 \log[I^-] \quad (3)$$

To confirm the formed species, we followed the evolution of the equilibrium potential (E_{eq}) of the platinum electrode according to the reference electrode (SCE).

The equilibrium potential E_{eq} has been determined at different concentration of KI (from 10⁻²M to 1M) in 0.3M HCl. E_{eq} , stabilizing less than one minute, shows a linear variation as function of the logarithm of the concentration of the ions I⁻. The obtained slope is equal to 57 mV/dec. (Figure 5), and it indicates that the electrochemical reaction related to I⁻ is mono-electronic. This result indicates the formation of I₂Cl⁻ instead of I₃⁻, thus the relation of Nernst can be written as follow:

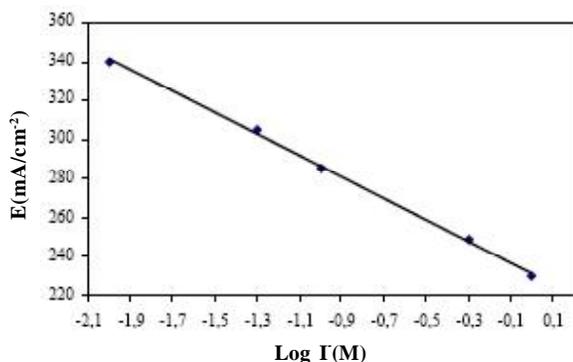


Figure 5: Variation of Eeq as function of the logarithm of the concentration of the ions I

$$E_{eq} = E^{\circ} + 0.03 \log[I_2Cl] - 0.03 \log[Cl] - 0.06 \log[I] \quad (4)$$

The apparent potential E° can be determined from the origin value (228 mV/SCE).

The concentration of I_2Cl can be calculated from the concentration of the iodine determined in 0.3M HCl, and the constant of the formation of the complex I_2Cl is 0.2^[18]. The concentration of the iodine is dosed by the ions thisulfates according to the following reaction:



The results obtained reveal that $[I_2] = 9.10^{-4}M$ and $[I_2Cl] = 4.3 \cdot 10^{-4}M$. The apparent potential E° is then equal to 312 mV/SCE. This value is in good agreement with the literature^[18].

CONCLUSION

We have studied the effect of the presence of the halogen ions in 0.3M HCl on the lead electrode by the use of cyclic voltammetry. The results obtained demonstrated that the addition of halogen ions act on the anodic behaviour of the lead follow the sequences:

- $F^{-} > Br^{-} > I^{-}$ at low concentrations ($C \leq 10^{-1}M$)
- $Br^{-} > F^{-} > I^{-}$ at high concentrations ($C \geq 5 \cdot 10^{-1}M$)

The shape of the cyclic voltammograms is not modified in the presence of halogen ions in solution

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