Asian Journal of Chemistry Vol. 6, No. 1 (1994), 143–148

Effect of Electronegativity and Covalent Radius of Halide Ions on Adsorption on Lead in Acid Medium

MOSTAFA H. WAHDAN† and GAMAL K. GOMMA*
Chemistry Department, Faculty of Education
Tanta University, Kafr El-Sheikh. Egypt

The corrosion rate of lead in 0.1 M chloroacetic acids with and without different additives of Cl, Br and I has been calculated gravimetrically and potentiokinetically. The results indicate that halide ions adsorbed on the electrode surface inhibit the dissolution reaction. Asorption occurs according to Langmuir isotherm. The inhibition effect increases in the order $I^- > Br^- > Cl^-$, which seems to indicate that radii and electronegativity of halogens play an important role.

INTRODUCTION

Halides inhibit the corrosion of some metals in strong acids and this effect depends on ion size and charge[1], the electrostatic field set up by the negative charge of the anion on adsorption sites[2] and the nature and concentration of halide ions[3]. In acidic solution, halides shift the corrosion potential to more negative values and decrease the corrosion current[4,5]. At high Cl^- ion concentration, solid metal chloride is preaccepted on metal surface. Due to the ability of halide ions to be absorbed on the metal surface, many attempts explain the different action of halides. Polarisation and atomic radii have shown that the ability increases in the direction $I^- > Br^- > Cl^-$[6]. The aim of the present work is to study the adsorption isotherm for Cl^-, Br^- and I^- on lead in chloroacetic acid solutions, and the effect of electronegativity and covalent radius on adsorption.

EXPERIMENTAL

Pure lead sheets were used. All measurements were carried out in 0.1 M mono-, di-, and trichloracetic acid at 30°C containing solutions of potassium salts of Cl^-, Br^- and I^- at varying concentrations (10^{-3}–10^{-1} mole/l). The corrosion rate was determined gravimetrically and potentiokinetically. Potentiodynamic studies were performed using a corrosion measurement system, a model 273 soft corrosion software potentiostat/galvanostat. The anodic and cathodic polarisation measurements were obtained at scan rate of 120 mV/min. and the potential ranging from –500 to +2000 mV. Potentials were measured against saturated calomel electrode (SCE) in deaerated solutions. The corrosion rate was obtained by linear polarisation and Tafel extrapolation methods.

---

†Chemistry Department, Faculty of Science, Assiut University, Egypt.

The coverage (θ) of the lead surface adsorbed halide ions was evaluated by the equation[7].

$$\theta = 1 - W_1/W_2$$

where W_1 and W_2 are corrosion rates in acid solutions with and without halide ion respectively.

RESULTS AND DISCUSSION

The corrosion rate of lead specimen as a function of log C of inhibitors is shown in Fig. 1. There is a linear dependence indicating that the corrosion rate depends upon the anion concentrations. Fig. 2 represents the relationships between θ and halide concentration (monochloro as example). From this figure, it could be seen that the halide anions inhibit the corrosion of lead in 0.1 M chloroacetic acids. The inhibitive effect decreases in the order $Cl^- > Br^- > I^-$ and in the order of tri- > di- > monochloracetic acid solutions.

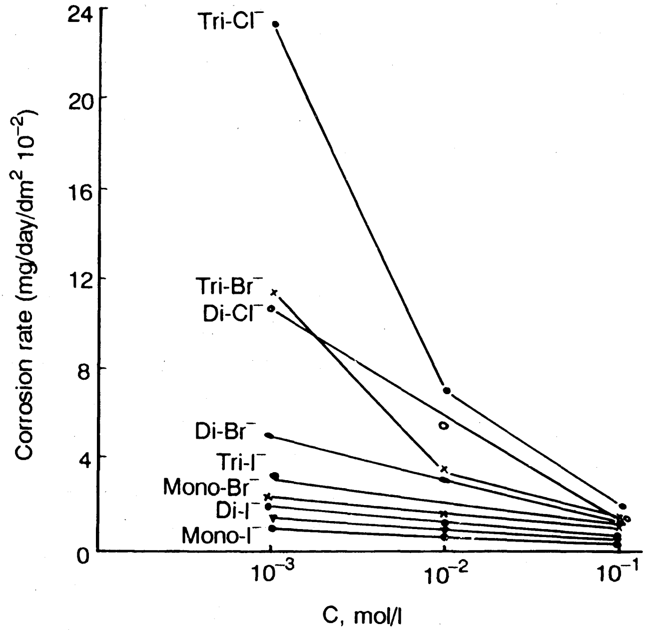

Fig. 1 The relation between corosion rate of lead in mono-, di- and trichloroacetic acid and concentrations.

The decrease in the inhibitive efficiency at higher halide ion concentrations is probably associated with the formation of a three-dimensional film[8].

The results carried out potentiokinetically showed that the corrosion potential values are shifted towards a more negative direction with increasing additive concentration. Such behaviour may be due to the adsorption of halide anions on the metal surface.[9] The negative shift in the values of corrosion potential in

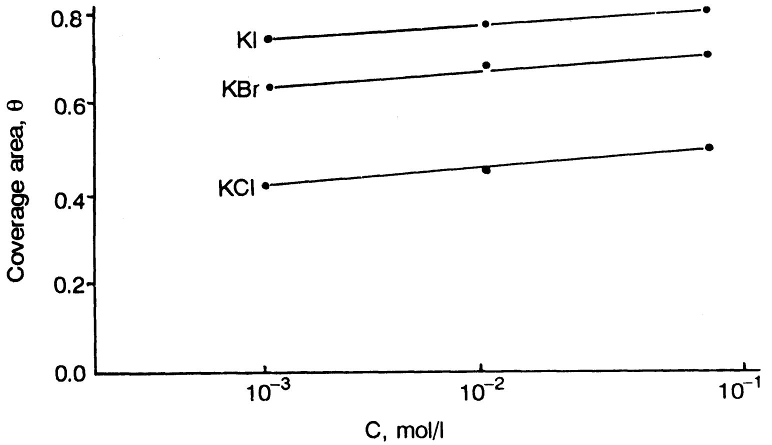

Fig. 2 Surface average area θ as a function of concentration of halides in 0.1 M monochloroacetic acid solution.

presence of Cl^-, Br^- and I^- is higher as compared to the effect of changing the respective concentrations of chloroacetic acid solutions, free from halide ions.

By applying the data given in Table 2 to Langmuir adsorption isotherms, it was concluded that the halide anions examined were adsorbed on the lead surface according to the Langmuir adsorption isotherm (1).

$$\frac{\theta}{1-\theta} = AC \exp\left(\frac{Q_a}{RT}\right) \qquad (1)$$

where A is a constant, C is the concentration of inhibitor in the solution, and Q_a is the heat of adsorption for Cl^-, Br^- and I^- ions on the electrode surface.

Thus,
$$\log\frac{\theta}{(1-\theta)} = \log A + \log C + \frac{Q_a}{2.3RT} \qquad (2)$$

To test the conformity of our results with this simple model, $\log\frac{\theta}{(1-\theta)}$ was plotted vs log C which should give a fit-in with straight lines, which cover three concentrations of Cl^-, Br^- and I^- solutions. However, the gradient is much less than unity (0.08, 0.10 and 0.12 for Cl^-, Br^- and I^- respectively monochloroacetic acid 0.05, 0.06 and 0.10 for Cl^-, Br^- and I^- respectively in di-, and 0.04, 0.05 and 0.09 for Cl^-, Br^- and I^- respectively in trichloroacetic acid). Such a discrepancy may be explained on the premise that a considerable area of holes is left through which lead ions can still pass. Graham[10] pointed out that the Langmuir constant K (slope of the straight line), which he named the equilibrium function, can possibly be less than unity for adsorption on heterogeneous surfaces in general and much smaller than unity when there is no lateral interaction between molecules.

From thermodynamic data calculated from the experimental results it is seen that the highest heat of adsorption is obtained for I^- and increases in the order

KI < KBr < KCl, which means that repulssive forces between the adsorbed anions vary in the above order.

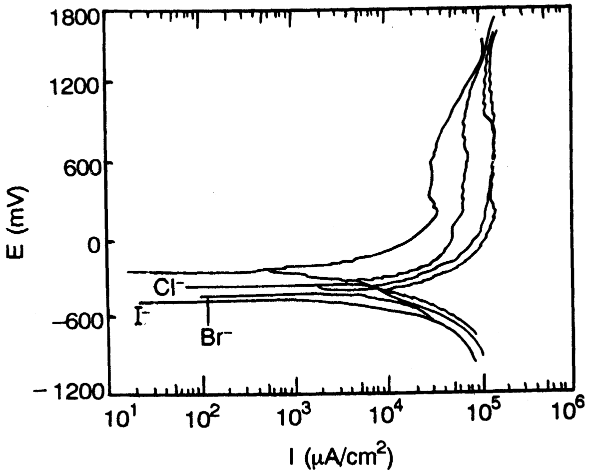

Fig. 3 Polarization curves for lead in 0.1 M trichloroacetic acid.

Polarisation results obtained for lead in 0.1 M chloroacetic acids without and with halide ions added are given in Fig. 3. The halide additives affect both cathodic and anodic curves by shifting polarisation curves to a lower current densities. However, the anodic process is more strongly affected than the cathodic process. Corrosion potentials and corrosion currents obtained are given in Table 1. Weight-loss and electrochemical measurements of the corrosion rate of lead in chloroacetic acid solutions containing halide ions give the same order of increasing rates, $I^- < Br^- < Cl^-$. Coverage area θ calculated on the base of corrosion currents differs from that based on weight loss measurements, but the same sequence is observed (Table 2).

TABLE 1
CORROSION POTENTIAL AND CORROSION CURRENTS FOR LEAD IN 0.1 M TRICHLOROACETIC ACID IN ABSENCE AND PRESENCE OF HALIDE IONS

Solutions		$-E_{corr.}$ (mV)			$i_{corr.}$ $(A/cm)^2$		
0.1 M Tri-		306			12384.91		
		KI	KBr	KCl	KI	KBr	KCl
0.1 M Tri-	+0.1 M	525	474	425	2644	3818	4421
0.1 M Tri-	+0.01 M	471	415	380	4068	5462	6832
0.1 M Tri-	+0.001 M	430	390	316	6494	7579	9198

Adsorption of halides on lead metal according to Langmuir isotherm indicates that chemisorption occurs. The chemisorbed film is immobile, and adsorption equilibrium settles slowly. Compounds subject to strong chemisorption possess a high electron density around the atom forming bonds with metal, and have the ability to form coordination bonding. There is no unanimity about the type of surface compounds formed by halides with lead. Halide ions are good ligands because they exhibit a low electronegativity (less than 3.5)[6]. Electronegativity decreases from Cl^- to I^-, [Cl^- = 3.16, Br^- = 2.96, I^- = 2.66], while covalence radius increases from Cl^- to I^- [Cl^- = 0.99, Br^- = 1.14, I^- = 2.33]. Thus lead can form compounds with halide ions. Thus halide ions inhibit corrosion of lead in chloroacetic acids which may be due to that under these conditions, the surface compounds of lead with halides are scarcely soluble. The inhibitive effect increases in the order $Cl^- < Br^- < I^-$, which seems to indicate that the radii of halogen ions may also play a role. With increasing ionic radius polarisation of electron cloud is facilitated, *i.e.* they are deformed more easily when adsorbed on lead metal surface. Therefore I^- (radius 1.33 Å) is more predisposed to adsorption than are Br^- (radius 1.14 Å) and Cl^- (radius 0.99 Å).

TABLE 2

THE RELATIVE SURFACE COVERAGE θ_W AND θ_P OBTAINED WITH WEIGHT-LOSS AND ELECTROCHEMICAL METHOD RESPECTIVELY

Concentrations (mol/l)		θ_W			θ_P		
		KI	KBr	KCl	KI	KBr	KCl
0.1 mono-	+0.1	0.890	0.760	0.690	0.87	0.83	0.70
0.01 mono-	+0.01	0.850	0.720	0.670	0.85	0.75	0.62
0.001 mono-	+0.001	0.770	0.700	0.570	0.82	0.71	0.55
0.1 Di-	+0.1	0.840	0.720	0.630	0.81	0.73	0.68
0.01 Di-	+0.01	0.800	0.690	0.610	0.78	0.68	0.60
0.001 Di-	+0.001	0.750	0.670	0.520	0.75	0.65	0.48
0.1 Tri-	+0.1	0.800	0.700	0.600	0.78	0.69	0.64
0.01 Tri-	+0.01	0.780	0.650	0.550	0.67	0.55	0.44
0.001 Tri-	+0.001	0.700	0.580	0.450	0.47	0.38	0.25

Since the potential of zero charge for lead is –0.65 V[11,12] and the corrosion potential in 0.1 M trichloroacetic acid is –0.306 V, the lead surface is positively charged at the corrosion potential, at potential ranging from –0.65 to –0.306 V, and at potentials more positive than –0.306 V. Consequently halide anions are able to affect both the anodic and cathodic polarisation curves for lead.

REFERENCES

1. M.J. Pryor, *Z. Electrochem.*, **62** 782 (1958).
2. G.H. Cartledge, *J. Phys. Chem.*, **60**, 32 (1952).
3. W.J. Lorenz, *Corros. Sci.*, **5**, 121 (1965).
4. A.J. Arvia and J.J. Podesta, *Corros. Sci.*, **8**, 203 (1968).
5. K.E. Heusler and G.H. Cartledge, *J. Electrochem. Soc.*, **108**, 732 (1961).
6. K. Snyder, in *Chemi. Stru. and Reac.* (eds. Holt, Richard and Winston (1966).

7. G. Trabanelli and Carassiti, Advances in Corrosion Science and Technology (eds. M.G. Fontana and R.W. Stachle Vol. 1, 147, Plenum Press, New York p 147 (1970).
8. J.N. Putilova, S.A. Balezin and W.P. Barannik, Inhibitory Korrozii Metalloy, Goskhimizdat, Moscow (1958).
9. Y.M. Kolotyrkin, *Chem. Soc.*, **54**, 8247 (1960).
10. D. Graham, *J. Phys. Chem.*, **57**, 665 (1953).
11. A.N. Frumkin, *Z. Electrochem.*, **59**, 807 (1955).
12. Z.A. Jofa, V.V. Batrakov and Kho Ngok Ba, *Electrochim. Acta*, **1**, 1645 (1964).

(*Received*: 20 February 1993; *Accepted*: 15 May 1993) AJC–614