Electrochemical Behaviour of Lead in 0.3M HCl in Presence of Pyrazolic Compounds

B. Hammouti*, R. Salghi and S. Kertit[1]

Laboratoire de Chimie Analytique Appliquee, Faculte des Sciences d'Guida, MOROCCO

[1] Laboratoire de Physico-Chimie des Materiaux, Ecole Normale Superieure de Takaddoum, B.P. 5118 Rabat, MOROCCO

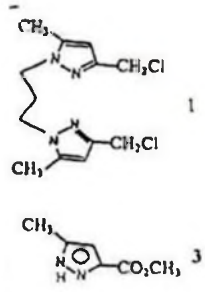
Several pyrazoles have been evaluated as corrosion inhibitors for lead in 0.3 M hydrochloric acid using potentiodynamic measurement. A comparison of results among these pyrazoles showed that bis(3-carbomethoxy-5-methyl-1-pyrazolyl) methane was the best inhibitor. Its current density attained a minimum at 10^{-3} M. Polarization data suggested that the pyrazoles acted as cathodic inhibitors without changing the mechanism of the cathodic reaction. It has been found that the anodic peak current increased with rise in temperature without modifying the peak potential.

Lead is considered as one of the vital metals because of its wide industrial applicability, particularly in lead-acid batteries. It is known that lead undergoes corrosion in dilute hydrochloric acid solution. When the concentration of acid exceeds 0.4M HCl, inhibitive $PbCl_2$ layer is formed. Inhibition of lead corrosion by organic additives has been studied by electrochemical methods [1-5]. Pyrazoles have been used as good inhibitors for lead [5] and iron [6].

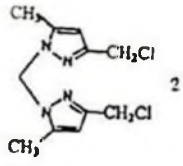
In the present investigations, corrosion of lead in 0.3M HCl in the absence and in presence of new pyrazolic compounds have been studied by employing electrochemical methods.

EXPERIMENTAL DETAILS

Pure lead electrode (99.99%) of area 0.56 cm^2 was used. The organic compounds were synthesised as described elsewhere [7].

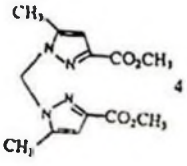


1



2

3



4

1: 1,3-Bis(3'-chloromethyl-5-methyl-1'-pyrazolyl) propane
2: Bis(3-chloromethyl-5-methyl-1-pyrazolyl) methane
3: 3(5)-carbomethoxy-5(3)-methyl pyrazole
4: Bis(3-carbomethoxy-5-methyl-1-pyrazolyl) methane

HCl solutions were prepared from HCl 37% (Riedel de Haen) with bidistilled water. The polarization curves were carried out with a potentiostat (Amel 550), connected to a generator (Amel 567) and X-Y recorder (Amel 580). A saturated calomel electrode (SCE) and platinum

© E.C.S.I. Bangalore

electrode were used as reference and auxiliary electrodes, respectively. The scan rate was 300 mV/min. All experiments were performed at specified temperature ±1°C in a conventional electrochemical cell of three electrodes. The electrode surface was polished with emery paper prior to each experiment. The magnetically stirred electrolyte was degassed by passing purified nitrogen through the solution for 2 hours before starting the experiments.

RESULTS AND DISCUSSION

Comparison of different inhibitors

The cathodic and anodic polarization curves of lead are recorded at 30°C in 0.3M HCl in absence of inhibitors and also in presence of 10^{-3} M different pyrazole compounds [1-4]. It is clear from the plot (Fig. 1) that the cathodic and anodic current densities at potential near the free E_{corr} are mainly associated with the activation control. On the cathodic side the current density decreased for the inhibitors in the order 4 < 3 < 2 <1. The anodic part of the polarization curve shows a peak corresponding lead dissolution [8], but the current density is independent of the presence of inhibitor.

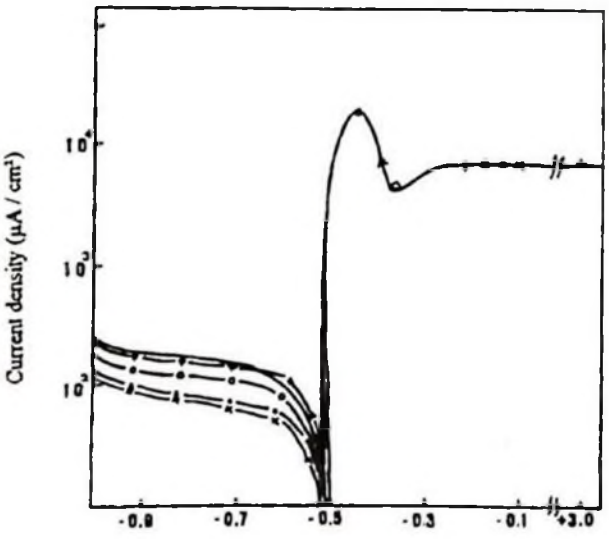


Fig. 1 Current - *vs* - potential curves
Lead in 0.3 M HCl and in 0.3 M HCl + 10^{-3} M of different pyrazole compounds.
(—)0.3 M HCl. (+) Inh 1. (o) Inh 2. (●) Inh 3. (X) Inh 4

Table 1

E_{corr} in presence of Different Inhibitors

Medium 0.3 M HCl without & with 10^{-3} M of the inhibitor
Reference electrode SCE

inhibitor	nil	1	2	3	4
E_{corr}(mV)	-515	-498	-517	-523	-528

The value of E_{corr} is presented in Table 1. It can be noted that change in E_{corr} is very slight but the order is the same as current density (4<3<2<1).

The extent of corrosion inhibition is expected to be dependent on the magnitude of electron charge density on the active centre. Introduction of electron donating substituent (CO_2CH_3) in inhibitors 3 and 4 enhances the adsorption of the inhibitors and hence increases corrosion inhibition.

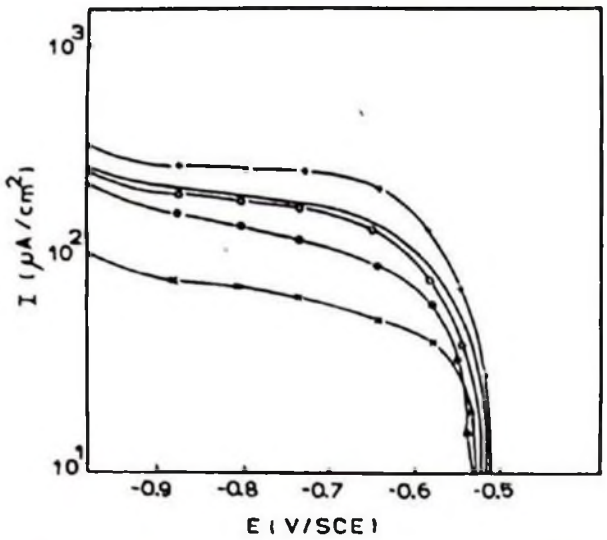


Fig 2 : Cathodic Potentio Kinetic Polarization Curves od Lead in 0.3 M HCl in Presence of Different Concentrations of Compound 4
(—)0.3 M HCl. (+) 10^{-5}, (o) 10^{-4}, (•) $2x10^{-4}$, (X) 10^{-3}

Effect of Concentration

The effect of concentration of inhibitor 4 on the polarization of lead at 30° in 0.3 M HCl shows that current density on the cathodic side decreased with inhbibitor concentration. It can be observed that the mechanism of the cathodic reaction is independent of the addition of pyrazoles. However the anodic current density is independent to the concentration of the inhibitor 4.

In chloride media, a passive $PbCl_2$ film may be formed which decreases the number of active sites available for adsorption. This may be cause for the lack of effect of the inhibitors on the anodic polarization curve.

Effect of Temperature on the Anodic Corrosion

The plots of anodic polarization curves of

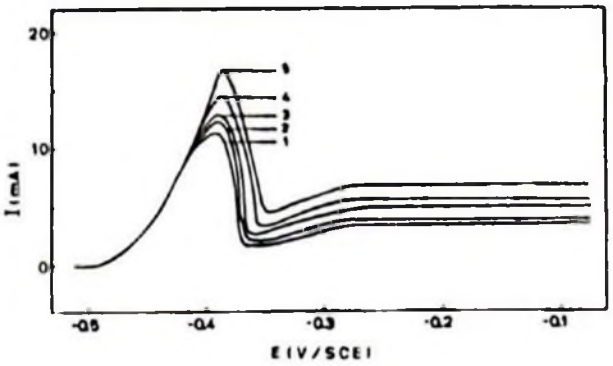


Fig 3 : Effect of temperature on anodic curves of the lead electrode in 0.3 M HCl (1) 20°C, (2) 25°C (3) 30°C, (4) 40°C, (5) 50°C.

lead in 0.3 M HCl at different temperatures (20-50°C) in Fig. 3 shows that the peak current (I_p) increases with temperature without any change in anodic peak potential. The current observed after passivation also increases. The solubility of $PbCl_2$ is known to increase with rise in temperature [10].

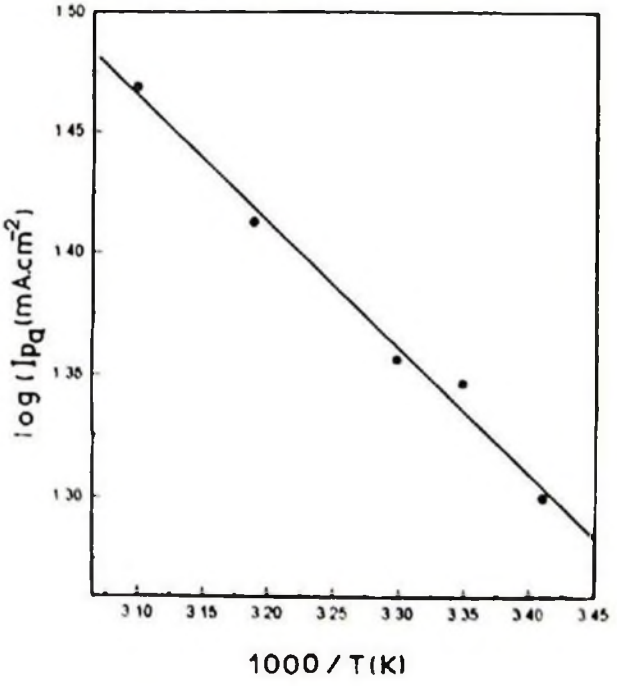


Fig 4 : Arrhenius plots
Variation of the logarithm of the peak current with the reciprocal of temperature.

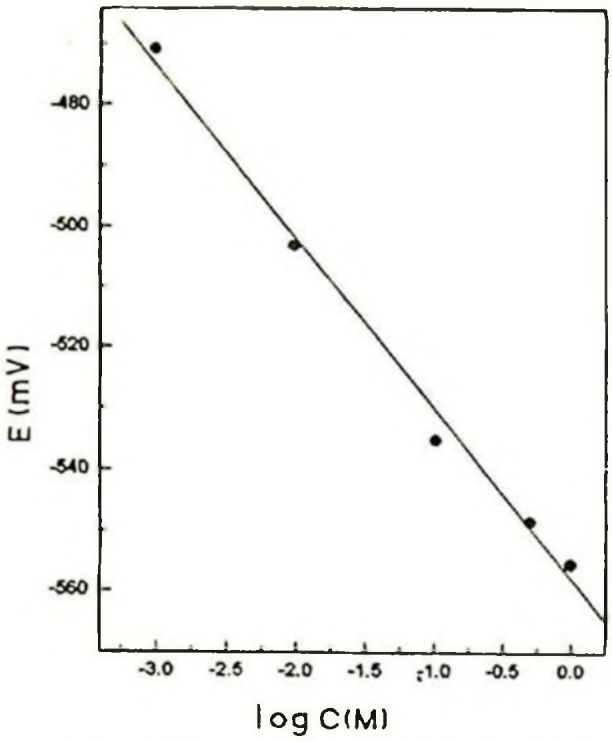


Fig. 5 : Variation of the equilibrium potential of the lead with the logarithm of Cl^-.

Fig. 4 shows Arrhenius plot for the anodic process. The following equation permits the calculation of the apparent activation energy E_a :

$$\log I_p = C^{te} - E_a / 2.3\ RT \qquad (1)$$

E_a has been found to be 9.8 kJ mol^{-1}. This value is different from that obtained by Badaway *et. al.* (E_a = 5.53 kJ mol^{-1}) [5]. The equilibrium potentials at various concentrations of HCl (0.002-1M) (Fig. 5) and the mathematical study of the plot E - log i in the anodic range (500 to 470 mV) both showing a linear variation with a constant slope of 32 mV/decade, suggest the anodic reaction to be :

$$Pb + 2Cl^- \longrightarrow PbCl_2 + 2e^- \qquad (2)$$

REFERENCES

1. S. Sankarapapavinasam, F. Pushpanaden, M.F. Ahmed, *Bull. Electrochem.*, **5** (1989) 319; *J. Electrochem. Soc. India* **41** (1992) 43; *Br. Corros. J.* **24** (1989) 39.
2. H. Mansour, N. Gaber and M.J. Mahmoud, *J. Electrochem. Soc. India* **38** (1989) 73.
3. M.Y. Mourad, A.S. El Gaber, *India J. Techno.*, **127** (1989) 439.
4. S.M. Abd El-Wahaab, S.A. Hassan, M. Murad, *Process Eng. (Coburg. Red. Repub. Ger)* **(1-2)** (1981) 16.
5. W.A. Badawy, N.M. Hefny and S.S. El Egamy, *Corrosion Science*, **36** (1990) 978.
6. A. Aouniti, B. Hammouti, M. Brighli, S. Kertit, F. Berhili, S. Elkadiri and A. Ramdani, *J. Chim. Phys.*, **93** (1996) 1262.
7. G. Tarrago, G.S. ElKadiri, C. Marzin and C. Coquelet, *New J. Chem.* **15** (1991) 677.
8. R.G. Barradas, K. Belinko and J. Ambrose, *Can. J. Chem.*, **53** (1975) 389.
9. R.J. Meakins, *J. Appl. Chem.*, **13** (1963) 339.
10. R.C. West, *Handbook of Chemistry and Physics*, 62nd Ed., **CRC Press, Inc., USA** (1982) B111.