

hetero atoms in the hetero-aromatic ring, the conjugation of each of these compounds is expected to follow the order VI > V > II. This behaviour results in reducing the stability of the compounds in the same direction and therefore the reducibility of these compounds and hence the II > V > VI. Furthermore, compound VIII is characterized by high reducibility relative to VII. This can be ascribed to the role of intramolecular hydrogen bonding established in VIII between OH group and the central nitrogen azomethine atom. This leads to the distinctly more stabilized polarizability of N=CH in case of the VIII relative to VII. Thus, the absorbability and reducibility of VIII is expected to be higher than those of VII.

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#### Inhibition by Halide Ions of Lead Dissolution in Chloroacetic Acids

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The inhibiting effect of Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> on the dissolution of lead by mono-, di-, and tri-chloroacetic acids has been investigated by measuring potentials of lead electrodes (versus SCE) at different time intervals. The addition of Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> brings about considerable shift of potential. The mass-loss technique and galvanostatic anodic polarization measurements show that the corrosion rate of lead in chloroacetic acid solutions decreases by the addition of halide ions in the order I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>. The magnitude of inhibitive effect increases by increasing the halide ion concentration.

BRASHER<sup>1</sup> has shown that the oxide films on Pb and Cd formed in aerated neutral solutions of corrosive salts are unstable, hence, true passivation is not possible. The present work deals with the study of the effect of Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> ions on the corrosion of lead in mono-, di-, and tri-chloroacetic acid solutions. The mass-loss and galvanostatic techniques have been employed to throw light on the corrosion behaviour of lead.

Solutions of mono-, di-, and tri-chloro acetic acids

(0.1M) containing different concentrations of the potassium salts of Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> (AR quality) were prepared in doubly distilled water. The concentration range selected for the halide anions for this investigation was 10<sup>-3</sup>-10<sup>-1</sup>M. Solutions were always prepared fresh.

Lead electrodes (1 cm length and 1 cm diam.) were always machined afresh for each experiment from BDH granulated lead and were welded to a hard copper wire fixed in a glass tube by means of neutral wax. The immersed area of electrode was effectively outside the tube. Before being used, the electrodes were abraded successively with 1 and 00 grade emery papers and then degreased with acetone. The pyrex glass electrode vessel, without rubber connections, could accommodate 50 ml of the test solution.

The potential-time measurements and mass-loss techniques employed were the same as described before<sup>2</sup>.

The study of critical current density of passivation ( $I_{crit}$ ) and its dependence on salt solution concentration was carried out using Uhlig and Woodside<sup>3</sup> galvanostatic anodic polarization procedure.

Experiments were carried out at 27°±1°C and potential of lead electrode was measured relative to saturated calomel electrode.

Potential-time studies of lead electrode in 0.1M solutions of mono-, di-, and tri-chloroacetic acids containing Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> ions in the concentration range 10<sup>-3</sup> to 10<sup>-1</sup>M were carried out by studying the variation of electrode potential under open circuit conditions (curves are not shown). The potential of lead electrode in these solutions fluctuates till the steady state is attained. It is observed that the potential decreases linearly with increase in halide ion concentration and the data fit the linear equation (1),

$$E = a - b \log C \quad \dots (1)$$

where  $a$  and  $b$  are constants depending on the nature of electrolyte and surface preparation<sup>1,4</sup>. The slopes obtained from the linear plots ( $b$  values) are collected in Table 1. Similar relationship has been found for steel<sup>5,6</sup>, zinc<sup>7,8</sup> in neutral salt solutions and for cadmium<sup>9</sup> in acid solutions. The decrease in  $b$ -values was explained as due to the decrease in aggressiveness of the anion (i.e. an increase in its inhibitive function).

The results of weight-loss technique show that the weight-loss increases linearly with time during a period of 40 hr (the duration of experiment). The corrosion rates computed from the linear plots, given in Table 2, show that the rate decreases with increase in halide ion concentration and reaches a minimum in 10<sup>-1</sup> M KX (X=Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>). The data fit in the equation of the type (2).

$$W = a C^{-b} \quad \dots (2)$$

where  $W$  is the corrosion rate in mg/day/dm<sup>2</sup>,  $C$  is the molar concentration and  $a$  and  $b$  are constants which depend on the type of anion. Constant  $b$  has

TABLE 1 — VALUES OF  $b$  OBTAINED FOR  $\text{Cl}^-$ ,  $\text{Br}^-$  AND  $\text{I}^-$  IONS IN 0.1M MONO-, DI- AND TRI-CHLOROACETIC ACIDS

0.1M Chloroacetic acid	$b$ Values in presence of		
	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$
Mono-,	-6	-18	-27
Di-,	-14	-24	-34
Tri-,	-16	-30	-31

TABLE 2 — CORROSION RATE OF LEAD IN CHLOROACETIC ACID SOLUTIONS WITH AND WITHOUT HALIDE ANIONS AS INHIBITIVE IONS

[Anion] M	Corrosion rate (mg/day/dm <sup>2</sup> × 10 <sup>-2</sup> ) in 0.1M		
	$\text{ClCH}_2\text{COOH}$	$\text{Cl}_2\text{CHCOOH}$	$\text{Cl}_3\text{CCOOH}$
Nil	3.36	45.60	81.60
IN PRESENCE OF $\text{Cl}^-$			
$1 \times 10^{-3}$	3.39	10.47	23.44
$5 \times 10^{-3}$	2.19	5.37	9.12
$1 \times 10^{-2}$	1.70	4.47	7.08
$5 \times 10^{-2}$	—	2.51	2.69
$1 \times 10^{-1}$	0.96	1.70	2.00
IN PRESENCE OF $\text{Br}^-$			
$1 \times 10^{-3}$	1.78	5.01	11.22
$5 \times 10^{-3}$	1.51	3.16	5.37
$1 \times 10^{-2}$	1.29	2.88	4.68
$5 \times 10^{-2}$	1.12	—	2.34
$1 \times 10^{-1}$	1.11	1.55	1.70
IN PRESENCE OF $\text{I}^-$			
$1 \times 10^{-3}$	0.76	1.12	1.95
$5 \times 10^{-3}$	0.60	0.98	1.70
$1 \times 10^{-2}$	0.48	0.83	1.32
$5 \times 10^{-2}$	—	0.72	1.26
$1 \times 10^{-1}$	0.37	0.69	1.12

values of (0.275, 0.400, 0.550) for  $\text{Cl}^-$ , (0.250, 0.280, 0.380) for  $\text{Br}^-$  and (0.125, 0.155, and 0.115) for  $\text{I}^-$  in 0.1M mono-, di-, and tri-chloroacetic acid solutions respectively.

The decrease in the corrosion rate with increase in anion concentration suggests that the halide ions act as inhibitors. The inhibitive function of these ions may be associated with their ability to become adsorbed on the metal surface thereby retarding the entry of  $\text{Pb}^{2+}$  ions into the solution at the anodes. It is observed that the double logarithm relation between corrosion rate and salt concentration covers 3-4 decades. This may suggest that the corrosion of Pb in halide solutions is controlled by adsorption of anion on active sites<sup>10</sup>. The current density  $I_{\text{crit}}$  decreases linearly with increase in chloride ion concentration contained in 0.1M tri-chloroacetic acid solution. The value of  $I_{\text{crit}}$  has been taken as inhibitor<sup>11</sup>. It may be suggested that  $\text{PbCl}_2$  initially formed does not afford sufficient protection since  $\text{PbO}$  which will be subsequently formed on the bare metallic parts is unstable. Direct oxidation of the still uncovered areas to higher lead oxides takes place at the respective equilibrium potential values. In less concentrated  $\text{Cl}^-$  ions,  $\text{PbCl}_2$  is formed to a lesser

extent and the electrode continues to dissolve freely. The linear decrease of  $I_{\text{crit}}$  with decrease in concentration shows that the rate of entry of  $\text{Pb}^{2+}$  in solution becomes little affected by anion concentration<sup>10</sup>.

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### Electro-chemical Studies on the Electron-transfer Reactions of Uranyl Octacyanotungstate(IV)-(V) System

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Oxidation of  $\text{K}_2\text{UO}_2\text{W}(\text{CN})_8$  and  $(\text{UO}_2)_2\text{W}(\text{CN})_8$  has been carried out using Ce(IV), Cr(VI) and Mn(VII) as the oxidants. The standard potentials ( $E^\circ$ ) for the redox systems,  $\text{UO}_2\text{W}(\text{CN})_8^{2-} \rightarrow \text{UO}_2\text{W}(\text{CN})_8^- + e$  and  $(\text{UO}_2)_2\text{W}(\text{CN})_8 \rightarrow (\text{UO}_2)_2\text{W}(\text{CN})_8^+ + e$ , have been determined by the potential mediator method. Log  $K$  values have been calculated. The influence of  $\text{H}^+$  ions on the  $E^\circ$ , and log  $K$  values of the systems involving Mn(VII) and Ce(IV) have been investigated. The relationships  $E = E^\circ - 2.303.RT/nF \log \frac{[\text{UO}_2\text{W}(\text{CN})_8^-]}{[\text{UO}_2\text{W}(\text{CN})_8^{2-}] [\text{H}^+]^x}$  and  $E = E^\circ - 2.303.RT/nF \log \frac{[(\text{UO}_2)_2\text{W}(\text{CN})_8^+]}{[(\text{UO}_2)_2\text{W}(\text{CN})_8] [\text{H}^+]^x}$  have been found to hold good for these redox couples respectively.

THE composition and stability of uranyl octacyanomolybdate(IV) have been studied by spectrophotometric and conductometric methods<sup>1,2</sup> and the values of the dissociation constant and free energy of formation evaluated by different methods. Its properties in solution and structure in the solid state have also been determined<sup>3</sup>. We have taken up the study of  $\text{UO}_2^{2+}-\text{W}(\text{CN})_8^{4-}$  system, in order to investigate whether the central atom in uranyl octacyanotungstate exists in two oxidation states. The study involves oxidation of uranyl octacyano-