CORROSION BEHAVIOUR OF ZINC IN SOLUTIONS OF POLYELECTROLYTES

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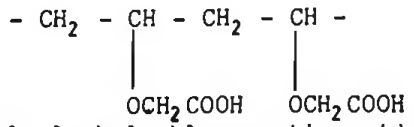
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The electrochemical corrosion behaviour of zinc in solutions of mono-, di-, Tri-, chloroacetic acids and their polyvinyl ether as aggressive media was studied. Weight loss measurements showed that, the polymerization of different chloroacetic acids with the polyvinyl alcohol reduced the aggressiveness of media to a larger extent. This behaviour was supported by measuring the open-circuit potential variation of zinc electrode with time and the values of cathodic protective currents. A suitable interpretation of the data obatained was suggested.

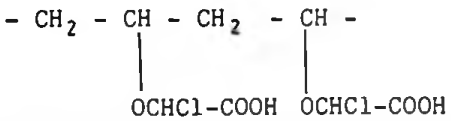
Corrosion inhibition of metals by polymeric materials was the subject of investigation carried out by many authors [1,4]. Hartman [5], has reported that the corrosion of Fe in HCl solution can be inhibited to a great extent by addition of partially polymerised diethyl amine, ethyl methacrylate and tetrabutyl amino ethyl methacrylate. A copolymer of acrilonitrile-vinyl pyridine provides corrosion protection in aerated artifical salt water. No blistering occured and most of the metal surface under these coatings remained perfectly shining after almost 1500 hr.

The study of the effect of free chloroacetic acids and their polyvinyl ether (poly-electrolyte) on the corrosion of zinc metal is reported here.

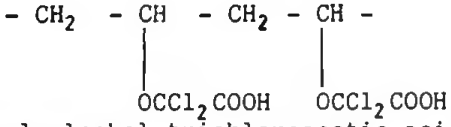
The three polymers are represented as :



Polyvinyl alcohol chloroacetic acid ether



Polyvinyl alcohol dichloroacetic acid ether



Polyvinyl alcohol trichloroacetic acid ether

EXPERIMENTAL

Preparation of polyelectrolyte

Polyvinyl alcohol (33g) was dissolved in aqueous NaOH solution (10%), and heated at 50-55°C for 3 hrs on a water bath. Mono-, di-, or trichloroacetic acid (0.635 mole) was then added and the reaction mixture was stirred at about 60°C for two hours then acidified with dilute HCl and filtered. The solid was dissolved in ethyl alcohol deionized by passing through a strong cation exchange resin, crystalized, filtered and dried on a sintered grass funnel.

The effect of free chloroacetic acids and the corresponding polyvinyl ether as aggressive media on the corrosion process of zinc metal was carried out using the weight loss technique [6]. Each experiment was carried out with 50 ml of unstirred, aerated corroding solution at 30 ± 0.1°C. All corrosion tests were made in duplicate.

Potential-time measurements were carried out under open-circuit conditions to obtain the steady state potential in different media.

RESULTS AND DISCUSSION

Weight loss measurements

The influence of time on the weight loss of zinc in 0.1 M and 0.2 M solutions of different chloroacetic acids is recorded in Table 1. It indicates that corrosion is sufficiently high and zinc is not passivated in these acids.

The results in Table 1 further show that the weight loss at corresponding time intervals decreased according to the order; trichoro. > dichloro. > monochloro acids.

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TABLE 1

EFFECT OF TIME ON WEIGHT LOSS OF ZINC IN CHLOROACTIC ACID SOLUTIONS AT 30 ± 0.1 °C.

Aggressive Media		Wt. loss (mg/cm^2) after				
		2hr.	4hr.	6hr.	8hr.	10hr.
Monochloroacetic acid	(0.1M)	3.2	6.4	11.3	16.2	20.5
	(0.2M)	7.6	14.3	24.1	30.5	35.8
Dichloroacetic acid	(0.1M)	9.2	13.5	17.0	21.0	26.3
	(0.2M)	21.2	29.5	36.5	39.5	46.9
Trichloroacetic acid	(0.1M)	36.0	55.0	70.0	87.0	102.0
	(0.2M)	80.5	130.5	152.5	178.5	189.0

The pK_a value of trichloroacetic acid (0.89) is lower than that of dichloroacetic (1.3) which is lower than that of monochloracetic acid (2.86). It is worth mentioning that the hydrogen produced during corrosion process at the cathodic areas may partially bring about dehalogenation of acid molecule and the HCl formed then increases the aggressiveness of the investigated haloacids [7]. Dehalogenation may take place as a result of hydrolysis in the aqueous medium.

The effect of polyvinylmonochloro-, dichloro- and trichloro-acetate as aggressive media, on the weight loss of zinc metal is tabulated in Table 2. It is to be noted that weight loss in the presence of the ethers of polyvinyl acetic acid is much less than that in presence of the corresponding free acids. This behaviour may be explained by two ways; (1) The higher adsorption of the long chain polymeric molecules at metal surface retards the corrosion reaction [8,13]; (2) The formation of intramolecular H-bonding in the polymeric ether decreases the acidity of the medium.

Open Circuit Potential Measurement

Results obtained from weight loss measurements were supported by the open circuit potential data of zinc electrode in polyvinyl ether and the free acid media.

Fig. 1 show the potential time curves of zinc electrode in 0.1 M and 0.2 M solutions of mono-, di-, and tri- chloroacetic acids. In monochloroacetic acid solutions, the potnetial shifts first towards less negative value until it reaches a maximum value and then shifts in opposite direction to reach a steady state potential finally. This behaviour can be ascribed to the formation of an insoluble layer of zinc oxide at the electrode surface, which increases the resistance of anodic areas, and therefore the potential values become more positive. These results are confirmed by the effect of time on the weight loss (Table 1). Here the corrosion rate is unchanged in the first period of imersion. The maximum of potential noticed in potential-time curves decreases as the concentration of monochloroacetic acid is lowered.

TABLE 2

EFFECT OF TIME ON WEIGHT LOSS OF ZINC IN POLYVINYL ETHER OF CHLOROACETIC ACID SOLUTIONS AT 30 ± 0.1°C
(values in the brackets show the percentage decrease of weight loss)

Aggressive Media		Wt. loss (mg/cm^2) after				
		2 hr	4 hr	6 hr	8 hr	10 hr
Polyvinyl mono-chloro-derivative	1%	1.0 (68.8	2.8 (56.3)	4.7 (58.4)	5.3 (67.3)	5.8 (71.7)
	2%	0.5 (93.4)	2.2 (84.6)	4.3 (82.2)	5.6 (81.6)	5.8 (83.8)
Polyvinyl di-chloro-derivative	1%	0.3 (96.0)	0.4 (97.0)	0.5 (97.0)	0.7 (96.7)	0.9 (96.6)
	2%	0.4 (98.0)	0.7 (97.6)	1.2 (96.7)	1.5 (96.2)	2.3 (95.0)
Polyvinyl tri-chloro-derivative	1%	7.0 (80.5)	8.7 (84.2)	12.3 (82.4)	15.3 (82.4)	17.7 (82.6)
	2%	10.5 (86.9)	15.6 (88.0)	19.2 (87.4)	23.5 (86.6)	27.0 (85.7)

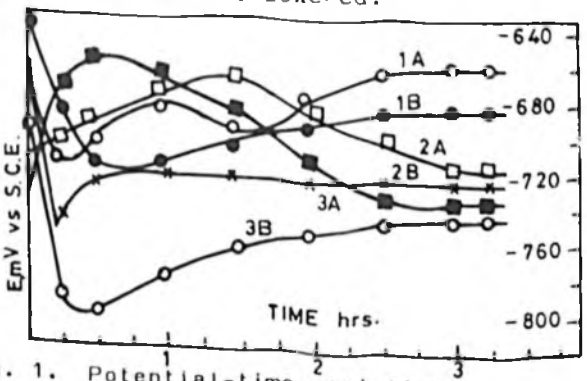


Fig. 1. Potential-time relations of zinc electrode in chloro acetic acids

Preliminary work showed that reaction of zinc metal with di- and tri- chloro- acetic acid was vigorous. This is because these acids are strong.

The steady state potential in di- and trichloroacetic acids is shifted towards positive direction by decreasing their concentration. This is understandable because of the strength of the acids.

Potentials of the zinc electrode in solutions of the corresponding polyvinyl ethers of chloroacids are shown in Fig. 2. The order of these potentials indicate that corrosion rate in different media or in the order polyvinyl trichloroacetic < polyvinyl dichloroacetic < polyvinyl monochloroacetic ethers. This may be attributed to higher specific viscosity (Table 3). Similarly corrosion is lower in higher concentration of the polymer. This result is supported by weight loss experiment (Table 2).

Cathodic Protection

Investigations were carried out on the effect of impressed cathodic current on the performance of the free chloroacetic acids and their polyvinyl ether as aggressive media. The results are given in Table 4.

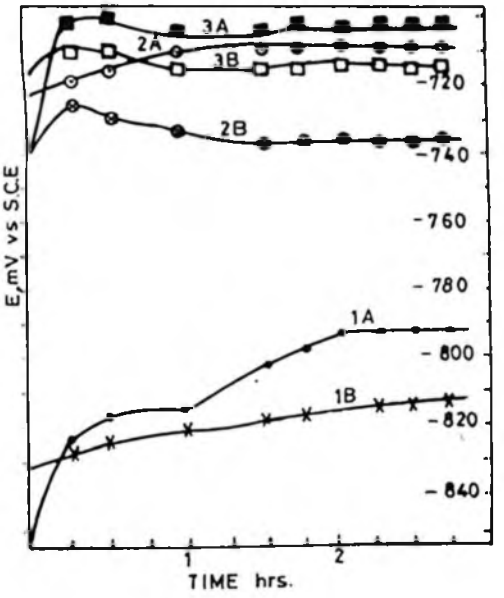


Fig. 2 Potential-time relations of zin electrode in poly-electrolytes.

TABLE 3

PROPERTIES OF POLYVINYL ETHER OF ACETIC ACID DERIVATIVES

Polyvinyl ether of	Acid No mg - KOH	Specific viscosity 0.05 g/10 m/H_2O at 25	Capacity in eguiv/g resin
Monochloroacetic acid	143	0.3010	2.416
Dichloroacetic acid	150	0.3040	2.602
Trichloroacetic acid	167	0.3092	2.655

TABLE 4

PROTECTIVE CURRENT AND POTENTIAL VALUES IN PRESENCE OF STUDIED AGGRESSIVED MEDIA

	Aggressive media		Protective current A/cm^2	Protective potential V vs. S.C.E
1	Monochloroacetic	(0.1M)	0.166	- 1.877
2	Dichloroacetic	(0.1M)	0.232	- 1.543
3	Trichloroacetic	(0.1M)	0.310	- 1.456
4	Polyvinylmonochloroacetic	(1%)	0.073	- 0.564
5	Polyvinyldichloroacetic	(1%)	0.061	- 0.611
6	Polyvinyltrichloroacetic	(1%)	0.048	- 0.632

In presence of polyelectrolytes (ether of polyvinyl alchol with different chloroacetic acids), as aggressive media, a very low values of protective currents were needed for complete protection of zinc metal, with respect to the values obtained in free chloroacetic acid solutions. The lower values support the aggressiveness of studied polyelectrolytes.

The order of protective current requirement follows the same pattern as indicated from the weight loss data. These values reveal that the aggressiveness of investigated media does not change under the effect of cathodic current. The cathodic protection of zinc metal in the studied polyelectrolytes can be considered as a practical suggestion due to the lower value of protective currents.

Full studies on the use of polyvinylchloroacetic acid as corrosion inhibitors are currently carried out in laboratory and will be published in future.

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