ANODIC DISSOLUTION OF ZINC IN AQUEOUS-METHANOLIC TRICHLOROACETIC ACID SOLUTIONS

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

Steady state current–potential curves for the anodic dissolution of zinc in aqueous-methanolic 0·25M trichloroacetic acid solutions were constructed for wide ranges of the solution composition and temperature. Analysis of the results reveal that the increase of the water content and rise of temperature of the solution increases the corrosion rate. The most plausible role of the solvent lies within the stabilization of the anodic dissolution reaction products by water molecules. The changes in the properties of the solution due to the presence of methanol which give rise to hindrance of the anodic dissolution reaction are adsorption of methanol, change of viscosity and pH of the solution. These factors seem to be of secondary importance.

Zinc is one of the active metals which is widely used in many applications. There is an extensive work on its electrochemical behaviour in aqueous solutions[1−3], but in methanolic-aqueous solutions it has scarcely been treated in literature. The corrosion rates of some metals similar to zinc decrease with the increase of the organic content of the solvent yet a mechanistic understanding of the partial roles of each of water and the organic solvent in the electrochemical behaviour needs further elucidation. It was suggested that the organic solvents inhibit the corrosion rate of aluminium in NaOH by increasing the viscosity and by decreasing the dielectric constant of the medium[4]. On the other hand, the decrease of the corrosion rate of aluminium in HCl with the increase of the alcohol content of the solution was interpreted in terms of the structural properties of the water–alcohol mixtures[5]. Also the organic solvent can decrease the conductivity of the corrosion medium which in turn decrease the corrosion rate[6].

Acetonitrile was shown to behave as an interface inhibitor in the anodic dissolution of iron in acidic solutions[7]. The dissolution reaction at high overvoltages was

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largely uninfluenced while the cathodic hydrogen evolution was inhibited by the presence of acetonitrile.

The influence of water on the corrosion behaviour of materials that can be passivated is significant. The anodic dissolution of beryllium in nonaqueous solutions was studied[8]. The effect of the low water content is to hinder the reforming of an oxide or a hydroxide film that protects beryllium from chemical attack. Under some conditions zinc behaves in a similar manner to either beryllium or iron. In water-free alcohols containing HCl, stainless steels 304 and 316 corrode actively[9]. With increasing the water content above a critical value, a transition to passivation is observed, the critical current density decreases and the passivation potential shifts to more active values.

EXPERIMENTAL

The experimental conditions and the arrangements are essentially the same as described before[3]. The corrosion media are 0·25M trichloroacetic acid methanolic-aqueous solutions in contact with air thermostated at the specified temperature in an air thermostat. AR grade chemicals and triple distilled water were used for preparation of solutions. The purity of the sample is 99·9% Zn. The working electrode is a stationary disc with an exposed area amounting to 0·2 cm^2. Before each experiment, the electrode was polished with emery paper grade 4/0, rinsed with distilled water, degreased by ethanol and dried in a stream of air. The auxiliary and reference electrodes are platinum wire and saturated calomel, respectively. Electrochemical polarization experiments were conducted potentiostatically using a Wenking potentiostat. The current response for each potential was followed with time till the steady state value was reached (less than five minutes), where it was recoreded.

RESULTS AND DISCUSSION

Beside the electrochemical corrosion test experiments carried out on zinc, chemical analysis experiments were made. A zinc sheet 20 cm^2 area was exposed to 250 ml of the test solution for one hour, thereafter the dissolved zinc was determined complexometrically. The corrosive medium is 0·25M trichloroacetic acid aqueous--methanolic solution. The corrosion rate, r_w decreases with the increase of the concentration of methanol in the solution, as given in Table I.

TABLE I

Decrease of the corrosion rate of zinc, r_w with the molar concentration of CH_3OH, at 25°C. For clarity, the concentration of methanol in mole fraction, x_A, is also given

$c(CH_3OH)$, mol l^{-1}	0	5	10·2	13·8	20·3
x_A	0	0·047	0·10	0·17	0·97
r_w, mg dm^{-2} min^{-1}	82	62	54	43	42

Potential–current $(E-i)$ curves for the anodic dissolution of zinc in the same test solutions at 25°C are shown in Fig. 1. Similar results have been obtained at 30, 40 and 50°C. There is a decrease in the anodic current with increase of c_{CH_3OH} at a given potential. This can be attributed to the decrease of the corrosion rate of zinc with the increase of c_{CH_3OH}. Figure 2 summarizes the dependence of the current i, at -0.85 V vs SCE, on temperature and solution composition. The last figure reveals that the presence of water is crucial for corrosion of zinc, since i approaches zero when the molar concentration of H_2O in the solution, c_{H_2O} approaches zero.

The overvoltage of the anodic dissolution of zinc in these media (0.25M trichloroacetic acid methanolic-aqueous solutions) is high as compared to the previous results[3,8] since $\partial E/\partial \log i \simeq 150$ mV. Since it is improbable that zinc is passivated under these conditions (weak acid solution)[10] thus this high overvoltage can be attributed to hindrance of the dissolution reaction by factors other than passivation such as decrease of the stability (solubility) of the anodic dissolution products[11-13].

The role of water (methanol) in enhancing (retarding) the corrosion rate of zinc may be elucidated from analysis of the foregoing results. One of the techniques that
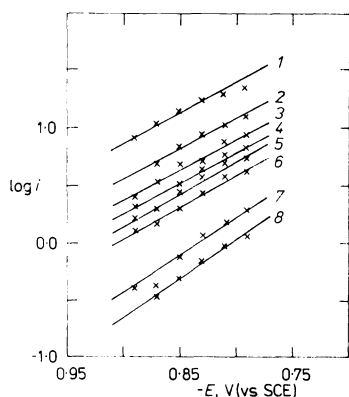

FIG. 1

Anodic polarization curves for dissolution of zinc at 25°C in 0.25M trichloroacetic methanolic-aqueous solutions with different molar concentrations of methanol (mol l^{-1}): 1 0; 2 5.0; 3 10.2; 4 13.8; 5 15.4; 6 17.9; 7 20.3; 8 22.7. i in mA cm^{-2}
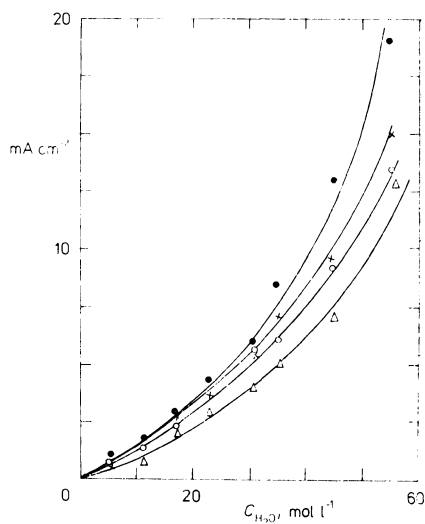
FIG. 2

Corrosion rate of zinc, r as inferred from the anodic dissolution studies, as a function of the solvent composition and temperature (°C): 25 ($\triangle$); 30 ($\bigcirc$); 40 ($\times$) and 50 ($\bullet$) at $E = -0.85$ V vs SCE

may be used to distinguish between alternative mechanisms is the value of the activation energy, E_a of the process under different experimental conditions[14]. The latter can be estimated by the aid of Arrhenius equation, $i = A \exp\left(-E_a/RT\right)$, where i is the current density at the absolute temperature T. The other symbols have their usual significance. E and A can be evaluated from plots of log i vs T^{-1}. The results indicate that in presence of methanol E_a amounts to 23 kJ and in its absence to 11 kJ, i.e., it increases by about 100% whereas A decreases by about 4%. Therefore one may conclude that the role of methanol in inhibiting the anodic dissolution of zinc is not a simple adsorption process. The latter mechanism for inhibition (adsorption) involves merely the profound decrease of the reactive surface area without a significant change in the activation energy of the process. The latter mechanism is common for inhibiting the hydrogen evolution reaction as a cathodic process by strongly adsorbed organic molecules[15]. The limited tendency for adsorption of methanol on the anodic sites of the zinc surface may be deduced from the small decrease of the parameter A in Arrhenius equation[16]. This may be confirmed from analysis of the dependence of the degree of surface coverage Θ on methanol concentration, c_{CH_3OH}. Θ was calculated using the familiar equation[3], $\Theta = 1 - i_2/i_1$, where i_1 and i_2 are the current densities in absence and presence of methanol, respectively.

It is well established that the adsorption of organic molecules on metallic surfaces leads to the replacement of the adsorbed water molecules. Adsorption of good inhibitors is characterized by the replacement of several water molecules from the surface by a single inhibitor molecule and/or a large decrease in the free energy of adsorption. The number of water molecules, n to be replaced by a single methanol molecule is related to c_{CH_3OH} and Θ by the Bockris and Swinkels equation[16]:

$$\frac{\left[\dfrac{\Theta}{(1-\Theta)^n}\right]\left[\Theta + n(1-\Theta)\right]^{n-1}}{n^n} = \frac{c_{CH_3OH}}{55\cdot5}\, e^{-\Delta G^0_{ads}/RT} .$$

n has been estimated by plotting $\log\left[\Theta/(1-\Theta)^n\right]\left[\Theta + n(1-\Theta)\right]^{n-1}/n^n$ vs log . . c_{CH_3OH} at 30°C for several values of n; viz. $\frac{1}{2}$, 1, 2, ,3 4 and 5. The slope of the last plot amounts to the theoretical one, viz. unity. For higher values of n the slope deviates positively; it increases. The weak adsorption of methanol on zinc was further confirmed from the small decrease in the standard free energy change of adsorption, ΔG^0_{ads}. The latter was calculated at $E = -0\cdot85$ V vs SCE, $c = 17\cdot9$ mol . . l^{-1} by plotting $\ln\left(79\cdot1\Theta\right)/\left[(1-\Theta)(1+\Theta)\right]^{1/2} c$ vs $1/T$. The value of ΔG^0_{ads} was found to be $-8\cdot4$ kJ. It is apparent that there is a small tendency for adsorption of methanol on the anodic sites of the zinc surface, since each of n and $-\Delta G^0_{ads}$ are relatively low. However the efficiency for inhibition is relatively high $\simeq 52\%$ and

69% as inferred from weight loss and anodic polarization experiments, respectively. Thus one may conclude that adsorption is not the fundamental mechanism giving rise to inhition.

The other mechanisms by which methanol can decrease the corrosion rate of zinc are decrease of the fluidity (inverse of viscosity) and/or acidity of the solution. Regarding the fluidity of the different solutions it had been found that the trend for the variation of the fluidity of the solution with composition is not monotonous, i.e., there is a minimum[4] at $c_{CH_3OH} \simeq 12$. There is no minimum in corrosion rate around this concentration (Table I, Fig. 2). Therefore the change in the fluidity of the solution alone cannot account for the decrease of corrosion rate with the increase of c_{CH_3OH}. On the other hand, the decrease of corrosion rate cannot be attributed totally to the slight increase of pH of the solution, because each of methanol and water are protic solvents and methanol is less basic than water but methanol has a lower dielectric constant[17].

In conclusion, the principal role of methanol in decreasing the anodic dissolution of zinc is the diminution of water in the solution. The reason for the slower kinetics of the anodic process can be a change in the mechanism of this process especially the steps involving H_2O reaction. Also water can increase the stability and/or solubility of each of the anodic reaction products. This conclusion accords with the fact that in the weakly acid solution the corrosion reaction of zinc occurs with the chemical control regime.

REFERENCES

1. Deslouis C., Duprat M., Tournillon Chr.: Corros. Sci. *29*, 13 (1989).
2. Walter G. W.: Corros. Sci. *16*, 573 (1976).
3. Gad Allah A. G., Hefny M. M., Salih S. A., El-Basiouny M. S.: Corrosion *45*, 574 (1989).
4. Abd El Naby B. A., Khalil N., Khamis E.: Surf. Technol. *22*, 367 (1984).
5. Abd El Naby B. A., Khalil N., Khamis E.: Corros. Sci. *25*, 225 (1985).
6. Duprat M., Lafont M., Dabois F., Moran F.: Electrochim. Acta *30*, 353 (1985).
7. Ahlberg E., Friel M.: Electrochim. Acta *34*, 187 (1989).
8. Johnson J. W., Chen S. C., Chang J. S., James W. J.: Corros. Sci. *17*, 813 (1977).
9. Hronsky P.: Werkst. Korros. *31*, 619 (1980).
10. Evans U. R.: *The Corrosion and Oxidation of Metals*. Arnold, London 1960.
11. Hurlen T.: Acta Chem. Scand. *16*, 1346 (1962).
12. Constantinescu E., Heitz E.: Corros. Sci. *16*, 857 (1976).
13. Lorenz W. J.: Corros. Sci. *5*, 121 (1965).
14. Antropov I.: *Theoretical Electrochemistry*, p. 394. Mir Publishers, Moscow 1972.
15. Al Shkel A. G., Hefny M. M., Ismail A. R., El-Basiouny M. S.: Corros. Prevent. Control *1987*, 155.
16. Bockris J. O' M., Swinkels D. A. J.: J. Electrochem. Soc. *111*, 736 (1964).
17. Sawyer D. T., Roberts J. L.: *Experimental Electrochemistry for Chemists*, p. 204. Wiley, New York 1974.