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Effect of dodecylamine on the corrosion behaviour of zinc in ammonium chloride solution

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Corrosion studies showed normal dodecylamine (NDDA) to be effective as an anodic inhibitor for zinc corrosion in ammonium chloride media. Its inhibiting effect was found to be associated with adsorption on active centres of the zinc surface. The adsorption is potential dependent and the inhibiting effect diminishes with positive shift of the zinc electrode during discharge. This feature makes it possible for NDDA to be used in zinc–manganese dry batteries as a substitute for the environmentally harmful mercury (salt) inhibitor.

1. Introduction

In the fairly long history of zinc–manganese battery production, soluble mercury salt is almost exclusively used as zinc corrosion inhibitor because the amalgamation of zinc surface through chemical displacement is effective in suppressing zinc corrosion during cell storage while not hindering zinc dissolution during cell discharge. However, mercury and its soluble salts are harmful pollutants, being highly toxic. With increasing awareness of the importance of environmental protection, it is imperative to avoid use of mercury in the zinc–manganese battery industry. This calls for alternative inhibitors for zinc corrosion.

It is known that in acidic or nearly neutral solutions, certain nitrogen or sulfur-containing organic compounds exhibit good inhibition of zinc corrosion [1–4]. This is attributed to the presence of electron donor groups in these compounds, which, by raising the overpotential of hydrogen evolution on zinc, decrease the rate of zinc corrosion, as does the amalgamation of zinc by mercury. Gad Allah *et al.* [5] studied the effects of several pyrazole derivatives on the corrosion rate of zinc in HCl solutions. All the substances studied show some inhibiting effect. The differences between the inhibiting effects of these pyrazoles were discussed from the view point of the electronic properties of their substituent groups.

Maja *et al.* [6] studied the inhibiting effects of various types of organic compound including aliphatic amines on zinc corrosion in NH_4Cl solutions with emphasis laid on observing the influence of these compounds on cathodic and anodic polarization behaviour of zinc. Positive shifts of zinc corrosion potential were observed with all substances that exhibited an inhibiting effect on zinc corrosion. Thus these substances are, in reality, anodic type inhibitors. But the authors did not discuss further whether they hinder zinc dissolution during cell discharge.

In searching mercury-substitute inhibitors for zinc–manganese dry batteries, we carried out extensive studies on the possibility of using organic additives. The present paper reports the effect of *n*-dodecylamine (NDDA) on the corrosion behaviour of zinc in NH_4Cl solutions. In conformity with the requirement for battery applications, emphasis is laid on observing the variation of the inhibiting effect of NDDA with the potential.

2. Experimental details

2.1. *Polarization measurement*

The zinc electrode was made of battery grade zinc rod composed of Zn (99.371 wt %), Pb (0.570 wt %), Cd (0.048 wt %) and Fe (0.011 wt %). The zinc rod was embedded in epoxy resin with an exposed cross-sectional area of 1.327 cm^2. Before each measurement it was finely polished and thoroughly cleaned by sonication in an ultrasonic water bath. The cell compartments were separated with a glass frit. The cell electrolyte, principally 26% NH_4Cl solution with or without added inhibitor, was prepared with AR grade reagents and deaerated by Ar purging before measurement. A platinum foil was used as counter electrode and a saturated calomel electrode as reference which is electrolytically connected to the zinc electrode via a Luggin capillary. The measurement of polarization curves was performed with a PAR model 273 potentiostat controlled by a microcomputer. After the potential of the immersed zinc electrode reached its steady value E_{corr} (changing no more than $2\,mV\,min^{-1}$), the measurement was carried out by sweeping the potential within predetermined limits from negative to positive at a rate of $1\,mV\,s^{-1}$.

2.2. *Electrochemical impedance study*

Electrochemical impedance spectra of zinc electrodes were obtained through a Solartron frequency response analyser in cooperation with a Solartron elec-trochemical interface under computer control.

The frequency range was 0.1 Hz to 10 kHz and the a.c. signal amplitude was 10 mV. The circuit elements of the electrode system were computed from the analysis of the impedance spectra with the aid of special EQUIVCRT software.

2.3. *Immersion test*

This provides a direct measure for evaluating the corrosion rate of a metal in liquid medium and hence the effectiveness of a specified substance as corrosion inhibitor. Sample zinc plates size 3 cm × 5 cm were cut out from battery grade zinc sheet. After degreasing, cleaning and weighing, they were immersed separately in NH_4Cl solution containing different addition agents. As a result of zinc corrosion, the hydrogen gas evolved during the immersion period was collected in a graduated glass tube. The immersion period usually lasted several weeks. The temperature was maintained at 45 °C for acceleration of reaction. The corrosion rate of the zinc plate can be evaluated, in principle, from its weight loss or from the volume of hydrogen evolved. Though the latter method has the advantage of being able to give continuous results during the course of the experiment, its accuracy was found to be inferior to that of the former method at very low corrosion rates owing to the effects of gas solubility, temperature fluctuation, etc. hence data of the former method were taken for evaluation.

3. Results and discussion

Figure 1 shows the linear sweep potentiostatic polarization curves of zinc in 26%NH_4Cl solutions containing different concentrations of NDDA. It is seen that, in the presence of NDDA, the corrosion current of zinc, i_{corr}, decreased markedly while the corrosion potential, E_{corr}, shifted positively indicating that NDDA is an anodic type inhibitor. Another feature to be noted from Fig. 1 is that in solutions containing NDDA, the slope of the anodic polarization curve gradually decreases at high anodic potentials, showing that the effect of NDDA is declining.

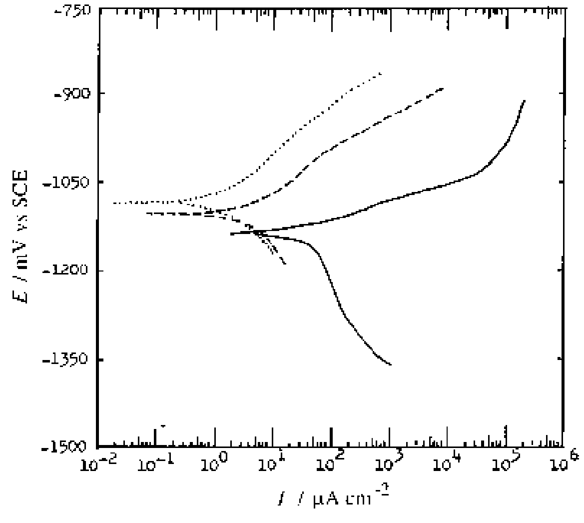

Fig. 1. Polarization curves of Zn electrode in 26% NH_4Cl solutions, (—) without inhibitor; (- - - -) with 0.025 M NDDA ; (.....) with 0.050 M NDDA.

Table 1. Results of immersion test of Zn in 26%NH_4Cl solutions

NDDA added / M	*Immersion period* / day	*Loss of sample weight* / g	*Rate of Zn corrosion* / g cm^{-2} day^{-1}
0	8	0.2182	0.000909
0.025	40	0.1353	0.000113
0.050	40	0.0511	0.000043
0.100	40	0.0427	0.000036

The immersion test also demonstrates that NDDA added to NH_4Cl solution can inhibit the corrosion of zinc, as is evident by comparison of the corrosion rates given in Table 1.

The inhibition of corrosion by organic molecules present may be caused either by a geometrical blocking effect or by chemical adsorption on active centres of the metal surface [7]. In the former case, the slopes of the cathodic and anodic polarization curves remain unchanged and so does the corrosion potential, E_{corr} of the metal. In the latter case, both the slopes and E_{corr} change to some extent. From Fig. 1 it can be seen that NDDA belongs to the latter category.

The adsorption of organic molecules on a metal surface usually changes the value of double layer capacity, *C*, of the interface. For a plain plate capacitor, $C = \varepsilon/4\pi d$ where ε denotes the dielectric constant of the medium and *d* the distance between the plates. Once chemical adsorption takes place, the water molecules within the interface are more or less replaced by larger sized organic molecules whose dielectric constant is much smaller than that of water. As a consequence, the double layer capactity decreases with increase in coverage by organic molecules, that is the extent of adsorption.

The double layer capacity of an electrode interface can be obtained by a.c. impedance measurement. Fig. 2 shows a typical Nyquist impedance spectrum of zinc electrode in 26% NH_4Cl solution. Bordering on a semicircle, the shape of this plot implies the

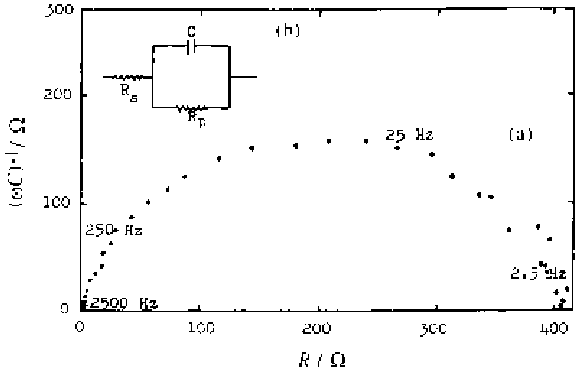

Fig. 2. (a) Typical Nyquist impedance spectrum of Zn electrode in 26% NH_4Cl solution; (b) equivalent circuit.

electrode interface under study can conditionally be expressed by a charge transfer resistance, R_p, in parallel with the double layer capacitor, C, the value of which is readily deduced by computer simulation. In this manner we obtained the double layer capacity C of the zinc electrode at open circuit conditions, that is at $E = E_{corr}$, as a function of concentration of NDDA in the NH_4Cl solution and time. The results are shown in Fig. 3. On introducing a zinc electrode into NH_4Cl solution, the electrode capacity C is seen to initially decrease gradually; after about one hour or more, it approaches a stable value. For pure 26% NH_4Cl solution without NDDA, the stable value of C is about 30 $\mu F\,cm^{-2}$ which is a little lower than the value of 40 $\mu F\,cm^{-2}$ obtained by Baugh *et al.* [8] for zinc in 29.5 wt % NH_4Cl solution, probably because the zinc electrode used by Baugh *et al.* had been etched before measurement, making the true surface area of the electrode somewhat greater. With NDDA added to the solution, C assumes smaller values until the concentration of NDDA reaches 0.1 M, when it reachs a stable value of about 17 $\mu F\,cm^{-2}$.

Thus, NDDA is an anodic type inhibitor capable of inhibiting the anodic reaction of zinc corrosion when adsorbed on active zinc centres. A question now arises: if it is used in a zinc cell , will it hinder the anodic dissolution of zinc during cell discharge? To address this question, we carried out further investigations on the inhibiting effect of NDDA as a function of zinc electrode potential.

Let $f = I'/I$, where I' and I denote the anodic current desities of a zinc electrode at the same anodic shift from rest potential in NH_4Cl solutions with and without NDDA, respectively. The variations of f with anodic potential shift were determined from zinc anodic polarization curves. The results are depicted in Fig. 4. It can be seen that at anodic shifts less than 150 mV from E_{corr}, f is practically zero , with further anodic shift of zinc electrode potential, f appears to rise first slowly then quickly. This indicates that NDDA loses its inhibiting effect by a positive potential shift of 200 mV or more.

The effect of NDDA on the anodic dissolution of zinc at closed circuit was further studied by recording chronopotentiometric curves of the zinc electrode at constant discharge current. Measurements were made with bare zinc, as well as zinc electrodes with preadsorbed NDDA. In the latter case , electrodes were first immersed in solutions containing NDDA for 24 hours to reach adsorption equilibrium before they were transferred into pure 26% NH_4Cl solution for measurement. The results are depicted in Fig 5. It can be seen that for zinc electrodes with preadsorbed NDDA , potential humps appeared at the initial stage of constant discharge. This is attributed to the need for a potential surge to initiate the breakthrough and desorption of the adsorbed NDDA. The more NDDA preadsorbed, the higher is the necessary potential surge. At later stages, the chronopotentiometric curves approach each other, showing a diminishing effect of NDDA after gradual desorption.

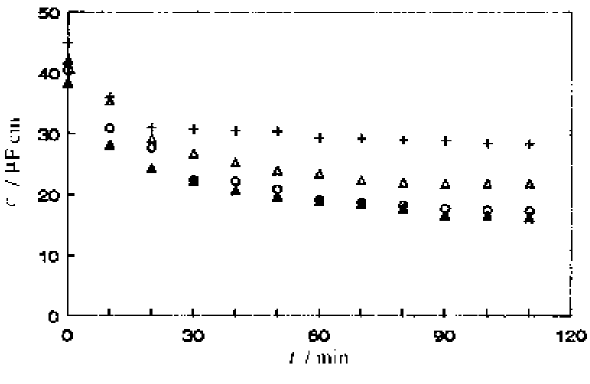

Fig. 3. Variation of Zn electrode capacitance at open circuit potential with immersion time, (+) in 26% NH_4Cl solution; (△) in 26% NH_4Cl + 0.025 M NDDA solution; (o) in 26% NH_4Cl + 0.05 M NDDA solution; (▲) in 26% NH_4Cl + 0.1 M NDDA solution.

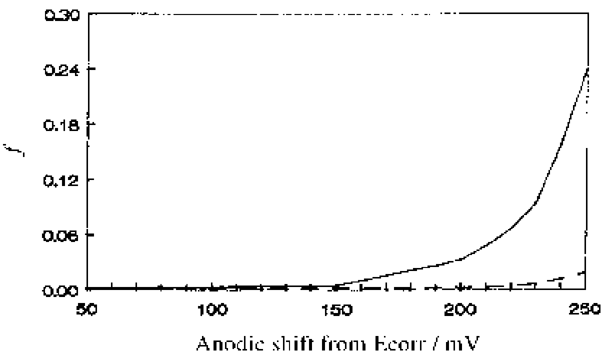

Fig. 4. Plots of f against anodic shift from E_{corr} for Zn in 26% NH_4Cl solutions with, (——) 0.025 M NDDA added; (----) 0.050 M NDDA added.

4. Conclusion

The aliphatic amine NDDA manifests itself as an anodic type inhibitor. The inhibition of zinc corrosion in NH_4Cl solution results from the adsorption of

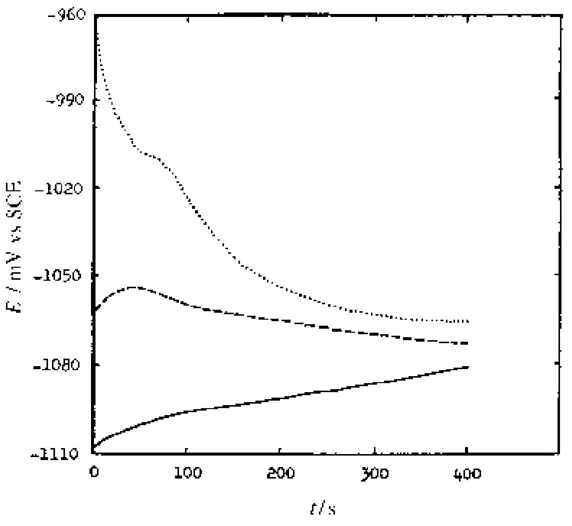

Fig. 5. Anodic chronopotentiometric curves of Zn electrode at i = 100 $\mu A\,cm^{-2}$ in 26% NH_4Cl solution. (——) Bare Zn electrode; (---) Zn electrode having been immersed in 0.025 M NDDA solution for 24 h before measurement; (.....) Zn electrode having been immersed in 0.050 M NDDA solution for 24 h before measurement.

the organic molecule on the active centres of zinc surface. The effect of NDDA on anodic dissolution of zinc diminishes with positive shift of the zinc electrode potential. This feature makes it a possible substitute for mercury salt as the corrosion inhibitor in zinc–manganese dry batteries.

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