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Explanation of Some Electrochemical Phenomena with the Theory of Disproportionation of Atoms—3: Effect of Anions on the Corrosion of Aluminium in Sodium Hydroxide Solution

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In the present work the effect of anions on the corrosion of aluminium in sodium hydroxide solutions has been described.

INTRODUCTION

Studies on the electrodic and corrosion behaviours of aluminium-sodium hydroxide solutions in presence of different anions are being carried out in our laboratory[1-3]. Among the anions investigated, only the chromate ion exhibited strong inhibitive action on the corrosion of the metal. In a recent study on the mechanism of hydrogen evolution at aluminium cathode in NaOH containing sodium nitrite, it was observed that above 10^{-2} M $NaNO_2$, the nitrite ions retarded the cathode reaction[4]. It was, therefore, expected that this ion would be useful in supressing the corrosion of the metal. The present paper describes the corrosion behaviour of aluminium in presence of sodium nitrite.

EXPERIMENTAL

The electrodes used for measuring the corrosion potential were prepared from extra pure aluminimum rods, 3 mm in diameter (Shering-Kahlbaum Company). The potential of the electrode was followed as a function of time over a period of 3 hrs. In all solutions studied the potential became constant within *ca.* 2 hrs. All measurements were carried out at 30°C in an air thermostat controlled to ± 0.5°C. The potentials were corrected to the normal hydrogen scale.

Determination of the corrosion rate was carried out using the weight loss technique. Experiments were performed on pieces of aluminium measuring 5 x 10 cm and 0.8 mm thick, cut from AnalaR aluminium sheet. The test pieces were first degreased with acetone, washed with conductivity water, dried in alcohol and ether and then weighed.

Corrosion tests were carried out in a wide 200 ml jar, in which the specimen was suspended for 2 hrs in the test solution. The specimen was then removed, rinsed with conductivity water and finally dried and weighed. All corrosion tests were carried out in aerated unstirred solutions. Results were duplicated and the mean was computed.

Galvanostatic corrosion currents were measured using a cell constructed of arsenic-free hard borosilicate glass (*Hysil*), and composed of 2 compartments. These were connected by a glass tube in which a tap and sintered glass disc were sealed. The pure NaOH solution was put in one compartment, while the other compartment contained the same NaOH solution together with the sodium nitrite salt. The two electrodes dipped in these solutions were cut from AnalaR aluminium sheet, and had equal areas of 4 cm^2 each. A microammeter was used to measure the current flowing beween these electrodes. The potentials of these electrodes were also measured (during the passage of the galvanostatic current) via built-in lugging capillaries, which led to saturated calomel electrode. Before each experiment, the cell was cleaned with a mixture of nitric and sulphuric acids (A.R.) and thoroughly washed with conductance water. All solutions were prepared from A.R. materials.

RESULTS AND DISCUSSION

Corrosion Potential and Corrosion Rate

The potential of the aluminium electrode was measured in 0.01-0.2 M NaOH

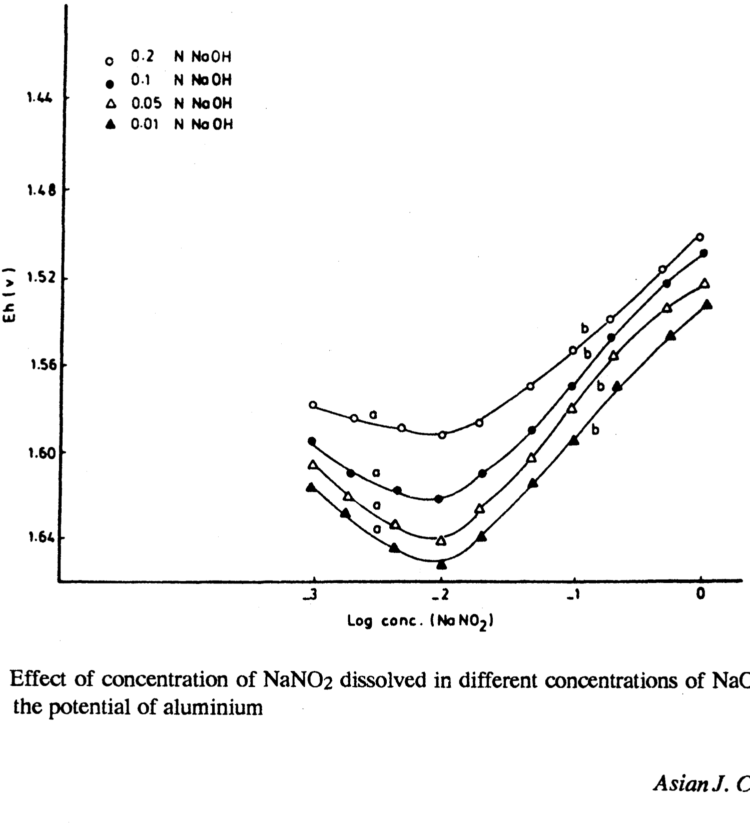

Fig. 1. Effect of concentration of NaNO2 dissolved in different concentrations of NaOH on the potential of aluminium

solutions containing 0.001–1 M $NaNO_2$. The steady state potentials obtained 3 hrs after immersion are plotted against the logarithm of the molar nitrite concentration for the different NaOH solutions. As evident from Fig. 1, the plots are composed of 2 parts:

(i) The first part (a) covers the concentration range 10^{-3}–10^{-2} M NO_2. In this part the potential decreases slightly with increase of nitrite concentration. With increase of NaOH concentration, the potential remains however nearly constant.

(ii) The second part (b) shows a considerable increase of potential with nitrite concentration.

The corrosion rate, V_{corr}, has also been determined in the different solutions and the results are shown in Fig. 2. Here, the corrosion rates in the corresponding pure NaOH solutions are represented by dotted lines; these are taken as reference values to those obtained in presence of the different nitrite concentrations. The plots are divided to two parts (a′ and b′) corresponding to the parts of the pot-log C relationships.

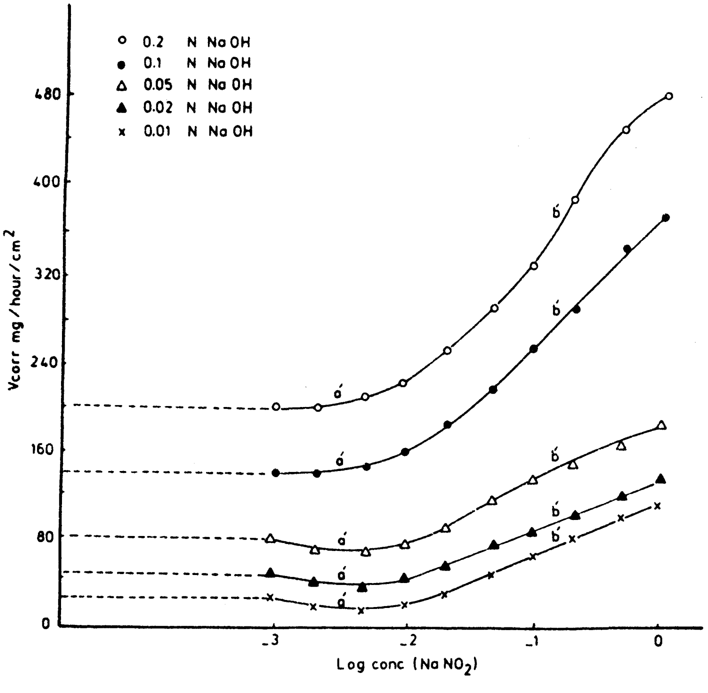

Fig. 2. Effect of nitrite concentraation on the corrosion rate of aluminium in NaOH Solutions.

(i) the first part (a′) covers the concentration range 10^{-3}–10^{-2} M $NaNO_2$. At these concentrations the nitrite ions hardly affect the corrosion rates. However, in very dilute alkali solutions (0.01–0.2 M NaOH) addition of small amounts of nitrite leads to the decrease of the corrosion rate down to a minimum value at 0.005 M $NaNO_2$.

(ii) The second part (b′) covers the concentration range 0.01–1 M nitrite. In this range increase of nitrite concentration brings about marked increase in the corrosion rate in all NaOH solutions studied. The increase is more considerable as the alkali concentration is increased.

It is mention-worthy that in these experiments hydrogen is evolved. However, above 0.2 M $NaNO_2$ we smelled the odour of ammonia. This was taken to indicate that a part of the nitrite ion undegoes reduction to NH_3.

The results of corrosion potentials and rates are interesting as far as Brasher's equation is concerned[5]. This equation requires that, for a corrosion-activating anion the potential of the corroding metal decreases linearly with the logarithm of the anion concentration. In the present investigation, increase of the corrosion rate is accompanied by increase of the corrosion potential, E_{corr}. This points out (according the Evans' diagram[6]) to the acceleration of the cathodic reaction.

Galvanostatic Corrosion Currents

One of the important techniques in corrosion studies is the measurement of the so-called "galvanstatic currents". In this technique the current is measured, which passes in a cell containing two electrodes, one immersed in the pure alkali

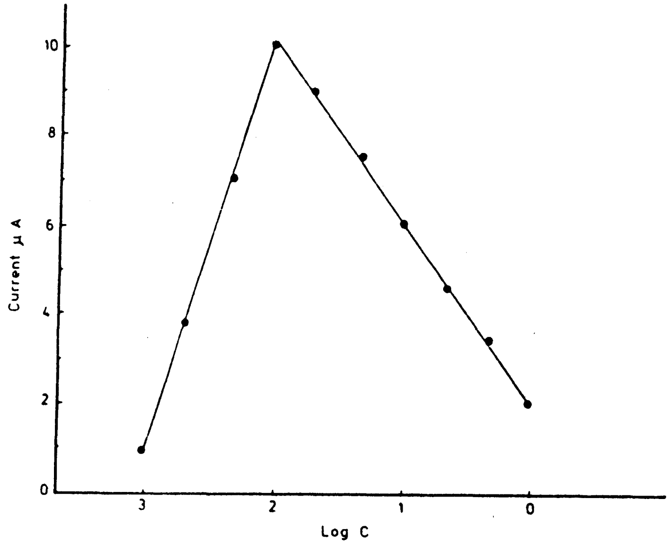

Fig. 3a Corrosion current of aluminium in 0.2N NaOH at different concentration of $NaNO_2$.

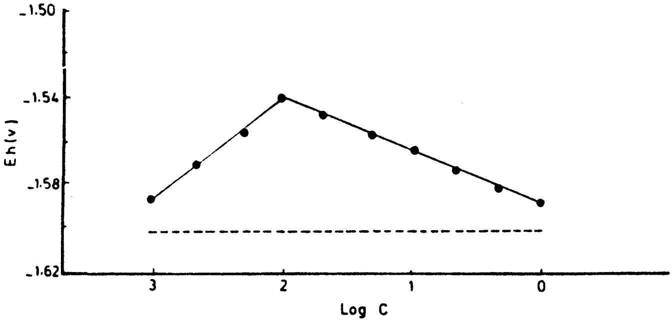

Fig. 3b Effect of concentration of nitrite dissolved in 0.2N NaOH, on the potential of aluminium

solution and referred to as "reference electrode", and the other immersed in the same alkali solution containing sodium nitrite, "test electrode". The difference in corrosion potential brought about by the nitrite leads to the passage of the galvanostatic corrosion current. Hence, the galvanostatic currents (as well as the potentials during the passage of these currents) in the different solutions were followed as a function of time within a period of 2 hrs. The steady state values are plotted versus log C of NO_2^- for the different NaOH solutions; the results in case of 0.2 M NaOH are depicted in Figs. (3a) and (3b). From these diagrams it is obvious that the potential of the test electrode increases linearly with log C of $NaNO_2$ up to 0.01M and then decrease with further increases of the salt concentration. As a result of increase of the potential with nitrite ion concentration, galvanostatic corrosion current flows from the reference electrode (–ve pole), which undergoes anodic reaction, to the test electrode (+ve pole) at which a cothodic reaction proceeds. (Hence a negative sign is assigned to the values of current). In analogy to the potential, the corrosion current increases with NO_2^- concentration up to 0.01 M and then decreases on further addition of NO_2^-. It is concluded that at low concentrations, NO_2^- ions accelerate the cathodic reaction, wheres at concentrations higher than 0.0 1 M this accelerating effect diminishes. These results contradict with the values of E_{corr}, and V_{corr}, which indicates that above 10^{-2} M, the nitrite ions accelerate markedly the cathodic reaction.

Results of Polarisation Studies

Cathodic polarisation of aluminium in NaOH solutions containing nitrite ions has already been studied[4]. The reaction was nothing but hydrogen evolution, and, yet, the Tafel slope is 0.04 V, and not 0.12 V as well-known for this reaction at aluminium cathodes in pure alkaline solutions[7]. It was, therefore, suggested that the nitrite ion is reduced to an intermediate compound (hyponitrous acid, HNO_2^-), which dissociates liberating hydrogen. From the Tafel slope and the dependence of the reaction rate on pH, the following expression was deduced for the cathodic current[4]:

$$i = K[H^+]^2 \cdot [NO_2^-] \exp\left(\frac{-3\Delta\varphi F}{2RT}\right) \quad (1)$$

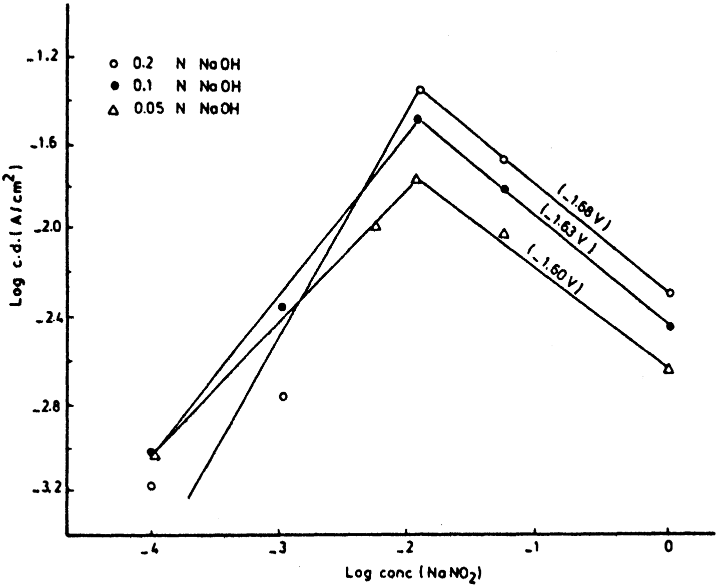

Fig. 4. Relation between log c.d. and log concentration of $NaNO_2$ at constant cathode potential

This equation requires that, at constant potential and pH, the cathodic current is directly proportional to the nitrite ion concentration. On plotting log i, at given constant potential, versus log $[NO_2^-]$, we obtained the curves shown in Fig. 4 for the different NaOH solutions[4]. The slope of the curve corresponding to the low NO_2^- concentration (10^{-4}–10^{-2} M) is positive amounting to 0.85, in agreement with the theoretical reaction order, "one". Above 10^{-2} M, the curve has a negative slope, indicating that the anion becomes inhibitive when the concentration exceeds 10^{-2} M. These results are in excellent agreement with the results of galvanostatic current measurements, but contradict again with the results of corrosion rate determination.

Since the results of cathodic polarisation deviate from the kinetic equation at high concentrations, it is very likely that this deviation is due to adsorption of the nitrite ions[4]. However, one must be cautious in accepting the idea of adsorption, because the ion thought to be adsorbed is itself the species which is reduced to the intermediate HNO_2^-; and this means that adsorption ought to favour the cathodic reaction.

The apparently contradicting results exhibited by aluminium in alkaline sodium nitrite solutions can be understood in the light of the theory of disproportionation of metal atoms[8]. This theory suggests that the surface atoms disproportionate partially into positive and negative metal ions, e.g.,

$$2Al \rightleftarrows Al^+ + Al^- \tag{2}$$

an equilibrium is established amongst the various species; thus:

$$\frac{[Al^+][Al^-]}{[Al]^2} = K \tag{3}$$

It has also been claimed that the first step in cathodic processes is the neutralisation of the positive ions at the cathode surface, with electrons received from the external source[9]. Thus:

$$Al^+ + e \longrightarrow Al \tag{4}$$

The resulting atoms disproportionate to regenerate Al^+, and create Al^- ions, which deliver electrons to the electron acceptor in solution.

With this model, one can proceed to account for the behaviour of aluminium in alkaline nitrite solutions as follows. So long as the surface pattern remains almost unchanged, the rate of the cathodic reaction, during cathodic polorisation, is proportional to the nitrite concentration. Above 10^{-2} M, the negatively charged nitrite ions start to be adsorbed on the positive ions, Al^+. The decrease in the number of these centres leads, according to equations[4], to the decleration of the cathodic reaction rate (cf. the curve with negative slope in Fig. 4).

Considering the corrosion behaviour, one has first to recognise that the situation in corrosion processes is quite opposite to the situation during cathodic polarisation, which agrees admirably with the results of cathodic polarisation of a previous publication. This contradiction was discussed in the light of the concept of disproportionation of the surface metal atoms. Thus, adsorption of NO_2^- on the positive centers, Al^+, leads to the inhibition of the cathodic reaction rate in polarisation experiments. The subsequent increase of the number of the negative species, Al^-, favours the corrosion of the metal in weight loss experiments.

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