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Formation and dissolution of anodic oxide films on zirconium in NaOH: kinetic studies

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The open circuit behaviour of a mechanically polished zirconium electrode in NaOH solution revealed that the oxide building or dissolution process depended on NaOH concentration. Anodic oxide films formed at and below 30 V are fairly stable in NaOH solutions below 1 M. The oxide film is highly unstable, however, when immersed in NaOH at concentrations higher than 1 M. In such cases, oxide dissolution occurs preferentially over oxide building although its extent is much lower if compared with that occurring in acid medium. The results are in accord with the duplex nature of the oxide formed on zirconium.

1. Introduction

The increasing tendency for the application of Zr in the chemical industry, particularly in aggressive media, has lately necessitated extensive knowledge of its electrochemical properties. Zr, which is classified as a valve metal, has a natural covering of a very thin oxide layer. Such a film is responsible for the apparent behaviour of the metal under open-circuit conditions or under the influence of an alternating field, since the film acts as a source or sink for electrons which participate in the electrochemical reaction.

Although Zr has attracted the attention of numerous investigators, a kinetic study of the oxide formation and dissolution in NaOH seems to be lacking. Kinetic studies on Zr have been reported in HCl [1] and H_2SO_4 [2]. Oxidizing ions led to pitting corrosion of Zr in HCl solutions. Bardina and Lukovestev noticed that the state of the film on Zr differed in acid and alkaline media [3–5]. A study of the kinetics of hydrogen adsorption by Zr during galvanostatic cathodic polarization in H_2SO_4, Na_2SO_4 and NaOH [6] showed that hydrogen diffusion was rate controlling.

The purpose of the kinetic study reported here is to clarify the effect of an aggressive medium, such as NaOH of high pH, on Zr and to compare the results with those in the literature of low pH values [1, 2].

2. Experimental details

The electrical circuit used was a high-precision a.c. impedance bridge of the symmetrical Wein type [7]. The electrolytic cell, surface pretreatment of the electrode and details of the experimental procedures were as described elsewhere [8, 9]. The electrode was cut from a spectroscopically pure zirconium rod (Johnson-Matthey, London) and prepared as described previously [2]. The electrode area exposed to the test solution was $0.46\,\mathrm{cm}^2$.

Anodic oxide formation and dissolution experiments were carried out in naturally aerated solutions. All measurements were carried out in a double-walled electrically controlled air thermostat at 25 ± 1° C. All solutions used were prepared from AnalaR grade or chemically pure reagents and triply distilled water. A saturated calomel electrode was used as reference electrode for potential measurements. Values of the electrode potential were then referred to the normal hydrogen electrode.

3. Results

3.1. *Effect of NaOH concentration on the abraded Zr surface*

The variation of open circuit potential with log time shown in Fig. 1 reveals that the abraded surface behaves in a manner dependent on the NaOH concentration. Below the concentration of 0.5 M NaOH, the potential shifts to more noble values indicating oxide building, while above 1 M NaOH the potential drifts to more negative values, indicating dissolution of the air-formed oxide, until the potential attains a steady value. The 1.0 M NaOH is apparently the critical concentration as the potential drifts first to more negative values. The figure thus provides an appropriate index for the extent of surface reactivity of Zr metal in NaOH solutions.

Figure 2 confirms the previous results. Concerning the value of C_m^{-1}, a relative measure of oxide thickening [10], in dilute NaOH C_m^{-1} increases with $t^{1/2}$, while for concentrations > 1.0 M, C_m^{-1} decreases for the first 30 min which indicates oxide dissolution, then more or less stabilized values are reached. For 1 M NaOH, oxide building is observed for the first 30 min, after which rapid dissolution takes place. It should be pointed out that the rate of oxide thickening at concentrations < 1.0 M increases with decreasing concentrations. Similar behaviour was observed for Ti in NaOH [11].

The variation of resistance with $t^{1/2}$ was found to reflect the same results as in Fig. 2. For highly con-

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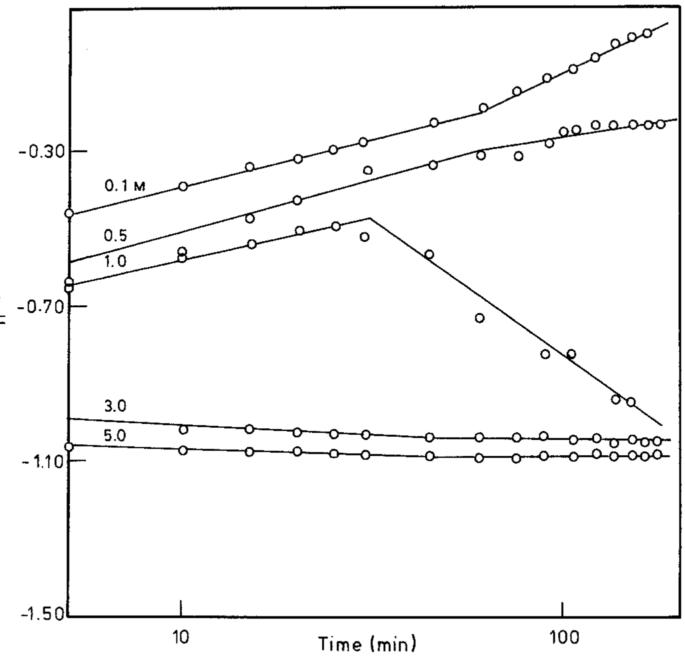

Fig. 1. Variation of E_h with log time for mechanically polished zirconium electrode in NaOH solutions of different concentrations.

ducting solutions C_m is large and R_m is small [12]. Thus, for the same surface state, C_m and R_m can be correlated as follows: $C_m = K/R_m$, where the proportionality constant K depends upon the specific resistance of the solution, apparent electrode area and reactivity of surface. In the present case the reactivity of the surface should include the effect of NaOH concentration as implied from the present results.

3.2. *Effect of formation voltage on the dissolution of the anodic oxide film*

Oxide films were formed at a current density of 2.17 mA cm^{-2} in 0.5 M H_2SO_4 solution up to polarization intervals of 10, 25, 50 and 70 V. After each formation voltage was reached, the applied current was interrupted and the corrosion potential and impedance

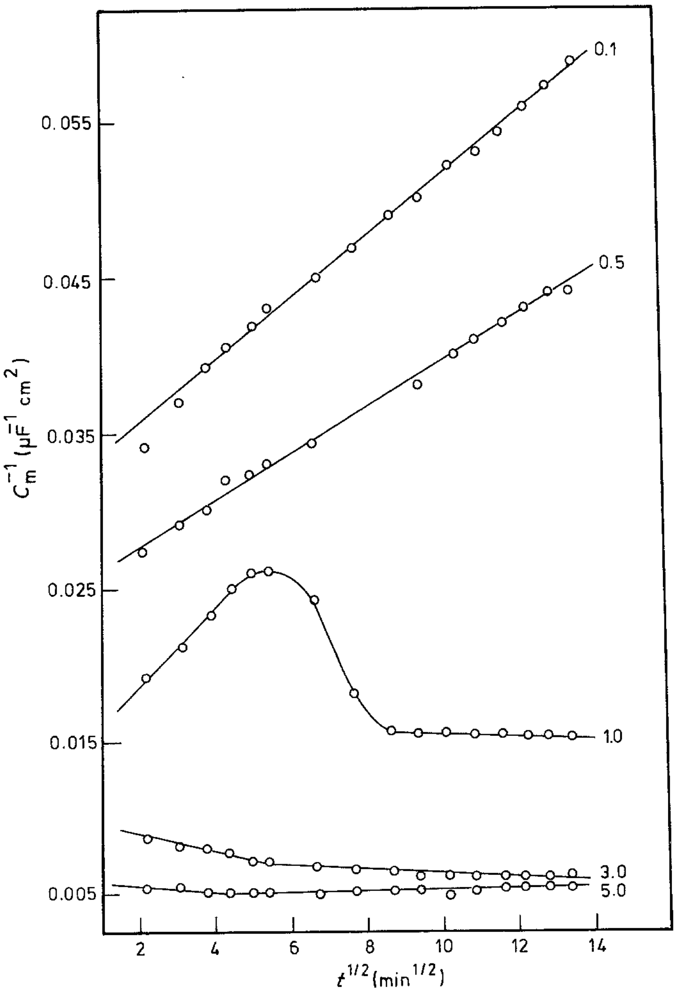

Fig. 2. Variation of the reciprocal capacitance, C_m^{-1}, with the square root of time in NaOH solutions of different molar concentrations.

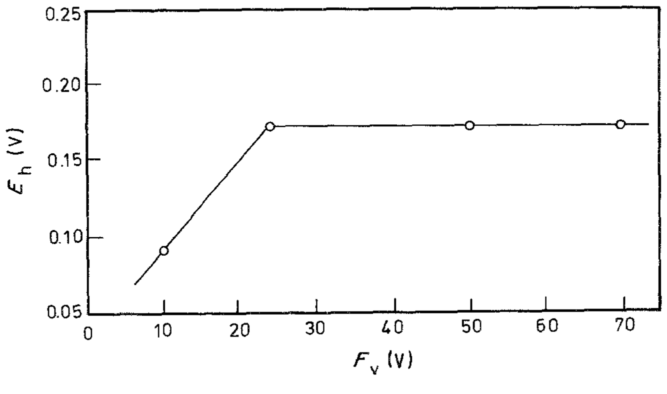

Fig. 3. Variation of final E_h (after 3 h immersion) with formation voltages in 1.0 M NaOH solutions.

of the surface oxide film were followed with time in 1.0 M NaOH solutions. The open-circuit potential was observed to shift to more noble values with increasing formation voltage. Figure 3 shows the variation of the final open-circuit potentials with formation voltage for the anodized electrode.

The results of the variation of C_m^{-1} and R_m, which are more sensitive indices of surface reactivity, are shown in Figs 4 and 5, respectively. The variation of C_m^{-1} with $t^{1/2}$ can be represented by the relation: $C_m^{-1} = \alpha - \beta t^{1/2}$ where α and β are constants, calculated and listed in Table 1. The oxide thickness before dissolution, α_1, increases with the formation voltage, whereas α_2, which is the C_m^{-1} value at the inflection point, increases linearly with formation voltage as shown in Fig. 6. The corresponding resistance, R_m, also increases linearly with formation voltage, Fig. 6. The rate constant of the dissolution process, β_1, increases with increase of oxide thickness, reflecting the increasing tendency of the outer anodic oxide film for dissolution. Meanwhile, the rate constant of the dissolution process of the inner layer, β_2, indicates that the outer layer possesses a higher tendency for dissolution, as observed in other instances [2, 11].

3.3. *Effect of NaOH concentration on the dissolution of the anodic oxide film on Zr*

The anodic oxide film was formed at a current density of 2.17 mA cm^{-2} up to 25 V vs SCE in 0.5 M H_2SO_4. The potential and impedance components of the electrode were followed as functions of time in NaOH solutions of concentrations ranging from 0.1 to 5.0 M. The variation of final open-circuit potential with NaOH concentration, Fig. 7, shows that the potential drifts to less noble values with increasing concentration of NaOH.

Figure 8 represents the variation of C_m^{-1} with $t^{1/2}$. The dissolution/thickening behaviour is dependent, to a great extent, on concentration. The concentration between 1.0 and 0.5 M (Fig. 8) is critical, which indicates that it may possess a critical pH value [13]. Such an observation indicates that either C_m^{-1} does not truly represent the film thickness, or that other factors are involved in the process of film dissolution at higher pH values [14]. In all cases an inflection point is reached at $\simeq$ 30 min (Fig. 8), after which more or less stable conditions are reached. Table 2 summarizes values of α_1, α_2, β_1 and β_2 as a function of NaOH concentration.

4. Discussion

The results in general are in accord with the behaviour of an oxide of a duplex nature [1, 3]. The dependence of potential on the pH of the electrolyte, as inferred from Fig. 1, indicates that hydrogen ions participate in the net reaction occurring at the electrode surface and may be rate controlling. The thermodynamic potentials of the systems

$$Zr + 2H_2O = ZrO_2 + 4H^+ + 4e \qquad (1)$$

$$2H^+ + 2e = H_2 \qquad (2)$$

are -1.340 and 0.000 V, respectively [15]. For dilute solutions, the observed potentials start at about -0.500 V and reach -0.055 and -0.255 V, but for concentrated solutions a value of -1.100 V is reached.

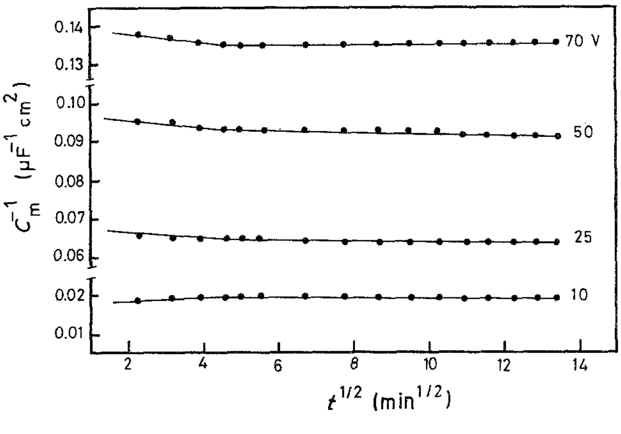

Fig. 4. Variation of the reciprocal capacitance, C_m^{-1}, of the anodized zirconium electrode to the different formation voltages with $t^{1/2}$ in 1.0 M NaOH solutions.

Table 1. Dissolution coefficients as a function of formation voltages, measured in 1.0 M NaOH solutions

Formation voltages (V)	$\alpha_1 \times 10^2$	$\alpha_2^* \times 10^2$	$\beta_1 \times 10^4$	β_2
10	1.7	2.0	8.5	0
25	6.6	6.4	6.0	0
50	9.7	9.3	10.0	0
70	13.9	13.5	12.5	0

* $\alpha_2 = C_m^{-1}$ at the inflexion point (Fig. 5).

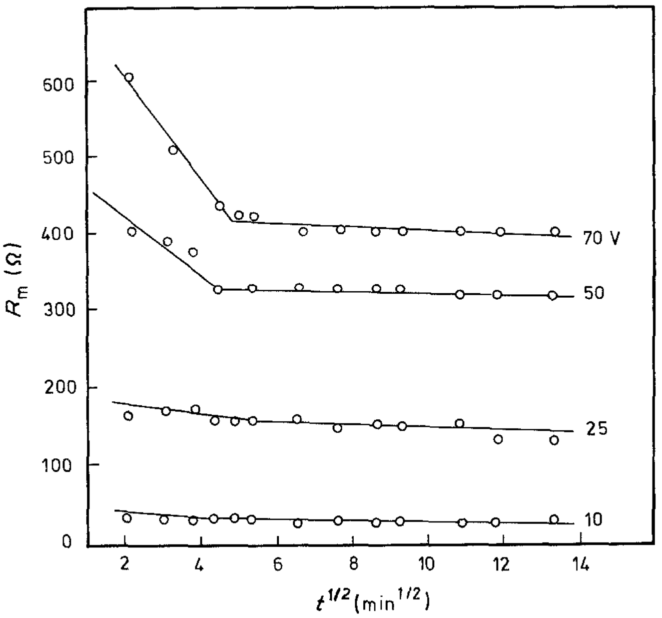

Fig. 5. Variation of the resistance of the oxide film formed at different formation voltages, R_m, with $t^{1/2}$ in 1.0 M NaOH solutions.

Such a variation in potential indicates that reaction 1 is the anodic process and reaction 2, for the concentrated solutions is the cathodic one. The net reaction is therefore

$$Zr + 2H_2O = ZrO_2 + 2H_2 \qquad (3)$$

leading to the formation of ZrO_2. In NaOH > 1.0 M, the oxide becomes more hydrated, causing its dissolution [16].

Under the present experimental conditions, the results indicate progressive film formation in dilute solutions at the expense of the anodically active centres with the result that the anodic process becomes more polarized and the potential becomes more positive. With increase of pH the potential should be expected to become less positive, as substantiated experimentally.

Further confirmation is obtained from Fig. 2, where oxide thickening is observed in dilute solutions and dissolution is observed at higher concentrations. A concentration of 1 M NaOH seems to be critical in that dissolution is observed only at and above this concentration. The R_m relation reflects, in general, the same picture observed for C_m^{-1} with $t^{1/2}$.

Although Zr can be subjected to anodic polarization in aqueous media to very high voltages (*ca* 200 V), parasitic reactions cause the cessation of oxide building at higher voltages [17]. Before the commencement of parasitic reactions, which include any reactions opposing the main process of oxide building, side reactions occur which involve high electronic currents [18]. The present results indicate progressive oxide thickening with increasing voltages up to 70 V, as denoted by the α_1 values (Table 1). On interruption of the current the oxide film suffers dissolution with a rate dependent on the formation voltage as shown in Table 1 (β_1 values). The dissolution is quite clear for oxides formed above 25 V (Figs 4 and 5). Increase of oxide thickness increases the defects within the oxide leading to an increased chemical dissolution.

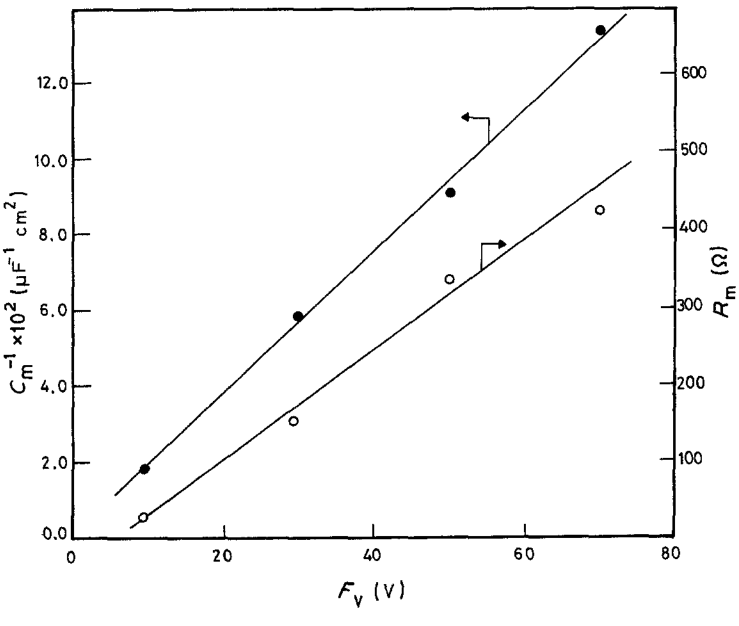

Fig. 6. Variation of each of reciprocal capacitance and resistance of the oxide film at the inflexion point with the formation voltages in 1.0 M NaOH solutions. (▲) $\alpha_2 = C_m^{-1}$ and (○) R_m.

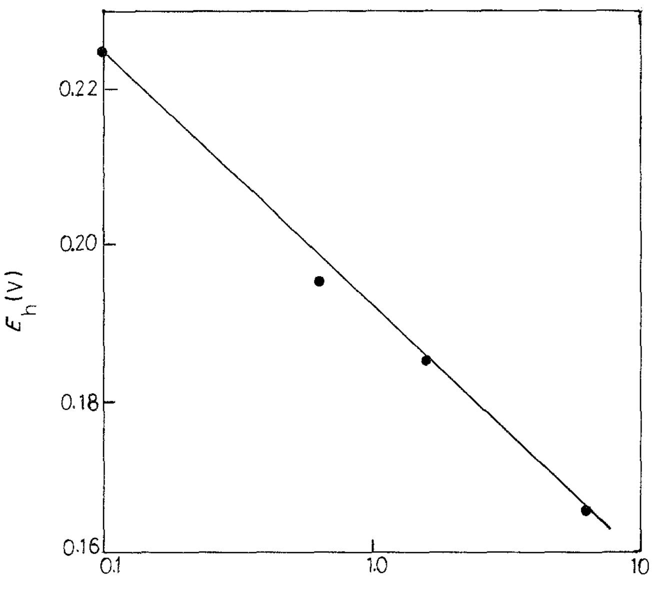

Fig. 7. Variation of final open-circuit potential, E_h, for the anodized zirconium electrode (F_v = 25 V) with log [OH$^-$].

The increase in the rate of dissolution is related to the structural and mechanical defects within the oxide through which OH$^-$ ions are incorporated forming the hydrated oxide [19]. The differences in the values of β_1 and β_2 are in favour of a barrier film of a duplex nature [1, 2].

The decrease of the value of β_2, after the inflection point, to zero is probably related to a change in the mechanism of the dissolution process. The occurrence of the inflection point (Figs 4 and 5) at the same time interval as that for oxide dissolution in H_2SO_4 [2] indicates that the inflection is connected with structural and/or compositional changes in the profile of the oxide film. The relation between these changes and the inflection is clear, as it occurs in both NaOH and H_2SO_4, independent of the concentration of both. It is obvious that the outer oxide film contains a higher concentration of defects.

Comparison of the values of β_1, in NaOH and H_2SO_4 [2], as a function of concentration for the oxide formed under the same experimental conditions shows that they are much higher in the latter case, the comparison being restricted to higher concentrations only where dissolution is observed in NaOH. This may be partly due to the greater solubility of the species produced on dissolution of the oxide film in acid medium as compared to that produced in alkaline medium. On the other hand, if the solubilities of both species are comparable then the lower solubility in NaOH could suggest that OH$^-$ ions have less incorporating power as compared to SO_4^{2-}. This may be readily explained if the bulkier size of SO_4^{2-} as compared to OH$^-$ is considered, together with the specific adsorption of each. Since the dissolution action appears to be due to the hydronium ion [20], it seems that their action is restricted by the SO_4^{2-} ions occupying the defect sites and therefore hindering the action of OH$^-$ ions to some extent. This may explain the process of film growth at very low OH$^-$ concentrations. The concentration of OH$^-$ ions is then below the limit necessary to attack the oxide and, thus, oxide growth is favoured.

The relatively low values (or zero values) of β_2, Table 2, indicate that the oxide does not suffer dissolution because the concentration of OH$^-$ ions is also less than the limit necessary for activation of the dissolution process of the inner layer, as previously

Table 2. Dissolution coefficient as a function of [OH$^-$] concentrations for the oxide film formed at 25 V vs SCE

[OH$^-$] (M)	$\alpha_1 \times 10^3$	$\alpha_2^* \times 10^2$	$\beta_1 \times 10^4$	$\beta_2 \times 10^4$
0.10	78.8	8.0	2.0†	0
0.25	68.1	6.9	3.0†	0
0.50	66.4	6.8	3.2†	0
1.00	66.4	6.4	6.0	0
2.50	64.6	6.2	6.0	1.0
5.00	64.5	6.1	6.5	1.0

* $\alpha_2 = C_m^{-1}$ at the inflexion point (Fig. 9).
† Oxide thickening.

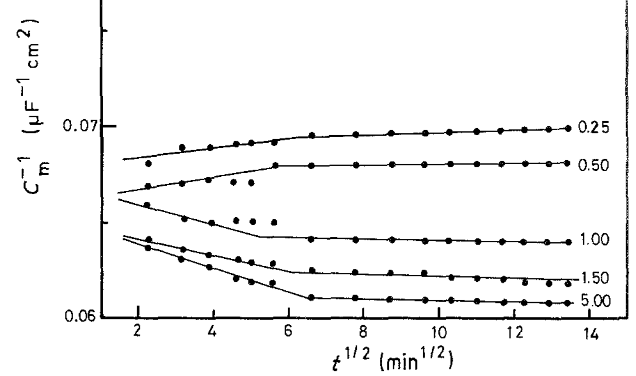

Fig. 8. Variation of the reciprocal capacitance of anodized zirconium electrode (F_v = 25 V), C_m^{-1}, with $t^{1/2}$ in NaOH solutions of different concentrations.

reported for iron based alloys in the presence of Cl^- ions [21]. The concentration limit necessary for activation of dissolution varies according to the nature of the layer as substantiated from the present results.

The relation shown in Fig. 7 may be put in the form

$$E_h = a - b \log [OH^-] \qquad (4)$$

where a and b are constants, depending on the type and concentration of electrolyte and also on the metal used.

The same relation was observed for Ni in chloride solutions where film repair and thickening occur [22] as well as in case of Fe [23], Zr [24, 25], Cd [25] and Pb [25] where active dissolution is observed. It has been shown that this equation describes a general phenomenon, irrespective of whether the anodic reaction leads to film destruction or film repair. In all cases it has been explained that the specific adsorption of the anion on the surface of metal or oxide is the reason [22]. The E_h-log concentration relation should also possess a slope equal to $2.303RT/ZF$ ($59/Z$ mV at 25° C). The value of b in the present case is 37 mV, so that it appears that the OH^- ion behaves as if it was a bivalent anion (29.5 mV at 25° C). A similar observation in the case of Br^- ions [22] was explained on the premise that the ions are adsorbed in the dimeric form, Br_2^{2-}. Although there is no further evidence to support such an assumption, it appears that the only plausible explanation for the low value of b in the present case is that the OH^- ions adsorb, at least partially, in the dimer form, $(OH)_2^{2-}$.

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