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# Valve metal behaviour of bismuth in NaOH

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Galvanostatic anodization of bismuth in different media indicates that the formation of the oxide film depends simultaneously on both pH and the anions present in the anodization medium. Dissolution of these films in NaOH supports this observation. The film is formed of two layers. Open circuit impedance and potential measurements in NaOH indicate film growth. The anodic film formed in NaOH dissolves, however, in NaOH solutions following a zero order mechanism. A number of factors including formation voltage, NaOH concentration, current density and temperature are investigated. The activation energy of the oxide film dissolution is calculated. It may be concluded that the outer layer, in addition to being of a more defective structure, is probably of a higher oxidation state than the inner layer.

## 1. Introduction

Bismuth occupies a special place among valve metals [1] as it appears to have a somewhat more complex behaviour than, for example, tantalum. Galvanostatic anodic film growth on bismuth has been comparatively well investigated in various aqueous and non-aqueous electrolytes. The data available indicated that the anodization of bismuth occurred under lower fields than those for typical valve metals, e.g. Ta, Nb, Ti, etc. [2].

Literature data show that the anodization kinetics of bismuth are strongly affected by the electrolyte nature and concentration [3, 4]. Reports on the characteristics of oxide films formed at constant potential on bismuth show that the field strength is higher in solutions of $ZnSO_4$ and $K_2SO_4$ than NaOH solutions [5–7]. In KOH solutions, Borshchevskii and Skorchelletti [8] reported the formation of $Bi_2O_3$ over a series of non-stoichiometric oxides of lower valency during oxidation of bismuth. The anodization of polycrystalline bismuth in various solutions produces an anodic film, having a thickness which depends on the nature of the anion present, the pH of solution and the polarization current density [4].

Recently, a study of the kinetics of the dissolution behaviour of anodic films on bismuth in $H_2SO_4$ was reported [9]. This investigation deals with the mode of dissolution in NaOH solutions, and the various factors which may influence the dissolution process.

## 2. Experimental details

The electrical circuit, cell and method were those used earlier [10]. The electrode was made from 99.99% bismuth rod. It was fixed in a glass tube with an adhesive resin so that a cross section area of $0.196\,cm^2$ was in contact with the test solution. The electrode was mechanically polished with successive treatments by finer grades of metallurgical papers. The final polish was made with fine tissue paper. All solutions were prepared from A.R. reagents and triply distilled water. No stirring was employed in all experiments. Measurements were conducted in an air thermostat at $30 \pm 0.5°$ C, unless otherwise stated.

Oxide growth was affected galvanostatically [4]. Current was supplied by a stabilized constant current electronic instrument, and potential was read on a valve voltmeter. The current densities employed were above $10^{-4}\,mA\,cm^{-2}$ to avoid the sharp decrease in potential of the bismuth anode recorded during galvanostatic oxidation at low current density [11]. For open circuit measurements, the electrode was washed with triply distilled water before being immersed in the test solution. For anodic oxide film formation experiments, the electrode was first immersed in 0.1 N NaOH for 30 min before connecting the circuit. To study the effect of formation voltage the oxide was formed at constant current density (c.d.) of $0.5\,mA\,cm^{-2}$ in the same solution to the required formation voltage. The electrode was then removed to break the circuit, washed with distilled water and immersed in the test solution, which was a fresh portion of 0.1 N NaOH solution. To study the effect of concentration of dissolution medium, the oxide was formed in 0.1 N NaOH at a c.d. of $0.5\,mA\,cm^{-2}$ up to 50 V. The electrode was transferred to the test solution, which was NaOH solution of various concentrations. To study the effect of c.d., the oxide was formed in 0.1 N NaOH up to 50 V at a constant c.d. of 0.25, 0.50 or $1.00\,mA\,cm^{-2}$. The test solution was 0.1 N NaOH. The effect of temperature was studied by forming the oxide in 0.1 N NaOH at a c.d. of $0.5\,mA\,cm^{-2}$ up to 50 V. The test solution was 0.1 N NaOH at 21, 25, 30, 41 or 45° C.

The measured series capacitance, $C_s$, and resistance, $R_s$, of the impedance of the bismuth electrode were traced at 1 kHz. Potentials were recorded vs a saturated calomel electrode (SCE), then referred to the normal hydrogen electrode (NHE).

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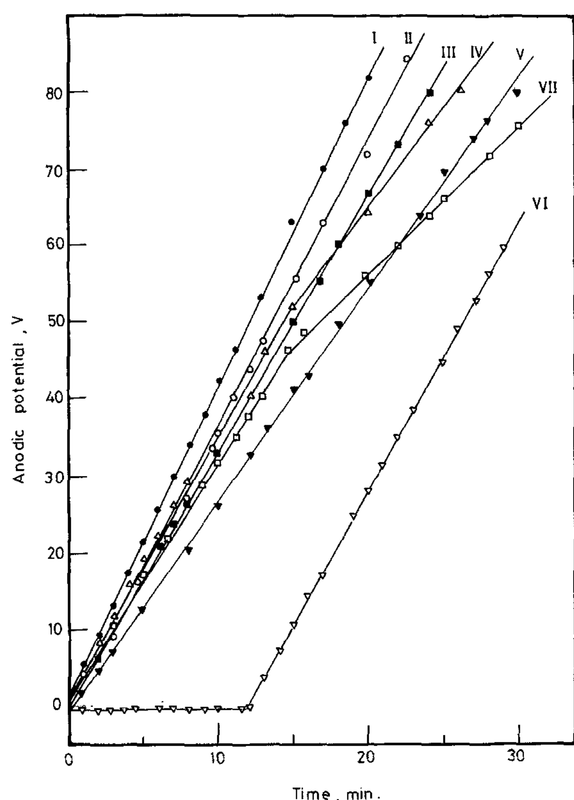


Fig. 1. Anodic charging curves in 0.1 N solutions (c.d. = 0.5 mA $cm^{-2}$). (I) $Na_2CO_3$, (II) $H_3PO_4$, (III) $Na_2B_4O_7$, (IV) $Na_2SO_4$, (V) NaOH, (VI) $(COOH)_2$, (VII) $H_2SO_4$.

## 3. Results

### 3.1. *Effect of medium on formation and dissolution of the anodic film*

Figure 1 shows the anodic charging curves obtained in 0.1 N solutions of $Na_2CO_3$, $H_3PO_4$, $Na_2B_4O_7$, $Na_2SO_4$, $H_2SO_4$, NaOH and $(COOH)_2$ at a c.d. of 0.5 mA $cm^{-2}$. The potential–time curve for oxalic acid shows an induction period after which a linear rise in potential is observed. This induction period is associated with the appearance of some crystals on the metal electrode. After completion of the induction period the crystal size and number increase together with the increase in electrode potential [12].

For $H_2SO_4$ there is a decrease in slope in the linear relation probably due to an increase in the dissolution process. The results indicate that anions influence the process of anodic oxidation. Comparison of the results in $H_2SO_4$ and $Na_2SO_4$ reveals that the rate of formation of the anodic film is the same in both media for the first 15 min before the dissolution action of $H_2SO_4$ starts influencing the rate of formation.

The influence of anions was tested by forming the anodic film till 50 V; the electrode was then transferred to the impedance cell containing 0.5 N NaOH. Capacitance measurements showed a dependence on the formation medium. Figure 2 shows the variation of $C_s^{-1}$ with time, where $C_s^{-1}$ is taken to be proportional to film thickness [13]. Decrease in $C_s^{-1}$ indicates prevalence of the dissolution process. In all cases the abrupt change of slope indicates that the film is formed of two layers. Oxides of metals exhibiting more than one

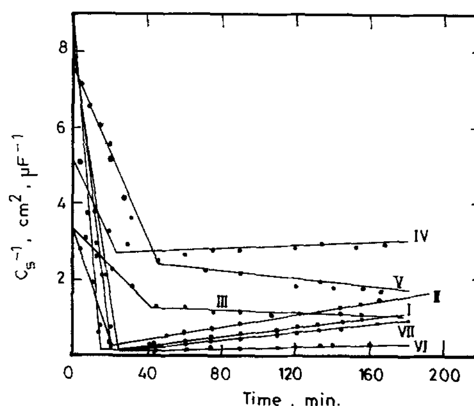


Fig. 2. Variation of $C_s^{-1}$ with time in 0.5 N NaOH for anodic films formed at 0.5 mA $cm^{-2}$ up to 50 V in 0.1 N solutions. (I) $Na_2CO_2$, (II) $H_3PO_4$, (III) $Na_2B_4O_7$, (IV) $Na_2SO_4$, (V) NaOH, (VI) $(COOH)_2$, (VII) $H_2SO_4$.

oxidation state are likely to be composed of layers of oxides differing in their chemical and electrochemical nature [14]. The changes of slope in Fig. 2 are associated with a change in the rate of dissolution. Before the inflection the rate of dissolution is high. A decrease in the rate of dissolution is observed in some cases, e.g. NaOH, and film thickening in other cases, e.g. $H_3PO_4$. This indicates that the film is of a duplex nature and that the outer layer is more susceptible to dissolution.

The dissolution process follows a zero order mech-

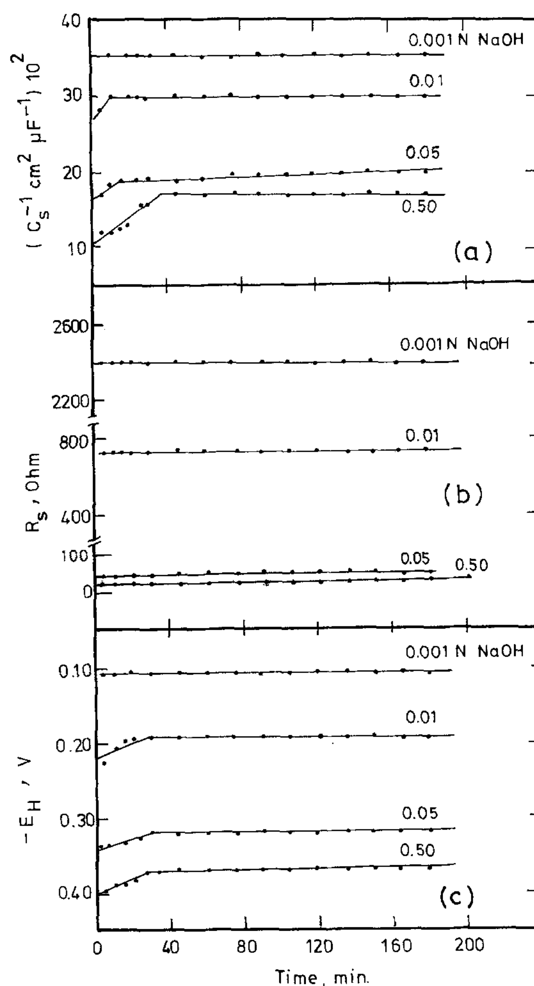


Fig. 3. Variation of (a) $C_s^{-1}$, (b) $R_s$ and (c) $E_H$ with time for the abraded bismuth electrode in NaOH of different concentrations.

anism that may be represented by

$$\frac{-\mathrm{d}C_s^{-1}}{\mathrm{d}t} = k \qquad (1)$$

where $C_s$ is the measured capacitance in $\mu$F cm$^{-2}$ at time $t$, $(-\mathrm{d}C_s^{-1}/\mathrm{d}t)$ is the rate of dissolution, and $k$ is the dissolution constant (cm$^2$ $\mu$F$^{-1}$ min$^{-1}$).

### 3.2. *Open circuit behaviour of bismuth metal in NaOH*

The results of impedance and potential measurements under open circuit conditions are shown in Fig. 3. The relations shown in Fig. 3a show that very dilute solutions do not affect the Bi metal. With increase of NaOH concentration an increase in film thickness is first observed. Both the increase of film thickness and the time required for film thickening increase with increase of NaOH concentration. After the initial film formation $C_s^{-1}$ attains a constant value which indicates that the formation/dissolution processes are at equilibrium.

The same results are reflected in Fig. 3b. However, the variation in $R_s$ is somewhat limited since the resistance is a less sensitive index for determination of variation in film thickness than capacitance [16]. Also the tendency of $E_H$ values to more noble values, Fig. 3c, is in agreement with the concept of film growth.

### 3.3. *Effect of formation voltage on the dissolution of the anodic film in NaOH*

Figure 4a indicates clearly the duplex nature of the film formed anodically to different formation voltages. Measurements of the rate of dissolution of the anodically formed film in dilute acid was also interpreted in terms of a two-layer model for the film [16]. The results show that the outer layer dissolves much faster than the inner layer which indicates that the former possesses a more defective structure. Increase in formation voltage increases the rate of dissolution of both layers (i.e. leads to formation of a more defective oxide film). The variation of resistance follows the same sequence, Fig. 4b.

The tendency of $E_H$ to less noble values, Fig. 4c, indicates the dissolution of both layers. Increase of formation voltage leads to increase in the rate of decrease of $E_H$ for the outer layer. Variation in $E_H$ for the second layer is very limited.

### 3.4. *Effect of NaOH concentration on the dissolution of the anodic film*

Increase in NaOH concentration causes dissolution of the film, Fig. 5. The rate of dissolution of the outer layer increases systematically with increase in concentration of NaOH. However, the rate of dissolution of the inner layer increases up to 0.3 N NaOH. For 0.5 N NaOH, there is a decrease in the rate of dissolution. At 1.0 N NaOH there is an increase in $C_s^{-1}$ which could be

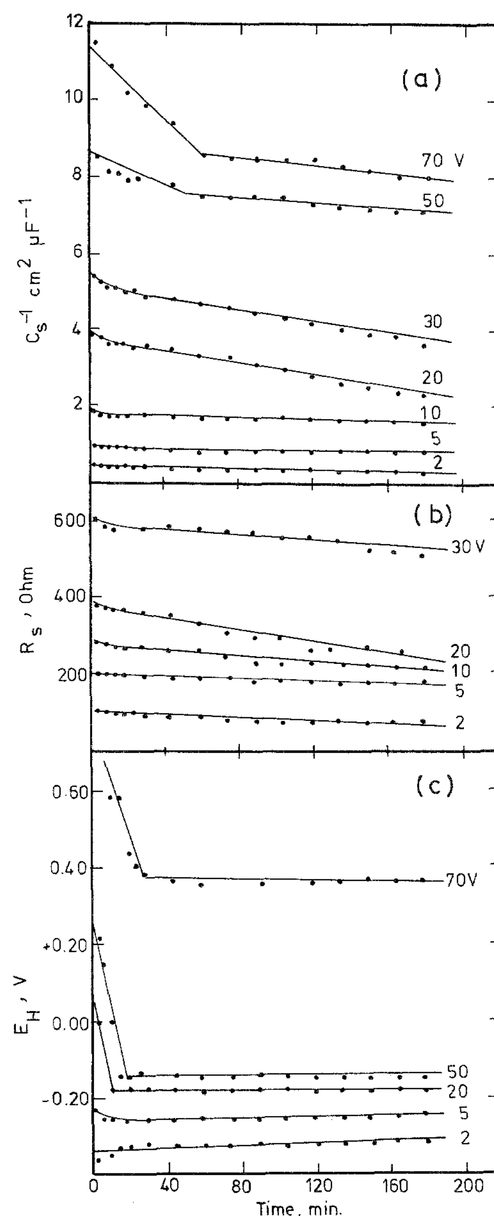


Fig. 4. Variation of (a) $C_s^{-1}$, (b) $R_s$ and (c) $E_H$ with time for the bismuth electrode anodized to different formation voltages.

explained by a dissolution–precipitation process sealing cracks in the outer layer. This is supported by the tendency of $E_H$ to more noble values at the same concentration.

### 3.5. *Effect of the formation current density on dissolution of the anodic film on Bi*

The variation of $C_s^{-1}$ with time in 0.1 N NaOH for the film formed at different current densities is shown in Fig. 6. The results indicate that the total thickness of the film ($C_s^{-1}$ at zero time) increases as the c.d. decreases. The rate of dissolution of the outer layer increases slightly with c.d. It is apparent that the dissolution of the inner layer occurs at a much lower rate and is nearly the same for the three current densities studied.

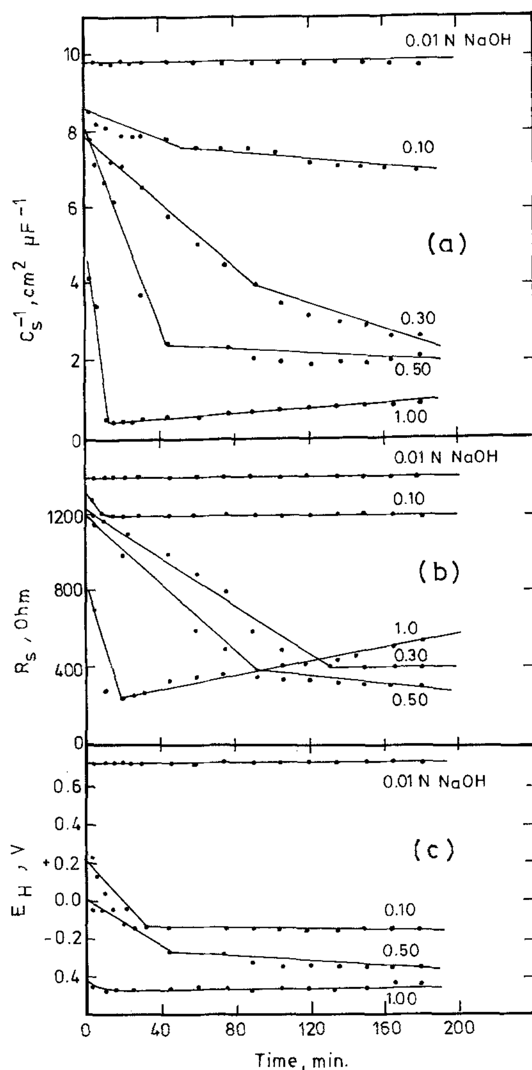


Fig. 5. Dependence of (a) $C_s^{-1}$, (b) $R_s$ and (c) $E_H$ on time for the anodized bismuth electrode in NaOH solutions of different concentrations.

### 3.6. *Effect of temperature on the dissolution of the anodic film in 0.1 N NaOH*

Dissolution of the anodic film in 0.1 N NaOH was studied at temperatures ranging from 21 to 45° C. Although this range of temperature is somewhat limited, the dissolution appears to be rather sensitive to slight changes in temperature as shown in Fig. 7. The effect is more pronounced for the dissolution of the outer layer, as revealed by the increase in the rate of dissolution with temperature. The rate of dissolution of the inner layer is also affected by temperature but to a limited extent.

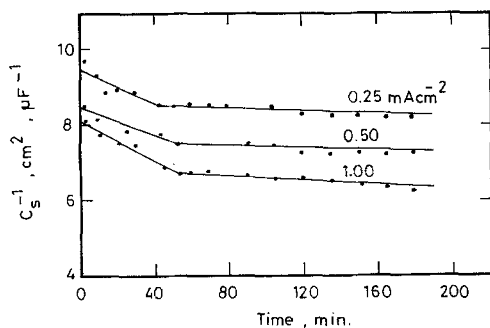


Fig. 6. Variation of $C_s^{-1}$ with time as function of anodizing current density.

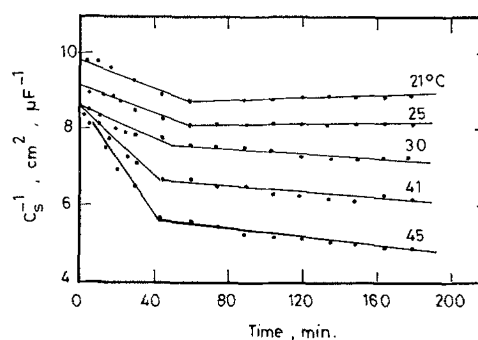


Fig. 7. Effect of temperature on the variation of $C_s^{-1}$ with time for the anodized bismuth electrode.

The results agree with observations of increase of solubility of the oxide with increase in temperature due to retardation of the film growth process on Bi [17].

## 4. Discussion

The anodic charging curves show that the solution composition and pH affect the type of anodic film formed on Bi. The structure of anodically formed layers, especially in the case of Bi, is a matter of some debate. Bi can be oxidized to one of the ionic species $Bi^{3+}$, $Bi(OH)^{2+}$, $BiO^{+}$ or to $Bi_2O_3$, with the possibility of further oxidation of $Bi_2O_3$ to higher oxides [4].

The appearance of an induction period in the galvanostatic oxidation of Bi in oxalic acid has been observed previously [12]. It has been shown that the films were composed from $Bi(OH)_3$ or $Bi_2O_3 \cdot CO_2 \cdot H_2O$ [12].

The other media studied differ in the rate of formation of the anodic film. Lower rates are observed in $H_2SO_4$ and NaOH which may be attributed to the increased partial dissolution of the films in acid and alkaline solutions. The somewhat higher rate obtained in $H_3PO_4$ probably indicates that pH and type of anions affect simultaneously the rate of formation.

The dissolution of these films in 0.5 N NaOH shows clearly that both the thickness (initial $C_s^{-1}$) and the nature of the two layers depend on the formation medium. The rate of dissolution of the outer layer is higher for thicker films, which may be associated with higher structural defects. The results indicate clearly that the pH of solution is not the only factor affecting the nature of the film formed anodically. The nature of anions present plays a role probably through contaminating the anodic film [18].

Film building is manifested by the open circuit behaviour of Bi metal, Fig. 3. The results indicate that the film reaches a thickness which depends on NaOH concentration after which equilibrium occurs between film thickening and film thinning. It is probable that the film formed naturally is a thin adherent layer of $Bi_2O_3$ which is the most stable oxide of Bi [19].

It may be gathered from the results in Fig. 2 for the film anodically formed in 0.1 N NaOH and dissolving

*Table 1. Rates of dissolution as function of formation voltage*

| | Formation voltage (V) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 20 | 30 | 50 | 70 |
| $k_1 \times 10^2 (cm^2 \mu F^{-1} min^{-1})$ | – | – | 1.0 | 1.0 | 1.3 | 2.6 | 4.8 |
| $k_2 \times 10^3 (cm^2 \mu F^{-1} min^{-1})$ | 0.6 | 0.6 | 1.7 | 6.9 | 6.7 | 3.9 | 5.0 |

*Table 3. Rates of dissolution as function of temperature*

| | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | 21 | 25 | 30 | 41 | 45 |
| $k_1 \times 10^2 (cm^2 \mu F^{-1} min^{-1})$ | 1.6 | 1.9 | 2.6 | 5.0 | 7.5 |
| $k_2 \times 10^4 (cm^2 \mu F^{-1} min^{-1})$ | 0.0 | 0.0 | 38.5 | 40.2 | 58.4 |

in 0.5 N NaOH, and the results for the naturally formed film, Fig. 3a, that the nature of the film covering Bi metal differs according to the conditions of formation.

Variation in formation voltage yields relations formed of two lines in accordance with Equation 1. The change of slope occurring indicates a change in the rate of dissolution and becomes very clear at high formation voltage. This may be interpreted in terms of a two layer model of the film [16]. The constants $k_1$ and $k_2$ for the dissolution of the outer and inner layers, respectively, are given in Table 1 as function of formation voltage. It is clear that the rate of dissolution of the inner layer is much lower than that of the outer layer. This agrees with the concept of different chemical and electrochemical nature of the oxides [14]. The increase of $k_1$ with formation voltage indicates that structural and mechanical defects increase with increasing film thickness; this has been observed previously [20]. Reports indicate the highly defective structure of anodic bismuth oxide films formed in NaOH [21]: evidence is given for the existence of the electronic space charges in the anodic oxide layers [22].

The data given in Table 1 agree with reports that the anodic oxide layers grown on Bi consist of a thin barrier layer overlaid by a thicker cracked and porous layer [23]. The present results show that the defects in the outer layer are much greater than those in the inner one. It has been reported that the rate of nucleation of the anodic oxide film on Bi in 0.1 N NaOH is limited by the electrochemical reaction at the uncovered metal surface or surface diffusion to the periphery of a spreading oxide patch, not by incorporation in the growing lattice [23].

The concentration of NaOH affects the rates of dissolution of both layers to a great extent. The rate of dissolution of the outer layer, $k_1$ (Table 2) increases sharply with NaOH concentration, while $k_2$ is also affected but in a different manner. This may be due to a difference in the basic character of the outer and inner layers. An increase is observed first in $k_2$ up to 0.3 N NaOH followed by a decrease at 0.5 N NaOH. At 1.0 N NaOH film thickening predominates. This is not strange in view of the amphoteric character of the

*Table 2. Rates of dissolution as function of NaOH concentration*

| | NaOH concentration (N) | | | | |
|---|---|---|---|---|---|
| | 0.01 | 0.10 | 0.30 | 0.50 | 1.00 |
| $k_1 \times 10^2 (cm^2 \mu F^{-1} min^{-1})$ | 0.00 | 2.6 | 4.5 | 13.5 | 30.0 |
| $k_2 \times 10^3 (cm^2 \mu F^{-1} min^{-1})$ | 0.00 | 3.9 | 16.6 | 2.9 | 3.0* |

* Rate of formation.

anodic oxide films on Bi [24] which possess semiconducting properties [3, 24]. The results shown in Fig. 5a indicate that the isoelectric point of the oxide forming the inner layer lies between 0.5 and 1.0 N NaOH.

A test was carried out by studying the behaviour of the film formed in $Na_2SO_4$ at a c.d. of 0.5 mA cm$^{-2}$ up to 50 V. Dissolution behaviour in NaOH followed the same trend. The film dissolution occurred at $\leqslant 0.5$ N NaOH and film formation at a concentration $\geqslant 0.7$ N NaOH. This shows that the film formed in $Na_2SO_4$ is probably the same forming the inner layer in the present case (i.e. when NaOH is the formation medium). A recent study indicated that most probably $Bi_2O_3$ is formed anodically in $Na_2SO_4$ [9].

During anodic polarization of the Bi electrode in 0.1 N NaOH above 100 $\mu$A cm$^{-2}$, the potential was found to remain constant at the $Bi/Bi_4O_7$ [25]. This suggests that a higher oxide, probably $Bi_4O_7$, forms the outer layer of the oxide film.

The $R_s$ and $E_H$ relations (Fig. 5b and c) follow the same trend as $C_s^{-1}$. This indicates that impedance and potential measurements reflect the same picture for the dissolution process.

Changes in c.d. apparently affect the thickness of the film. It is apparent that the lower c.d. is associated with formation of a thicker film. Increase of c.d. increases somewhat the rate of dissolution of the outer layer; in the same time a longer time interval is required for dissolution of this layer which indicates that the outer layer thickness increases with c.d. However, the rate of dissolution of the inner layer is apparently not affected by changes in c.d.

Increase in temperature enhances dissolution of both layers, as indicated by Table 3.

The effect is more significant above 30° C, which

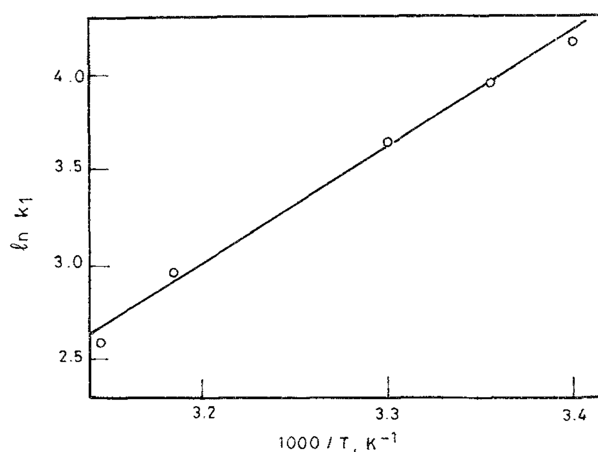


Fig. 8. Arrhenius plot for dissolution of the oxide film in 0.1 N NaOH.

indicates that the formation/dissolution process of the oxide is shifted more towards dissolution with increase of temperature. Thus, the main controlling step would be the chemical step and the dissolution is of a purely chemical nature [25]. Increase in dissolution is probably aided by increase in the diffusion coefficient of the dissolved species at higher temperature and increase in porosity of the oxide [26].

The activation energy for the dissolution process, $-\Delta H$, was calculated to be equal to $51.9\,\mathrm{kJ\,mol^{-1}}$ from the Arrhenius plot shown in Fig. 8. This was obtained from the relation [27]

$$R\mathrm{d}\ln[-(\mathrm{d}C_s^{-1}/\mathrm{d}t)_{C_s^{-1}}]/\mathrm{d}(1/T) = -\Delta H \quad (2)$$

This value of $\Delta H$ is somewhat higher than $24.2\,\mathrm{kJ\,mol^{-1}}$ for Bi in $H_2SO_4$ [9]. This may be attributed to the difference in nature of the outer porous oxide formed in each case as well as their solubilities in NaOH and $H_2SO_4$.

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