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Anodic formation of thin CdS films.
II. Dependence of the kinetics on S^{2-}-concentration

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The kinetics of anodic formation of CdS films is examined in 1.0 mol dm^{-3} $NaHCO_3$ solutions with different concentrations of Na_2S. It is confirmed that films formed initially under galvanostatic conditions grow according to the high field assisted migration of ions. The exchange current density is first-order with respect to the concentration of Na_2S. This dependence can be accounted for with a process at the anodic film/solution interface as the rate determining step. Such a step is usually not considered to be rate determining in the formation of anodic films according to the high field model of growth. The surface density of the species participating in the rate determining step is calculated and compared to the concentration of various species in the bulk of the solutions. This calculation shows that S^{2-} is the species participating in the rate determining step across the inner Helmholtz layer. The concentration of HS^-, which may be thought to participate in the rate determining step, is higher, by six orders of magnitude, than the concentration of the species participating in the rate determining step. A rate equation for the process in the inner Helmholtz layer as the rate determining step is developed and discussed.

1. Introduction

In the preceding paper [1] the kinetics of the anodic formation of thin CdS films are analysed under potentiodynamic and galvanostatic conditions at different temperatures. Under both conditions, growth proceeds according to the known model of high field assisted formation of ions at the metal/anodic film interface and their migration through the film. The frequency factor, N, used in the rate equation to fit to the model and which gives the surface density of ions in the rate determining step, is significantly lower than in the case of anodic hydroxide films at Pt, Ni and other electrodes [2–6]. These films, too, grow according to the high field model. A low value of N for CdS precludes a process at the Cd/sulphide film interface as the rate determining step [1].

In this paper, work on the kinetics of CdS formation under galvanostatic conditions in solutions of different concentrations of Na_2S is described. Data from different concentrations are expected to help distinguish between the rate determining step within the anodic film and that at the anodic film/solution interface.

2. Experimental details and results

The experimental procedure, electrode pretreatment, solution preparation, cell and instrumentation were the same as in the previous work [1]. Constant current charging experiments were conducted at 22° C in 0.01, 0.1 and 1.0 mol dm^{-3} Na_2S in 1.0 mol dm^{-3} $NaHCO_3$. The pH values of the solutions were adjusted to 9.0.

In all the solutions, the shape of the galvanostatic charging curves at different currents were similar to those reported in the first paper [1] for the 0.1 mol dm^{-3} Na_2S + 1.0 mol dm^{-3} $NaHCO_3$ solution. In Fig. 1, potential–charge density (V–q) traces at three current densities are shown for the 1.0 mol dm^{-3} Na_2S + 1.0 mol dm^{-3} $NaHCO_3$ solution. Although the V–q traces of the different concentrations are similar (compare Fig. 1 with Fig. 5 in [1]), both the position of the linear portions of the V–q traces with respect to the V axis, and their slopes for the same current density are affected by the solution concentration. Thus, V_0, the intercepts of the linear V–q traces at different current densities decrease with increasing concentrations of Na_2S. To determine V_o in a

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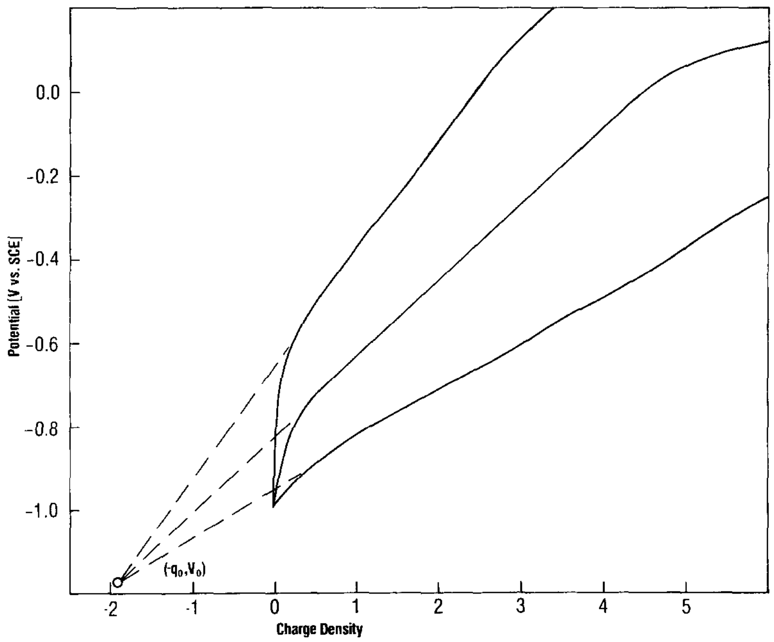

Fig. 1. Galvanostatic charging curves at 7.9×10^{-6} A cm^{-2} (bottom), 7.9×10^{-5} A cm^{-2} (middle line) and 7.9×10^{-4} A cm^{-2} (top line) in 1.0 mol dm^{-3} Na_2S + 1.0 mol dm^{-3} $NaHCO_3$ solution. The charge density is 3.94×10^{-4} C cm^{-2} per division. The data are not corrected for roughness of the electrode surface.

given solution it was important to keep the experimental conditions, at different current densities, as nearly the same as possible. This was achieved in this work when a low current density, e.g. 10^{-6} A cm^{-2}, was first applied to a freshly polished electrode as soon as it was immersed into the solution and then, when a given potential was reached, a test current higher than 10^{-6} A cm^{-2} was applied (see [1]). This procedure was previously adapted to determine V_0 for the growth of anodic films of $Ni(OH)_2$ [4]. In Fig. 2, V_0 values are plotted against the concentration of Na_2S. It appears that V_0 decreases about 30 mV as the concentration of Na_2S increases 10 times, i.e. $\partial V_0/\partial \log [Na_2S] \approx -2.3RT/(2F)$.

The slopes of the V–q traces are affected by solution concentration. This is evident from Fig. 3 in which the $\partial V/\partial q$ slopes at three concentrations are plotted against the logarithm of the applied current density (i). For each concentration there is a distinct linear dependence of $\partial V/\partial q$ on $\log i$ extending for a few decades of current density. The lower the concentration the higher the lines are placed along the $\partial V/\partial q$ axis. The slopes of these lines are, however, independent of concentration i.e.

$$\frac{\partial^2 V}{\partial q \partial \log i} = 2.3\, n \neq f(i, c_{Na_2S}). \qquad (1)$$

The parameter n is nearly equal to 85 VC^{-1} cm^2 when correction for the roughness of the electrode surface is made. $\partial V/\partial q$ versus $\log i$ lines appear to be regularly displaced with concentration (c) along the $\partial V/\partial q$ axis. It is significant that the displacement of the $\partial V/\partial q$ versus $\log i$ lines for the two lower concentrations is numerically equal to the slope of the $\partial V/\partial q$ versus $\log i$ lines. In Fig. 4, $\partial V/\partial q$ values at a given current density are plotted against the logarithm of the concentration. From this plot it appears that:

$$\frac{\partial^2 V}{\partial q \partial \log [Na_2S]} = 2.3\, m \approx -2.3\, n. \qquad (2)$$

3. Discussion

3.1. *The rate equation*

Kinetic data at any concentration leads to the following empirical rate equation (see [1]):

$$i = i_0 \exp\left[\frac{V - V_0}{n(q + q_0)}\right] \qquad (3)$$

with i_0 and V_0 being dependent on the concentration of Na_2S. As discussed previously [1], this equation agrees with the rate equation expected for the high field assisted growth of insulating anodic films [7, 8]. For this model, parameter q_0

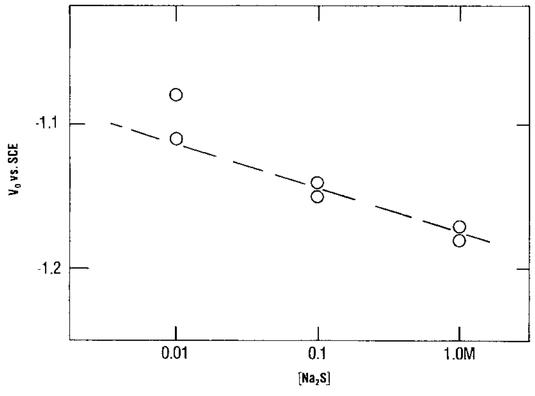

Fig. 2. V_0 as a function of Na_2S concentration. The broken line indicates a $dV_0/d\log c(Na_2S)$ slope of — 30 mV.

is expected to be independent of concentration, as observed to be the case in the growth of anodic films at Pt and Ni electrodes [3, 9]. Parameter n for the high field model contains the half-jump distance and, therefore, is also expected to be independent of concentration, as observed (Fig. 3).

The exchange current density, i_o, can be calculated in a simple way from the value of $\partial V/\partial q$ at $i = 1\ \mathrm{A\,cm^{-2}}$. It is given by

$$\ln\frac{i_o}{i^0} = \frac{-1}{n}\left(\frac{\partial V}{\partial q}\right)_{i=1} = f(c_{\mathrm{Na_2S}}). \tag{4}$$

Here, i^0 is a unit of current density and is introduced into the equation to render the term in the logarithm dimensionless. Assuming that the dependence of $(\partial V/\partial q)_{i=1}$ on $\log c(Na_2S)$ is linear with the slope $2.3\,m$ (see Fig. 4), an assumption that will be discussed below, it is possible to write

$$\left(\frac{\partial V}{\partial q}\right)_{i=1} = \left(\frac{\partial V}{\partial q}\right)_{c=1,i=1} + m\ln\frac{c(\mathrm{Na_2S})}{c^0} \tag{5}$$

where c^0 is a unit of concentration. Introducing Equation 5 into Equation 4, i_o as a function of the concentration of Na_2S is given by:

$$i_o = i^0\left[\frac{c(\mathrm{Na_2S})}{c^0}\right]^{-m/n}\exp\left[-\frac{1}{n}\left(\frac{\partial V}{\partial q}\right)_{c=1,i=1}\right]. \tag{6}$$

Since $m \simeq -n$, and denoting the exponential term with a constant K, Equation 6 assumes the following simplified form

$$i_o = i^0 K\frac{c(\mathrm{Na_2S})}{c^0}. \tag{7}$$

The most important result of this study is that the exchange current density depends on the concentration of Na_2S and that this dependence is linear. The exchange current densities are equal to 3.7×10^{-9}, 3.7×10^{-8} and $2.1\times10^{-7}\ \mathrm{A\,cm^{-2}}$ for 0.01, 0.1 and 1.0 mol $\mathrm{dm^{-3}}$ Na_2S, respectively. It may be noted that both m and n are affected by the roughness of the electrode surface. However, their ratio is not effected, provided that the roughness remains the same in all the experiments.

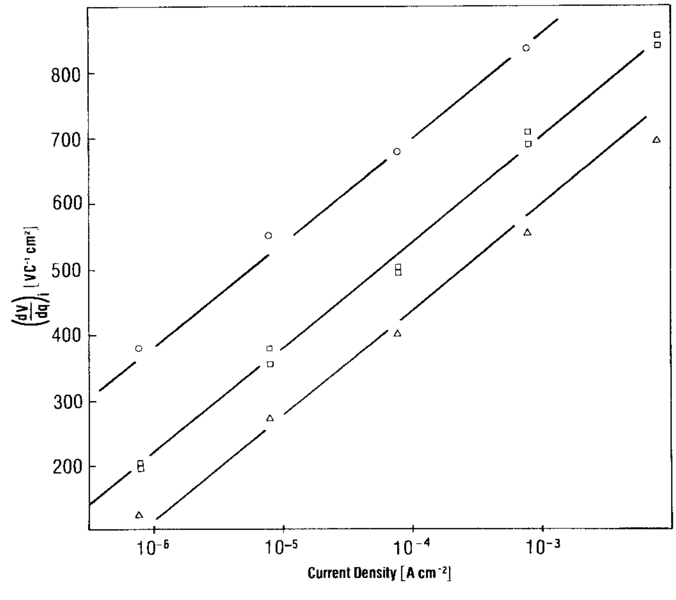

Fig. 3. Slopes of galvanostatic charging curves at various constant current densities in 1.0 mol $\mathrm{dm^{-3}}$ $NaHCO_3$ and 1.0 (△), 0.1 (□) and 0.01 mol $\mathrm{dm^{-3}}$ (○) Na_2S solutions. Data are not corrected for roughness of the electrode surface.

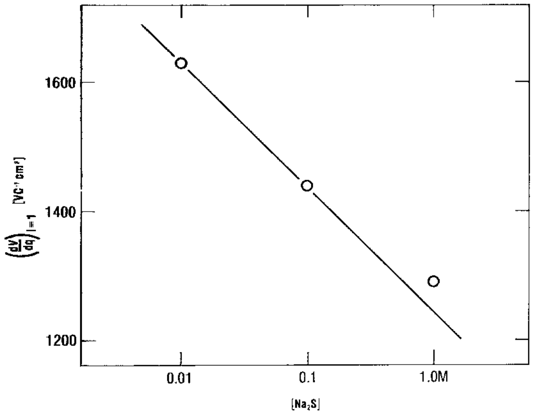

Fig. 4. $\partial V/\partial q$ values extrapolated to a constant current density of 1 A cm^{-2} as a function of Na_2S concentration. The line indicates a slope of $2.3\,m = -2.3\,n$. Data are corrected for roughness of the electrode surface ($RF = 1.2$).

The dependence of i_o on the concentration of Na_2S is not expected for a process either at the Cd/CdS interface or within the CdS film as the rate determining step. The observed dependence strongly suggests that a process at the CdS/solution interface is the rate determining step. Such a step is frequently ignored in studies of anodic formation of insulating films [10]. Recently, however, it was shown that for the growth of anodic oxide films at Pt [5] and Ni [4] electrodes a process at the oxide film/solution interfaces is the rate determining step.

For the high field assisted growth with the rate determining step at the anodic film/solution interface, the following rate equation can be derived [7, 8]

$$i = Nvze\exp\left[\frac{-\Delta G^*}{RT}\right]\exp\left[\frac{ze\lambda\Delta V_i}{kT\delta_i}\right] \tag{8}$$

Here, ΔV_i is the potential difference across the inner Helmholtz layer of thickness δ_i. The significance of the other symbols is the same as given previously [1]. It should be pointed out that N now represents the surface density (in cm^{-2}) of the species in the inner Helmholtz layer participating in the rate determining step. λ may still be called the 'half-jump' distance. It gives the distance ions participating in the rate determining step migrate from their equilibrium positions before the rate determining step to the position of their highest energy when 'crossing' the activation energy barrier. Note that with the latter definition λ/δ_i is equivalent to the symmetry factor in electrode kinetics.

When there is no surface charge at the outermost surface of the anodic film, the relationship

$$\frac{\Delta V_i}{\delta} = \frac{\epsilon_f}{\epsilon_i} \times \frac{\Delta V_{of}}{d}, \tag{9}$$

where d is the thickness of the sulphide film, should hold, and Equation 8 could be transformed to

$$\begin{aligned} i &= Nvze\exp\left[\frac{-\Delta G^*}{RT}\right]\exp\left[\frac{\epsilon_f ze\lambda\Delta V_{of}}{\epsilon_i kTd}\right] \\ &= i_o\exp\left(\frac{\epsilon_f}{\epsilon_i} \times \frac{\alpha\Delta V_{of}}{d}\right). \end{aligned} \tag{10}$$

This equation is valid when the rate determining step is a process at the anodic film/solution interface. It is similar to the rate equation with the rate determining step either at the metal/anodic film interface or within the anodic film. It differs from the latter in that the field term in the exponent is multiplied by the ratio of the dielectric constants, ϵ, of the film, f, and inner Helmholtz layer, i. Two comments are in order at this point.

First, ΔV_{of} cannot be directly related to $V - V_o$ in the experimental rate equation. Equation 10 is developed for the model of two double layers at the anodic film/solution interface. The significance of V_o in the observed rate equation depends on the model assumed [10]. For the two double layer model, $V - V_o$ is the potential difference, not across the anodic film itself, but rather across the film and the inner Helmholtz layer [1]. In this case, V and V_o are, respectively, the potentials of the underlying metal and inner Helmholtz plane with respect to the same reference point. V_o is a measure, therefore, of the potential difference across the outer Helmholtz layer with respect to this reference. For a given temperature and concentration, V_o was found to be independent of current density. On the other hand, ΔV_{of} in Equation 10 is the potential difference across the anodic film only. Since the potential difference across the inner Helmholtz layer is not constant but varies with current density, the measured potential, V, cannot be related directly to ΔV_{of}. Therefore, experimental rate equations cannot be related directly to Equation 10. Equation 10, as such, cannot be subjected to direct experimental verification.

The difficulty discussed in the preceding paragraph is overcome when $\Delta V_{\mathrm{of}}/d$ in Equation 10 is replaced according to the following relationship:

$$\frac{\Delta V_{\mathrm{of}}}{d} = \frac{\phi_{\mathrm{m}} - \phi_{\mathrm{i}}}{d + \delta\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}}} = \frac{V - V_{\mathrm{o}}}{d + d_0}. \qquad (11)$$

This relationship follows from Equation 9. Here, d_{o} (= $\delta\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}}$) is the 'corrected' thickness of the inner Helmholtz layer, and $\phi_{\mathrm{m}} - \phi_{\mathrm{i}}$ (= $V - V_{\mathrm{o}}$) is the potential difference across the anodic film and inner Helmholtz layer. With Equations 10 and 11, the equation for the rate determining step at the anodic film/solution interface can be written in the form

$$\begin{aligned} i &= N\nu ze \exp\left[\frac{-\Delta G^*}{RT}\right] \exp\left[\frac{(\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}})\alpha(V - V_{\mathrm{o}})}{d + d_{\mathrm{o}}}\right] \\ &= i_{\mathrm{o}} \exp\left[\frac{(\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}})\alpha(V - V_{\mathrm{o}})}{d + d_{\mathrm{o}}}\right]. \qquad (12) \end{aligned}$$

Now, V and V_{o} are the potentials of the metal and inner Helmholtz layer with respect to the same reference point. If the increase of the positive charge density in the metal surface with the applied current density is counterbalanced only by an increase of negative charge density in the inner Helmholtz plane, then V_{o} is independent of current density, as observed. V is the potential of the anode with respect to a reference electrode (to which V_{o} also refers). $V - V_{\mathrm{o}}$ in Equation 12 can now be directly related to the $V - V_{\mathrm{o}}$ in the observed rate equation.

For completeness of the discussion, the rate equation for the same model with two double layers but with the rate determining step either at the metal/anodic film interface or within the film itself is given here. It is

$$\begin{aligned} i &= N\nu ze \exp\left[\frac{-\Delta G^*}{RT}\right] \exp\left\{\frac{ze\lambda(\phi_{\mathrm{m}} - \phi_{\mathrm{i}})}{kT[d + (\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}})\delta]}\right\} \\ &= i_{\mathrm{o}} \exp\left[\frac{\alpha(V - V_{\mathrm{o}})}{d + d_{\mathrm{o}}}\right]. \qquad (13) \end{aligned}$$

Note, that Equations 12 and 13 differ only by the factor $\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}}$ in the denominator in the exponent of Equation 12. The exchange current densities in both equations contain the same terms. However, the numerical values of N are expected to be different. N in Equation 12 can be related to the concentration of ions in the solutions that are participating in the rate determining step, as will be discussed below.

A second comment related to Equation 10, and now also to Equation 12, is that for the process at the anodic film/solution interface as the rate determining step, the experimentally obtained parameter n should be compared to $\epsilon_{\mathrm{i}}kT/(\epsilon_{\mathrm{f}}ze\lambda)$ instead of to $kT/(ze\lambda)$, as usually done in various analyses of anodic film formation. From Equations 12 and 13 it follows that n can be related to $kT/(ze\lambda)$ only when the rate determining step is located either at the metal/anodic film interface or within the anodic film itself. In the first paper [1], λ was calculated from Equation 13, i.e. without taking $\epsilon_{\mathrm{i}}/\epsilon_{\mathrm{f}}$ into account since the process at the anodic film/solution interface was not considered at that time to be the rate determining step. The half-jump distance then obtained was 2.3 Å, i.e. about twice as large as expected. For the rate determining step at the anodic film/solution interface, Equation 12 should be used and λ should be corrected by the factor $\epsilon_{\mathrm{i}}/\epsilon_{\mathrm{f}}$. With the best estimates of ϵ_{i} (= 6) and ϵ_{f} (= 8.6 [11]), λ is now calculated as 1.6 Å. This value is far more reasonable for a half-jump distance.

It is interesting to note that values calculated for λ in anodic oxide film formation were frequently significantly higher than expected. For the anodic growth of hydroxide film at Pt and Ni electrodes, higher values for λ than expected were also obtained if no correction was made for $\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}}$. At these electrodes it was demonstrated recently that the rate determining step is located at the oxide film/solution interface [5, 12]. If the correction of λ for $\epsilon_{\mathrm{f}}/\epsilon_{\mathrm{i}}$ was made then more reasonable half-jump distances would have been obtained. A question can be asked about whether the values of λ can be used as an additional criterion to discriminate between the rate determining steps. This will depend on the accuracy with which parameter n can be determined and how well the dielectric constants are known. With well controlled experimental conditions and a reasonably accurate determination of surface roughness, it appears possible to determine n with sufficient accuracy. If the dielectric constants are known reasonably well, an attempt may be made to discriminate between the rate determining steps.

The observed dependence of i_{o} on the concentration of Na_2S can now be analysed by comparing Equations 7 and 12. The only factor in the exchange current density that is expected to depend on the concentration is N. This factor can be calculated from the activation energy, ΔG^*, and i_o at a given concentration. ΔG^* was previously determined to be 10.6 kcal mole^{-1} [1]. With $\nu = 10^{12}$ s^{-1}, as usually taken for a vibrational frequency [13], and $z = 2$, for Cd^{2+} or S^{2-} as the species migrating in the rate determining step, N values are equal to 5×10^5, 5×10^6 and 3×10^7 cm^{-2} for 0.01, 0.1 and 1.0 mol dm^{-3} Na_2S solution, respectively. As expected, N for the 0.01 mol dm^{-3} solution is 10 times less than for the 0.1 mol dm^{-3} solution. N for the 1.0 mol dm^{-3} solution is somewhat less than expected in comparison with 0.1 mol dm^{-3} solution. This deviation at the highest concentration is due most probably to the fact that concentrations rather than activities are taken in these calculations. This also provides a justification for the assumption made above that a linear dependence exists between $(\partial V/\partial q)_{i=1}$ and log $c(Na_2S)$. Evidently, N in the exchange current density is the factor that relates linearly to the concentration of Na_2S.

It is possible to learn about the species participating in the rate determining step by the following approximate analysis. N is first converted to the concentration in mole cm^{-2}, or surface coverage, of the species in the inner Helmholtz plane that are participating in the rate determining step. This concentration can then be compared to the concentrations of various species in the bulk of the solutions [5, 12]. Now, N of 5×10^6 cm^{-2} in a 0.1 mol dm^{-3} solution of Na_2S corresponds to 7.7×10^{-18} mole cm^{-2}. This is indeed a very low surface concentration. (So low a concentration indicates the absence of specific absorption.) Assuming that the thickness of a monolayer of the species in the inner Helmholtz layer is 2 Å, this surface concentration can be expressed as the bulk concentration. It is 4.2×10^{-7} mole dm^{-3}. For 0.01 and 1.0 mol dm^{-3} Na_2S solutions, the bulk concentrations, calculated in the same way, equal 4.2×10^{-8} and 2.3×10^{-6} mole dm^{-3}, respectively. These concentrations should now be compared to the concentration of various sulphur containing species in solution.

S^{2-} ions from the dissociated Na_2S molecules hydrolyse to HS^- according to

$$HS^- \rightleftarrows S^{2-} + H^+. \qquad (14)$$

Since the dissociation constant for this process is very low, only 1.2×10^{-15} [14], and the equilibrium is almost entirely shifted to the left, it can be assumed that most of the S^{2-} ions, which are formed by the dissociation of Na_2S, are hydrolyzed to HS^-. The concentration of HS^- may then be taken as equal to the concentration of Na_2S. The concentration of S^{2-} in 1.0 mol dm^{-3} Na_2S + 1.0 mol dm^{-3} $NaHCO_3$ at pH 9 is then essentially equal to 1.2×10^{-6} moles dm^{-3}. In 0.1 and 0.01 mol dm^{-3} Na_2S solutions, the concentrations of S^{2-} are equal to 1.2×10^{-7} and 1.2×10^{-8} mole dm^{-3}, respectively. These concentrations are surprisingly close to the concentrations of the species reacting in the rate determining step as calculated in the preceding paragraph from N. This simple correlation of N, obtained from i_o and ΔG^*, and calculated concentrations of S^{2-} confirm that the rate determining step is located at the anodic film/solution interface and shows that S^{2-} rather than HS^-, is the species participating in the rate determining step. As S^{2-} ions in the inner Helmholtz plane are consumed in the process of growth, they are replenished not by the diffusion of S^{2-} from the bulk of the solution, which is a slow process, but rather by the fast dissociation of HS^- in or close to the double layer.

Different values for the dissociation constant have been reported. They range from 1.1×10^{-12} [15] to 1.0×10^{-17} [16]. In the above calculation, a value close to the middle of the range, 1.2×10^{-15} [14], was used. Different values for the dissociation constant will affect the calculated concentrations of S^{2-}. The wide range of the dissociation constant tends to decrease, and even annul, the significance given to the agreement discussed above. However, the concentration of S^{2-}, as calculated with any dissociation constant, is so much closer to the concentrations of the species participating in the rate determining step, as determined from N, than the concentration of HS^-. The concentration of HS^- is at least a few orders of magnitude higher than the concentration of the ions participating in the rate determining step. Thus, irrespective of the scattering of the values for the dissociation constant, it appears that S^{2-}, and not HS^-, is the species participating in the rate determining step. On the basis of the present data, the dissociation constant given by Kolthoff and Menzol [14] is preferred.

A problem with the comparison of the concentrations of S^{2-} calculated from the dissociation constant with those obtained from the values of N is that the former give the concentrations in the bulk of the solutions, whereas the latter represent the concentration in the inner Helmholtz plane. Because there is a potential difference across the outer Helmholtz layer, it seems hardly probable that these two concentrations can be compared. The concentration of ions in the inner Helmholtz plane can be related to the concentration in the bulk by the condition of electrochemical equilibrium across the outer Helmholtz layer. It has been shown in studies of anodic oxide films at Pt [5] and Ni [12] electrodes, both of which grow according to the same mechanism and rate determining step as the CdS films, that this equilibrium condition is included in the activation energy as an additional energy term. Consequently, values of N, calculated with the help of this overall activation energy, are not the densities of ions in the inner Helmholtz layer. They are already 'corrected' for the effect of the potential difference across the outer Helmholtz layer and should relate to the concentration of the ions in the bulk of the solution. The calculations of the concentrations and the comparisons of the concentrations discussed in the preceding paragraphs, therefore, are justified.

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