

A STUDY OF THE INHIBITED REACTION OF ALUMINIUM SINGLE CRYSTAL IN AQUEOUS SOLUTION OF SODIUM HYDROXIDE

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The effect of sodium tartrate and calcium ions on the kinetic behaviour of the $\{110\}$ plane of an aluminium single crystal in aqueous solution of NaOH was investigated in dependence on the concentrations of the substances added, and optimum concentrations for attaining the highest inhibiting effect were established. The effect of temperature and concentration of NaOH on the inhibiting efficiency was also examined. The mechanism of the inhibiting effect is discussed.

Aluminium corrosion in alkaline media and its inhibition have been largely studied on polycrystalline material¹⁻¹⁰. The effect of water on the corrosion of aluminium single crystal has been examined by Lelong and Hérenguel¹¹, the chemical behaviour of aluminium single crystal in alkaline media has been studied by us previously^{12,13}. Inhibition of the reaction of aluminium single crystal in alkaline solution, however, has not been as yet described.

The present work is concerned with the inhibited dissolution of an aluminium single crystal with an oriented section in the $\{110\}$ plane in aqueous solution of sodium hydroxide, with regard to the fact that owing to its purity and well-defined surface, a single crystal is better suited to this study than a polycrystalline material. The aim of the experiments was to examine the effect of sodium tartrate in the absence and in the presence of Ca^{2+} ions (added as CaCl_2) on the kinetic behaviour of an aluminium single crystal in aqueous solution of NaOH, find an inhibitor mixture exhibiting the highest inhibiting efficiency at a chosen temperature and NaOH concentration and evaluate changes in the inhibiting efficiency of this mixture with varying temperature and NaOH concentration.

EXPERIMENTAL

The experimental arrangement and methodology have been described in ref.¹². The reaction rate $v = \Delta m / \Delta t$ was derived from the slope of the straight line plot of dependence of the amount of aluminium dissolved from a unit area (in kg m^{-2}) on time (in h). The inhibiting effect was evaluated as⁹

$$I = (v_0 - v) / v_0 \quad (1)$$

and expressed in per cent values; here v_0 and v are the reaction rates in the absence and in the presence of inhibitor, respectively. The temperature of 298.2 K and NaOH concentration of 1 mol dm^{-3} were chosen as the basic conditions. The results of kinetic measurements reported in this paper are averages of three replicate measurements, their reproducibility being 5–7%.

RESULTS AND DISCUSSION

Effect of Sodium Tartrate on the Course of Aluminium Dissolution in NaOH

The time course of dissolution of Al {110} remained linear over the interval of 0–2 hours during the investigation of all concentration and temperature dependences, some of which are presented in Fig. 1. This is apparently due to the establishment of a steady state at the metal/electrolyte interface, the corrosion products formed being transported off into the reaction mixture bulk.

The effect of sodium tartrate on the dissolution of Al {110} was investigated over the tartrate concentration region of 10^{-5} – $10^{-1} \text{ mol dm}^{-3}$. The dependences are shown in Fig. 2. The inhibiting efficiency was highest (though low) at tartrate concentrations of 10^{-4} – $10^{-2} \text{ mol dm}^{-3}$, whereas at concentrations in excess of $10^{-2} \text{ mol dm}^{-3}$ a gradual stimulation of the dissolution process was observed. The slight inhibiting effect of sodium tartrate can be interpreted in terms of the donor-acceptor properties of the metal-ligand system. In a strongly alkaline solution,

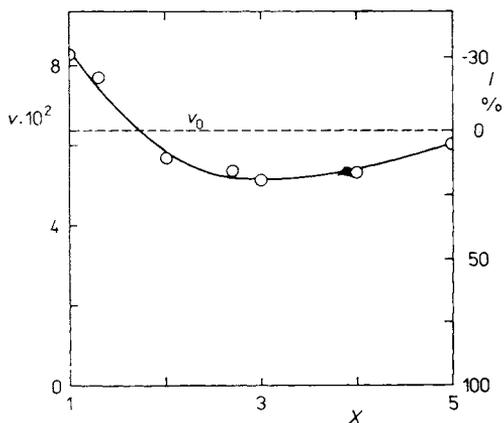


FIG 1

Time dependence of mass m (kg m^{-2}) of Al {110} dissolved in 1M-NaOH at 298.2 K; $c(\text{C}_4\text{H}_4\text{O}_6\text{Na}_2)$, $c(\text{CaCl}_2)$ (mol dm^{-3}): 1 0, 0; 2 10^{-1} , 0; 3 $2 \cdot 10^{-3}$, 0; 4 $1 \cdot 10^{-3}$, $1 \cdot 10^{-3}$

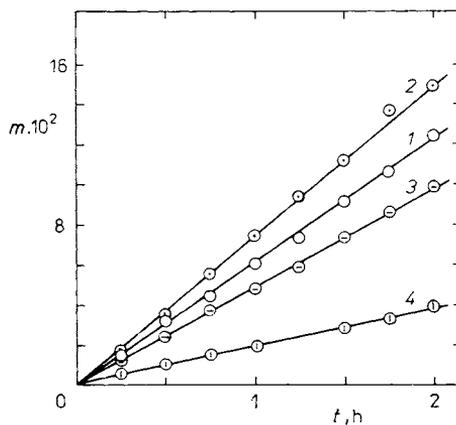


FIG. 2

Dependence of rate of dissolution v ($\text{kg m}^{-2} \cdot \text{h}^{-1}$) of Al {110} (inhibiting efficiency I) in 1M-NaOH at 298.2 K on X ($\equiv \log(1/c(\text{C}_4\text{H}_4\text{O}_6\text{Na}_2))$). Dashed line refers to v_0 in the absence of inhibitor

conditions exist for sodium tartrate to occur in its ionic form. With regard to the negative charge at the aluminium surface¹⁴, it can be assumed that the electrostatic repulsion of the tartrate anion will counteract its tendency to adsorb on the metal surface via the oxygen lone electron pairs, so that this adsorption, associated with an inhibiting effect, will be not very pronounced. The stimulating effect of sodium tartrate can be so explained that by its tendency to adsorb, the anion stabilized in aqueous NaOH by hydration effects transports towards the metal surface a component of the medium promoting its corrosion disturbance; the concentration of this component in a close vicinity to the surface increases to the extent that the depolarization reaction, associated with evolution of hydrogen⁸, is thereby accelerated.

Effect of Addition of Calcium Ions on the Inhibiting Efficiency of Sodium Tartrate

For enhancing the slight inhibiting effect of sodium tartrate, calcium ions were added with a view to combining the effect of electrostatic attraction with that of the donor-acceptor interaction: since Ca^{2+} ions are preferentially adsorbed on the negatively charged aluminium surface^{8,14}, the negative charge of the latter is lowered, whereby the adsorption of the organic anion, forming a chemisorbed protective complex at the metal surface⁵, is facilitated.

The tartrate-to-calcium ion concentration ratio was varied while maintaining the sum of their concentrations constant at $2 \cdot 10^{-3} \text{ mol dm}^{-3}$, and the rate of dissolution of Al {110} was found lowest if the two substances were present in equal concentrations (Fig. 3). Clearly, the Ca^{2+} ions facilitate the formation and stabilization of the forming surface complexes, whose stability depends appreciably on the mutual concentration ratio of the substances.

The rate of dissolution of Al {110} was also measured in dependence on the concentration of calcium chloride or sodium tartrate while keeping the concentration of the other component constant at $10^{-3} \text{ mol dm}^{-3}$ (Fig. 4). Increasing concentration of the variable component brought about decrease in the dissolution rate down to a limiting value, attained at a concentration of $10^{-3} \text{ mol dm}^{-3}$ in either case, i.e., equal to that of the unvaried component. Thus the equimolar ratio again appears as optimum, bearing out the hypothesis that the mechanism of the effect of the two substances is adsorption controlled.

The decrease in the reaction rate implies an increase in the inhibiting efficiency, up to a limiting value (Fig. 4); the dependence of this quantity on the variable concentration c_i can be described by a relation analogous to the adsorption isotherm⁹, viz.

$$I = I_{\max} c_i / (a + c_i), \quad (2)$$

where I_{\max} is the limiting inhibiting efficiency and a is a parameter whose value,

determined from the plot of c_i/I vs c_i , is $7.5 \cdot 10^{-5} \text{ mol dm}^{-3}$ for variable concentration of sodium tartrate and $13.4 \cdot 10^{-5} \text{ mol dm}^{-3}$ for variable concentration of calcium chloride.

Effect of Temperature on the Inhibiting Efficiency

The inhibiting effect of the mixture with the optimum composition was also studied at various temperatures over the region of 288.2–313.2 K by comparing with data obtained in the absence of the inhibitor mixture¹². The data are given in Table I. The value of the apparent activation energy of the inhibited reaction, $E_1^* = 71.1 \text{ kJ} \cdot \text{mol}^{-1}$, obtained from the linear plot of $\log v$ vs $1/T$ indicates that the inhibitor mixture does not affect the nature of the controlling phenomenon, i.e., also the inhibited reaction proceeds in the kinetic region similarly as observed in refs^{9,10}. The increase in the apparent activation energy as compared to that of the uninhibited system¹² ($E^* = 48.9 \text{ kJ mol}^{-1}$) is consistent with the inhibiting effect of the mixture used.

From the point of view of interpretation of the effect of the inhibitors on the kinetic behaviour of Al {110} it is of importance that over the temperature region examined, the inhibiting effect of the optimum mixture remained preserved, only a slight

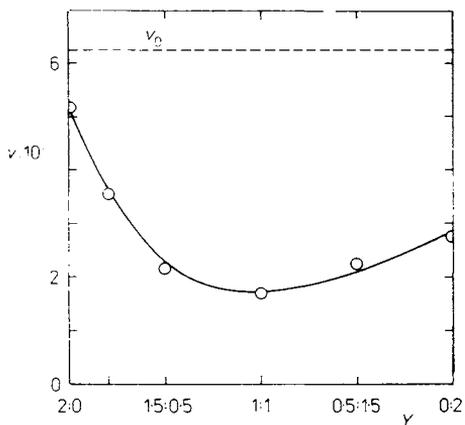


FIG. 3

Dependence of rate of dissolution v ($\text{kg m}^{-2} \cdot \text{h}^{-1}$) of Al {110} in 1M-NaOH at 298.2 K on the tartrate-to-calcium ion concentration ratio Y ; $c(\text{C}_4\text{H}_4\text{O}_6\text{Na}_2) + c(\text{CaCl}_2) = 2 \cdot 10^{-3} \text{ mol dm}^{-3}$. Dashed line refers to v_0 in the absence of inhibitor

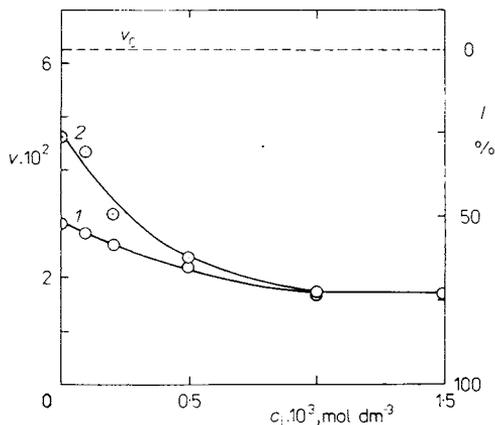


FIG. 4

Dependence of rate of dissolution v ($\text{kg m}^{-2} \cdot \text{h}^{-1}$) of Al {110} (inhibiting efficiency I) in 1M-NaOH at 298.2 K 1 on $c(\text{C}_4\text{H}_4\text{O}_6\text{Na}_2)$ at $c(\text{CaCl}_2) = 10^{-3} \text{ mol dm}^{-3}$, 2 on $c(\text{Ca}^{2+})$ at $c(\text{C}_4\text{H}_4\text{O}_6\text{Na}_2) = 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

decrease in the inhibiting efficiency (about 20%) being observed with increasing temperature. This again is consistent with the concept of the inhibitor being bonded to the metal surface by chemisorption, because if physical adsorption were involved, temperature increase would bring about desorption of the inhibitor and loss in its protective effect.

Effect of Hydroxide Concentration on the Inhibiting Efficiency

The inhibiting effect of the mixture whose composition was optimum in 1M-NaOH dropped rapidly with increasing sodium hydroxide concentration (Fig. 5); after attaining the maximum dissolution rate the system behaved as free from inhibitors^{1,2},

TABLE I

Effect of temperature on the rate of dissolution of Al {110} in 1M-NaOH; $c(\text{C}_4\text{H}_4\text{O}_6\text{Na}_2) = c(\text{CaCl}_2) = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$

T K	$v_0 \cdot 10^2$ $\text{kg m}^{-2} \text{ h}^{-1}$	$v \cdot 10^2$ $\text{kg m}^{-2} \text{ h}^{-1}$	I %
288.2	2.6	0.5	80.8
293.2	3.7	0.9	75.7
298.2	6.3	1.5	74.6
303.2	8.4	2.3	72.6
308.2	11.6	3.4	70.7
313.2	14.0	4.4	68.6

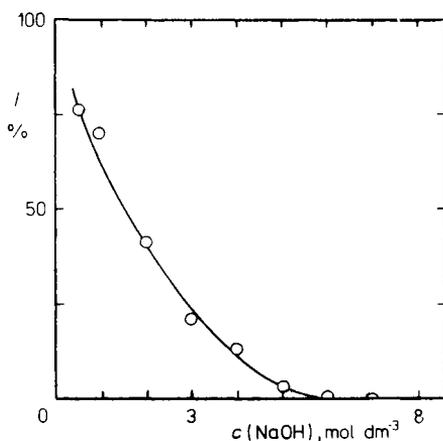


FIG. 5

Dependence of inhibiting efficiency of mixture of sodium tartrate and calcium ions ($c(\text{C}_4\text{H}_4\text{O}_6\text{Na}_2) = c(\text{CaCl}_2) = 1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) with respect to dissolution of Al {110} at 298.2 K on the concentration of sodium hydroxide

¹², i.e., the inhibiting effect of the substances added was nil. This lowering and ultimately vanishing of the inhibiting effect of the sodium tartrate-calcium chloride mixture with increasing sodium hydroxide concentration is probably due to a proportion change in the competition of the process of restoration of the metal surface and the process of adsorption of inhibitor on it: while the rate of the former process increases with increasing aggressivity of medium, that of the latter process does not vary, whereupon the inhibiting effect decreases correspondingly.

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