

## The Effect of Molybdate Ion on the Behaviour of Tin in Sodium Hydroxide Solution

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The effect of molybdate ion on the potential of tin electrode was measured in different concentrations of sodium hydroxide solutions and the steady state potential vs. pH of the solution showed that tin behaves as Sn/SnO couple. The potential of tin was measured also in the pure alkali and containing different concentrations of molybdate ion. The results showed that potential decreases with increase of molybdate concentrations indicating the acceleration of cathodic reaction. Anodic polarisation measurements showed that increase of molybdate ion concentration delays the onset of passivity. Cathodic polarisation curves were also measured. The results confirmed the acceleration of the cathodic reaction with increase of molybdate concentration.

### INTRODUCTION

In the study of the anodic behaviour of tin in alkaline solution, Forester and Dolch<sup>1</sup> observed that thin anodes passed into sodium hydroxide solutions as divalent ions until a definite concentration was obtained. At this point the potential changes almost instantaneously to a more positive value; the dissolved tin was oxidised to the tetravalent state and oxygen was liberated at the anode which had become passive. Volessi<sup>2</sup>, on the other hand, found that tin anodes in sodium hydroxide solutions dissolved directly as sodium stannite and sodium stannate, and the electrode became covered with powderlike tin metal. Awad and Kassab<sup>3</sup> studied the potential of tin anode with current density in different concentrations of sodium hydroxide, and showed that tin oxidised to stannous oxide which dissolves in alkali forming sodium stannate.

In the present investigation the effect of molybdate ion on the behaviour of tin in sodium hydroxide was studied.

### EXPERIMENTAL

The polarisation measurements on the tin electrode were carried out in a cell described in an earlier publication<sup>4</sup>. This cell is constructed from the arsenic-free hard borosilicate glass, Hysil, and thus it permits the vigorous purification of the solutions under investigation through pre-electrolysis. For this purpose we used a platinum electrode (2 cm<sup>2</sup> platinum sheet welded to a platinum wire sealed to glass).

The electrodes were prepared from extra-pure tin rods, 3 mm in diameter (Shering Kahlbaum Company). The electrode area was 1 cm<sup>2</sup>. Each run was

carried out with a new electrode. All solutions were prepared from A.R. materials. Before each run, the cell was cleaned with a mixture of nitric and sulphuric acids (A.R.) and thoroughly washed with a conductance water.

For measuring the corrosion potential, the potential of the tin 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  $\pm 0.5^\circ\text{C}$ .

### RESULTS AND DISCUSSION

The potential of tin electrode was measured in 0.1–2 M sodium hydroxide solutions. In Fig. 1 the steady state potentials, observed 3 hrs after immersion are

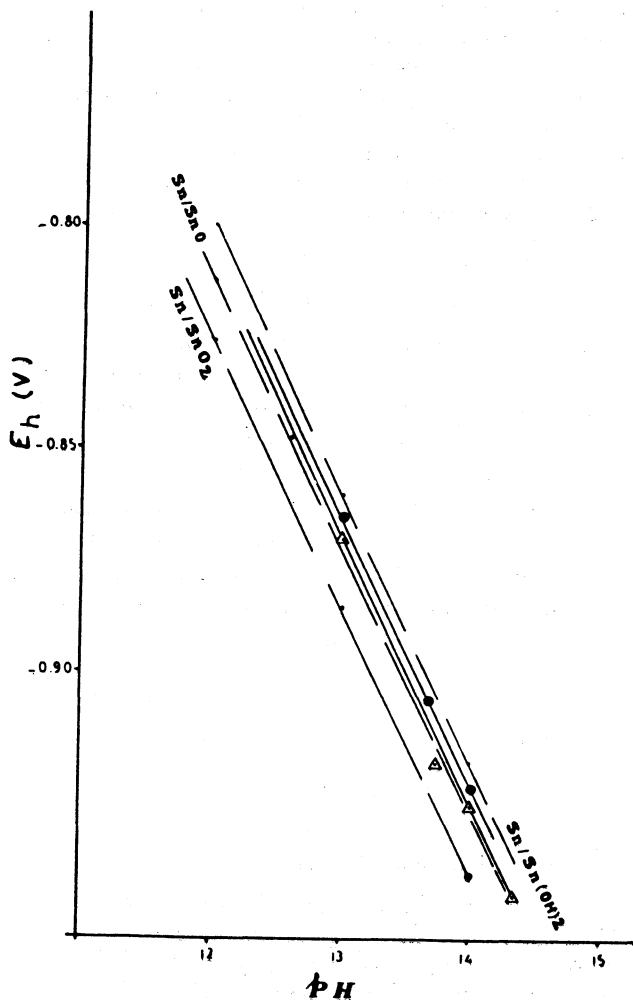
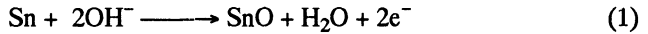


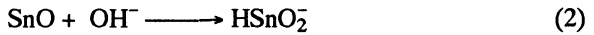
Fig. 1. Effect of pH on the  $E_h$  potential of tin in ▲ pure NaOH, ●  $\text{MoO}_4^{2-}$

plotted as a function of the pH values of the solution. The dotted lines in this figure represent the theoretical potential/pH relation of the Sn/SnO, Sn/Sn(OH)<sub>2</sub> and Sn/SnO<sub>2</sub> systems. These systems are characterised by standard potentials (at 1 M OH<sup>-</sup>) of -0.932, -0.920 and -0.945 volt respectively. It is clear from Fig. 1 that the experimental values coincides fairly with that of Sn/SnO couple.

Thus, the anodic reaction is represented by



The corrosion rate of the metal,  $V_{\text{corr}}$ , was measured in the pure alkali solution and the results showed that the metal corrodes slightly in these solutions. One can therefore conclude that the oxide is not quite protective, due most probably to dissolution in the alkaline solutions forming stannite through the action of OH<sup>-</sup> ions.



It follows that the metal surface is partially oxide free.

**Effect of MoO<sub>4</sub><sup>2-</sup>**

To test the effect of molybdate on the corrosion potential of tin, the potential was measured in 0.1–2 M NaOH containing 0.001–1 M Na<sub>2</sub>MoO<sub>4</sub>. In Fig. 2 the

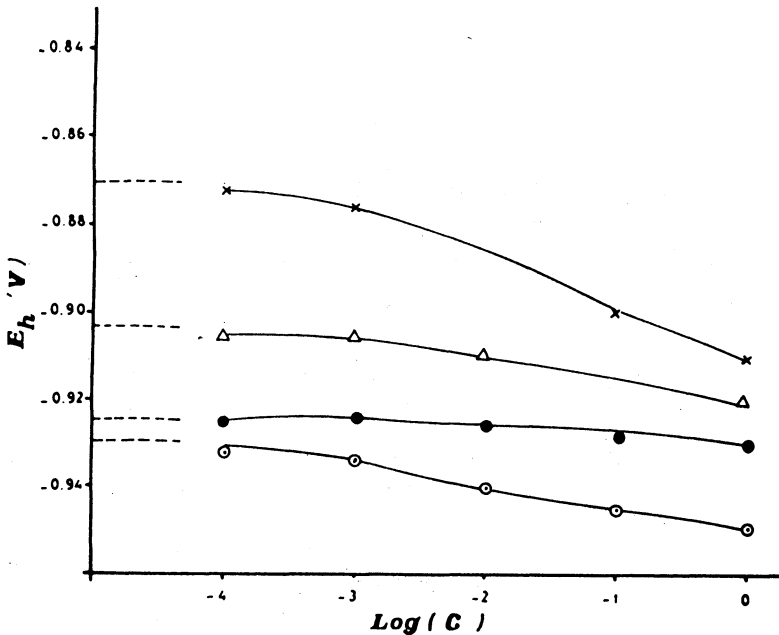


Fig. 2 Effect of concentration of Na<sub>2</sub>MoO<sub>4</sub> containing ⊙ 2 M NaOH, ● 1M NaOH Δ 0.5 M NaOH and × 0.1 M NaOH

steady state potentials are plotted as a function of the molar concentration of molybdate, for the different alkali solutions. In this figure the steady state potentials in the corresponding NaOH solutions are represented by dotted lines; these are taken as reference values to those obtained in presence of  $\text{MoO}_4^{2-}$ . From Fig. 2, it is inferred that the potential decreases with increase of molybdate concentration. The above results are interesting as far as Brasher's work is concerned.<sup>5</sup> The shift of potential to more negative values denotes an acceleration of the cathodic reaction.

### Anodic polarisation

In order to throw light on the corrosion behaviour of tin in the molybdate solution anodic polarisation measurements were carried out in 2 M NaOH containing 1, 0.1, 0.01 and 0.001 M molybdate. The results are given in Fig. 3. Polarisation was conducted within the current density range  $10^{-4}$ – $10^{-1}$  A/cm<sup>2</sup>.

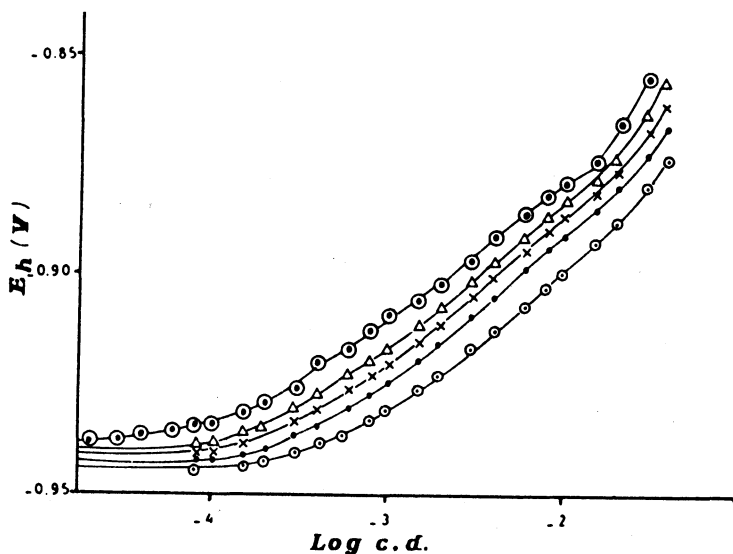
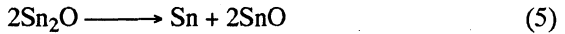
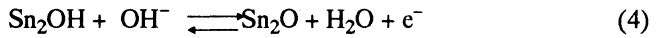
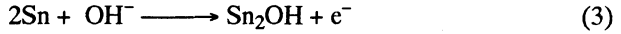


Fig. 3. Anodic polarisation of Sn in 2 M NaOH containing  $\circ$  1 M  $\text{MoO}_4^{2-}$ ,  $\bullet$  0.1  $\text{MoO}_4^{2-}$   $\times$  0.01  $\text{MoO}_4^{2-}$ ,  $\Delta$  0.001 M  $\text{MoO}_4^{2-}$ ,  $\ominus$  Pure NaOH

Generally, the polarisation curves exhibit a region of stationary potential, which extends up to a certain current density, dependent on the molybdate concentration. The potential then exhibit a linear logarithmic relation, with a slope of about 0.03V. At higher currents, the potential shows rapid increase with the current density indicating the onset of passivity.

As is obvious from Fig. 3, the polarisation curve is shifted to more negative potential with increase of the molybdate concentration. This is consistent with the result of measurements of corrosion potential [c.f. Fig. 2]. The observed Tafel slopes are almost equal to the values previously obtained for the anodic dissolution

of tin in pure alkali solutions (Awad and Kassab<sup>3</sup>). These results had been taken to indicate that the metal dissolves in two successive steps as follows:



The last reaction is the rate determining step. The observation of the same Tafel slope in the presence of molybdate indicates that this ion does not change the mechanism of the anode reaction. However, as evident from Fig. 3, the linear logarithmic part is extended to higher currents as the molybdate concentration is increased, a fact which means that increase of  $\text{MoO}_4^{2-}$  concentration delays the onset of passivity.

The onset of passivity is usually ascribed to the incomplete removal of the oxide as stannite. Hence, the oxide accumulates on the anode surface, leading to rapid increase of potential. Accordingly, one expects that increase of the alkali concentration (at a given molybdate content), delays the onset of passivity. Therefore, potential current density relations were measured in 1 M  $\text{Na}_2\text{MoO}_4$ , in presence of 0.1, 0.5, 1 and 2 M NaOH. As evident from Fig. 4, the current

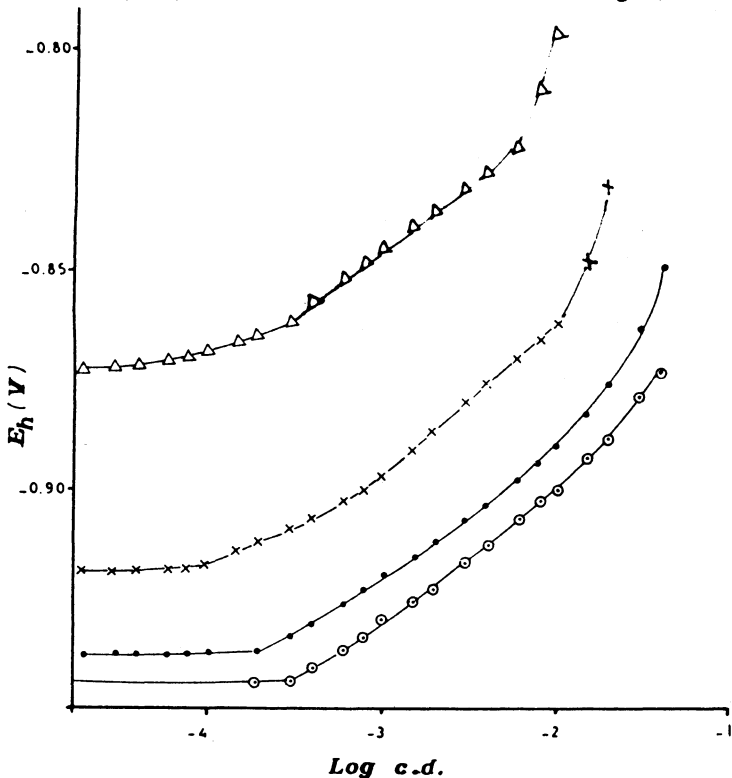


Fig. 4. Anodic polarisation of Sn in 1 M  $\text{MoO}_4^{2-}$  containing in  $\odot$  2 M NaOH,  $\bullet$  1 M NaOH,  $\times$  0.5 NaOH,  $\Delta$  0.1 NaOH.

density at which the metal is passivated, increases, although slightly, with increase of the alkali concentration.

### Cathodic Polarisation

Cathodic polarisation measurements were carried out in 2 M NaOH solutions, in presence of 0.001, 0.01, 0.1 and 1 M  $\text{Na}_2\text{MoO}_4$  and the results are shown in Fig. 5. It is evident that the potential remains stationary within a current density range, that increases with increase of the molybdate concentration. Then the potential decreases markedly with the current density. The stationary potential decreases with increase of molybdate concentration, in good agreement with the results of  $E_{\text{corr}}$  measurements [c.f. Fig. 2].

The observed stationary potential in Fig. 5 ranges from  $-0.933$  to  $-0.936$  V. These values are near the standard potential for hydrogen evolution  $-0.858$  V.

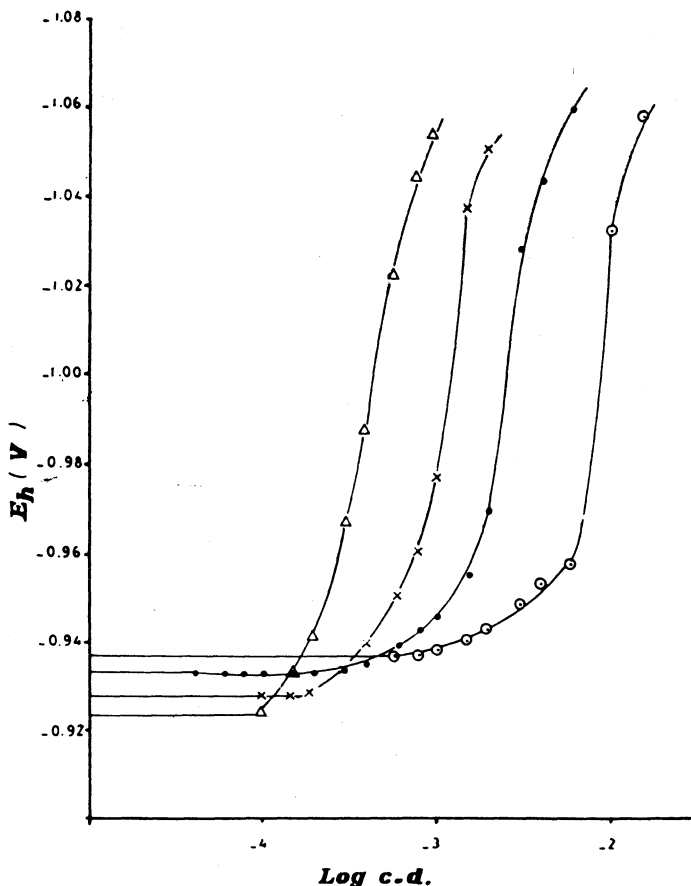


Fig. 5. Cathodic polarisation of Sn in 2 M NaOH containing  $\odot$  1 M  $\text{MoO}_4^{2-}$ ,  $\bullet$  0.1  $\text{MoO}_4^{2-}$ ,  $\times$  0.01  $\text{MoO}_4^{2-}$  and  $\Delta$  0.001  $\text{MoO}_4^{2-}$

So, the cathodic reaction is the evolution of hydrogen. Since the standard potential for the reduction of molybdate is  $-0.6\text{ V}$  (Latimer<sup>6</sup>), it is quite possible that reduction of this ion might contribute in the cathode reaction. Hence, the potential remains constant to higher current densities as the molybdate concentration is increased.

### CONCLUSION

The potentials of tin were measured in 0.1–2 M NaOH solutions containing  $10^{-4}$ –1 M  $\text{Na}_2\text{MoO}_4$ . Results showed that the potential decreases with increase of molybdate concentration.

This indicates the acceleration of the cathodic reaction. Anodic polarisation showed that the increase of  $\text{MoO}_4^{2-}$  concentration delays the onset of passivity.

Cathodic polarisation curves were also measured; the results confirmed the acceleration of the cathodic reaction with increase of molybdate concentration.

### REFERENCES

1. F. Forester and M.Z. Dolch, *Electrochem.*, **16**, 559 (1909).
2. E. Volessi, *Boll. Soc. Enstachianaist. Sci. Univ. Camerino*, **31**, 1 (1933). *Chem. Zentr.*, **II**, 2818 (1933).
3. S.A. Awad and A.J. Kassab, *Electroanal. Chem.*, **26**, 127 (1970).
4. S.A. Awad, *Electrochim. Acta*, **7**, 677 (1962).
5. D.M. Brasher, *Nature (London)*, **193**, 868 (1962).
6. W.M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs, N.J., 2nd edn., p. 252 (1952).

(Received: 15 September 1992; Accepted: 20 October 1992)

AJC-515