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ABSTRACT

The corrosion behaviour of both vibrated and stationary tin electrodes in aerated solutions of KCl, K_2SO_4, HCl and NaOH was examined by means of potential-time measurements. The effect of temperature on the electrode potential was also studied. The results of present study indicate that the shift of corrosion potential becomes more negative for the vibrated one than its values for the stationary case. The potential-temperature diagrams obtained within the temperature range 25-60 C_0 were interpreted in the light of the theory of lattice defects. The E'_o values vary linearly with temperature with a coefficient of -3 mV/Cs. The potential is governed by the $Sn/Sn^{++++}/SnO^{++}$ system. At pH 5-11 the $Sn/Sn(OH)_2$ potential predominates, whereas at higher pH values stannite ions are formed and their activity governs the electrode potential.

INTRODUCTION

Local corrosion sometimes produces small black spots which may grow into damaging pits. The occurrence of this local corrosion has been studied by Schultz [1] and by Brennert [2] and the electrochemistry of its action on pure tin has been investigated by Hoar [3]. Both Brennert and Hoar showed that the first change on a tin surface immersed in a neutral solution was the reinforcement of the air-formed oxide film by precipitation of oxide or hydroxide at point where tin ions emerged through the film. In a more general theory of the course of pitting, Hoar [4] has pointed out that when most of the surface becomes covered by a protective film, the anodic current density on the areas still unprotected would be sufficient to cause a levelling down of pH of the solution and there by to prevent further healing of the surface pores by insoluble salts. Britton and Michael [5] reported that the local corrosion of tin by dilute chloride solution was increased by lowering the pH. Bannister [6] reported that the corrosion product on an ancient specimen of pure tin is composed of 43 % hydrated stannous oxide and 55 % anhydrous stannic oxide. Yang [7] and Thomas [8] belived that at room temperature the oxide film on tin consists of stannous oxide. The electrode surface was conceived to be covered with a thin impervious layer of tin dioxide overlayered with oxygen doublets, its lattice being most probably deficient in oxygen. The effect of temperature on such mobile oxygen layers has proved to provide a more or less similar picture regarding the mode of oxidation of metals with oxygen-deficient oxide lattices [9]. All of these studies were carried out in the case of stationary tin electrode. The present study deals with the corrosion behaviour of both stationary and vibrated tin electrode in different media.

EXPERIMENTAL

Material and methods:

The electrode used was in the form of rode of spectroscopically pure tin (Johnson and Matthey London), each 1 cm long and 1 cm in diameter. Before each measurement the electrode surface was efficiently polished to attain a smooth bright surface, thoroughly washed with redistilled water and then with the solution to be used. Experiments were made in hydrochloric acid, sodium hydroxide, potassium chloride and potassium sulphate solutions with different concentrations. All experiments were carried out at 25 °C. The behaviour of tin electrode was investigated by the potential-time technique and effect of temperature is also studied The circuit used is shown in fig. 1.

RESULTS

Potential-time results:

The steady state potential values of stationary and vibrated tin electrodes are shown in table (1).

The potential of tin electrode immersed in conc. HCl shifts towards more negative values with time for both stationary and vibrated tin electrodes. The shift of vibrated tin electrode potential immersed in concentrated hydrochloric acid (5M-4M) in the negative direction is more than observed for stationary electrode. But the trend is reversed if the electrode immersed in diluted HCl (from 1M to 10^{-1}M). The obtained results for potential of tin electrode in sodium hydroxide, potassium chloride and potassium sulphate show that the negative shift of vibrated tin electrode with time exceeds the values of stationary electrodes.

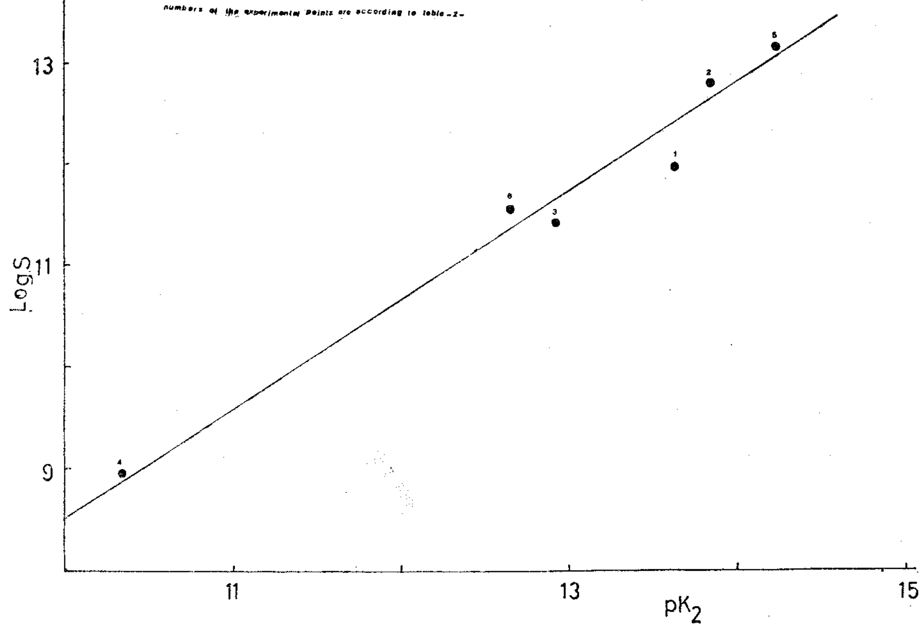

fig.1. Relationship between logS and pK$_2$

numbers of the experimental points are according to table-2-

Table 1

Solutions	Molar Concentrations	Steady state potential mV.	
		Stagnant	Vibrated f=20, A=1
KCl	1 M	-520	-525
	1×10^{-1} M	-435	-520
	1×10^{-2} M	-295	-330
	1×10^{-3} M	-285	-310
K_2SO_2	1×10^{-1} M	=540	-570
	1×10^{-2} M	-440	-530
	1×10^{-3} M	-320	-420
	1×10^{-4} M	-185	-290
NaOH	1 M	-1180	-1200
	1×10^{-1} M	-1960	-1105
	1×10^{-2} M	-760	-960
	1×10^{-3} M	-450	-639
	1×10^{-4} M	-100	-320
HCl	5 M	-685	-690
	4 M	-665	-685
	2×10^{-1} M	-515	-460
	1×10^{-2} M	-360	-250

Table 2. Steady-state potential results for stagnant and vibrated tin electrode at different amplitude and/constant frequency.

Solutions	Molar Conc.	Steady-state potential mV.			
		stagnant		vibrated f=10	
			1 amp.	2 amp.	3 amp.
KCl	1×10^{-1} M	-495	-490	-525	-510
K_2SO_4	1×10^{-2} M	-470	-370	-415	-420
NaOH	1×10^{-1} M	-1060	-1000	-870	-1005
HCl	2×10^{-1} M	-515	-300	-305	-310

From fig. (2, 3) and table (2) it is clear that the effect of varition of different amplitude at constant frequency (f=10), leads to a maximum increase at amplitude = 2 and f= 10 for KCl. In case of K_2SO_4, the potential increases with increasing amplitude. But in NaOH solution the potential decreases by increasing the amplitude. Further increase of amplitude leads to increase in potential. This indicates that the product of amplitude x frequency or the velocity of electrode affects its potential. Figs. (4), (5), (6) and (7) shows the relationships between steady state potential values and logarithm of molar concentration of NaOH, HCl, K_2SO_4 and conc. HCl respectively in stationary and vibrated case. The steady-state potential of tin electrode shifts yo more active values (towards negative direction) with increasing the molar concentration of solution. It is also shown that the steady-state potential has highly negative values in vibrated case comparing with those obtained for the stationary electrode potentials at the same concentration.

Effect of Temperature.

The results obtained for the study of temperature on stationary tin electrode show that the potential varies with time at all the investigated temperatures within narrow limits, showing drifts towards more active values. Steady-states are approached within 2-3 hours from immersion in the tested aerated solutions. By plotting E_H-pH plots obtained with electrode subjected alternately to the reducing action of hydrogen are all characterized by a sudden potential jump occurring at about pH 11-13 at 30 C^o.

Table 3

pH values	4	5	6	7	8	9	10	11	12	13
EH mV.	440	480	510	580	650	700	780	785	790	1000

The Eo' values which obtained by extrapolating the corresponding E_H-pH plots for tin electrode are shown in table (4).

Table 4

Temperature	25°	30°	35°	40°	45°	50°	55°	60°
E'_0 mV.	485	480	467	452	453	390	475	445

By plotting Eo' against temperature, fig. (8) obtained which passes through a minimum and a maximum within the investigated temperature range 30-50°.

DISCUSSION

Potential-time discussion

The results of the present study in both stagnant and vibrated electrode indicated that the potential of tin metal depends on the diluted range from 10^{-4} to 1M. The relation between steadystate potential "E" and logarithm of molar concentration "C" of the aggressive anions in the concentration range 10^{-4} to 1M is approximately of the form

$$E = a - b \log C$$

where (b) is approximately constant and equals 125 mV. and (a) is a constant depends upon the nature of the anion. From fig. (4) it is obvious that solution of NaOH is more aggressive in both stagnant and vibrated cases.

It is well known that the hydrogen overpotential of tin is very large; it follows from this that acid and moderately alkaline solutions free from oxidizing agents will be only slightly corrosive when tin is pure. Thus in acid solution in presence of air, tin is corroded by mineral acids [10] as HCl. But in case of oxidizing acids such as nitric acid are generally corrosive, and the addition of small quantities of oxidizing agent causes an increase in the corrosion to a limite values. In alkaline NaOH solutions the pH is sufficiently high to dissolve the film of oxide (SnO_2) already existing on the metal. It is also found that when the pH is sufficiently high, the dissolution of tin again depends to a large extend on the presence of oxidizing agent as in case of acid [11]. In case of KCl and K_2SO_4 solutions i.e. neutral solutions (pH=6.9 for KCl and 7 for K_2SO_4) a passivation occures, this passivation would correspond to the metal being covered with a layer of stannic oxide SnO_2. This solution causes back stains to appear on the surface of the metal [3, 12]. The oxide film pre-existing on the metal has weak points when corrosion begins and consequently a new protective layer, made up of a mixture of stannous and stannic oxides; can be formed at the point of attack, these stains occur in KCl and K_2SO_4 which do not form a precipitate with stannous ions. Thus the dissolution of tin in neutral or alkaline solutions gives rise to the formation of stannous hydroxide $Sn(OH)_2$, an amphoteric hydroxide which dissolves in acid media as stannous ions Sn^{++} and in alkaline media as stannite ions $HSnO_2^-$ and stannate ions SnO_3^{--}. A greater degree of oxidation leads to the formation of stannic hydroxide $Sn(OH)_4$, an amphoteric hydroxide which dissolves in acid media as stannic ions Sn^{++++} and in alkaline media as stannate ions SnO_3^{--}. The hydroxides $Sn(OH)_2$ and $Sn(OH)_4$ are thermodynamically less stable than the corresponding oxides SnO and SnO_2, and tend to change into these oxides with affinities respectively of 590 and 9080 cal. [13]. When a rotating electrode was used, it was found that critical potential rises considerably [14] which is in agreement with our results that the vibration accelerate the dissolution of the metal [15].

Effect of Temperature.

The potential recorded by Sn electrode after being subjected to the reducing action of hydrogen reveal that such pretreatment made the electrode surface active. The results obtained in air can be explained on the premise that Sn is oxidized forming a thin layer of SnO_2 on which oxygen from the atmosphere persists as charged doublets, rendering the electrode surface passive and contributing an overvoltage effect. The decrease of Eo' values obtained with the rod electrode from 30-40 °C, shows that raising the temperature activates the local action process set up in solution between the metal-metal oxide and the oxide-oxygen film interfaces as anode and cathode respectively, leading to increased depolarization of oxygen doublets. The fact that the potential varies linearly with temperature along the range 30-45 °C with a coefficient of-3mV. / °C shows that the electrodic behaviour is governed by a stable system presumably the SnO^{++} / Sn^{++++} oxidation-reduction couple. The lower temperature coefficient may be related to the counteracting oxidation effect brought about by discharged OH^- ions, thus

$$OH^- + OH^- = O + H_2O + 2e \qquad (1)$$

It has to be recognized that as long as there exists bare metal parts on the electrode surface, the process of OH^- ion discharge will be enhanced opposing thus the depolarizing effect of increasing temperature. Accordingly, a temperature would be reached at which the discharge process overweighs the desorption process, leading to increased oxidation of the bare metal parts and subsequently to the accamulation of oxygen doublets on the electrode surface rendering it passive. This behaviour is substatituted by the minimum occurring at — 43 C°, followed by sharp potential rise towards a maximum Eo' value attained at 51 °C. At temperatures higher than ~ 43 C°. oxygen evolved by the discharge process accumulates on the electrode surface after the process of oxidation has been completed leading to the observed overvoltage effect. The rapid fall of Eo' with rise of temperature from — 51 — 60 C°, indicating that the adsorbed oxygen is progressively desorbed being incapable to persist on the electrode surface at such relatively high temperature. The ease with which oxygen is desorbed suggests that the gas is loosely held to the electrode surface, presumably by Van der Waal's molecular forces, rather than being chemisorbed. This is explained on the fact that, Van der Waal's molecular forces is characterized by low heat of adsorption ranging from (5-10 kcal per mol) of gas compared with the highly value associated chemisorption from 10-100 kcal. mol^{-1} [16]. The difference in potential between the minimum and maximum values obtained at 43° and 51 °C respectively, amount to 43 mV. This value corresponds to 3.5 kcal., associating the discharge of one mole of oxygen on the electrode surface according to reaction (1), this value (3.5 kcal) which is comparable with quantity encountered in physical adsorption.

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