MECHANISM OF ANODIC DISSOLUTION OF LEAD IN SODIUM HYDROXIDE SOLUTIONS

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INTRODUCTION:

From studies on the anodic dissolution of tin in alkaline solutions[1], it was suggested that the surface tin atoms exist as diatomic molecules, a suboxide (Sn_2O) is first formed, which undergoes self oxidation to stannous oxide.

The study is now extended to lead. Although much work has been published on the electrochemical behaviour of Pb in acid solutions, its behaviour in alkaline solutions has received, relatively little attention. Jones et al[2] found that lead anodes dissolved in 1N KOH first as plumbite and then passivated by a film of PbO_2. On the other hand, Khamudkhamova[3] found that lead anodes dissolved directly in KOH solutions with the formation of $HPbO_2^-$ and PbO. After complete covering of lead surface with oxides, the potential increased, the formation of PbO_2 began and O_2 evolved.

The electrochemical behaviour of PbO in deaerated NaOH solutions has been studied by Abdul Azim et al[4]. They observed that the porosity of the initially formed PbO_2 is maximal in 2N NaOH.

It was observed that no mention is made in the literature of the kinetics of the anodic reactions of lead. In the present investigation, the mechanism of its anodic dissolution in alkaline solutions is examined.

EXPERIMENTAL:

Polarisation measurements on the lead anode were carried out in a cell (constructed from the arsenic-free hard borosilicate glass, Hysil) which permitted the rigorous purification of the solutions under investigation through anodic pre-electrolysis[5]. For this purpose a platinum anode (2 cm.^{2} platinum sheet welded to a platinum wire sealed to glass.

The electrodes were prepared from extra pure lead rods, 3 mm in diameter (Schering-Kahlbaum Company). The electrodes area was 1 cm.^{2}. 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 thorough washed with conductance water. The test solution was then introduced into the pre-electrolysis compartment of the ce and pre-electrolysis was conducted at 10^{-3} - 10^{-1} A cm.$^{-2}$ for 30 h. The lead electrode was then introduced into the anode compartment of the cell and adjusted to touch the Luggin capillary which lid, via a salt bridge, to a satura ed calomel electrode. Some of the pre-electrolysed soluti was then transferred to the anode compartment, and the Taf line was determined from low to high current densities and then downwards again. After each overpotential run, the concentration of the electrolyte was determined analytical

All measurements were carried out in an air-thermostat, the temperature of which was kept constant wit ± 0.5 °C. The current density value was calculated using apparent surface area. All potentials are recorded on the normal hydrogen scale.

RESULTS AND DISCUSSION:

The potential of the lead anode was measured 30 °C in 0.1 - 10 N NaOH as a function of the current dens

within the range of 10^{-6} - 10^{-1} A cm.$^{-2}$. At any current density the potential was constant within few minutes. In each solution, six potential-current density relations (on six electrodes and solutions) were measured; the results were reproducible to ± 5 mV. At very low anodic polarisation, the anodic potential did not change with current, and a stationary potential was measured in each of these solutions. These stationary potentials are given in Table (1) together with the pH values of the different solutions.

1. Nature of anode reaction:

The stationary potentials represent, or at least closely approach, the reversible potentials for the reaction taking place at the anode. We can, therefore, define the nature of this reaction by comparing the experimentally observed stationary potentials with the theoretical values for all possible reactions involving lead in alkaline solutions.

The following oxidation reactions have been suggested as being the most probable to occur on the surface of the lead anode,

	E^o_B (at pH 14 and 25 °C) V (NHE)	
$Pb + 2\ OH^- \longrightarrow Pb(OH)_2 + 2\ e$	-0.562	(1)
$Pb + 2\ OH^- \longrightarrow PbO + H_2O + 2\ e$	-0.580	(2)
$Pb + 3\ OH^- \longrightarrow HPbO_2^- + H_2O + 2\ e$	-0.540	(3)
$Pb + 4\ OH^- \longrightarrow PbO_2 + 2\ H_2O + 4\ e$	-0.166	(4)

The standard potentials E^o_B for the above reaction, at unit hydroxyl ion activity, are calculated from the standard free energy of formation[6] of the different products, OH^- and H_2O.

Since the standard potentials are little affected by temperature[7], the above values may be taken as the standard potentials at 30 °C. In Fig. (1), the observed potentials are plotted as a function of the pH value of the solution. The dotted lines represent the theoretical potential / pH relations

of the oxidation reactions suggested above. These are drawn on the basis that the potential varies with pH by the same gradient as that for the hydrogen electrode (60 mV at 30 °C). It is clear from Fig. (1) that the experimental potential / pH relation coincides with that of the Pb / PbO couple, indicating that the anode reaction is represented by equation (2). The oxide dissolves as plumbite through the action of OH^- ions, with the result that the electrode surface remains active.

2. Mechanism of anode reaction:

The discussion made so far indicates that the overpotential (difference between the potential measured at a given current density and the stationary potential) at the lead anode is associated with the formation of PbO. The mechanism of the reaction can be elucidated from the observed parameters and characteristics of overpotential. These are summerized below:

(a) Slope of overpotential-log current density relations:

The mean values of overpotential, η, were plotted against the logarithm of the current density; some representative relations (which are usually called Tafel lines) are given in Fig. (2). It is clear that the Tafel lines exhibit a linear logarithmic part. The mean values of the slopes of these parts amount to 28-34 mV (see Table 1).

(b) The electron number:

This is the number of electrons required to complete one act of the rate-determining step. This parameter is calculated from the exchange current of the Tafel line, i_o, and the slope of the overpotential-current density relation at low values of η; the expression for the electron number, λ, is:

$$\lambda = (RT/i_o F)(\partial i/\partial \eta)_{\eta \to o} \qquad (5)$$

Examples of the relations between η and current density at low anodic polarization are shown in Fig. (3). The slopes of such relations, together with the exchange current for the different Tafel lines and the calculated values for the electron number, are given in Table (1).

It is obvious from Table (1) that the experimental values of λ are very near to 4. This value is peculier, since on the basis of the stationary potentials, the oxidation to the tetravalent state is excluded.

Reconciliation between the dissolution of lead as plumbite and the doubled value of the electron number can be made by assuming that the surface lead atoms exist (or at least participate in electrochemical reactions) as diatomic molecules. An analogous assumption has accounted satisfactorily for the cathodic[8] and anodic[9] behaviour of tellurium and tin[1].

(c) Effect of pH on overpotential:

One of the important means which help to distinguish between the different possible mechanism is the dependence of overpotential, at a constant current density and temperature, on the pH of the solution. The overpotential of lead anodes was found to be almost independent of the alkali concentration, as is clear from Table (1), in which the values of at 10^{-3} A cm.$^{-2}$ are given. This behaviour will give an indication as to whether the suboxide is oxidised anodically:

$$Pb_2O + 2\ OH^- \longrightarrow 2\ PbO + H_2O + 2\ e \qquad (6)$$

or undergoes a self-oxidation process:

$$2\ Pb_2O \longrightarrow 2\ PbO + Pb_2 \qquad (7)$$

(d) Effect of neutral salts on overpotential:

Neutral salts affect the structure of the double layer at the anode-solution interface, and hence they affect the concentration of OH^- at that interface. It follows that they affect the velocity of the anode reaction. The effect

of neutral salts can thus exist in elucidating the proper reaction mechanism. The overpotential was measured in 0.1 and 0.3 N solutions which contain excess (1 M) Na_2SO_4. The results indicated that the Tafel line is not affected by neutral salts, for instance, the overpotentials at 10^{-3} a. cm.$^{-2}$ are the same as for the corresponding pure solutions (see Table 1). We concluded that the expression for η does not include the zeta potential (ζ).

On the basis of the above mentioned features of overpotential, the mechanism of anodic dissolution of lead in alkaline solutions was formulated as follows:

$$\text{Step I:} \quad Pb_2 + OH^- \overset{V_1}{\underset{V_1'}{\rightleftharpoons}} Pb_2OH + e \qquad (8)$$

$$\text{Step II:} \quad Pb_2OH + OH^- \overset{V_2}{\underset{V_2'}{\rightleftharpoons}} Pb_2O + H_2O + e \qquad (9)$$

$$\text{Step III:} \quad Pb_2O \xrightarrow{V_3} Pb_2 + 2\ PbO \qquad (10)$$

Reaction (10) is the rate-determing step, since it requires 4 electrons. To confirm this mechanism, the Tafel line slope is theoretically deduced and compared with the experimentally observed values. The velocities of the different steps in the anodic direction are refsrred to as V_1, V_2 and V_3, and V_1' and V_2' repreaent the velocities of the first two step in the cathodic direction. Since the velocity of the reverse of reaction (10) is negligible, the general expression for the overall rate is:

$$V_1 - V_1' = V_2 - V_2' = V_3 \qquad (11)$$

It is assumed that in the anodic direction, step II is faster than step I, and hence, reaction (9) is governed by reaction (8). It follows that:

$$V_2 = V_1 \qquad (i)$$

On the other hand, step II is assumed to be slower than step I in the cathodic direction. Thus, reaction (8) is governed by reaction (9), and accordingly:

$$V_1' = V_2' \qquad (ii)$$

Substituting V_1' by V_2' (cf. condition ii), or V_2 by V_1 (cf. condition i), equation (11) reduces to:

$$V_1 - V_2' - V_3 = 0 \qquad (12)$$

It is important to mention that if reaction (9) is sufficiently fast in the anodic direction, Pb_2OH is rapidly converted into Pb_2O, with the result that the surface concentration of Pb_2OH is neglected. On the basis of a symmetrical energy barrier, the rate V_1, which represents the rate of the anode formation of Pb_2O, is given by:

$$V_1 = k_1(1-x)[OH^-]_{d.l.}\exp(\Delta\phi F/2RT) = a_1(1-x) \quad (13)$$

where k_1 is the specific reaction rate, a_1 is the electrochemical rate constant, x is the fraction of the surface covered with Pb_2O, (1-x) is the bare fraction of the metal surface, $[OH^-]_{d.l.}$ is the activity of hydroxyl ions in the outer Helmholtz double layer; and $\Delta\phi$ is the potential difference between the electrode and this Helmholtz layer. The rate V_2', which represents the rate of cathodic reduction of Pb_2O, is given by:

$$V_2' = k_2'(x)\exp(-\Delta\phi F/2RT) = a_2'(x) \quad (14)$$

The rate of the self-oxidation process (reaction 10) is:

$$V_3 = k_3(x^2) = a_3(x^2) \quad (15)$$

The steady state corresponding to a constant coverage, current and potential, is represented by equation (12). The self-oxidation process governs the dissolution of lead under the condition[10]:

$$(a_1 + a_2') \gg 10\, a_3 \quad (16)$$

From equations (12) - (16), the total surface coverage becomes:

$$x = a_1 / (a_1 + a_2') \quad (17)$$

Under conditions when a_1 is much smaller than a_2',

$$x = a_1 / a_2' = k_1 / k_2'[OH^-]_{d.l.}\exp(\Delta\phi F/RT) \quad (18)$$

The net anodic current is given by:

$$i = 4FV_3 = 4Fk_3(k_1/k_2')^2[OH^-]^2_{d.l.}\exp(2\Delta\phi F/RT) \quad (19)$$

The tafel line slope according to equation (19) is 0.03 V at 30 °C, in agreement with the experimental values.

Equation (19) satisfies also the requirement that the overpotential is independent of the alkali concentration. This is revealed by substituting $[OH^-]_{d.l.}$ by $[OH^-]\exp(\zeta F/RT)$,

(where $[OH^-]$ is the OH^- concentration in the bulk of solution), and $\Delta\phi$ by $(\Delta\phi_r + \eta - \zeta)$, (where $\Delta\phi_r$ is the reversible potential in the given solution). Thus:

$$i = k[OH^-]^2 \exp(2\zeta F/RT) \exp(2(\Delta\phi_r + \eta - \zeta)F/RT) \quad (20)$$

and hence,

$$\eta = \text{const.} + (RT/2F)\ln i - (RT/F)\ln[OH^-] - \Delta\phi_r \quad (21)$$

Since $\Delta\phi_r = E_B - (RT/F)\ln[OH^-]$, it is clear that at a constant current density, η = constant.

The absence of ζ from equation (21) accounts also for the fact that addition of neutral salts brings about no effect on the overpotential.

Derivation of the rate equation on the basis that the suboxide is oxidised anodically (reaction 6), leads to the expression:

$$\eta = \text{const.} + (RT/2F)\ln i - (1.5RT/F)\ln[OH^-] - \Delta\phi_r \quad (22)$$

This relationship requires that addition of excess neutral salt (which causes ζ to approach zero), the overpotential decrease 30 mV for ten-fold increase of the alkali concentration. Experiment showed that η remained practically constant in 0.1 and 0.3 N NaOH containing excess neutral salts (cf. Table 1). This result supports the self-oxidation mechanism.

3. Heat of activation:

The heat of activation, $\Delta H^{\#}$ of the anode reaction at the reversible potential can be evaluated from the effect of temperature on the exchange current; the expression being:

$$d\log i_o/d(T^{-1}) = -\Delta H^{\#}/2.303R \quad (23)$$

The overpotential was, therefore, measured at 20, 30, 40 and 50 °C in 0.5, 5 and 10 N solutions. Fig. (4) shows the Tafel lines at different temperatures for the 10 N solution. The values of $\log i_o$ for the different solutions are plotted against 1/T in Fig. (5). It is obvious that the exchange current is almost unaffected with temperature; this means that the heat of activation is equal to zero. This result can be understood in the light of the theory of absolute reaction

rates, which shows that the parameter that determines the reaction rate is the free energy of activation ΔG^{*}, and not ΔH^{*}. Since $\Delta G^{*} = \Delta H^{*} - T\Delta S^{*}$, the value of ΔH^{*}, and consequently, the temperature effect on i_o, depends on the value of ΔS^{*}. In the case under consideration, ΔS^{*} is evidently negative, and its numerical value is such that $T\Delta S^{*}$ compensates for ΔG^{*}, i.e., $\Delta G^{*} = -T\Delta S^{*}$, and accordingly $\Delta H^{*} = 0$. It is reasonable that the formation of the activated complex $(Pb_2O)_2$ from two Pb_2O entities is accompanied by decrease in the order of the system, and hence, ΔS^{*} is negative, Table (2).

4. Passivity of lead:

When the current density is such that the rate of formation of plumbous oxide exceeds the rate of its chemical dissolution, the potential was found to rise rapidly, showing a tendency towards passivity. The current density at which passivity occured, increased as the concentration of the alkali hydroxide was increased.

SUMMARY:

The potential of the lead anode was measured as a function of current density in 0.1 - 10 N NaOH solutions at 20 - 50 °C.

The overpotential is independent of pH in pure solutions as well as in solutions containing excess neutral salts. From the electron number value (4), it was suggested that the surface lead atoms exist as diatomic molecules. A suboxide (Pb_2O) is first formed, which undergoes self-oxidation to PbO. This latter step governs the overall reaction rate. The effect of temperature was also investigated. The exchange current is almost unaffected with temperature; this means that the heat of activation is equal to zero.

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Table 1

Stationary potentials and parameters of overpotential for lead anodes in different solutions at 30 °C.

$[NaOH]/mol\ l^{-1}$	pH	Stationary potential/V NHE	Tafel slope/ mV	i_o A cm.$^{-2}$ 10^{-5}	$(\partial\eta/\partial i)_{\eta=0}$ / VA^{-1} cm.$^{-2}$	λ	η /mV at 10^{-3} A cm.$^{-2}$ Pure soln.	Soln. containing 1 M Na_2SO_4
0.1	12.89	-0.521	32	7	80	4.65	33	34
0.3	13.32	-0.532	32	17.85	36.6	3.99	32.5	33
0.5	13.54	-0.548	30	15.85	36.7	4.49	23	
1	13.83	-0.570	31	19.95	31.7	4.12	20	
2	14.15	-0.591	28	17.78	36.7	3.99	21	
5	14.68	-0.636	27	12.95	53.3	3.88	24	
10	15.04	-0.655	28	7.5	96.7	3.60	29	

Table 2

Effect of temperature on the exchange current for lead anodes in different NaOH solutions.

Temperature T	Log. i_o 0.5 N	5 N	10 N	ΔS^*
20	-3.8	-3.95	-4.10	-0.0/40
30	-3.8	-3.90	-4.125	-0.0/36
40	-3.75	-3.90	-4.14	-0.0/32
50	-3.75	-3.85	-4.14	-0.0/28

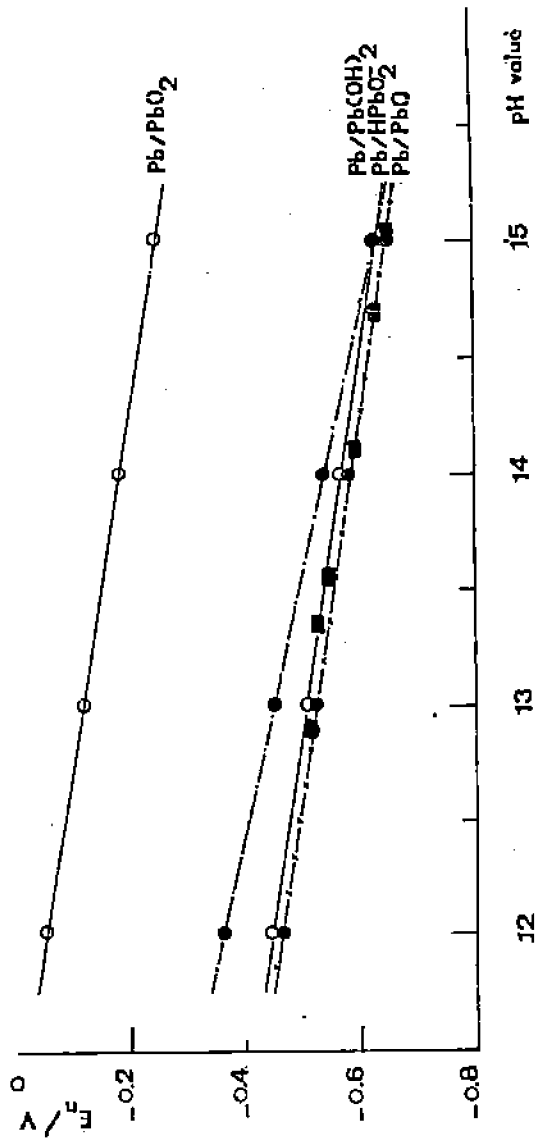


Fig (1): Effect of pH on the reversible potential of lead anodes.

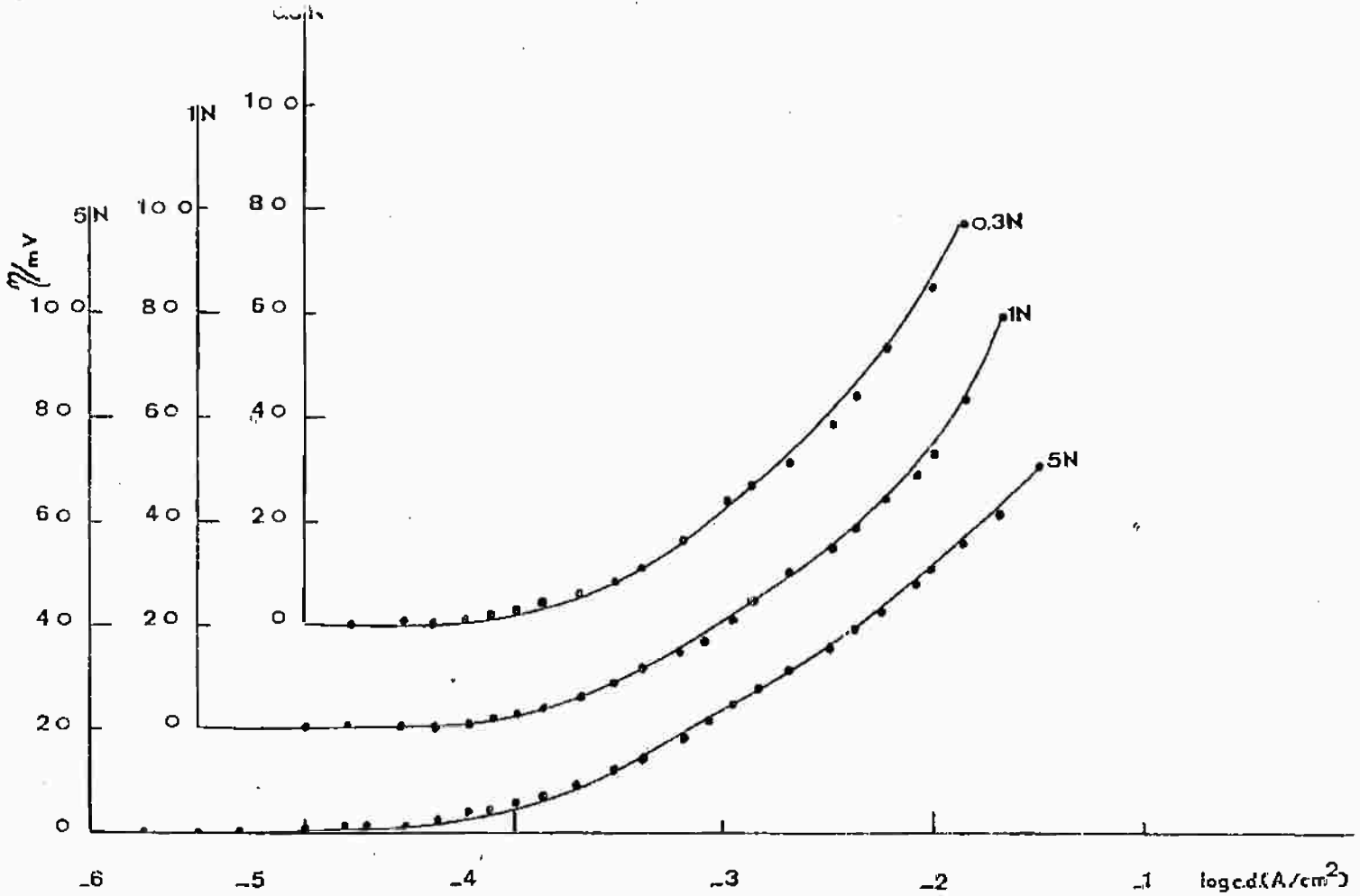


Fig.(2): Tafel lines for lead anodes in NaOH solutions at 30°C.

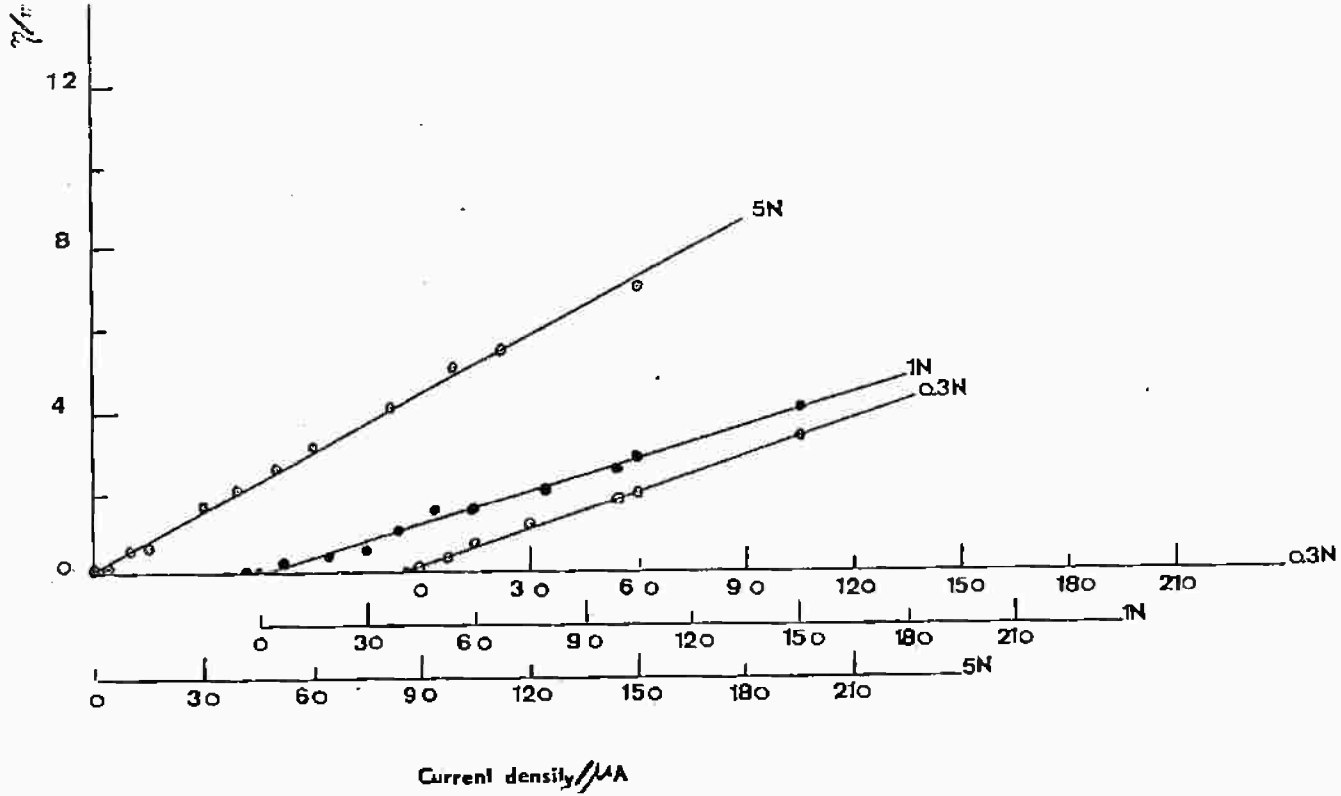
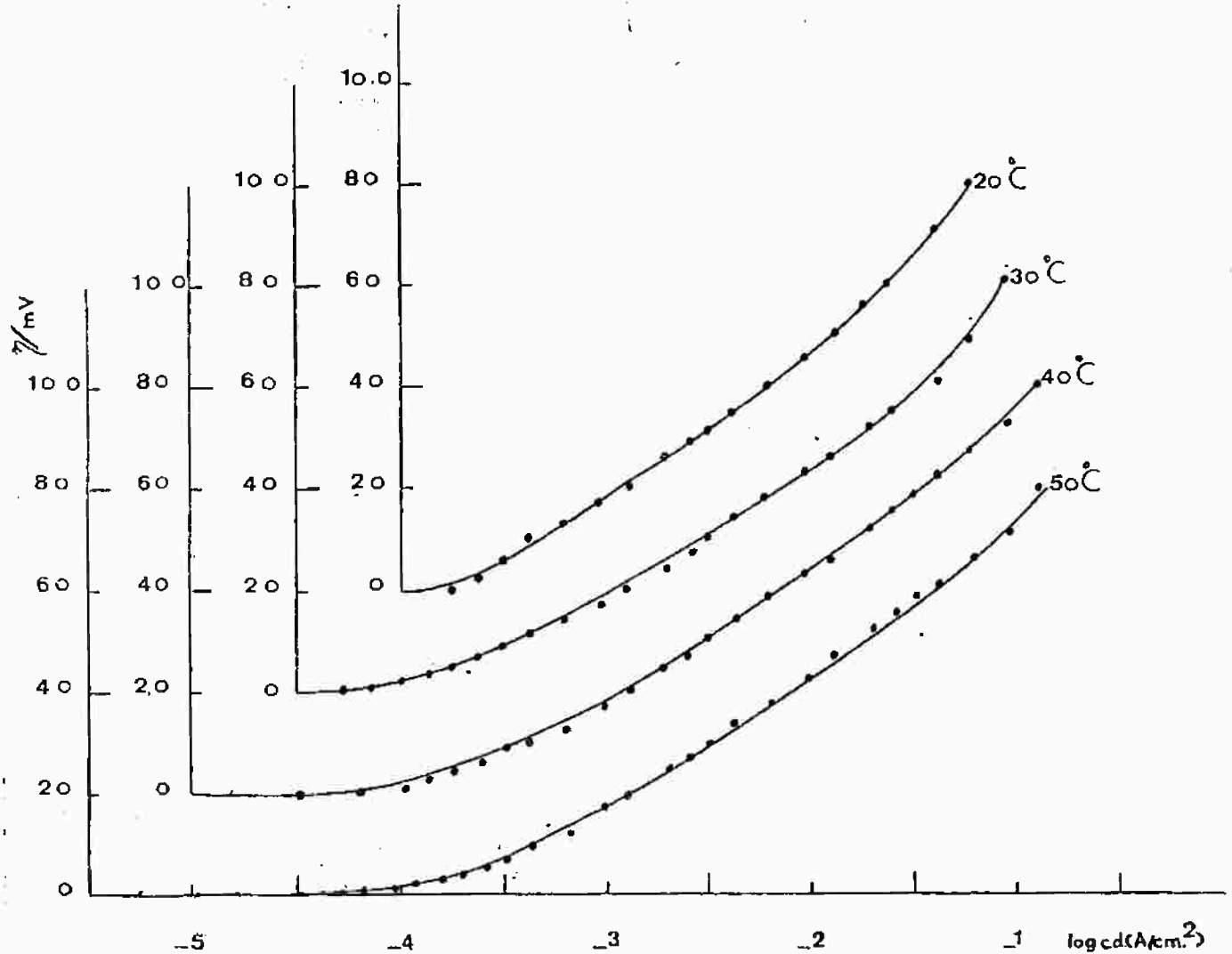


Fig (3): Relation between current density and overpotential at low anodic polarisation of lead.


η/mV
10.0
8.0
6.0
4.0
2.0
0
20°C
30°C
40°C
50°C
-5
-4
-3
-2
-1
log cd(A/cm.²)

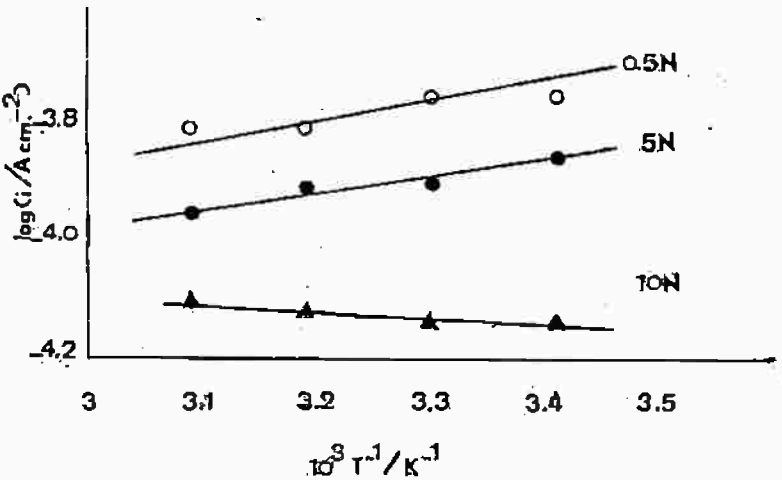


Fig (5): Effect of temperature on the exchange current for lead anodes in different NaOH solutions.