

THE BEHAVIOUR OF MOLYBDENUM ON CATHODIC POLARISATION WITH REFERENCE TO THE EFFECT OF ANIONS ON ITS HYDROGEN OVERPOTENTIAL

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The overpotential of hydrogen is measured in pure HCl solution of concentration ranging from 5.91 – 0.003N. Within this concentration range and at current densities = 1×10^{-3} – 1.8×10^{-4} amps./cm² the Tafel-line slope amounts to 0.06, which suggests a dual electrochemical-catalytic mechanism. At lower acid concentrations than 0.1 N and at higher currents than 1.8×10^{-4} , the Tafel-line slope increases continuously up to 0.116 in 0.003 N-HCl. Borate and nitrate ions possess a pronounced effect on the slope of the Tafel lines, but the effect of phthalate is small.

In a previous investigation involving a study on the behaviour of chromium in the course of cathodic and anodic polarisation (Issa, Ammar and Khalifa, *J. Phys. Chem.*, 1955, 59, 492), we observed that the anions, present in the buffer solutions used, possessed considerable influence on the Tafel-line slopes. The observed increase was attributed to the specific adsorption of such anions whence the evolution of hydrogen took place on a surface partly covered by these anions. In order to find out whether this is true of other metals or not, we have carried out a detailed study on the hydrogen overvoltage on molybdenum in pure hydrochloric acid and sodium hydroxide solutions or in a mixture of these and alkali phthalate, borate, phosphate or nitrate.

EXPERIMENTAL

The electrodes (Fig. 1) used in this investigation were spectroscopically pure rods, 5 mm. in diameter and 2 cm. in length, welded to glass tubings. Electric contact was maintained through a spiral copper wire fitted well around the tapering end of the rod lying inside the tube.

The electrolytic cell was essentially similar to that of Bockris and Potter (*J. Chem. Phys.*, 1952, 20, 614). It was constructed from pyrex glass and cleaned with chromic acid.

The electrolytes were pre-electrolysed (Azzam, Bockris, Conway and Rosenberg, *Trans. Faraday Soc.*, 1950, 46, 918) for periods of 5 to 10 hours at a platinum gauze cathode, before immersion of the molybdenum electrode, while bubbling a stream of hydrogen, purified by the method of Honigschmidt (*Z. anorg. Chem.*, 1927, 163, 78). The electrolysis was continued for another hour at the molybdenum cathode before the measurements were started. The Tafel lines were traced in unstirred solutions from a higher current density of 1.8×10^{-3} amps./cm². to a lower one of 1×10^{-5} amps./cm². The same results were obtained for both the periods.

Measurements were made in pure HCl solutions of concentrations varying from 5.9 to 0.003 N (p_H 1.05 to 2.55) and in 0.1 N-NaOH solution (p_H 13.0), either alone or when admixed from the start with phosphate, borate, nitrate or phthalate ions. HCl solutions were prepared from the constant boiling acid



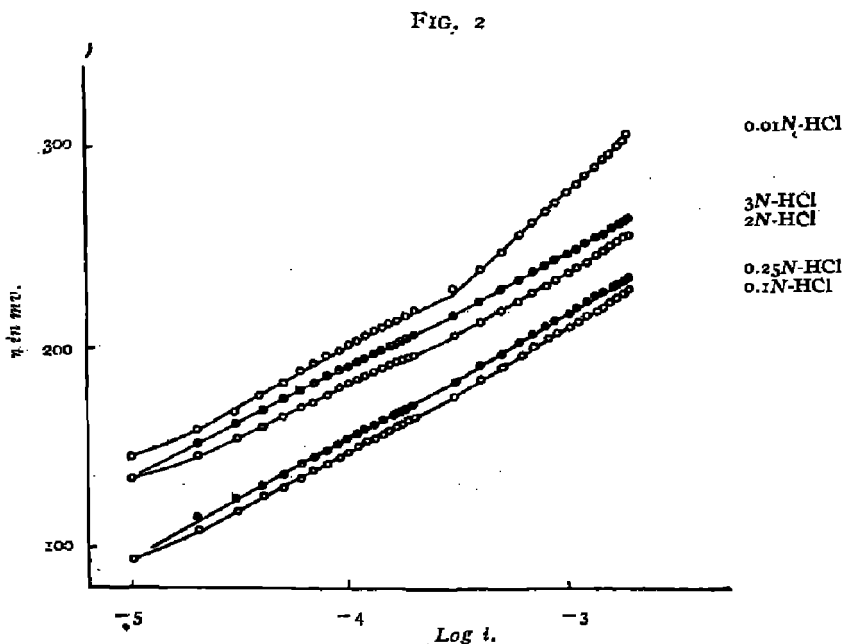
FIG. 1

(5.91 *N*) by appropriate dilution with water (twice distilled from alkaline permanganate). The salts used were of the Analar samples. The calculated amounts were dissolved in acid or alkali hydroxide solutions to make them 0.05 or 0.1 molar with respect to the above anions. NaOH solutions were prepared by diluting the concentrated carbonate-free solution. The water used was twice distilled from alkaline permanganate.

The p_H of the solutions was measured at the end of each experiment using the hydrogen electrode.

Behaviour in Pure Hydrochloric Acid Solutions

Fig. 2 shows representative Tafel lines obtained in pure HCl solutions of ~ 5.9 to 0.003 *N*, using current densities ranging from 1×10^{-5} to 1.8×10^{-3} amps./cm² at 25°.



The Tafel lines possess two slopes, one covering the current density range of 1×10^{-5} to 1.8×10^{-4} and the other within the range of 2×10^{-4} to 1.8×10^{-3} amps./cm². with the respective slopes 0.05 - 0.06 and 0.065 - 0.116v. In Table I are recorded the values of the slopes b_1 within the lower current-density range together with the respective i_{01} values, and the values of hydrogen overpotential η at the current densities 5×10^{-5} , 1×10^{-4} and 1.3×10^{-4} amps./cm². The values of b_2 and i_{02} within the higher current-density range together with η at the current densities 5×10^{-4} and 1.3×10^{-3} amps./cm². are listed in Table II:

TABLE I

Hydrogen overpotential at molybdenum cathodes in HCl solns

Normality of HCl	5.90	5.0	4.0	3.0	2.0	0.50	
p_H	-1.05	-0.930	-0.848	-0.598	-0.305	0.42	
b_1	0.056	0.051	0.051	0.052	0.051	0.057	
i_{01} amp./cm ² × 10 ⁻⁸	3	1.5	1.5	2.5	2.90	4.0	
α	1.0	1.15	1.15	1.1	1.15	1.0	
η in mv.	{ c.d. 5×10^{-5}	174	182	185	175	165	151
	{ c.d. 1×10^{-4}	198	199	201	191	182	171
	{ c.d. 1.3×10^{-4}	205	205	207	197	188	177
Normality of HCl	0.25	0.10	0.05	0.02	0.01	0.003	
p_H	0.82	1.09	1.38	1.76	2.00	2.55	
b_1	0.058	0.060	0.064	0.060	0.060	0.060	
i_{01} amp./cm ² × 10 ⁻⁸	2.5	3.2	5.5	4.6	4.6	4.6	
α	1.0	0.95	0.90	0.95	0.95	0.95	
η in mv.	{ c.d. 5×10^{-5}	136	129	134	181	182	178
	{ c.d. 1×10^{-4}	155	147	152	200	202	200
	{ c.d. 1.3×10^{-4}	162	155	159	207	209	207

TABLE II

Hydrogen overvoltage at molybdenum cathodes in HCl solns.

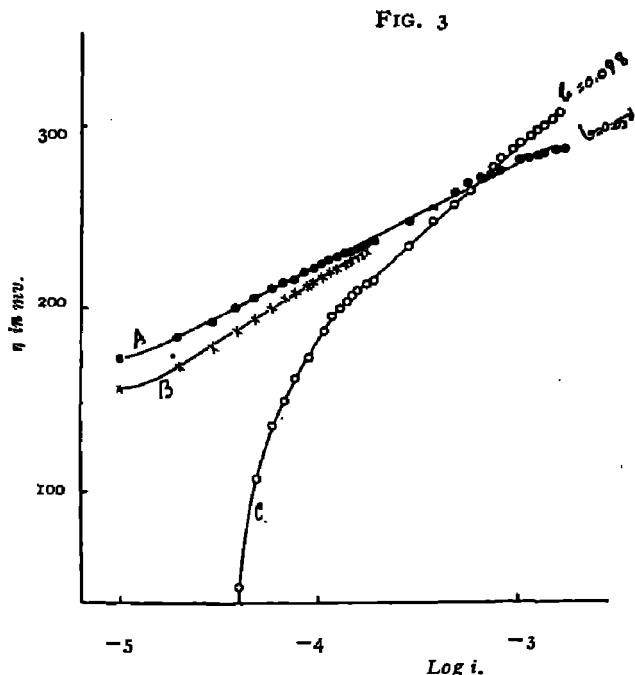
Normality of HCl	5.9	5.0	4.0	3.0	2.0	0.50	
p_H	-1.05	-0.930	-0.848	-0.598	-0.305	0.42	
b_1	0.066	0.064	0.065	0.060	0.066	0.072	
i_{01} amp./cm ² × 10 ⁻⁸	10	7.8	7.5	10	2.2	2.2	
α	0.85	0.90	0.90	0.95	0.85	0.80	
η in mv.	{ c.d. 5×10^{-4}	238	236	238	228	217	212
	{ c.d. 1×10^{-4}	257	255	257	247	237	235
	{ c.d. 1.3×10^{-4}	265	263	264	255	241	244
Normality of HCl	0.25	0.10	0.05	0.02	0.01	0.003	
p_H	0.82	1.09	1.38	1.67	2.00	2.55	
b_1	0.073	0.076	0.090	0.095	0.100	0.116	
i_{01} amp./cm ² × 10 ⁻⁷	1.7	2.2	6.3	2.5	1.6	2.5	
α	0.8	0.75	0.65	0.60	0.60	0.50	
η in mv.	{ c.d. 5×10^{-4}	196	191	197	244	248	254
	{ c.d. 1×10^{-4}	218	211	220	267	277	287
	{ c.d. 1.3×10^{-4}	227	218	228	275	290	302

The above data show that η numerically decreases between 4N and 0.1N-HCl with $d\eta/dp_H$ amounting to 29 mv. At lower acid concentrations (0.1-0.003 N), η remains approximately constant at lower currents (5×10^{-5} - 1.8×10^{-4}) but increases numerically by ~ 60 mv per unit p_H at higher currents (5×10^{-4} - 1.8×10^{-2} amps./cm²). Above 4 N-HCl the values of η exhibit slight variations with p_H .

Effect of Anions on the Discharge of Hydrogen on Molybdenum

As was previously observed (Issa, Ammer and Khalifa, *loc. cit.*), anions possess a considerable effect on the slopes of the Tafel lines and on the values of η on chromium.

The same effect was observed in the case of molybdenum, as shown in Table III. The anions studied include phthalate, borate, phosphate and nitrate.



A: p_H 0.085 HCl + phosphate.
 B: " 1.15 " + phthalate.
 C: " 1.0 " + nitrate.

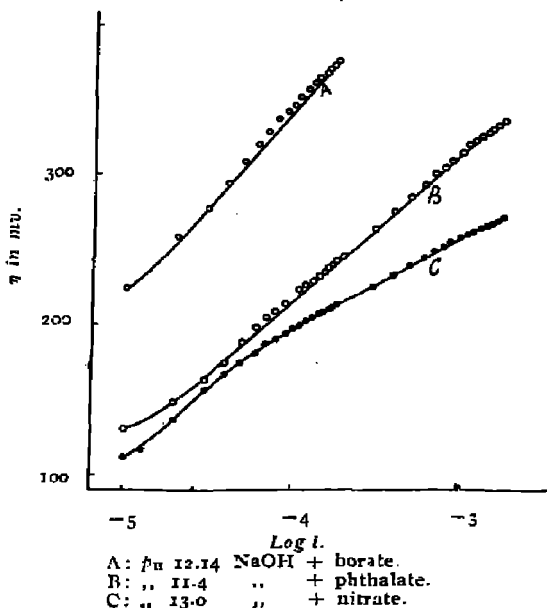
Nitrate anions produce a pronounced effect on the values of η and on the Tafel-line slope. Curve A in Fig. 3 shows that η in 0.1N-HCl + nitrate ($p_H \approx 1.0$) and at low current densities is very small, amounting to 50 mv but rises rapidly such that the slope of the curve is 0.4 volt. On increasing i above 10^{-4} amps./cm², the curve becomes linear with a slope of 0.098, approximating thus the behaviour in pure acid solution, $b_2 = 0.073$. In alkaline solutions, the effect of the nitrate ion is much less pronounced and above 10^{-4} amps./cm², the behaviour is exactly similar to that in pure NaOH solution.

TABLE III

Solution.	C.D. = $10^{-6} - 10^{-4}$ amp./cm ² .			C.D. = $2 \times 10^{-4} - 1.8 \times 10^{-3}$ amp./cm ² .	
	p_H .	b_1 .	i_0 .	b_2 .	i_0 .
Pure HCl	1.0	0.058	3.0×10^{-5}
HCl + borate	1.12	0.060	3.2×10^{-5}	0.050	7.1×10^{-1}
" + "	7.93	0.129	2.4×10^{-7}	0.246	6.3×10^{-6}
" + "	8.12	0.131	2.2×10^{-7}	0.193	1.8×10^{-6}
Pure borate	8.71	0.131	2.3×10^{-7}	0.172	1.5×10^{-6}
HCl + phthalate	1.15	0.054	2.0×10^{-5}	0.078	2.8×10^{-1}
" + phosphate	0.085	0.053	2.0×10^{-5}
" + nitrate	1.0	0.098	1.0×10^{-5}
Pure NaOH	13.0	0.072	3.2×10^{-5}	0.092	2.4×10^{-1}
NaOH + borate	12.14	0.082	1.3×10^{-7}
" + phthalate	11.90	0.075	3.2×10^{-5}	0.092	1.5×10^{-1}
" + phosphate	12.00	0.100	6.7×10^{-7}
" + nitrate	13.00	0.076	6.3×10^{-5}

In acid solutions phosphate anions have no effect on the slope of the Tafel line

FIG. 4



(b amounting to ~ 0.053) or on the value of η (curve B, Fig. 3). The slope of the Tafel line observed in pure NaOH solution of p_H 13.0 is higher than in pure HCl solutions, amounting to 0.072 and 0.092 within the lower and higher current-density range (curve A, Fig. 4). In presence of phosphate (p_H 12.0) and borate (p_H 12.14) the slopes are higher, amounting to 0.1 and 0.082 throughout the whole current-density range. A striking phenomenon, however, is that the borate anion has a pronounced effect on the Tafel-line slope obtained in solutions (HCl + borate) of p_H higher than 7. Thus, at p_H 7.03 and 8.12, slopes amounting to 0.129, 0.132 are obtained at lower currents and 0.246, 0.193 at higher ones respectively (see Table III). Similarly, the respective values obtained in 0.05 N pure borate

solution of p_H 8.71 amount to 0.131 and 0.172, as compared to 0.06 and 0.09 in HCl + borate solution of p_H 1.12.

DISCUSSION

The values of parameters for the hydrogen evolution on molybdenum were calculated from the relations

$$\eta = RT/2F \ln i_0/i_0 \quad \text{or} \quad b = 2.303 RT/\alpha F$$

in which i_0 is the exchange current and i_c , the current density corresponding to the overpotential η , and α is a constant. The parameters as found experimentally are listed in Tables I and II for the lower and higher currents respectively. The most probable value of α is "one" which is not in accordance with the observations previously made by Pecherskaya and Stender (*J. Appl. Chem. Russ.*, 1946, 19, 1303) who obtained for α the value 0.5 in 2 N-H₂SO₄, and Bockris and Parsons (*Faraday Soc., Disc.*, 1947, 1, 325, 95; *Trans. Faraday Soc.*, 1948, 44, 860) who obtained 0.5-1.5 in 1N-HCl.

The fact that the Tafel-line slope in concentrated and dilute acid solutions up to a current density of 1.8×10^{-4} amps./cm². amounts to ~ 60 mV indicates that the process of hydrogen evolution cannot be accounted for by any of the known simple mechanism. Thus, the slow discharge is characterised by a slope of 0.116 and a value of h (the electron number) = 1. The electrochemical mechanism has two slopes of 0.116 and 0.039 at high and low current densities respectively and a value of $h = 2$. The catalytic mech-

anism has at low current densities a slope of 0.03 and a value of $k = 2$. However, a dual mechanism, combining an electrochemical and catalytic processes, possesses a slope of 0.059 which lies near our experimental value (Ammar, Ph.D. Thesis, London). The mechanism remains the same at higher current densities in solutions more concentrated than 0.5 N-HCl. In more dilute solutions and at higher current densities than 1.8×10^{-4} , the slope increases up to 0.073 and 0.116 in 0.25N- and 0.003N-HCl respectively (Table II), indicating a change in the mechanism, possibly to pure electrochemical. Dual mechanisms were suggested for nickel by Frumkin and his co-workers (Frumkin, *Faraday Soc. Disc.*, 1947, 1, 63) in which the reaction was controlled over a part of the electrode by a discharge step and over the remaining area by a combination of hydrogen atoms. Similarly Bockris and Conway (*Trans. Faraday Soc.*, 1949, 45, 989) suggested a dual rate-determining desorption step involving recombination of hydrogen atoms and electrochemical desorption.

Although the effect of p_H on η at low current densities in the more dilute solutions is in agreement with the dual electrochemical-catalytic mechanism, this is not the case at higher currents when the average value of $d\eta/dp_H$ amounts to ~ 60 mv.

The effect of the anions on the hydrogen overvoltage on molybdenum can be explained on the premise that they are specifically adsorbed on the metal.⁶ At lower currents the nitrate ions, on account of their oxidising properties, are reduced at the electrode surface. This behaviour resembles depolarisation of oxygen, when not rigidly removed from the solution prior to electrolysis. At higher currents, the process of adsorption decreases, but instead hydrogen deposition occurs and the Tafel line behaves normally. Phthalate anions, on the other hand, are without effect on the Tafel line slope, obtained in an acid solution of p_H 1.15 and with but a slight effect in an alkaline solution of p_H 11.9, indicating a slight tendency of being adsorbed.

Borate ions, on the other hand, bring about a pronounced increase of both b and γ values, especially at higher p_H , but the exact reason for this is not clear.