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Inhibition effect of potassium iodide on corrosion of stainless steel in hydrochloric acid solution

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The inhibition effect of potassium iodide on the corrosion of stainless steel has been examined using weight loss and electrochemical measurements. Potassium iodide was found to be an excellent inhibitor for stainless steel types 316, 430 and 440 (efficiency more than 95%), and moderate for type 304. The corrosion rates in 1 M HCl and in presence of potassium iodide fit an Arrhenius equation. The presence of potassium iodide lowered both the activation energy and the rate of reaction. Polarization measurements indicated that potassium iodide acts as an anodic inhibitor particularly at higher concentrations and as a cathodic inhibitor at lower concentrations. The synergistic effect of potassium iodide on the inhibitive efficiency of the organic substances was studied.

1 Introduction

Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial cleaning, acid descaling and oil-well acidizing. Because of the general aggressiveness of the acid solutions, the practice of inhibition is commonly used to reduce the corrosive attack on metallic materials [1]. In order to minimize the loss of metal, acid inhibitors are added to the pickling baths; these are usually organic compounds containing oxygen, nitrogen or sulphur and are characterized by high molecular weights, and in particular by stereo-chemical structures and the presence of polar groups [2–7]. Nowadays it is common practice to use a mixture of inhibitors, each one characterized by different but complementary modes of action which confer additional or synergistic inhibiting properties to the mixture [8–11].

2. Experimental procedure

The compositions of the stainless steels used in these experiments are given in Table I.

For weight loss measurements, rectangular specimens of stainless steel of size 1.0 × 5 × 0.1 cm with a small hole ≃ 2 mm diameter near the upper edge of the specimen, were used for the determination of the corrosion rate. Prior to use each specimen was mechanically polished, degreased in acetone, dried and weighed to the nearest 0.1 mg. For electrochemical measurements, test specimens were cut as strips, 10 cm long by 0.5 cm wide. A strip was inserted into the sample holder tube except for a 1 cm section at the end. The test area was scoured clean just prior to use.

TABLE I Compositions of the stainless steels (wt %)

Type of specimen	Cr	Ni	Mo	C
304	18.20	8.12	–	0.08
316	16.18	10.14	2–3	0.08
430	14.18	–	–	0.12
440	16.18	–	0.75	0.60

3. Results and discussion

3.1. Weight-loss measurements at room temperature

Corrosion tests for different types of stainless steel in 1 M hydrochloric acid solution in the absence and presence of potassium iodide conducted over a period of 6 h (curves are not shown), revealed that the loss in weight increased linearly with time. The corrosion rate derived from the straight lines thus obtained are given in Table II. It can be seen that the corrosion rate progressively decreased with increase in the concentration of potassium iodide.

Fig. 1 shows that the inhibitive efficiency of potassium iodide increases with increasing concentration for the different types of stainless steel, except for 0.1 M potassium iodide in stainless steel type 316. Potassium iodide was found to be an excellent inhibitor for stainless steel types 316, 430 and 440 (efficiency more than 95%) and a moderate inhibitor for type 304.

3.2. Effect of temperature

The effect of temperature (30–80 °C) on the corrosion inhibition of different types of stainless steel in the absence and presence of potassium iodide (0.1 M) is shown in Table III. It can be seen that weight loss increases with increasing temperature. The corrosion

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TABLE II Effect of different concentrations of potassium iodide on the corrosion rate of stainless steel in 1 M HCl at 30 °C

Concentrations of potassium iodide (M)	304		316		430		440	
	Corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)	Efficiency (%)	Corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)	Efficiency (%)	Corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)	Efficiency (%)	Corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)	Efficiency (%)
–	0.036	–	0.064	–	0.580	–	0.260	–
0.1	0.011	69.4	0.023	64.0	0.018	96.9	0.015	94.2
10^{-2}	0.012	66.6	0.002	96.8	0.019	96.7	0.031	88.0
5×10^{-3}	0.012	66.6	0.004	93.7	0.036	93.8	0.060	76.9
10^{-3}	0.015	58.3	0.009	85.9	0.140	75.8	0.130	50.0
10^{-4}	0.015	58.3	0.009	85.9	0.230	60.3	0.150	42.3

TABLE III Effect of temperature on the corrosion rate of different types of stainless steel in 1 M HCl and in the presence of 0.1 M potassium iodide

Temperature (°C)	304 corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)		316 corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)		430 corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)		440 corrosion rate ($\mathrm{mg\,cm^{-2}\,h^{-1}}$)	
	1 M HCl	1 M HCl + 0.1 M KI	1 M HCl	1 M HCl + 0.1 M KI	1 M HCl	1 M HCl + 0.1 M KI	1 M HCl	1 M HCl + 0.1 M KI
30	0.036	0.011	0.064	0.023	0.58	0.018	0.26	0.015
40	0.27	0.019	0.250	0.008	3.50	0.040	2.60	0.020
50	0.40	0.018	0.500	0.016	10.50	0.060	6.20	0.020
60	0.52	0.020	0.700	0.021	17.50	0.600	14.00	0.060
70	1.05	0.024	1.500	0.021	32.00	0.200	23.00	0.160
80	1.53	0.025	2.800	0.022	41.00	0.520	37.00	0.460

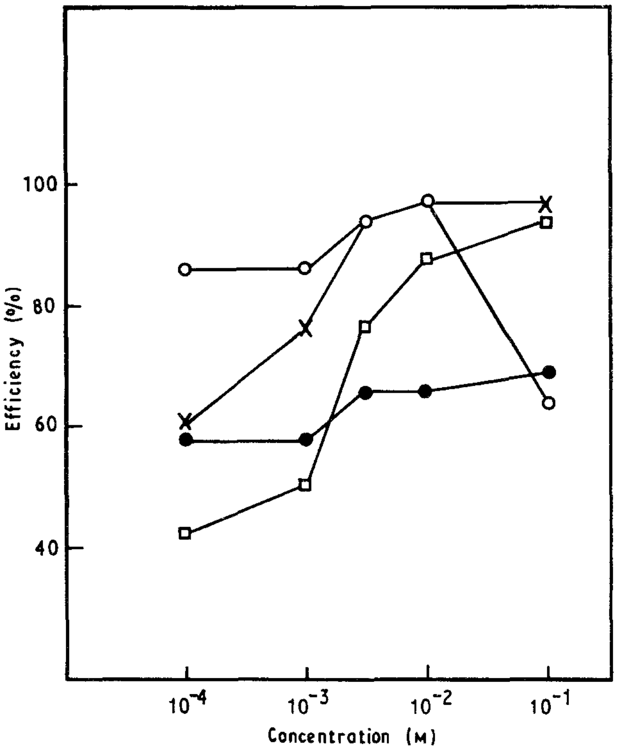

Figure 1 Inhibitive efficiency of different types of stainless steel against concentration of potassium iodide: (●)304, (○) 316, (×) 430, (□) 440.

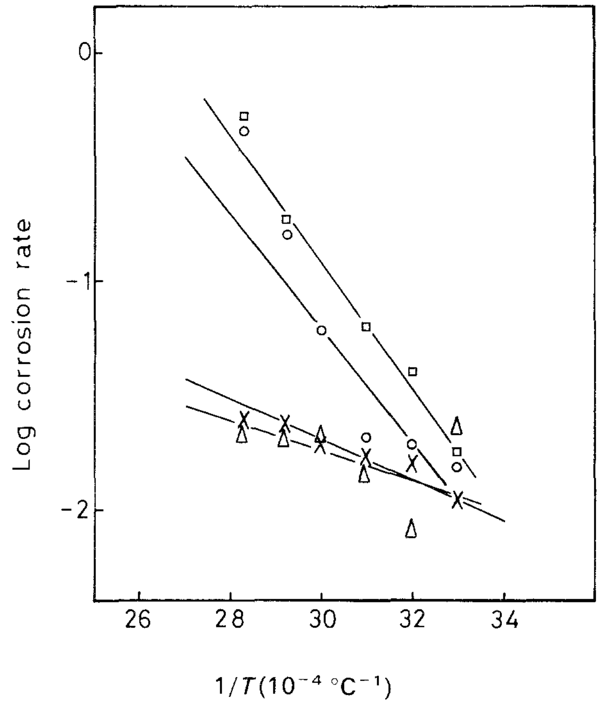

Figure 2 Arrhenius plot for different types of stainless steel in 1 M HCl and in presence of potassium iodide: (×) 304, (△) 316, (□) 430, (○) 440.

rate derived from weight-loss measurements was plotted against $1/T$. These measurements conform the relation of the type

$$\log \text{rate} = \frac{-E}{RT} + \text{constant} \qquad (1)$$

where E is the activation energy, R the gas constant and T the absolute temperature.

Fig. 2 represents Arrhenius plots of stainless steels as a function of $1/T$ for uninhibited acid and in the presence of 0.1 M KI. The activation energies calculated from the slopes of the curves for the different types of stainless steel in the absence and presence of the inhibitor are given in Table IV. The value of activation energies obtained in free acid solution are of the same order of magnitude as those observed by Riggs [12], 14.2 kcal mol^{-1}, and Podesta and Arvia [13] for the corrosion of carbon steels in phosphoric acid and chloride solutions respectively, Schorr and Yahalom [14], R. M. Hudson *et al.* [15] and Dhirendra *et al.* [16], 15.18 kcal mol^{-1}, for the corrosion of stainless steel in HCl. Based on the above conclusions regarding the cathodic process, the estimated E values may be allocated to the discharge of hydrogen ions in the cathodic reaction and the rate-determining steps for the corrosion of the different types of stainless steel are of the order of magnitude of activated adsorption. It is interesting that the presence of potassium iodide lowers both the activation energy, E, and the rate of reaction, more than for the uninhibited solution. The inhibitor is believed to be firmly held on the metal surface, sometimes by chemisorption, as a result of which the surface area of the metal covered by inhibitor molecules increases as temperature rises [17]. These results agree with Machu's [18] studies of the influence of temperature on inhibitor action, which concluded that with a "powerful" inhibitor, the activation energy was lower for the inhibited than for the uninhibited reaction. According to Riggs and Hurd [19] and Anoschenko [20], the mechanism is changed in the presence of an inhibitor from activation-controlled to a diffusion-controlled process. The underlying mechanism may be in harmony with the above results.

TABLE IV Activation energy for the different types of stainless steel in 1 M HCl in the absence and presence of 0.1 M potassium iodide

KI concentration	Activation energy (k cal mol^{-1})			
	304	316	430	440
	17.04	16.58	16.58	16.12
0.1 M	4.15	2.76	12.40	11.50

3.3. Galvanostatic measurements

Anodic and cathodic polarization measurements were conducted separately for different types of stainless steel. Fig. 3a–d show the polarization curves in 1 M HCl solution without and with potassium iodide. Tafel regions extend over about a decade of the current axis. The reproducibility of the cathodic Tafel slopes was somewhat better than those of the anodic Tafel slopes (± 5 mV/decade and ± 10 mV/decade, respectively). The corrosion current and the corrosion potential were given by the intersection of extrapolated anodic and cathodic Tafel lines. Electrochemical parameters determined for all samples studied in 1 M HCl with and without potassium iodide are summarized in Tables V–VIII. It can be seen that the addition of inhibitor shifts the corrosion potential for all the samples towards the positive direction and, at the same time, the corrosion current density decreases. The cathodic Tafel slope, b_c, is appreciably increased for stainless steel types 304, 316 and 440 compared with the additive-free solutions except at lower concentration (10^{-4} M), while b_c for type 430 decreases with the addition of potassium iodide. The values of the anodic Tafel slopes, b_a, decrease in the presence of potassium iodide, except at the two concentrations (10^{-3} and 5×10^{-3} M) for type 440.

The inhibitive efficiencies calculated from the polarization method are listed in Tables V–VIII. It can be seen that there is a good coincidence between the

TABLE V Electrochemical parameters of stainless steel type 304 in 1 M HCl in the absence and presence of potassium iodide

Potassium iodide conc. (M)	Rest potential, E_{rest} (mV)	Corrosion potential, E_{corr} (mV)	Corrosion current, I_{corr} (μA cm^{-2})	Efficiency (%)	b_a (mV/log$i$)	$-b_c$ (mV/log$i$)
0	− 150	− 200	33.11		84	133
0.1	− 31	− 116	9.12	72.4	37	227
10^{-2}	− 58	− 103	10	69.8	60	190
5×10^{-3}	− 34	− 140	10	69.8	70	123
10^{-3}	− 57	− 170	19.05	42.5	73	137
10^{-4}	− 71	− 150	19.05	42.5	43	113

TABLE VI Electrochemical parameters of stainless steel type 316 in 1 M HCl in the absence and presence of potassium iodide

Potassium iodide conc. (M)	Rest potential, E_{rest} (mV)	Corrosion potential, E_{corr} (mV)	Corrosion current, I_{corr} (μA cm^{-2})	Efficiency (%)	b_a (mV/log$i$)	$-b_c$ (mV/log$i$)
0	− 81	− 136	28.84		90	100
0.1	+ 26	− 16	15.14	47.5	33	200
10^{-2}	− 2	− 56	3.98	86.2	46	153
5×10^{-3}	− 6	− 66	7.94	72.46	47	176
10^{-3}	− 32	− 70	12.58	56.38	30	147
10^{-4}	− 63	− 86	15.14	47.5	17	66

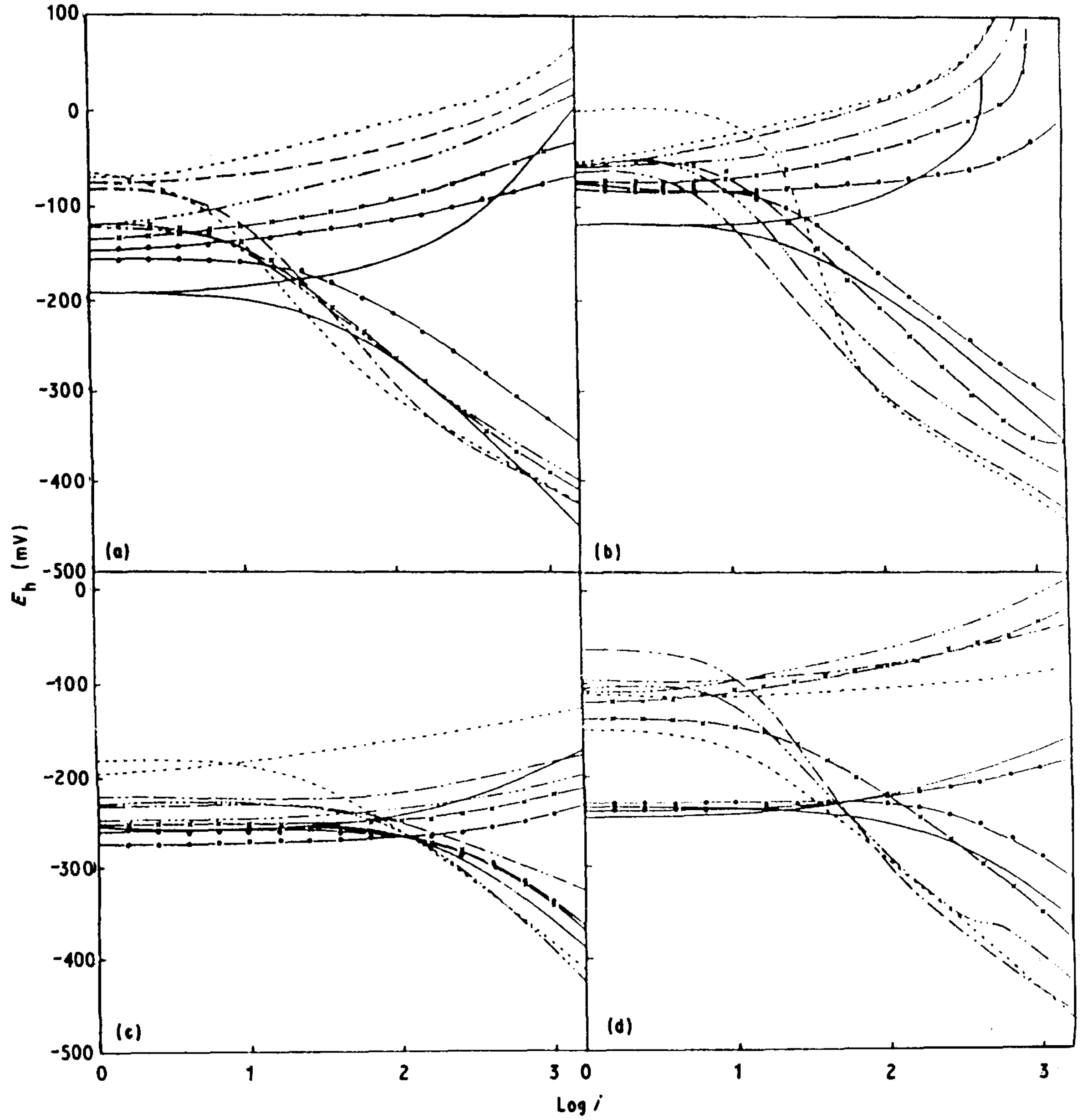

Figure 3 Polarization curves for different types of stainless steel in 1 M HCl solution in the absence and presence of potassium iodide. (a) 304, (b) 316, (c) 430, (d) 440. (——) 1 M HCl, (– – –) 0.1 M KI, (–·–·–) 10^{-2} M KI, (–····–) 5×10^{-3} M KI, (–×–) 10^{-3} M KI, (–●–) 10^{-4} M KI.

TABLE VII Electrochemical parameters of stainless steel type 430 in 1 M HCl in the absence and presence of potassium iodide

Potassium iodide conc. (M)	Rest potential, E_{rest} (mV)	Corrosion potential, E_{corr} (mV)	Corrosion current, I_{corr} (μA cm^{-2})	Efficiency (%)	b_a (mV/log$i$)	b_c (mV/log$i$)
0	− 242	− 256	144.54		80	124
0.1	− 141	− 183	13.8	90.4	27	83
10^{-2}	− 199	− 230	38	73.7	30	57
5×10^{-3}	− 203	− 240	57.5	60.2	20	83
10^{-3}	− 236	− 256	69.2	52.1	27	47
10^{-4}	− 240	− 270	120.2	16.8	27	54

inhibitive efficiency obtained by the polarization method and by the weight-loss measurements.

The corrosion potential, E_{corr}, for the different types of stainless steel in inhibited solution moved towards more noble values with increasing inhibitor concentration. As a result of these observations it may be assumed that anodic inhibition predominates for potassium iodide, particularly at higher concentration. At lower concentration the inhibitor shows a tendency to cathodic inhibition. This is in agreement with Heusler and Cartledge [21] and Cavallaro and Felloni [22] who found that iodide ions exert a slight inhibition on the cathodic reaction and a marked action on the anodic reaction.

The rest potential, E_{rest}, shows a tendency towards a more positive value for all types of stainless steels. The maximum shifts ranges from 100–180 mV.

3.4. Potentiodynamic measurements

Fig. 4a–d shows the potentiodynamic *E–I* polarization curves for the different types of stainless steel in 1 M HCl in the absence and presence of different concentration (0.1–10^{-4} M) of potassium iodide solutions. The *E–I* curves of stainless steel types 304 and 316 show one peak in free acid at potential values 20 and 0 mV, respectively. The presence of an inhibitor shifts the potential peak towards the noble value with increasing inhibitor concentration. The anodic polarization curves for stainless steel type 430 possess two anodic current maxima in free acid at potentials − 40 and 160 mV, respectively. The presence of different concentrations of potassium iodide causes the disappearance of the second anodic maximum; this may be attributed to the strong adsorption of the inhibitor on the metal surface. *E–I* curves of stainless steel type 440 show no anodic current maximum.

The corrosion potential, E_{corr}, and pitting potential for the different types of stainless steel are shifted towards more noble potential with increasing potassium iodide concentrations. The corrosion current decreases with increasing inhibitor concentrations.

From the previous results it can be seen that there is a good coincidence between the inhibitive efficiency obtained by potentiodynamic, galvanostatic and weight-loss measurements.

3.5. Weight-loss measurements for different types of stainless steel in a 1 M HCl-containing mixture of inhibitors

In the series of tests with single inhibitors, as far as the inhibiting efficiency values were concerned, it was observed that, even in the most favourable case, the corrosion rate generally remained too elevated to be considered acceptable in the treatment of well-acidizing. Eventual synergistic effects were researched by using binary mixtures of organic inhibitor and potassium iodide which had already been tested singly.

Table IX shows the corrosion rate and the efficiencies for the different types of stainless steel in the presence of different inhibitors (hexamine, quinoline and thiourea) and mixtures of them with potassium iodide. Mixtures of hexamine or quinoline with potassium iodide tended to improve the inhibitive efficiency to a greater extent (more than 90%) for stainless steel types 316 and 430 and to induce a moderate inhibition for the other two types, 304 and 440. The presence of potassium iodide with thiourea increases only the efficiency of stainless steel type 304.

From the previous results it can be seen that the mechanism of inhibition is essentially one of mixed control with a prevalence of anodic or cathodic action according to the acid concentration. The halogen anions, derived from potassium iodide in acid solution, are probably strongly adsorbed on the surface of the stainless steel, decreasing the positive charge of the metal and thereby facilitating the adsorption of organic cations. The inhibitive efficiencies can be closely correlated with the rate of oxidation of iodide ions to iodine [23].

TABLE VIII Electrochemical parameters of stainless steel type 440 in 1 M HCl in the absence and presence of potassium iodide

Potassium iodide conc. (M)	Rest potential, E_{rest} (mV)	Corrosion potential, E_{corr} (mV)	Corrosion current, I_{corr} (μA cm^{-2})	Efficiency (%)	b_a (mV/log*i*)	$-b_c$ (mV/log*i*)
0	− 278	− 223	100		43	107
0.1	− 96	− 133	7.58	92.4	20	143
10^{-2}	− 148	− 110	13.8	86.4	37	226
5×10^{-3}	− 170	− 156	15.85	84.1	83	170
10^{-3}	− 199	− 153	30.2	69.8	73	133
10^{-4}	− 217	− 226	79.4	20.6	26	36

TABLE IX Corrosion rate and the efficiency for different types of stainless steel in the presence of different inhibitors and mixtures of them

Concentration of inhibitor (M)	304		316		430		440	
	Corrosion rate (mg cm^{-2} h^{-1})	Efficiency (%)	Corrosion rate (mg cm^{-2} h^{-1})	Efficiency (%)	Corrosion rate (mg cm^{-2} h^{-1})	Efficiency (%)	Corrosion rate (mg cm^{-2} h^{-1})	Efficiency (%)
10^{-1} hexamine	0.022	38.8	0.034	46.87	0.200	65.5	0.07	73.07
10^{-2} quinoline	0.024	33.3	0.038	40.62	0.120	78.5	0.05	80.76
10^{-2} thiourea	0.026	27.7	0.014	78.10	0.130	77.6	acc.	acc.
10^{-4} potassium iodide	0.015	58.3	0.009	85.90	0.230	60.3	0.15	42.30
10^{-1} hexamine + 10^{-4} KI	0.010	72.2	0.004	93.70	0.044	92.4	0.06	76.90
10^{-2} quinoline + 10^{-4} KI	0.010	72.2	0.006	90.60	0.042	92.7	0.084	67.70
10^{-2} thiourea + 10^{-4} KI	0.010	72.2	0.010	84.40	0.140	75.8	0.26	0.00

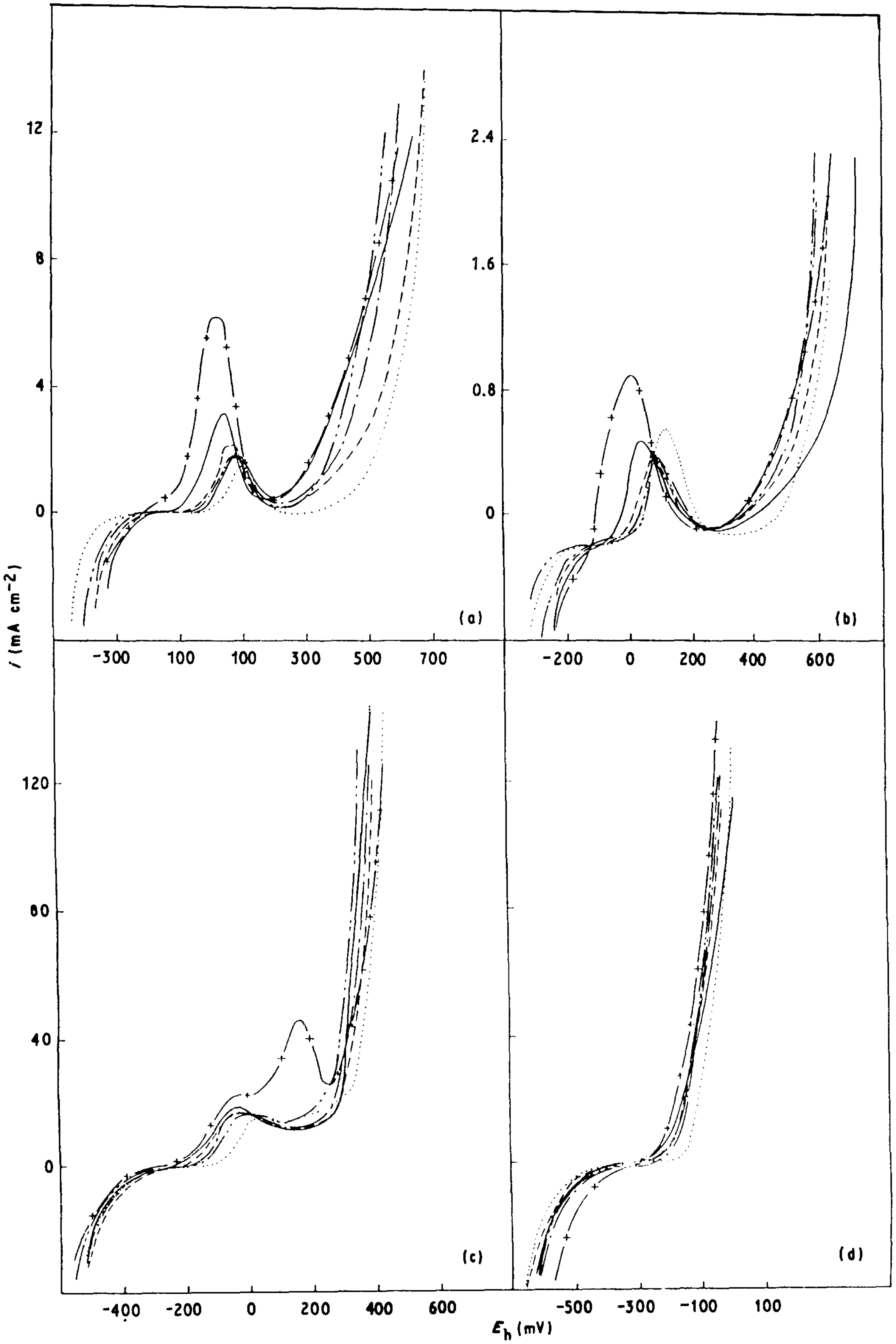

Figure 4 Potentiodynamic curves for different types of stainless steel in the absence and presence of potassium iodide. (a) 304, (b) 316, (c) 430, (d) 440, (— + —) 1 M HCl, (···) 0.1 M KI, (–··–) 10^{-2} M KI, (–·–) 5×10^{-3} M KI, (–––) 10^{-3} M KI, (———) 10^{-4} M KI.

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