

- The temperature dependence of the surface tension of liquids found in this way corresponds to that observed experimentally.
- The surface tension and its variation with temperature can be represented, in the cases of pure metals and liquids, in the same form:

$$\sigma = k_1 \delta p u^2 / \gamma \text{ and } \sigma(T) = \sigma(0) \exp \left\{ -k_2 \int_0^T \alpha(T) dT \right\},$$

k_1 and k_2 being constants obtained by calculation.

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EFFECT OF ADSORBED HALIDE IONS AND ORGANIC CATIONS ON THE ELECTRO-CHEMICAL DISSOLUTION OF COBALT IN ACID SOLUTIONS

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Many workers¹⁻⁵ have studied the action of adsorbed halide ions on electrochemical processes occurring at an iron electrode in acid solutions, but in the case of the cobalt electrode this effect has not been investigated in detail. It has been established that α -cobalt has a more negative stationary potential than its β modification, and dissolves more rapidly in 1 N H_2SO_4 by a factor of 45.⁶ Addition of halide ions to $CoSO_4$ solution diminishes the rate of ionisation and discharge of cobalt⁷. Electrolytic cobalt, representing a very pure specimen of the α hexagonal modification, has been used in the present work†.

Polarisation curves have been obtained by a galvanostatic method in 6 N and 1 N H_2SO_4 containing KI, KBr, and KCl at 20°. Fig. 1 shows the curves obtained under stationary conditions (continuous lines) in 6 N H_2SO_4 containing KI; Fig. 2 gives, as functions of the logarithm of the KI concentration, mean values (of 4-6 experiments at each concentration) of the potential ϕ , of spontaneous dissolution, the logarithm of the corresponding current density $\log i_s$, and

† For analysis of the cobalt for impurities, and also the method and conditions for determining polarisation curves under stationary conditions, see Ref. 8.

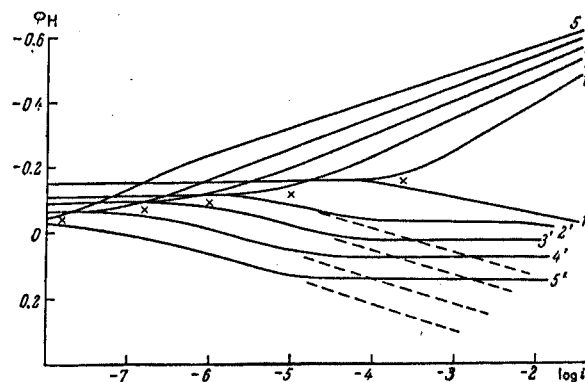


Fig. 1. Cathodic and anodic polarisation curves for cobalt in 6 N H_2SO_4 containing different concentrations of KI: 1), 1') 0 (no addition); 2), 2') 10^{-5} N; 3), 3') 10^{-4} N; 4), 4') 10^{-3} N; 5), 5') 10^{-2} N. The broken lines represent curves of ϕ_{max} against $\log i_a$ obtained oscillographically.

the cathodic and anodic potentials ϕ_c and ϕ_a at 0.001 A cm^{-2} . All potentials are given on the normal hydrogen scale. Figs. 1 and 2 show that halide ions, being adsorbed on the cobalt surface, as in the case of iron, increase the over-voltage both for the cathodic discharge of hydrogen ions and for the anodic ionisation of cobalt. Slowing down of these reactions diminishes the rate of spontaneous dissolution of cobalt. Owing to the more strongly retarded anodic reaction, ϕ_s is shifted to more positive potentials. With increase in the KI concentration, the slope of the semilogarithmic cathodic curves decreases from 0.150 to 0.082 V. In the presence of KI the anode potential at $i_a > 10^{-5}$ A cm^{-2} becomes almost independent of the anodic current density i_a , as has been observed in the case of iron^{2,5}. The polarisation curves obtained in the presence of Br^- and Cl^- ions in H_2SO_4 solutions are similar in shape, but the retarding effect of the anions on the rate of the above reactions diminishes in the sequence $I^- > Br^- > Cl^-$, and it falls also with decrease in the acid concentration. The accompanying Table (potentials given in mV) lists some data characterising polarisation curves obtained in the presence of Br^- and Cl^- .

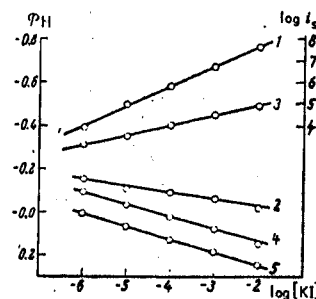


Fig. 2. Influence of logarithm of KI concentration in 6 N H_2SO_4 on: 1) $\log i_s$; 2) ϕ_s ; 3) ϕ_c ; 4) ϕ_a ; 5) ϕ_{max} .

TABLE.

Addition to 6 N H ₂ SO ₄	φ_s	$-\log i_s$	φ_c	φ_a	b_c
No addition	-145	3.68	-250	-110	-150
0.0001 N KBr	-93	5.10	-305	40	-135
0.01 N KBr	-40	6.05	-355	180	-122
0.01 N KCl	-90	4.85	-245	95	-135
0.1 N KCl	-85	5.16	-280	115	-135

In the case of high concentrations of halide salts, φ_s is established slowly, being displaced towards positive values. Figs. 1 and 2 and also the Table give values of φ_s obtained after a delay of 2 min.

Effect of Halide Ions on the Discharge of Hydrogen Ions

As in the case of iron, the observed decrease in the rate of discharge of hydrogen ions is due to chemisorption of halide ions on the cobalt surface. The increase in the hydrogen overvoltage is probably caused by strengthening of the bond between the chemisorbed halide ion and the cobalt atom, resulting in desorption and a decreased surface concentration of atomic hydrogen and in a diminution in its energy of adsorption. If the surface is assumed to be uniform, the rate of this reaction can be represented by the equation:

$$i_c = k_1 [H_3O^+] (1 - \theta) \exp\{-\alpha \varphi_c F / RT\} + k' [H_3O^+] \theta \exp\{-\alpha \varphi_c F / RT\}, \quad (1)$$

where θ and $(1 - \theta)$ are respectively the fractions of the surface occupied by adsorbed halide ions and free from them. If $k'' \ll k'$, i.e. if the rate constant on the occupied surface is small in comparison with that on the unoccupied surface, the second term in Eqn. (1) can be neglected, and the following equation is obtained for the potential:

$$\varphi_c = a - \frac{RT}{\alpha F} \ln i_c + \frac{RT}{\alpha F} \ln [H_3O^+] + \frac{RT}{\alpha F} \ln (1 - \theta). \quad (2)$$

On this hypothesis, the value of i_c when φ_c and $[H_3O^+]$ are constant should diminish with decrease in the free electrode surface:

$$(1 - \theta) = \left(\frac{i_c}{i_c^0} \right)_{\varphi_c, pH} \quad (3)$$

where i_c and i_c^0 represent the cathodic current density in the presence and in the absence of halide ions in the solution at the same potential. The values of $\log(1 - \theta)$, given below for a series of values of φ_c in one of the solutions (6 N H₂SO₄ + 10⁻⁴ N KI), show that cathodic polarisation is accompanied by desorption of I⁻ ions:

φ_c	-0.20	-0.25	-0.30	-0.35	-0.40
$\log(1 - \theta)$	-1.68	-1.54	-1.34	-1.18	-0.99

According to this calculation, the free electrode surface is doubled by an increase in φ_c of 100 mV. These values of $(1 - \theta)$, computed from kinetic data, are perhaps too low, and hence those of θ are somewhat overestimated. Though direct determination of the adsorption of I⁻ ions on Co, for example by a radioactive tracer method, has not yet been undertaken, from the effects of I⁻ ions on the hydrogen overvoltage on cobalt and iron^{2,4}, it can be assumed that the adsorption of these ions does not greatly differ on the two metals. At φ_s in 1 N H₂SO₄, less than half a monolayer

of I⁻ is adsorbed on iron $[(1 - \theta) > 0.5]$ during the first 20–30 min,^{5,9} which is less than the value calculated by the above method. This result may indicate that the chemisorption of I⁻ involves a change in the state of the cobalt surface even on the portions not occupied by these ions, for example a decrease in the energy of adsorption of atomic hydrogen in the vicinity of an adsorbed I⁻ ion.

Effect of Halide Ions on the Anodic Ionisation of Cobalt

The slowing down of the anodic reaction can also be explained by a low rate of ionisation of cobalt at sites occupied by adsorbed halide ions. If this latter effect is neglected, we can write the equations:

$$i_a = k_2 (1 - \theta) \exp \{2\beta \varphi_a F / RT\}, \quad (4)$$

$$\varphi_a = a_2 + \frac{RT}{2\beta F} \ln i_a - \frac{RT}{2\beta F} \ln (1 - \theta). \quad (4a)$$

Desorption of halide ions is responsible for the above fact that the anodic polarisation curve passes, with increase in i_a , into a portion along which φ_a is practically independent of i_a (Fig. 1). At each anodic current density a kinetic equilibrium is established between the rates of adsorption and desorption, the former being proportional to the halide ion concentration in the solution and to the surface which is free from the ions⁵

$$v_{ads} = k_{ads} (1 - \theta) c_{I^-}. \quad (5)$$

The rate of desorption increases with rise in the anodic potential

$$v_{des} = k_{des} \theta \exp \left\{ \frac{3\beta \varphi_a F}{RT} \right\}. \quad (6)$$

However, the effect of anodic polarisation is not direct, since we should expect a decrease rather than an increase in the desorption of anions with increase in the anodic potential. Desorption is obviously caused by dissolution of the metal and removal of adsorbed ions with the surface atoms of cobalt undergoing ionisation. As is evident from Eqns. (4) and (6), the rate of this process increases with increase in i_a or φ_a . This is confirmed by the φ - t curves obtained when the anodic current is switched on.

In order to obtain such a curve, the electrode was kept without current (at φ_s) for 2 min, the previously established current density i_a was switched on, and a φ - t oscillogram was recorded by means of an ENO-1 oscillograph. A curve like that in Fig. 3 was obtained for each current density and KI concentration. Immediately after the current was switched on, while the surface layer of metal atoms still remained, the maximum adsorption and the corresponding anode potential φ_{max} were rapidly attained, and it was only after the whole of the initial surface layer of metal atoms had been removed that the rates of adsorption and desorption of halide ions became equal and the stationary anode potential φ_a was established. Owing to the comparative slowness with which halide ions are bonded to the cobalt atoms and adsorption equilibrium is established, the values of φ_a and φ_s depend on the rate at which the polarisation curves are determined. Fig. 2 gives values of φ_a obtained after a given current density has been passing for 1–2 min, together with the maximum values φ_{max} obtained oscillographically, as a function of the logarithm of the KI concentration. The broken lines in Fig. 1 represent φ_{max} plotted against $\log i_a$. The slope of these curves $\partial \varphi_{max} / \partial \log i_a$ is the same (~ 0.060 V) for all KI concentrations. Calculation

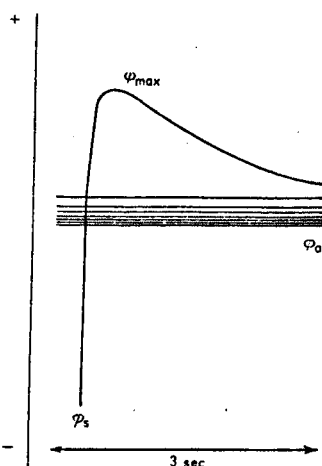


Fig. 3. Diagrammatic oscillogram.

based on a formula analogous to Eqn. (3) shows that, when the anodic reaction takes place with maximum adsorption of I^- ions, the proportion of surface unoccupied ($1 - \theta$) is very small, and diminishes with increase in $\varphi_{\max}$, as can be seen from the following data:

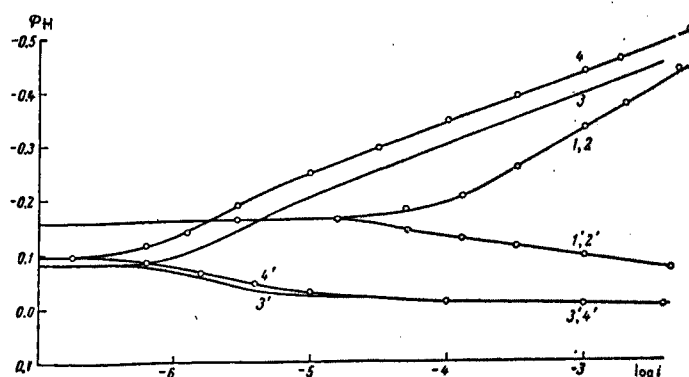
$\varphi_{\max}, V$	-0.050	0.00	0.050	0.100
$\log(1 - \theta)$	-3.6	-4.2	-4.6	-5.1

Under stationary conditions (at φ_s), the removal of a considerable proportion of the adsorbed I^- ions from the anode surface together with the ionised Co atoms results in $1 - \theta$ being considerably larger than these values.

Experiments show that the action of the halide ions, and hence also their adsorption, diminish with decrease in the acid concentration, probably for two reasons — owing to φ_s becoming more negative and because of an increase in the chemisorption of OH^- — which diminish the adsorption of halide ions and themselves stimulate the anodic process⁹.

Action of Cationic Inhibitors in the Presence of Halide Anions

The experiments showed that, as in the case of iron, the cationic type of inhibitors are ineffective in the absence of halide anions, obviously owing to their low adsorption on a cobalt surface. Up to concentrations of 0.01 M, tetrabutylammonium sulphate produces no appreciable increase in cathodic or anodic polarisation in 1 N and 6 N H_2SO_4 , probably because the cobalt surface bears a positive charge practically throughout the range of potentials measured. The stationary potential of cobalt in H_2SO_4 solutions is more positive than the zero-charge potential. In 1 N and 6 N H_2SO_4 the values of φ_s are respectively -0.160 and -0.145 V. Divergent values are given for the zero-charge potential: -0.58 and -0.68 V have been calculated from the electron work function by Vasenin¹⁰, and -0.51 V by Antropov¹¹; Kheifets and Krasikov¹² obtained experimental values between -0.32 and -0.48 V over the pH range 1–6, and -0.23 V in 2 N H_2SO_4 . The presence of halide anions in an acid solution results in the adsorption of organic cations and an additional retarding effect on electrochemical reactions.

Fig. 4. Curves for the polarisation of cobalt in 1 N H_2SO_4 containing:

1), 1') no addition; 2), 2') 10^{-3} N $N(C_4H_9)_4^+$; 3), 3') 10^{-4} N KI; 4), 4') 10^{-4} N KI + 10^{-3} N $N(C_4H_9)_4^+$.

Fig. 4 gives polarisation curves for a cobalt electrode in 1 N H_2SO_4 containing KI and $[N(C_4H_9)_4]_2SO_4$ alone and together. The effect of $N(C_4H_9)_4^+$ on the cathodic reaction in the presence of KI is smaller with cobalt than with iron, and decreases with increase in the KI concentration in the acid solution. Thus the increases in the hydrogen overpotential produced by adding 0.001 N $N(C_4H_9)_4^+$ to 6 N H_2SO_4 containing 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} N KI are respectively 50, 38, 28, and 15 mV.

Qualitatively similar regularities are observed in the presence of Br^- and Cl^- ions. The increase in the hydrogen overvoltage produced by adding the 0.001 N cation to the 6 N H_2SO_4 is respectively 40 and 30 mV in the presence of 0.01 N and 0.1 N KCl. Chemisorbed halide anions probably make the zero-charge potential of cobalt more positive, thereby facilitating the adsorption of organic bases. The retarding effect of $N(C_4H_9)_4^+$ on the anodic ionisation of cobalt in the presence of KI and KBr is observed only close to φ_s ; elsewhere in the range of anodic polarisation it is very small (less than the experimental error). A possible explanation of this last fact is that, in contrast to conditions with iron, the adsorption of these anions on cobalt, while making the zero-charge potential more positive, does not change the surface charge from positive to negative.

SUMMARY

1. The presence of halide salts (KI, KBr, KCl) in sulphuric-acid solutions slows down the discharge of H_3O^+ and the ionisation of cobalt, the effect on the latter reaction being the greater.
2. The occurrence at high current densities of a section of the anodic polarisation curve along which the potential is practically independent of current density is due to the finite rate of adsorption of halide ions on cobalt and the passage into the solution of chemisorbed halide ions with the ionised metal atoms.

3. The effect and hence the adsorption of I^- ions diminish with increase in the cathodic potential, and become more marked with rise in the anodic potential.
4. Tetrabutylammonium cations have hardly any influence on these electrochemical reactions on cobalt in sulphuric acid solutions, probably because of the positive surface charge on cobalt.
5. Addition of tetrabutylammonium cations to an acid solution containing KI results in further retardation of the cathodic reaction, but has little effect on the rate of the anodic ionisation of cobalt.

We examined the effect of non-aqueous solvents on one of the simplest redox reactions:



The behaviour of this system in aqueous solutions has been studied by a number of workers^{4,5}, KI serving as a source of iodide. They observed two types of polarisation — concentration and chemical. In the anodic process the latter predominates and in the cathodic process the former.

We chose tetraethylammonium iodide of "analytical reagent" grade as the source of I^- . We investigated the cathodic and anodic processes for 0.001 M $(C_2H_5)_4NI$ and 0.001 M I_2 by the temperature-kinetic method⁶ using a rotating platinum disc electrode of area $S = 0.12 \text{ cm}^2$. The design of the electrode, developed by Gorbachev and Belyaeva, eliminated the effect of the ohmic factor and prevented the breakdown of the hydrodynamic regime. To prevent variations in the rate of rotation due to mains voltage fluctuations, an SD-09M synchronous motor was used. The polarisation was measured by the direct compensation method, an M91/A mirror galvanometer serving as the null instrument.

All the measurements were made at $2^\circ - 20^\circ$ and rates of rotation of the electrode between 600 and 3000 rev min^{-1} . Tetraethylammonium iodide was twice recrystallised and dried in a stream of nitrogen. Propanol of "purified" grade was treated with magnesium filings and twice distilled. All the investigations were made in a hermetically sealed system.

The results are presented in Figs. 1 and 2. The polarisation curves in these figures characterise the rates of reaction (1) in water and propanol as solvents at 20° and with various rates of rotation of the electrode. It is seen that (1) rotation considerably increases the rate of both the anodic and cathodic processes, and (2) the rates of the anodic and cathodic reactions differ by a factor of about 1.5. Similar curves were obtained also at other temperatures.

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EFFECT OF SOLVENTS ON THE KINETICS OF ELECTROCHEMICAL REDOX REACTIONS. I. ELECTROCHEMICAL OXIDATION-REDUCTION OF THE IODINE-IODIDE SYSTEM IN WATER AND PROPANOL

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Non-aqueous solvents have a considerable influence on the kinetics of reactions in solution. Menshutkin¹ was the first to turn his attention to this phenomenon, which was later investigated by Moelwyn-Hughes². The electrochemical properties of electrolytes in non-aqueous solvents have been investigated in detail by Izmailov and coworkers³. However, the effect of solvents on the kinetics of electrochemical reactions⁴, although one of the most important problems in physical chemistry in connection with the development of organic synthesis and polarography in non-aqueous media, remains virtually uninvestigated.

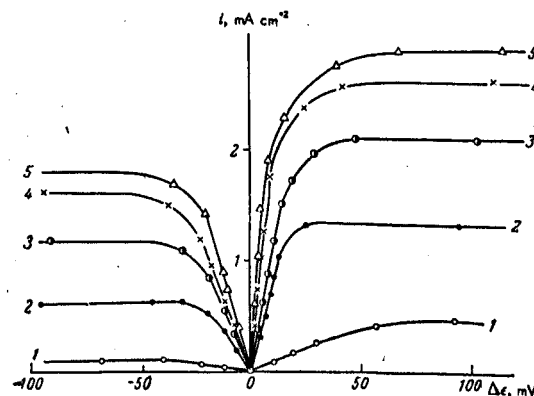


Fig. 1. Effect of the rate of rotation of the electrode on the rate of the anodic and cathodic processes in water at 20° and $(C_2H_5)_4NI$ and I_2 concentrations 0.001 M; rate of rotation n (rev min^{-1}): 1) 0; 2) 637; 3) 1190; 4) 1900; 5) 3000.