EFFECT OF CATION ON THE KINETICS AND MECHANISM OF THE REACTION OF COPPER SINGLE CRYSTAL IN ALKALI HYDROXIDE SOLUTIONS*

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The effect of the metal (Li, Na, K) on the kinetics and mechanism of the reaction of a copper single crystal in alkali hydroxide solutions was studied on the faces corresponding to the (100), (110), and (111) planes, with a special attention to the (100) plane. The differences in the kinetic behaviour are discussed in terms of the hydratability of the cations as well as of the physico-chemical characteristics of the hydroxide solutions, particularly their viscosity and the solubility of oxygen in them. Of the electrochemical parameters examined, only the E^0 value is affected by the cation.

Cations (similarly as anions) of the medium, even though not constituting the reactants, affect the course of homogeneous as well as heterogeneous reactions taking place in the system. In the electro-reduction of bromates on a mercury dropping electrode[1] the reduction rate depends on the cation of the indifferent electrolyte: it increases in the cation order $Li^+ < Na^+ < K^+$, which is also the order of their increasing adsorbing ability[2]. It has been found that rather than in a specific adsorption the effect of the cation lies in a formation of ionic associates, their disposition for this phenomenon increasing with their adsorbing ability[3]. In exchange reactions of MnO_4^- with MnO_4^{2-} ions or of $[Fe(CN)_6]^{3-}$ with $[Fe(CN)_6]^{4-}$ ions, the rate has been observed to increase in the cation order [4,5] $Li^+ < Na^+ < K^+$. In this case the partly dehydrated cation forms an ionic triplet of the $(MnO_4-K-MnO_4)^{2-}$ type; and as the weakly hydrated K^+ cation forms ionic associates with higher stability constants than the strongly hydrated Li^+ cation, it will accelerate the reaction to a higher extent.

One of the few papers concerned with the effect of cations on the spontaneous dissolution of metals in liquid media is the study[6] dealing with the reaction of aluminium in lithium, sodium, potassium, and ammonium hydroxide solutions. Based on the observation that the reaction rate in dependence on the concentration of hydroxide is directly proportional to the conductivity of the solution, and making use of

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other experiments as well, the authors were able to prove that the dissolution of aluminium proceeded on an electrochemical mechanism.

The present work is concerned with the effect of the alkali metal cation on the reaction of a copper single crystal in hydroxide solutions, and with the effect of the reaction conditions on the position of the maximum in the concentration dependence curves.

EXPERIMENTAL

The reaction kinetics was examined spectrophotometrically based on the time increment of copper-(II) ions in the solution stored in a thermostatted glass reaction vessel for four hours. Oriented sections (precision $\pm 2°$) of a copper single crystal grown by secondary recrystallization from poly-crystalline copper of spectral purity served as the experimental material. The measurements were conducted under pure oxygen at atmospheric pressure. The partial pressure of oxygen was reduced by rarefying with nitrogen, the mutual ratio of the two gases being controlled by flow meters. Each measurement was repeated three to five times and the averages were used for the plots. The mean error was $5-10\%$.

The potential of copper, monitored parallel with the kinetic measurements, was measured against a saturated calomel electrode connected with the reaction system *via* a saturated KCl solution bridge. The potential values obtained were converted to the hydrogen scale.

RESULTS AND DISCUSSION

The effect of LiOH, NaOH, and KOH appeared on all of the three basic planes of the crystal (Table I). The change was most marked on the (100) plane, as could be anticipated taking into account our previous study of the action of anions[7] in which this plane was affected by anions to the least extent (except for the strongly hydrated F^- anion). For this reason, we concentrated now our attention to this plane.

TABLE I

Rates of the reaction of a copper single crystal in alkali hydroxide solutions; $c_{MOH} = 0.5 \text{ mol l}^{-1}$, $t = 15°C$

Hydroxide	$v \cdot 10^2$, kg h^{-1} m^{-2}, for the plane		
	(100)	(110)	(111)
LiOH	0·82	0·31	0·70
NaOH	0·095	0·30	0·41
KOH	0·08	0·10	0·23

The rates of dissolution of the (100) plane in dependence on the hydroxide concentrations are plotted in Fig. 1; the rate in the maximum depends on the cation present, the order being $v_{LiOH} > v_{NaOH} > v_{KOH}$. The specific adsorption of the cations and their charge transfer ability, as mentioned above, decrease in the reverse order, which indicates that in this case it is probably other properties of the cation that control the effects at the metal–electrolyte interface.

The ratio of the rates in the maximum is $v_{LiOH} : v_{NaOH} : v_{KOH} = 1·8 : 1·0 : 0·7$, which is in a good agreement with the ratio of the adsorption coefficients $\alpha_{LiOH} : \alpha_{NaOH} : \alpha_{KOH} = 1·6 : 1·0 : 0·8$; hence, the concentration of oxygen in the solution is among the factors affecting appreciably the height of the maximum.

The dependence of the reaction rate on the concentration of the Li^+ and Na^+ ions in an LiOH—NaOH isomolar series with the total hydroxide concentration $0·5$ mol . . l^{-1} is shown in Fig. 2. Since the physico-chemical properties of the hydroxide solutions, such as the viscosity, conductivity, or solubility of oxygen, differ only slightly up to this concentration, the variations in the height of the maximum are obviously determined, in addition to the concentration of oxygen, also by the cation involved. This, however, implies that the reaction order, determined from the ascending branch of the concentration dependence, is to be considered also with respect to the MOH ionic system and not only with respect to the OH^- ions, as indicated in paper[9],
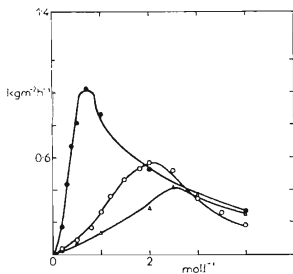

FIG. 1

Rates of dissolution of a copper single crystal in dependence on the hydroxide concentration; (100) plane, $P_{O_2} = 0·1$ MPa, $t = 15°C$.
● LiOH, ○ NaOH, △ KOH
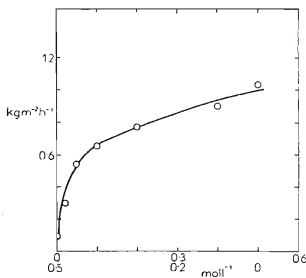

FIG. 2

Rate of dissolution of a copper single crystal in dependence on the lithium-to-sodium ratio for the total hydroxide concentration $0·5$ mol l^{-1}; (100) plane, $P_{O_2} = 0·1$ MPa, $t = 15°C$

because the cation, although not taking a direct part in the reaction, also affects the reaction rate.

In view of the fact that the oxygen concentrations in 0·5M-LiOH and NaOH solutions are roughly the same, the effect of the cation obviously consists in an influencing of the structure of molecules of the dissolved oxygen. The interaction of nonelectrolytes in electrolyte solutions has been a concern of Čeleda[10-12], who pointed out that ions can exert an effect upon the nonelectrolyte molecules by short-range forces and add them by a coordination bonding, and was able to prove the existence of such adducts experimentally.

The effect of the cation in the reaction under study can also be explained in terms of this concept: the cation exerts a short-range effect upon the oxygen molecules and polarizes them, whereupon the activation energy of their cleavage decreases. Moreover, owing to the addition of the oxygen molecule in the inner coordination sphere of the cation, the metal–O_2 distance shortens on the adsorption of the adduct on the metal surface, thus facilitating the charge transfer. As a consequence, the reaction rate will increase in the same order as the stability constants of the adducts, hence, from K^+ to Li^+.

The concentration dependence curve, involving a maximum, is typical of spontaneous dissolution of metals[6,8,9,13-15]. According to Akimov[16] the rate rise is due to the increase in the conductivity of the solution, leading to a higher corrosion current; the c_{max} concentration at which the rate is highest is determined by a combination of the effects of the solubility of oxygen and the conductivity, the ensuing deceleration being due to a lowering of the former. This concept has been confirmed in the work[6], in which c_{max} corresponded directly with the maximum of conductivity of the electrolytes used. However, as the experiments with the dissolution of germanium in KI and Na_2SO_4 solutions[14] indicated, these factors are not the sole ones and not even the primary ones, as two mutually different curves were obtained in a concentration region in which the concentration of oxygen changed only slightly and the conductivity of the two solutions was comparable. For the dissolution of germanium in nitric acid the c_{max} value depends on the stirring intensity, which has been interpreted in terms of an autocatalytic effect[15].

In this case the rate increase obviously is not governed by the conductivity of solution, because at a given concentration of hydroxide the conductivity increases in the order $\varkappa_{LiOH} < \varkappa_{NaOH} < \varkappa_{KOH}$, while the rate increases in the reverse order. The rate increase is due to the increasing concentrations of the cations, which accelerate the formation of copper(I) oxide according to the above mechanism, as well as of the hydroxyl anions, which accelerate the dissolution of the oxide. The position of c_{max} depends on the oxygen pressure (being higher at higher pressures) (Fig. 3, curves 1 and 2), on the viscosity (the viscosity of LiOH in the maximum, for instance, equals approximately that of KOH in the maximum), and also on temperature (Fig. 3, curve 3).

As follows from the literature and from our experimental data, the reaction mechanism governing the shape of the concentration dependence for the spontaneous dissolution of metals in electrolytes is conditioned by the physical properties of medium, and therefore cannot be generalized.

Along with the kinetics of the reaction, the potential of copper was also monitored. Examining the significance of the potential in the reaction of copper we found[17-20] that potential changes during the reaction are associated with the formation of oxides on the metal surface; the potential of copper in NaOH solutions at 15°C and oxygen pressure of 0.1 MPa was given by the relation

$$E = E° - (2RT/F) \ln a_{NaOH} + (RT/2F) \ln (\alpha/\alpha_0) . \qquad (1)$$

This equation can be applied also to LiOH and KOH solutions; in Fig. 4 the quantity $E_1 = E - (RT/2F) \ln (\alpha/\alpha_0)$ is plotted as a linear function of the hydroxide activity,

$$E_1 = E° - A \ln a_{MOH} . \qquad (2)$$

The values of the $E°$ and $A = RT/nF$ constants for LiOH, NaOH, and KOH are given in Table II; the proportionality factor values are found to be very close to one another irrespective of the cation involved.
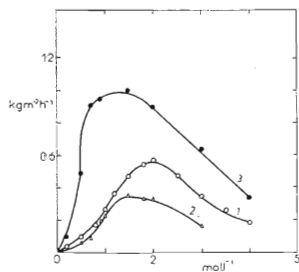
FIG. 3

Rate of dissolution of a copper single crystal in dependence on the concentration of NaOH at various oxygen pressures and temperatures; (100) plane. 1 $P_{O_2} = 0.1$ MPa, $t = 15°C$, 2 $P_{O_2} = 0.05$ MPa, $t = 15°C$, 3 $P_{O_2} = 0.1$ MPa, $t = 25°C$
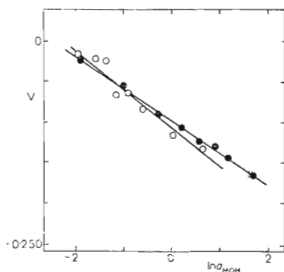
FIG. 4

Dependence of the copper potential at the (100) plane on the activity of the hydroxide; $P_{O_2} = 0.1$ MPa, $t = 15°C$. ○ LiOH, ● KOH

The potentials in the NaOH solutions were measured also at 25°C (Fig. 5, curve *1*). The slope of the straight line is $2RT/F$, identical with that at 15°C.

At a unity activity of NaOH and a pressure of oxygen of 0·1 MPa, E in Eq. (*1*) equals E^0 $(= -0.079$ V); at different oxygen pressures,

$$E = -0.079 + (RT/nF) \ln (P/P^0), \qquad (3)$$

where P^0 is the standard pressure of 0·1 MPa. So the proportionality factor can be determined if the E value is known for a pressure P and a unit activity of NaOH; for instance, at an oxygen pressure of 0·05 MPa the E value is -0.086 V (Fig. 5, curve (*2*), so that

$$-0.086 = -0.079 + (RT/nF) \ln (7.05/0.1), \qquad (4)$$

whence $(RT/nF) = 0.010$; the same value has been obtained also in the work[17] as the slope of the plot of potential *versus* the oxygen pressure.

TABLE II

Values of the parameters of Eq. (*2*) for the (100) plane

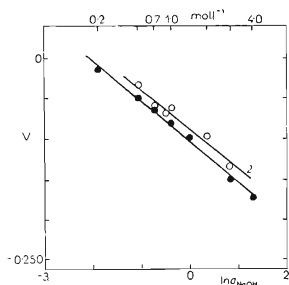| Hydroxide	E^0 V	A V	n
LiOH	−0·1045	0·048	0·5
NaOH	−0·079	0·048	0·5
KOH	−0·097	0·040	0·6

FIG. 5

Dependence of the copper potential at the (100) plane on the activity of NaOH at various oxygen pressures and temperatures. *1* $P_{O_2} = 0.05$ MPa, $t = 15$°C, *2* $P_{O_2} = 0.1$ MPa, $t = 25$°C

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