THE INFLUENCE OF THE NATURE OF THE CATIONS ON THE OVERVOLTAGE OF HYDROGEN LIBERATION FROM ALKALINE SOLUTIONS AT A MERCURY CATHODE

Z. A. Iofa and E. A. Maznichenko
(M. V. Lomonosov State University, Moscow)

Hydrogen overvoltage in alkaline solutions has been studied in less detail than in acid solutions. For a mercury cathode, the hydrogen overvoltage has been studied by the method of amalgam decomposition by S. I. Sklyarenko [1], G. I. Volkov [2], Bockris and Watson [3] and others. Examination of the literature shows, however, there are as yet no precise and reliable data on overvoltage at a mercury cathode in alkaline solutions, and on the relationship between this overvoltage and various factors, including the nature of the alkali metal cation. The fact that the experimental data of different authors do not agree is related to the fact that the process of hydrogen liberation from alkaline solutions is extremely sensitive to various types of impurity, since the process in such solutions is the result of discharge of water molecules at a relatively high negative potential. Foreign ions entering the double layer may alter the distribution of the lines of force of the field close to the water molecules and may have a marked accelerating or retarding effect on the discharge process. We shall give examples of the retarding and accelerating action of cations.

The relationship between the rate of hydrogen evolution and the potential has been measured directly from the cathodic polarization curves for a dropping mercury electrode in pure solutions of tetraalkylammonium bases, whose cations do not form amalgams. At the high negative potentials which are reached in these cases, the dropping period is greatly reduced, so that a capillary is chosen with an initial dropping period of at least 10 seconds. The area of the dropping cathode was calculated from the rate of flow of mercury and the dropping period for each value of the potential. The charging current, which must be subtracted from the measured current, was found from the charge on the electrode surface, calculated from the double layer capacity curves for these solutions.

Fig. 1 gives curves for the relationship between the potential (relative to a saturated calomel electrode) and the logarithm of the current density at 20° for 0.1 N $(CH_3)_4NOH$ (1) and 0.1 N $(C_4H_9)_4NOH$ (2). The figure shows that the rate of hydrogen evolution from the $(C_4H_9)_4NOH$ solution is much less, and the overvoltage much greater, (by 350 mv) than from $(CH_3)_4NOH$ solution at the same potential. The Table compares the overvoltage values for these solutions with the overvoltage values for other alkalies. Fig. 1 shows that the potentials at corresponding current densities for $(CH_3)_4NOH$ and $(CH_3)_4NI$ solutions coincide exactly. This feature is of particular interest and provides evidence that the rate of hydrogen evolution at a given concentration and potential is independent of the pH value in the layer next to the electrode. 0.1 N $(CH_3)_4NOH$ has pH ~ 13. When the experiment is carried out with $(CH_3)_4NI$, the originally neutral solution acquires a weakly alkaline reaction as a result of hydrogen evolution. Calculation using the Ilkovic equation has shown that for the current density range indicated in Fig. 1, the pH of the $(CH_3)_4NI$ solution varied between 10 and 11.6. The fact that the rate of hydrogen evolution is independent of the pH is in complete accordance with theory based on the assumption that the hydrogen is liberated from water molecules.

The question then arises: up to what pH value is it necessary to take account of the discharge of hydrogen ions in addition to the liberation of hydrogen from water molecules? In order to answer this question, let us examine the curves given in Fig. 2, which shows the relationship between the hydrogen overvoltage at a mercury

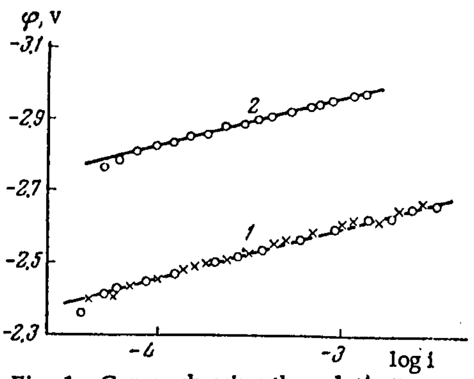

Fig. 1. Curves showing the relationship between the potential of the mercury electrode and the logarithm of the current density. 1) In 0.1 N $(CH_3)_4NOH$ (circles) and 0.1 N $(CH_3)_4NI$ (crosses); 2) in 0.1 N $(C_4H_9)_4NOH$ (circles).

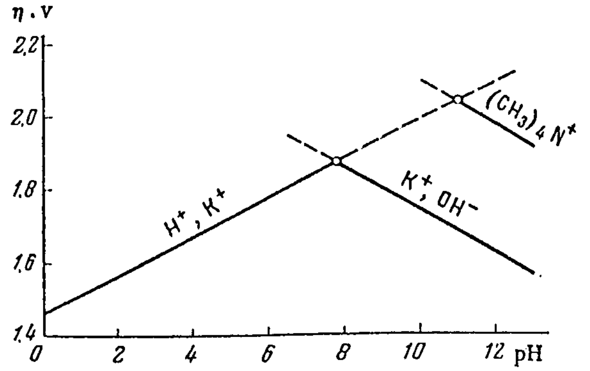

Fig. 2. Curves showing the relationship between the overvoltage at a mercury cathode and pH in 0.1 N solutions for acid and alkaline solutions [KOH and $(CH_3)_4NOH$].

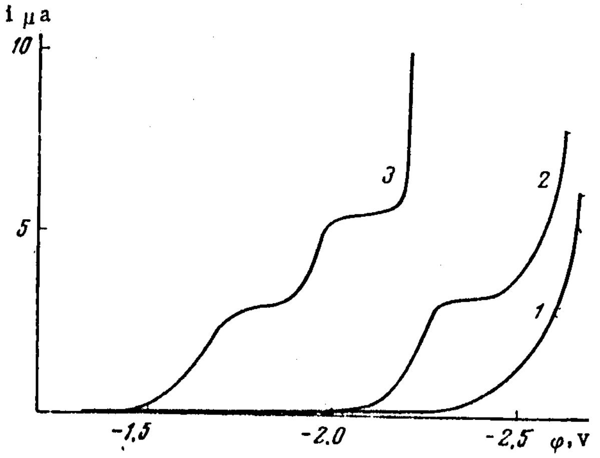

Fig. 3. i – φ curves recorded at a dropping mercury electrode in the solutions: 1) 0.1 N $(CH_3)_4NI$; 2) 0.1 N $(CH_3)_4NI$ + N $CaCl_2$; 3) 0.1 N $(CH_3)_4NI$ + 10^{-4} N HCl + N $LaCl_3$.

cathode and the pH, at constant concentration and current density, for the acid and alkaline regions. It can be seen that in the case of KOH solution, the evolution of hydrogen from hydrogen ions and from water molecules takes place at identical rates at pH 7.8 (point of intersection of the curves), and in the case of $(CH_3)_4NOH$, at pH 11. It therefore follows from Fig. 2, that hydrogen is liberated from water molecules only at relatively high pH values.

Calculation has shown, however, that this conclusion must be stated more precisely. Ordinary current densities may be achieved by means of the diffusion of hydrogen ions only at pH values less than 5. At higher pH values, hydrogen ions can be obtained only as a result of the dissociation of water molecules in the layer next to the electrode, and the maximum quantities of these which can be used up depends on the rate of dissociation of the water molecules and on the rate of supply of these molecules to the electrode surface. A limitation is thus set on the current due to H^+ -ions, i.e., this current acquires kinetic character. Calculation carried out by A. N. Frumkin* has shown that the kinetic currents due to hydrogen ions in weakly alkaline solutions are smaller than the measured currents by several orders of magnitude, so that the latter must be responsible for the direct liberation of hydrogen from water molecules.

As a result of the kinetic limitations applying to the hydrogen ions, the pH in the surface layer at which the rate of discharge of water molecules is comparable to the rate of discharge of hydrogen ions is shifted towards lower values, and it is possible to move along the straight line (η, pH) for alkaline solution to a more acidic value than is indicated by Fig. 2.

The table compares the overvoltage for 0.1 N alkali solutions with different cations for a current density of 10^{-3} amp/cm². The values of the Tafel equation constant a for a number of alkalies are also given.

---

*The calculation will be published in detail in Zhur. Fiz. Khim. Akad. Nauk SSSR (Journal of Physical Chemistry, USSR Academy of Sciences).

Overvoltages for 0.1 N Solutions of Alkalies With Different Cations

Solution	η $i = 0.001$ amp/cm^2	a $i = 1$ amp/cm^2	Author
	v		
$(C_4H_9)_7NOH$	1.88	2.27	Our measurements
$(CH_3)_4NOH$	1.53	1.93	" "
KOH	1.28	1.63	O. L. Kaptsan and Z. A. Iofa [4]
LiOH	1.29	—	Bockris and Watson [3]
NaCl$_{\text{sat.;}}$ pH = 12	1.47	—	G. I. Volkov [2]
HCl	1.08	1.46	Z. A. Iofa [5]

The table shows that the overvoltage in $(C_4H_9)_4NOH$ is 800 mv higher than in acid, and 600 mv higher than in KOH of the same concentration. These overvoltages (judging from the values for the constant a) in tetraalkylammonium bases are considerably greater than the limiting value for the Tafel equation constant a obtained on the bases of the adsorption theory of N. I. Kobozev, which is equal to 1.5-1.6 v [6].

The high overvoltage in alkaline solutions and its dependence on the nature of the cation may be explained if account is taken of the nonuniform distribution of the electrical field in the double layer. In acid solutions the discharge of hydrogen ions takes place in the region of maximum concentration of the lines of force of the double layer field, since these ions form the outer surface of the double layer. In the case of hydrogen evolution from alkaline solutions, the species being discharged are not ions, but neutral water molecules situated between the cations of the surface of the double layer or present in their sphere of hydration. For this reason, the conditions for the action of the electrical field in this case are much less favorable.* The greater the dimensions of the cation, the further the water moleculeslie from the region of positive charge localization, the lower the density of the lines of force of the field in the region of the double layer containing the water molecules which are being discharged, and, consequently, the more negative will be the potential for a given process rate, i.e., the higher will be the overvoltage.

The rate of hydrogen evolution from alkaline solutions, like any other electrochemical reaction, depends on the potential jump in the dense part of the double layer bringing about the discharge of the hydrogen in the water molecules. As a first approximation, it has been assumed [7] that thispotential jump is given by the equation

$$i = k\,[\mathrm{H_2O}]_S\, e^{\frac{-\alpha(\varphi-\psi_1)F}{RT}}$$

i.e., is proportional to the difference between the measured cathode potential and the ψ_1-potential – the average value of the potential at a distance from the electrode surface equal to the ionic radius.

It is more accurate, however, to consider a certain effective ψ_1-potential value. This effective value of the ψ_1-potential depends on the position of the water molecule relative to the positive charge on the cation. The greater the cation radius, the further will be the water molecule from the center of gravity of the positive

---

*In addition to the difference considered here, which is related to the influence of the electrical field, we must also take into account the fact that the energy barrier for rupture of the bond between the proton and the hydroxide ion in the water molecule is higher than that for rupture of the bond between the proton and the water molecule in the hydronium ion.

charges in the double layer, and, consequently, the more negative will be the value of ψ' appearing in the exponent in the above kinetic equation. This reduces the effective potential jump in the dense part of the double layer and also leads to a decrease in the rate of the process at a given cathode potential.

In addition to this effect, we must also take into account the fact that increase in the cation radius in solutions of tetraalkylammonium bases causes an increase in the extent to which the cathode surface is covered by these bases for a given charge, and as a result decreases the surface concentration of the water molecules, which also appears in the above kinetic equation (in the first degree). Preliminary calculations, carried out using the cation radius [8] and electrode surface charge, have shown that in the case of $(CH_3)_4NOH$ the extent to which the surface is covered at a current density of 10^{-3} amp/cm^2 is approximately 0.25, and in the case of $(C_4H_9)_4NOH$ is approximately 1. The decrease in the surface concentration of water molecules as a result of the covering of the electrode surface with tetraalkylammonium cations also reduces the rate of the process at the same potential.

We should also mention some further results of experiments on the study of the influence of added cations on the rate of hydrogen evolution from alkaline solutions. Fig. 3 gives curves showing the relationship between current and potential recorded at a dropping mercury electrode in pure 0.1 N $(CH_3)_4NI$ (Curve 1) solution and in the same solution (as supporting electrolyte) containing 0.001 N $CaCl_2$ (Curve 2). Comparison of the upper sections of these curves, which represent the waves for hydrogen liberation from water molecules, shows that small concentrations of calcium ions have no significant effect on the rate of this process in weakly alkaline solutions. Barium ions behave similarly.

Curve 3 (Fig. 3) is the curve for an acidified solution of the supporting electrolyte containing 0.0001 N $LaCl_3$. The curve consists of three waves: the wave for hydrogen evolution from H_3O^+, the La^{3+} discharge wave, and the wave for H_2 evolution from water molecules. Comparison of the position of the last wave with the position of the analogous wave for the supporting electrolyte shows that the lanthanum ions have a considerable accelerating effect on the evolution of hydrogen from weakly alkaline solutions: the wave for the discharge of water molecules is shifted to more positive potentials by 400 mv. A similar accelerating action by lanthanum ions has been observed by S. I. Zhdanov and A. N. Frumkin [9].

The above considerations lead to a qualitative explanation of the action of certain cations added to the solution. It is evident that the discharge conditions should be particularly favorable for water molecules present in the sphere of hydration of polynuclear cations in the double electrical layer. This effect is apparently clearly shown in the case of lanthanum ions.

It would however, be incorrect to extend this explanation to the effects observed in the presence of such ions as those of chromium, molybdenum, vanadium, etc. In these cases, a predominant part is played by the catalytic action of the metal, which is deposited at the surface of the mercury cathode.

LITERATURE CITED

[1] S. I. Sklyarenko, and B. A. Sakharov, Zhur. Fiz. Khim., 21, 97 (1947).

[2] G. I. Volkov, Zhur. Fiz. Khim., 27, 194 (1953).

[3] J. O'M. Bockris and R. Watson, J. chim. phys., 49, 1 (1952).

[4] O. L. Kaptsan and Z. A. Iofa, Zhur. Fiz. Khim., 26, 193, 201 (1952).

[5] Z. A. Iofa, Zhur. Fiz. Khim., 13, 1435 (1939).

[6] N. I. Kobozev, Zhur. Fiz. Khim., 26, 120 (1952).

[7] A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa and B. N. Kabanov, "Kinetika Elektrodnykh Protsessov" (The Kinetics of Electrode Processes), Izd. MGU, 1952).

[8] R. Robinson and R. Stokes, Electrolyte Solutions, London, 1955.

[9] S. I. Zhdanov and A. N. Frumkin, Zhur. Fiz. Khim., 29, 1459 (1955).