128. M. A. Loshkarev, L. M. Boichenko, and A. F. Nesterenko, Vopr. Khim. Khim. Tekhnol., No. 31, 67 (1973).
129. M. A. Loshkarev, A. F. Nesterenko, V. M. Vakulenko, and A. I. Silkina, Vopr. Khim. Khim. Tekhnol., No. 30, 80 (1973).
130. L. S. Zagainova and A. V. Kuzmicheva, Vopr. Khim. Khim. Tekhnol., No. 28, 88 (1973).
131. V. V. Losev, Dokl. Akad. Nauk SSSR, 107, 432 (1956).
132. B. N. Afanas'ev (Afanasiev), Coll. Czech. Chem. Commun., 33, 1186 (1968).
133. B. N. Afanas'ev, Élektrokhimiya, 1, 1449 (1965).
134. G. A. Dobren'kov, L. F. Gusev, and V. A. Golovin, Élektrokhimiya, 10, 122 (1974).

HYDROGEN OVERPOTENTIAL AT A MERCURY CATHODE IN ACIDIC ACETONITRILE SOLUTIONS

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UDC 541.138.3:546

The effect of the composition of the solution on the hydrogen overpotential in acetonitrile solutions was investigated. The conditions under which the presence of a small amount of water has practically no effect on the results were determined. It was shown that the discharge of hydrogen ions follows the laws of retarded discharge theory. The difference in overpotential between the aqueous and acetonitrile solutions amounts to ~120 mV.

Interest in electrode processes in nonaqueous media has increased in recent years. In the present work the hydrogen overpotential in an acetonitrile aprotic solvent with dielectric constant $\varepsilon = 37$ was investigated. Acetonitrile differs from water in its low basicity and weak structuring characteristics.

There are several methods for the purification of acetonitrile [1, 2]. We decided on a purification method similar in principle to that described in [3], which does not involve appreciable decomposition or polymerization of the solvent. The acetonitrile was first boiled with potassium carbonate for 2 h under a reflux condenser to remove the water and acetic acid and was then purified. Potassium permanganate and potassium carbonate were added to the distillate, and the solvent was distilled. At this stage the acetonitrile was purified from aromatic unsaturated compounds. The product was slightly acidified with twice-distilled concentrated sulfuric acid to remove ammonia which had formed in the previous stage. The precipitate was decanted. The distillate was redistilled, and the obtained product was kept in a refrigerator. Just before the experiment the acetonitrile was distilled on a fractionating column with glass packing. The height of the packing layer was 110 cm. The conductivity of the purified acetonitrile amounted to 10^{-7} to $10^{-8}\ \Omega^{-1}\cdot cm^{-1}$, and this agrees with the best published data. Thus, a solvent with a conductivity of $(0.7\text{-}1.5)\cdot 10^{-7}\ \Omega^{-1}\cdot cm^{-1}$ was obtained in [4] and $(4\text{-}6)\cdot 10^{-8}\Omega^{-1}\cdot cm^{-1}$ in [5]. In [6] it was shown that with a conductivity of $5\cdot 10^{-8}\Omega^{-1}\cdot cm^{-1}$ impurities could not be detected in acetonitrile either by chromatography or by the poisoning of a platinum electrode in the iodine–iodide system.

The other reagents were purified by normal methods. The mercury was distilled twice under vacuum. The lithium perchlorate and potassium iodide were recrystallized twice from twice-distilled water and dried under vacuum. The perchloric acid was distilled twice under vacuum at a residual pressure of 2-3 mm Hg.

A hydrogen electrode was used initially as reference electrode. The platinum was platinized in an aqueous solution of H_2PtCl_6. The platinized electrode was dried in a vacuum desiccator and was rinsed with acetonitrile just before the experiment. Cases of satisfactory operation of a hydrogen electrode in this solvent have been described in the literature [7, 8]. Other investigators [1] have found that a hydrogen electrode has insufficient stability and reproducibility of potential on account of its poisoning in acetonitrile solutions. We found that a hydrogen electrode operates stably for periods between one and several hours. The length of this

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 13, No. 8, pp. 1118-1121, August, 1977. Original article submitted September 1, 1975.

period was poorly reproduced. A rapid decrease of several hundreds of millivolts in the potential then occurs. This decrease in the potential is due largely to the appearance of impurities in the solution (probably the products from hydrogenation of acetonitrile), since replacement of the solution by fresh solution leads to reestablishment of the former potential in a short time (5-10 min).

In most of the experiments a glass electrode, which has been used before as an indicator for hydrogen ions in acetonitrile [1], was used. The potential of the glass electrode is established rapidly (5-10 min), and no changes occur with the electrode for several months. A glass electrode which had been previously soaked in acetonitrile (3 weeks) was calibrated with reference to a hydrogen electrode in perchloric acid solution with various concentrations (0.16, 0.05, and 0.01 N in lithium perchlorate as indifferent electrolyte and without an indifferent electrolyte) in a special cell, which contained two different compartments with electrodes of platinized platinum. The length of the calibration test was such that the stability of the potential of the hydrogen electrode was not destroyed. The potential difference between the hydrogen and glass electrodes in solutions with various compositions amounted to 380 ± 5 mV. In the intervals between the tests the glass electrode was kept in pure acetonitrile.

The overpotential was first measured on a quiescent mercury cathod (in solutions of perchloric acid in lithium perchlorate with a constant water content). Under these conditions, however, the hydrogen overpotential decreased by 30-90 mV with time and increased again with replacement of the cathode. Acetonitrile decomposition and reduction products probably accumulate on the electrode with time. This forced us to turn to a dropping mercury electrode. The overpotential (η) at the dropping mercury electrode was close to η at the freshly replaced quiescent electrode.

Perchloric acid is the only strong acid in acetonitrile [9]. Other acids such as hydrochloric acid [10] are weakly dissociated. For this reason all the experiments were carried out in perchloric acid solutions. The employed perchloric acid was 72%, i.e., each mole of the acid contained 2.4 M water. We therefore investigated the effect of water on the hydrogen overpotential in a solution of 0.01 N perchloric acid in a 0.8 N lithium perchlorate indifferent electrolyte (Fig. 1). As seen, under these conditions the addition of water in an amount considerably greater than the amount introduced with the acid (0.024 M) has a very slight effect on the hydrogen overpotential. Consequently, the presence of a small amount of water in the initial acid in experiments with an excess of the salt cannot have an appreciable effect on the results.

As shown in [11], alkali-metal cations are hydrated selectively in acetonitrile. On the basis of published data [11, 12] on the hydration constants for Li^+ and H^+ we determined the amount of free water and unhydrated H^+ ions (H_S^+) under our experimental conditions. These calculations showed that the concentration of free water was less than the concentration of H^+ ions and that the H_S^+ concentration was practically proportional to the concentration of the acid.

The polarization curves for various concentrations of perchloric acid in lithium perchlorate with an overall electrolyte concentration of 0.8 N are given in Fig. 2. The average slope of the curve in this series of experiments amounted to 97 mV, and the effective transfer coefficient was $\alpha_{av} = 0.6$. According to retarded discharge theory the change in overpotential with change in the concentration of the acid by an order of magnitude amounts to $(1-\alpha)/\alpha \cdot RT/F$, i.e., 40 mV, which is close to the observed value (45 mV). According to published data [13] perchloric acid, being the strongest acid in acetonitrile, is fully ionized but is not fully dissociated. The equilibrium constant for the dissociation of the ion pair $CH_3CNH^+ClO_4^- \rightleftarrows CH_3CNH^+ + ClO_4^-$ is $\sim 10^{-2}$. With an excess of lithium perchlorate the ratio of the concentration of free CH_3CNH^+ ions to the pairs is constant, and association does not thus affect the dependence of the overpotential on pH with a constant ionic strength.

Data for various lithium perchlorate concentrations are given in Fig. 3. The average slope amounts to 109 mV, and accordingly $\alpha_{av} = 0.55$. Consequently, $\partial\eta/\partial \log c = 50$ mV. The effect of the concentration of the salt is close in order of magnitude ($\sim$50 mV) to the value which should be observed according to the retarded discharge theory. However, this quantity cannot be compared directly with the theoretical value, since it presents the overall result from several effects.

On account of association of the salt the concentration of the dissociated electrolyte increases more slowly with increase in the concentration of the salt. It can therefore be expected that the overpotential will increase by less than 50 mV. Estimates made by means of data on the association constants [14] show that the expected effect amounts on the average to about 0.8 of the theoretical effect. However, on account of the association of the acid increase in the concentration of the ClO_4^- ion leads to a decrease in the number of free hydrogen ions, and this leads to a further increase of η by an average of 0.6 of $(1-\alpha)/\alpha \cdot RT/F$. Moreover, an

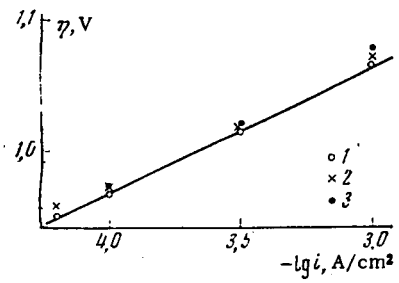

Fig. 1

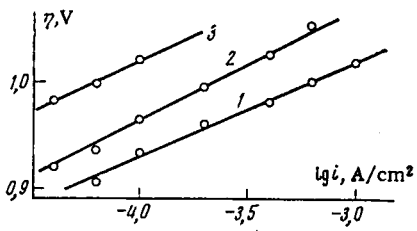

Fig. 2

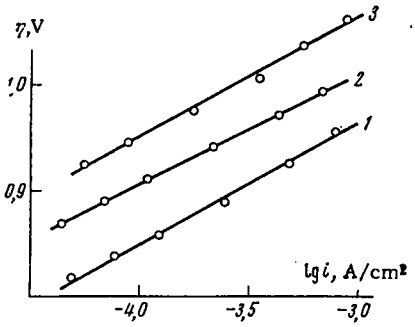

Fig. 3

Fig. 1. The η vs log i relation in solutions: 1) 10^{-2} N $HClO_4$ + $7.9 \cdot 10^{-1}$ N $LiClO_4$; 2) and 3) the same with the addition of 0.14 M H_2O and 0.24 M H_2O, respectively.

Fig. 2. The η vs log i relation in solutions: 1) 10^{-1} N $HClO_4$ + $7.0 \cdot 10^{-1}$ N $LiClO_4$; 2) 10^{-2} N $HClO_4$ + $7.9 \cdot 10^{-1}$ N $LiClO_4$; 3) 10^{-3} N $HClO_4$ + $7.99 \cdot 10^{-1}$ N $LiClO_4$.

Fig. 3. The η vis log i relation in solutions: 1) $8 \cdot 10^{-3}$ N $HClO_4$; 2) and 3) the same with additions of $8 \cdot 10^{-2}$ N $LiClO_4$ and $8 \cdot 10^{-1}$ N $LiClO_4$, respectively.

increase in the amount of salt leads to partial dehydration of the H^+ ions, and the concentration of the unhydrated H_S^+ ions increases a little which leads to a decrease of the overpotential by about $0.2(1-\alpha)/\alpha \cdot RT/F$. Thus, the overall effect amounts to approximately $1.2\ (1-\alpha)/\alpha \cdot RT/F$. The agreement with experiment can be considered satisfactory in view of the insufficient accuracy of the data on the association constants [14] and hydration constants [11, 12] used in the calculation.

From the data on the dependence of the overpotential on the composition of the solution it can be concluded that the discharge of hydrogen ions from acetonitrile in general follows the laws of the retarded discharge theory.

Our values for the hydrogen overpotential in acetonitrile are 120 mV less than the corresponding values in water [15]. In the literature there are data on the polarography of perchloric acid in acetonitrile [9, 16], from which the difference between the η values in water and acetonitrile was estimated as 0.8 V. In these works, however, the overpotential was not determined directly, and inaccurate data were used for its assessment. In addition, there were certain procedural difficulties, which will be discussed below. Vlček [16] determined the half-wave potential of hydrogen in a solution of $1.5 \cdot 10^{-3}$ N $HClO_4$ + $2 \cdot 10^{-3}$ N KI + TMA I_{sat} with reference to a potassium electrode in acetonitrile with various water contents and then extrapolated the difference of the half-wave potentials of hydrogen and potassium to zero water concentrations. Vlček indicates that he used data on the overpotential under analogous conditions during comparison with η in water. However, comparison of the overpotential in the presence of adsorbed ions in water and in acetonitrile is not strictly valid on account of the different adsorbabilities in these media.

We measured the hydrogen overpotential in a 0.1 N solution of perchloric acid in 0.1 N potassium iodide, and this was found to be ~400 mV lower than in the corresponding solution of lithium perchlorate. With the same current densities even in a more concentrated (1 M) solution of potassium iodide in water the iodide was desorbed from the mercury electrode and did not have an effect on the overpotential [17]. Consequently, a considerable part of the shift of η observed by Vlček in acetonitrile compared with aqueous solutions was due to the large change in the ψ' potential, which is practically absent in water. This effect could be further intensified on account of the effect of TMA on the adsorbability of I^- [18]. (We were unable to reproduce Vlček's data quantitatively, since the employed concentration of TMAI in the aqueous solution was not indicated in [16].) Kolthoff and Coetzee [9] recorded polarograms in perchloric acid in 0.1 M triethylamine perchlorate with various water contents against an aqueous calomel electrode. To determine the difference in overpotential from these data it is necessary to take account of the interphase potential jump and the difference between the equilibrium potentials of hydrogen in water and acetonitrile (AN). The sum of these values forms the emf of the cell:

$$H_2|H^+ 0.1\ N\ (AN)\,|KCl_{sat}(H_2O)\,|H^+ 0.1\ N(H_2O)\,|H_2,$$

which we measured and proved equal to ~350 mV. A correction must be made to this value in discussion of the data in [9]. In addition, in [9] the perchloric acid was dehydrated by heating a 71% aqueous solution of per-

chloric acid with a mixture of glacial acetic acid and acetic anhydride. Consequently, there was an excess of acetic acid, which could also be discharged at the cathode, in this system.

Thus, the published data [9, 16] substantially overestimate the difference between the hydrogen overpotential in water and acetonitrile. The $\Delta\eta$ value of ~120 mV obtained in the present work on the basis of direct measurement of η is more reliable.

LITERATURE CITED

1. J. M. Bulter, Adv. Electrochem. Electrochem. Eng., 7, 77 (1970).
2. C. K. Mann, Electroanal. Chem., 3, 57 (1969).
3. G. F. O'Donnell, I. T. Ayres, and C. K. Mann, Anal. Chem., 37, 1161 (1965).
4. I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, J. Am. Chem. Soc., 83, 3927 (1961).
5. W. S. Muney and J. F. Coetzee, J. Phys. Chem., 66, 89 (1962).
6. A. V. Chizhov, Yu. M. Povarov, P. D. Lukovtsev, and S. D. Pirozhkov, Élektrokhimiya, 8, 1089 (1972).
7. V. A. Pleskov, Zh. Fiz. Khim., 22, 351 (1948).
8. I. M. Kolthoff and F. G. Thomas, J. Phys. Chem., 69, 3049 (1965).
9. J. F. Coetzee and I. M. Kolthoff, J. Am. Chem. Soc., 79, 6110 (1957).
10. P. J. Elving and M. S. Spritzer, Talanta, 12, 1243 (1965).
11. M. K. Chantooni, Jr. and I. M. Kilthoff, J. Am. Chem. Soc., 89, 1582 (1967).
12. M. K. Chantooni, Jr. and I. M. Kilthoff, J. Am. Chem. Soc., 92, 2236 (1970).
13. J. F. Coetzee and D. K. Meguire, J. Phys. Chem., 67, 1810 (1963).
14. G. J. Janz and R. P. T. Tomkins, Nonaqueous Electrolytes Handbook, Vol. 1, Academic Press, New York–London (1972).
15. A. N. Frumkin, Adv. Electrochem. Electrochem. Eng., 1, 65 (1961).
16. A. A. Vlček, Coll. Czech. Commun., 20, 636 (1955).
17. Z. Iofa, B. Kavanov, E. Kuchinskii, and F. Chistyakov, Zh. Fiz. Khim., 13, 1105 (1939).
18. T'ja Ch'uan Hsin and Z. A. Iofa, Dokl. Akad. Nauk SSSR, 126, 1308 (1959).

KINETICS OF SELECTIVE ALLOY DISSOLUTION AND HYDROGEN SORPTION IN METALS AT LIMITING DIFFUSION

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UDC 621.357.7

Mechanisms are presented for the selective dissolution of alloys and hydrogen sorption in metals at limiting diffusion in a solid phase with respect to movement of the electrode/solution interface. The equations obtained were analyzed by conversion to a 10% approximation. The results obtained agree with data in the literature.

A study of selective alloy component dissolution (SACD) permits an understanding of the action of alloying additives and the characteristics of anodic dissolution and alloy corrosion [1-3]. One of the possible mechanisms of SACD is the non-steady-state diffusion of negative components from the bulk to the surface of the alloy/solution interface [4]. Electron and x-ray diffraction investigations of electrode surfaces directly confirmed an enrichment of the alloy surface layer during dissolution of its electropositive component [4-6], but did not yield quantitative data on the SACD kinetics.

A more promising method for understanding the mechanism of selective dissolution is studying the kinetics of individual alloy component transfer into the solution with the aid, for example, of the ring–disk elec-

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Translated from Élektrokhimiya, Vol. 13, No. 8, pp. 1122-1128, August, 1977. Original article submitted September 15, 1975.