HYDROGEN OVERPOTENTIAL IN DIMETHYL SULFOXIDE

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In the present work, hydrogen overpotential (η_{H_2}) has been studied at a mercury cathode in dimethyl sulfoxide (DMSO). Hydrogen evolution had been studied previously in this solvent [1], but, although from this work one can draw certain conclusions as to the mechanism of hydrogen evolution in DMSO, the quantity directly measured was the potential relative to an aqueous calomel electrode rather than η_{H_2}. In addition, the measurements at the quiescent mercury cathode were generally irreproducible, evidently because unpurified solvent had been used by the authors. It was the aim of the present work to measure η_{H_2} under sufficiently pure conditions.

According to literature data [2], DMSO is purified, either by recrystallization or by distillation with various drying agents (CaO, CaH_2, silica gel), but the solvent is known to undergo decomposition when boiled with calcium oxide or hydride. In the present work, the following purification procedure was adopted. The starting material (kh.ch. ["chemically pure"] grade) was frozen out (one third of the volume was discarded), then dried over calcined calcium oxide. After decantation the DMSO was twice distilled in vacuum (under a pressure of 3 to 5 mm Hg). The product obtained had a conductivity of 1 to $2 \cdot 10^{-8}$ Ω^{-1} cm^{-1}, which agrees with the best literature data [2] (2 to $3 \cdot 10^{-8}$ $\Omega^{-1}cm^{-1}$).

Mercury and sulfuric acid were twice distilled in vacuum. The salts used were recrystallized from twice distilled water and dried in vacuum. The HCl was obtained by adding concentrated H_2SO_4 (os.ch ["specially pure"] grade) to calcined NaCl (os.ch grade). The gas obtained was passed through concentrated H_2SO_4 for drying and then used to saturate the purified solvent.

Conflicting data exist in the literature concerning the behavior of the hydrogen electrode in DMSO. Thus, it is reported in review [3] that platinized platinum apparently decomposes the solvent by catalytically reducing it to sulfide, which poisons the platinum black. But satisfactory operation of a Pt/Pt electrode in DMSO is reported in [4]. We have investigated the behavior of the hydrogen electrode in DMSO. The electrodes were platinized from aqueous H_2PtCl_6 solution and dried in a vacuum desiccator. The potentials of the hydrogen electrodes were measured relative to an aqueous calomel electrode. Two electrodes tested simultaneously deviated no more than 1 mV. The potential was established quickly (5-10 min) and was stable in time (3 days). During polarization with small currents, the potential of the hydrogen electrode is a linear function of the current over the entire temperature range examined (20-60° C), and it returns to the original value when the current is disconnected. The potential change of the electrode which is provoked by changes of solution acidity at constant total electrolyte concentration ($H_2SO_4 + LiClO_4$) is following the Nernst equation. Sulfuric and perchloric acid are completely dissociated in DMSO; the H_2SO_4 is a monobasic acid in this solvent [5]. Thus, a hydrogen electrode of Pt/Pt is entirely adequate for measurements in DMSO.

The overpotential measurements were conducted at a quiescent mercury cathode in a cell with separate cathode and anode compartment. The solution in the cell was carefully purged with purified hydrogen. After establishment of the η_{H_2} value (10-15 min), the electrode was held for about 1 h at a particular value of current density. Then the cathode was replaced, and in doing so the overpotential did not change by more than 2-5 mV. When the cathode was replaced one day after beginning the measurements, η_{H_2} also changed in these limits.

One can conclude from [1] that hydrogen ion discharge from acidic DMSO solutions on the whole follows the slow-discharge mechanism; therefore, we did not examine in particular the dependence of η_{H_2} on solution composition in DMSO. Our data obtained with the aqueous calomel reference electrode are close to the results of [1].

The slope of the semilogarithmic straight-line plots obtained from measurements in $LiClO_4$ or LiCl solutions acidified with HCl is 112 to 120 mV; the absolute value of overpotential in 10^{-2} M HCl in a 1 M salt base electrolyte on an average is 0.60 V at a current density of 10^{-4} A/cm^2, i.e., is 0.45 V lower than in aqueous solution. We also studied the temperature dependence of hydrogen overpotential in DMSO. Polarization curves

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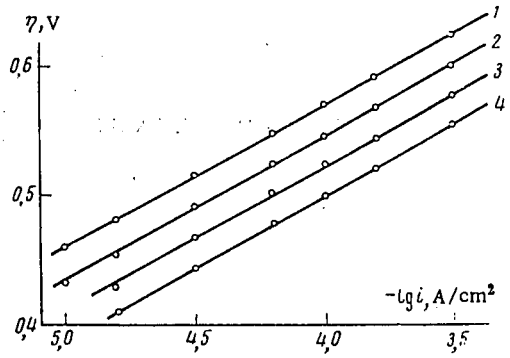

Fig. 1. Polarization curves in $2.3 \cdot 10^{-2}$ M HCl+1 M $LiClO_4$ solution at different temperatures: 1) 20, 2) 30, 3) 40, and 4) 50°C.

were recorded over the temperature range from 20 to 50°C. After solution heating the cell was cooled back to the original temperature, of 20°C; the value of overpotential then returned to the former value with an accuracy of 1 mV.

Typical polarization curves recorded in $2.3 \cdot 10^{-2}$ M HCl+1 M $LiClO_4$ solutions at different temperatures are presented in Fig. 1. The activation energy, A_0, at the equilibrium potential and the preexponential factor, K, calculated from these polarization curves are 15 kcal/mole and $10^{2.1}$ A/cm^2, respectively. Similar values were obtained in HCl solutions with LiCl as the base electrolyte, and sulfuric acid solutions with $LiClO_4$ as the base electrolyte. One can see that the preexponential factors for hydrogen discharge in water and DMSO are of the same order of magnitude (in water, log $K \simeq 3.7$ [6] with 0.1 M HCl solution in 0.9 M KCl as the base electrolyte, i.e., allowing for the concentration dependence of K in water, log K is 1.2 units higher). The difference of 0.45 V in the hydrogen overpotentials is due to the large difference in the activation energies, which is about 7 kcal (a value of $\Delta A_0 = 7$ kcal corresponds to $\Delta\eta = 0.60$ V when $\alpha = 1$ 2, while the Δ log $K = 1.2$ will give $\Delta\eta = -0.14$ V, which when added practically coincides with the experimental overpotential difference; the coincidence is important, as it shows the self-consistency of the entire set of experimental data).

The solvation energy of an ion should have no direct influence on its discharge activation energy [7]. According to available literature data, there is no quantitative relation between the values of overpotential and the solvation energies of the ions in different solvents, but qualitatively they have been found to run parallel [7]. According to our results, in DMSO there is not even a qualitative parallel trend between these two quantities. The solvation energy of the hydrogen ion in dimethyl sulfoxide is 0.34 eV higher than that in water [8], but η_{H_2} in DMSO is 0.45 V lower. This observation very clearly supports the theoretical conclusion that there should be no direct connection between overpotential and solvation energy.

LITERATURE CITED

1. D. Posadas and A. J. Arvia, Electrochim. Acta, 18, 205 (1973).
2. D. Martin and H. G. Hauthal, Dimethylsulfoxid, Akademie-Verlag, Berlin (1971).
3. J. M. Butler, Advan. Electrochem. Electrochem. Eng., 7, 77 (1970).
4. J. Courtot-Coupez and M. Le Demezet, C. R. Acad. Sci., Ser. C, 266, 1438 (1968).
5. I. M. Kolthoff and T. B. Reddy, J. Electrochem. Soc., 108, 980 (1961).
6. E. N. Potapova, L. I. Krishtalik, and I. A. Bagotskaya, Elektrokhimiya, 10, 49 (1974).
7. L. I. Krishtalik, Zh. Fiz. Khim., 31, 2403 (1957).
8. J. Courtot-Coupez, M. Le Demezet, A. Laouenan, and C. Madee, J. Electroanan. Chem., 29, 21 (1971).