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Overvoltage on Mercury in the Presence of Surface Active Electrolytes

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In previous papers by Frumkin[1], it was shown that the rate of the cathodic evolution of hydrogen depends upon the concentration of the hydrogen ions in the double layer. In consequence of this, in the equation connecting the current density i and the cathode potential φ, appears the value of the potential at the distance of one ionic radius from the metal surface, which is denoted by ψ_1 in the Stern theory of the double layer, and which determines the surface concentration of the hydrogen ions. In dilute solutions, as was indicated by Stern, ψ_1 may be identified with the electrokinetic potential ζ. Accordingly, in previous papers from this laboratory on the theory of overvoltage which referred to dilute solutions, the symbol ζ was used. The identification of ζ and ψ_1 is only an approximation even in the case of dilute solutions and would be quite misleading at higher concentrations. We shall therefore use in this paper the symbol ψ_1 and present the relation between φ and i in the form:

$$\varphi + \psi_1 = \frac{2RT}{F} \ln [\mathrm{H}^{\cdot}] - \frac{2RT}{F} \ln i + \text{const.}, \qquad (1)$$

or introducing the overvoltage η:

$$\eta = \psi_1 - \frac{RT}{F} \ln [\mathrm{H}^{\cdot}] + \frac{2RT}{F} \ln i + \text{const.} \qquad (1a)$$

In the derivation of equation (1), the assumption is made that the laws of ideal solutions apply both to the solution and to the ions in the double layer.

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[1] Frumkin, Z. physik. Chem., A **164**, 121 (1933); Frumkin, Acta Physicochimica URSS, **3**, 475 (1937).

If both the current strength and the hydrogen ion concentration in the solution are constant, the following relation should hold:

$$\varphi + \psi_1 = \text{const.} \tag{2}$$

As recent papers by Levina and Sarinsky[2] have shown, this relation is justified in the case of dilute solutions of acids and of acids with the addition of neutral salts.

The ψ_1-potential may be changed both in the direction of more positive and more negative values if surface active cations or anions are added to the acid solution. The concentration of hydrogen ions in the boundary layer and the value of the overvoltage (at $i = \text{const.}$) depending upon it, change correspondingly with a change of the sign and of the value of the ψ_1-potential. The shift of $\varphi_{\max}$, (the potential corresponding to the maximum of the electrocapillary curve), may serve as a measure of the change of the ψ_1-potential.

In the literature there are data concerning the effect of certain capillary active substances on the overvoltage. However, these substances possess a complex structure (quinine[3], codeine, morphine and others[4]) and are not stable with respect to cathodic reduction; it is therefore difficult to explain their action upon the overvoltage.

We did not find any data in the literature on the basis of which the question of the effect of surface active substances could be subjected to a theoretical examination. Therefore, for testing the theses advanced above, we carried out the present investigation which consisted in measuring the overvoltage on a mercury cathode in the presence of such adsorbed active ions which do not undergo any chemical change on the cathode.

Experimental method

The measurement of the overvoltage was carried out either with a small or with a large cathode. Since both these methods had served also for other investigations of the overvoltage on mercury, we shall describe them here in detail.

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[2] Levina a. Sarinsky, Acta Physicochimica URSS, 6, 491 (1937). Levina a. Sarinsky, Acta Physicochimica URSS, 8, 493 (1937).

[3] Herasymenko a. Slendyk, Coll. Czech. Chem. Comm., 6, 204 (1934).

[4] Pech, Coll. Czech. Chem. Comm., 6, 190 (1934).

Method of mercury drop

The apparatus[5] consisted in this case of a central reservoir *B* (see Fig. 1) which formed the cathodic vessel, and a side anodic vessel *A* separated from *B* by an internal ground glass stopper *p*[6].

The mercury is first poured into *g*. By turning the stop-cock *m*, a mercury drop is squeezed out through the tube onto the flat end of the capillary tube *q* where it serves as the main cathode K_1. Supply of current to it was effected by means of a tube filled with mercury with a platinum wire sealed into it. A platinum plate about 5 cm². in area served as the anode. The solution to be investigated was poured into *D* and into the small vessel *c*; and then hydrogen, obtained by electrolysis and purified in the usual manner, was passed through it. The hydrogen was saturated with the vapour of the solution being investigated in the vessel *c*, and then passed through the entire system including the solution in *D* for 10—12 hours

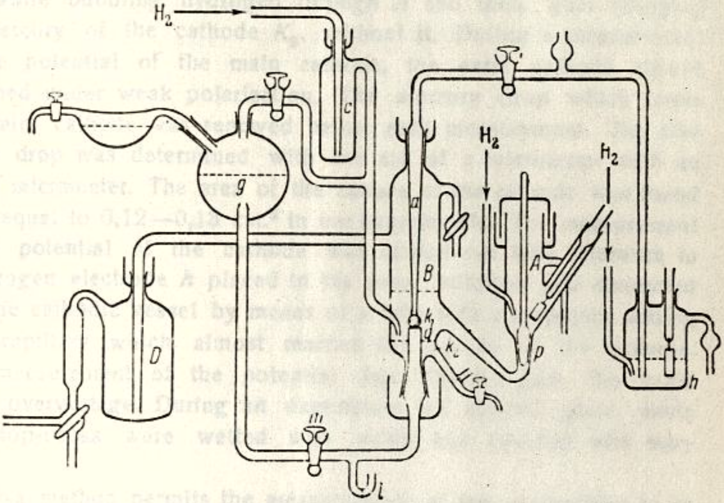

Fig. 1.

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[5] Constructed by B. N. Kabanov in the Karpov Institute.

[6] In many experiments the anode was separated from the cathodic space by a special siphon.

until the whole system was completely freed from oxygen. After this the solution under pressure of hydrogen was transferred from D into the cathodic vessel and from the latter, by raising the stopper p, into the anodic vessel A. In the cathodic vessel the solution was subjected to electrolytic purification from traces of impurities with the aid of a supplementary large mercury cathode K_2 using a current strength of $2 \cdot 10^{-5}$—10^{-4} A over a period of 12—14 hours, at first while bubbling hydrogen through B and then, after changing the mercury of the cathode K_2, without it. During a measurement of the potential of the main cathode, the extra cathode always remained under weak polarization. The mercury drop which forms the main cathode was renewed before each measurement. The size of the drop was determined with the aid of a microscope with an ocular micrometer. The area of the surface of the cathode was found to be equal to 0,12—0,13 cm.^{3} in our experiments. The measurement of the potential of the cathode was carried out with reference to a hydrogen electrode h placed in the same solution and connected with the cathodic vessel by means of a tube with a stop-cock ending in a capillary which almost reached the surface of the cathode. The measurement of the potential thus directly gave the value of the overvoltage. During an experiment all ground glass joints and stop-cocks were wetted with water and covered with mercury.

This method permits the measurements of the overvoltage to be made at current densities from about 10^{-6} to $5 \cdot 10^{-2}$ A/cm.^{2}, and possesses the advantage that the cathode, remaining stationary during the measurement, may be easily and quickly changed[7]. In such a manner one may obtain a clean, renewed surface and repeatedly test upon it the results of the measurements. A shortcoming of this method consists in the great difficulty of obtaining reproducible results for current densities lower than $5 \cdot 10^{-6}$ A/cm.^{2}. In this respect the second method using a large mercury cathode is much better.

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[7] In this respect, this method advantageously differs from the dropping mercury cathode. With a dropping cathode, to determine the true current density it is necessary to take into account the effects connected with a change in the surface tension of the mercury with polarization, and also with its continuous flow form the capillary.

Method of large mercury cathode

Fig. 2 presents the set- up with a large mercury cathode with which a check of the results obtained with the small cathode was carried out. The solution being studied was first poured into vessel *a*. After freeing the solution and the entire system from oxygen by prolonged passage of hydrogen, under pressure of the latter the solution was transferred from *a* into the cathodic vessel *b*. The mercury, which was previously well washed and subjected to repeated vacuum distillations, was transferred from the central part of the reservoir *g* into the vessel *b* where it served as the cathode. Its surface area was equal to ~ 10 cm.^{2}. The volume of the solution was 25 cm.^{3}. The current was led to the cathode from below by means of a narrow tube filled with mercury in which a platinum wire was sealed. This prevented the penetration of the mercury which had been in contact with the platinum into the cathodic space.

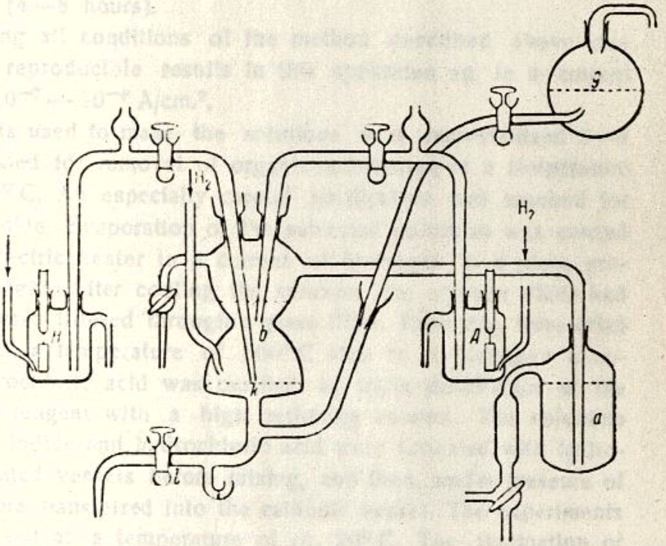

Fig. 2.

The solution under investigation in the cathodic vessel was then subjected to prolonged electrolytic purification (from 18 to 48 hours) on the same cathode *K* with the help of anode *A* using a current strength of about 10^{-4} A. During this time the mercury of the cathode was changed 2—3 times by pouring it off, together with a small quantity of the solution in contact with it, through stop-cock *l*. The measurement of the overvoltage was carried out with reference to a hydrogen electrode *H* in the same solution on a renewed mercury surface after a polarization of the latter lasting at least two hours. In most cases satisfactory results, especially for small current densities, are obtained only after a more prolonged polarization of the cathode (4—8 hours).

Observing all conditions of the method described above one may obtain reproducible results in this apparatus up to a current density of 10^{-7} — 10^{-8} A/cm.^{2}.

The salts used to make the solutions were recrystallized 3—4 times and heated for removal of organic substances at a temperature of 500—600° C. An especially careful purification was required for potassium iodide. Evaporation of the saturated solutions was carried out on an electric heater in a current of hydrogen in a place protected from light. After cooling the solution, the crystals which had settled out were filtered through a glass filter. Then they were dried and heated at a temperature of 500° C also in a hydrogen atmosphere. Hydrochloric acid was purified by triple distillation of the C. P. Merck reagent with a high refluxing column. The solutions of potassium iodide and hydrochloric acid were saturated with hydrogen in separated vessels before mixing, and then, under pressure of hydrogen, were transferred into the cathodic vessel. The experiments were carried out at a temperature of *ca.* 20° C. The fluctuation of the values of the potential, as measured during individual experiments, amounted to ± 3 mV and, for current densities lower than 10^{-5} A/cm.^{2}, to *ca.* ± 5—6 mV. In the region of small values of the current density, the difficulty in obtaining reproducible results is connected in the first place with the depolarizing action of impurities present both in the solution and in the mercury, and in the second place, the equilibrium in the presence of surface active ions at small cathodic polarization is established apparently very slowly.

The latter conclusion may be drawn from the fact that the direct (from small to large current densities) and the reverse course of the $\eta - \lg i$ curve in a certain region do not coincide with each other. If, after decreasing the current density, the current is increased then at first the points lie almost on the same curve; in the region where the slope of the curve increases, the curves separate and again coincide at higher current densities. The hysteresis loop for the potassium iodide solution is observed in the region of comparatively large values of the current density ($5 \cdot 10^{-5} - 2 \cdot 10^{-6}$ A/cm.^{2})

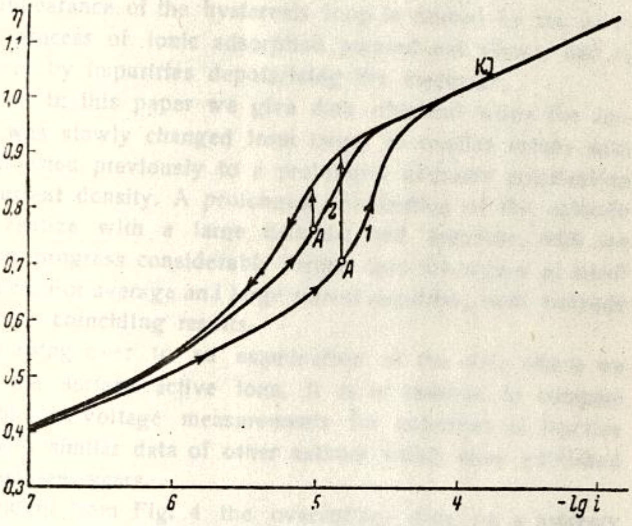

Fig. 3. Overvoltage curves for increasing and decreasing polarization in an acidified 1 N KJ solution: *1* — quickly increasing polarization, *2* — slowly increasing polarization.

(see Fig. 3); it is much less pronounced for KBr and KCl and lies at lower values of the current density. The slower the direct curve is obtained the smaller is the divergence of the curves (see Fig. 3, curves *1* and *2*). In Na_2SO_4 solutions effects of this kind are not observed.

If one stops at a point of the curve of increasing polarization, *e. g.*, at *A*, then the overvoltage will slowly and uniformly increase until it reaches the upper curve corresponding to slowly decreasing polarization. This rise of the overvoltage at constant current density in the region of the hysteresis loop takes place the quicker, the higher the current density.

These facts may lead to the conclusion that, with a decrease in current density, a slow adsorption of ions takes place on the electrode, which lowers the overvoltage. In a similar way, with an increase in the current density and simultaneously in the negative value of the potential, a slow process of desorption of these ions takes place, with a corresponding increase in the overvoltage. However, in view of the fact that after a prolonged cathodic polarization of the electrode the divergences of the direct and reverse curves significantly decrease, it cannot be said at present, to what degree the appearance of the hysteresis loop is caused by the slowness of the process of ionic adsorption pointed out above, and to what an extent by impurities depolarizing the electrode.

Farther on in this paper we give data obtained when the current density was slowly changed from larger to smaller values with a cathode subjected previously to a prolonged cathodic polarization at a small current density. A prolonged polarization of the cathode is easier to realize with a large cathode; and therefore, with the latter, one may progress considerably farther into the region of small current densities. For average and large current densities, both methods give completely coinciding results.

Before passing over to an examination of the data which we obtained for the surface active ions, it is of interest to compare our results of overvoltage measurements for solutions of inactive electrolytes with similar data of other authors which were published during the past few years.

As is evident from Fig. 4 the overvoltage data on a mercury cathode obtained by different authors markedly differ from each other both in magnitude and in dependence upon the current density. Curve *1* gives our results for 0,1 *N* HCl and curve *2* for 1*N* H_2SO_4 at 20° C. The crosses on curve *1* indicate the results of Levina and Sarinsky for 0,1*N* HCl, corrected for a small difference of temperatures in both series of experiments; as it is shown by Fig. 4, the agreement with our data is very good. The slope of the straight line $\eta - \lg i$ for the first solution is equal to 0,120, and for the second, to 0,117 V. Curve *3* presents the $\eta - \lg i$ relation for 2 *N* HCl and curve *4* for 2*N* H_2SO_4 according to the data of Naray-Szabo[8]. In another paper[9] the same author gives

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[8] Naray-Szabo, Naturwiss., **25**, 12 (1937).

[9] Naray-Szabo, Z. Physik. Chem., A **181**, 367 (1938).

a higher value of η for HCl (curves *5a* and *5b*) and somewhat lower for H_2SO_4 (curve *6*). However, upon comparison with our data, the overvoltage in both cases is markedly lowered for HCl and raised for H_2SO_4. The slope of the curves in all cases is extremely small (from 0,055 to 0,075 V). This disagreement, and especially the increase in the overvoltage for H_2SO_4 by 0,2 and 0,3 V in comparison with our data, cannot be explained by the influence of any kind of impurities.

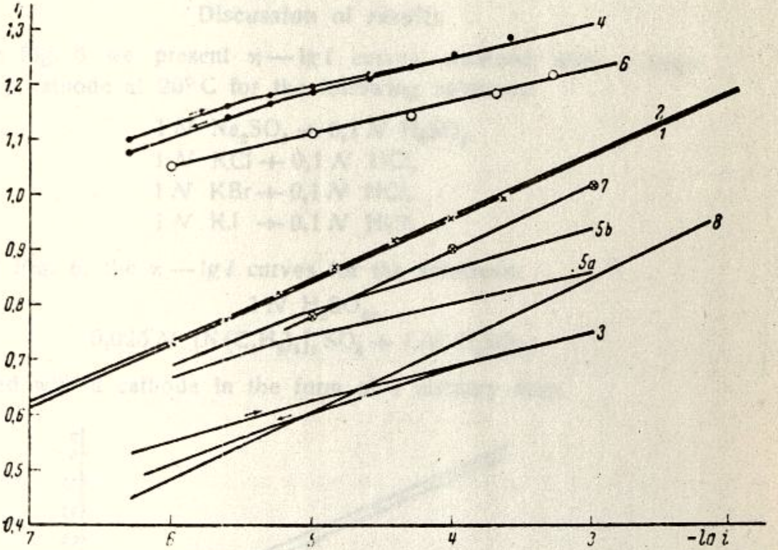

Fig. 4. η — lg i curves for mercury: *1* — our measurements in 0,1 *N* HCl; *2* — the same in 1 *N* H_2SO_4; *3*, *5a*, and *5b* — Naray-Szabo's data for 2 *N* HCl; *4* and *6* — the same for 2 *N* H_2SO_4; *7* — Novoselski's data for 0,5 *N* H_2SO_4; *8* — Harkins and Adam's data for 0,1 *N* H_2SO_4.

Curve *7* presents the results of Novoselski's experiments[10] with 0,5 *N* H_2SO_4; and curve *8*, Harkin's and Adam's experiments[11] with 0,1 *N* H_2SO_4. The slopes of the curves in both cases coincide with those obtained by us. However, the value of η obtained by the first author is lower by 65 mV; and by the second, by 200 mV. Within the limits of the data of these two authors, values for the

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[10] Novoselski, J. Phys. Chem. (Russ.), **3**, 309 (1938).
[11] Harkins a. Adams, J. Phys. Chem., **29**, 215 (1925).

overvoltage were also obtained by others[12]. If we do not consider the work of Naray-Szabo on H_2SO_4, whose results are difficult to explain in any way, then the lowering of the overvoltage found by other authors may be explained by an insufficient purification of the solution and incomplete elimination of depolarizing agents.

Discussion of results

In Fig. 5 we present $\eta - \lg i$ curves obtained with a large mercury cathode at 20° C for the following solutions:

$$1\,N\ Na_2SO_4 + 0{,}1\,N\ H_2SO_4,$$
$$1\,N\ KCl + 0{,}1\,N\ HCl,$$
$$1\,N\ KBr + 0{,}1\,N\ HCl,$$
$$1\,N\ KJ + 0{,}1\,N\ HCl;$$

and in Fig. 6, the $\eta - \lg i$ curves for the solutions:

$$1\,N\ H_2SO_4,$$
$$0{,}025\,N\ [N(C_4H_9)_4]_2SO_4 + 1\,N\ H_2SO_4,$$

obtained with a cathode in the form of a mercury drop.

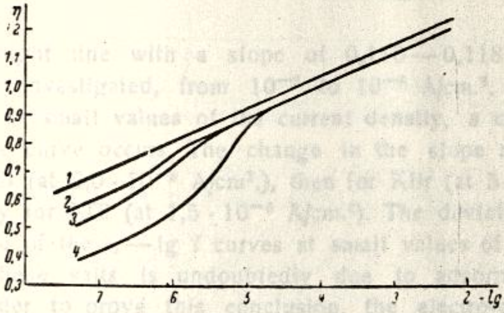

Fig. 5. $\eta - \lg i$ curves: 1—$1\,N\ Na_2SO_4 + 0{,}1\,N\ H_2SO_4$; 2—$1\,N\ KCl + 0{,}1\,N\ HCl$; 3—$1\,N\ KBr + 0{,}1\,N\ HCl$; 4—$1\,N\ KJ + 0{,}1\,N\ HCl$.

Upon examination of the curves of Figs. 5 and 6, the following facts are brought to attention. The curves for KCl, KBr and KJ coincide with each other if the current density exceeds $2{,}5 \cdot 10^{-5}$ A/cm.². The

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[12] Bowden a. Rideal, Proc. Roy Soc., **120**, 59 (1938); Bowden, ibid., **126**, 107 (1929).

overvoltage curve for an acidified solution of Na_2SO_4 lies by 40 mV higher than for acidified solutions of the halides, and for 1 N sulphuric acid in the presence of $[N(C_4H_9)_4]_2SO_4$, by 120 mV higher than for pure 1 N H_2SO_4.

The dependence of the overvoltage upon the current density in a solution of Na_2SO_4, as well as in H_2SO_4, is represented by a straight line with a slope of 0,116—0,118 V over the entire range investigated, from 10^{-2} to 10^{-8} A/cm.². For the remaining salts at small values of the current density, a change in the slope of the curve occurs. The change in the slope appears the earliest for KJ (at $2{,}0 \cdot 10^{-5}$ A/cm².), then for KBr (at $5 \cdot 10^{-6}$ A/cm.²), and finally for KCl (at $1{,}5 \cdot 10^{-6}$ A/cm.²). The deviation from the linear course of the $\eta - \lg i$ curves at small values of the current density for these salts is undoubtedly due to adsorption of the anion. In order to prove this conclusion, the electro-capillary curves for the same solutions[13], presented in Fig. 7, should be examined. These curves, like the overvoltage curves, are referred to a hydrogen electrode in the solution being investigated.

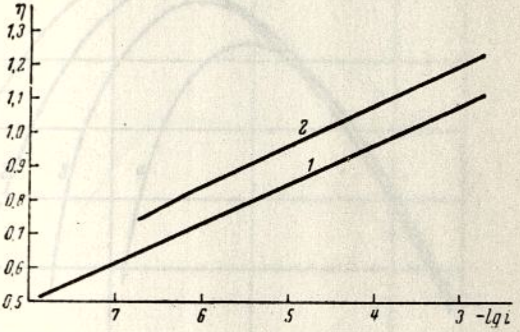

Fig. 6. $\eta - \lg i$ curves: 1 — 1 N H_2SO_4; 2 — 1 N H_2SO_4 + + 0,025 N $[N(C_4H_9)_4]_2SO_4$.

The cathodic branches of the electro-capillary curves of these solutions coincide with each other, like the overvoltage curves at higher current densities, in the region where, owing to electrostatic repulsion, the adsorption of the anion disappears. For the

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[13] Obtained by P. Agarkov, stud. chem.

Na_2SO_4 solution, the cathodic branch of the electro-capillary curve is shifted to the left by *ca.* 40 mV and accordingly the $\eta - \lg i$ curve is raised by the same quantity. This shift for Na_2SO_4 in both cases must be caused by the small value of the activity of the hydrogen ions in this solution in comparison with the other solutions, which was shown also by a direct measurement of the reversible hydrogen potential in these solutions. Indeed, a decrease of the concentration of hydrogen ions, if ψ_1 is constant, according to equation (1a) produces an increase of the overvoltage, equal to the change of the quantity $\frac{RT}{F} \ln [H^{\cdot}]$.

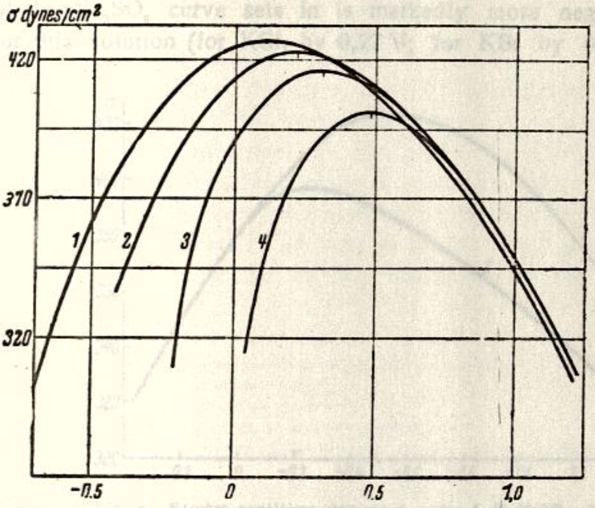

Fig. 7. Electro-capillary curves for acidified solutions: *1* — Na_2SO_4, *2* — KCl, *3* — KBr, and *4* — KJ, measured with reference to a hydrogen electrode in the same solution.

It may be expected that the deviation from the linear course of the $\eta - \lg i$ curve, and the beginning of the anomalous lowering of the overvoltage should occur at those potentials at which begins the adsorption of the given anion. These potentials, φ_σ, may be found from the electro-capillary curves. To determine φ_σ we chose that point on the electro-capillary curve which corresponds to a lowering of the surface tension by 0,5 dynes/cm. This magnitude for the KJ and KBr solutions was determined by comparison with the curve for the KCl solution. For the curve of the KCl solution, φ_σ was determined by comparison with the electro-capillary curve for Na_2SO_4, after the curves were shifted in such a manner that the lower part of the cathodic branches for both solutions coincided. The potential at which the deviation of the course of these curves from the course of the Na_2SO_4 curve sets in is markedly more negative than $\varphi_{max.}$ for this solution (for KCl, by 0,27 V; for KBr by 0,33 V; and for KJ, by 0,31 V). Let us now denote by φ_η the potential at which the overvoltage curve deviates from its linear course by 0,005 V, the smallest value which could be observed with certainty. As shown by Table 1, columns 6 and 7, φ_η and φ_σ do not coincide; namely, φ_η is more negative than φ_σ. Apparently a small adsorption, which cannot be detected on the electro-capillary curves, may already cause a noticeable decrease of the overvoltage.

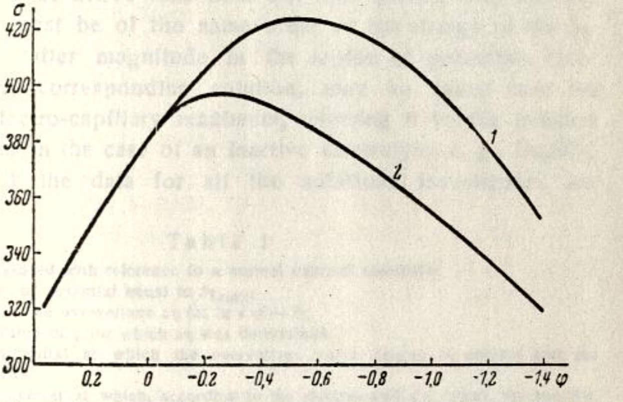

Fig. 8. Electro-capillary curves: 1 — for 1 *N* H_2SO_4, 2 — for 1 *N* H_2SO_4 + 0,025 *N* $[N(C_4H_9)_4]_2SO_4$, measured with reference to a normal calomel electrode.

In the case of ammonium tetrabutyl sulphate, the cation is the ion which is specifically adsorbed. This is evident from the shift of the maximum of the electro-capillary curve to the anodic side (see Fig. 8)[14]. Owing to this, the adsorption is especially pronounced at potentials corresponding to the negative branch of the electro-

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[14] These electro-capillary curves were obtained by S. Bezuglyi and are given with reference to a 1 *N* calomel electrode.

capillary curve; and, consequently, the effect connected with the introduction of this cation into the surface layer can be observed at medium and large current densities as shown by Fig. 6. Owing to the adsorption of a cation, the ψ_1-potential assumes a positive value and the overvoltage increases.

If we now consider the change of the overvoltage $\Delta\eta$ due to the adsorption of ions (it may be found by comparing the actual overvoltage with the continuation of that part of the $\eta - \lg i$ curve where adsorption of active ions does not take place), then we may expect that $\Delta\eta$ must be of the same order as the change of the ψ_1-potential. This latter magnitude in the region of potentials close to $\varphi_{\max}$ for the corresponding solution, may be found from the shift of the electro-capillary maximum, referring it to the position of the maximum in the case of an inactive electrolyte, *e, g.*, Na_2SO_4.

In Table 1 the data for all the solutions investigated are collected.

Table 1

Column 2 — $\varphi_{\max}$ measured with reference to a normal calomel electrode;
» 3 — change in ψ_1 potential equal to $\Delta\varphi_{\max}$;
» 4 — lowering of the overvoltage $\Delta\eta$ (at $\lg i = -7$);
» 5 — $\varphi_{\Delta\eta}$, the value of φ for which $\Delta\eta$ was determined;
» 6 — φ_{η}, the potential at which the overvoltage curve begins to deviate from its linear course;
» 7 — φ_{σ} the potential at which, according to the electro-capillary curves, the specific adsorption of anions sets in. 5, 6, 7 referred to hydrogen electrode in the same solution.

Neutral salt added	$\varphi_{\max.}$	$\Delta\varphi_{\max.} = \Delta\psi_1$	$\Delta\eta$	$\varphi_{\Delta\eta}$	φ_{η}	φ_{σ}
Na_2SO_4	—0,480	—	—	—	—	—
KCl	—0,560	—0,080	—0,050	—0,6	—0,79	—0,50
KBr	—0,653	—0,173	—0,105	—0,55	—0,86	—0,65
KJ	—0,820	—0,340	—0,230	—0,425	—0,94	—0,80
$[N(C_4H_9)_4]_2SO_4$	—0,230	0,25	0,120*	—	—	—

* In comparison with the curve for 1 *N* H_2SO_4 at $\lg i = -4$.

The most satisfactory explanation of the effect of an anion on the overvoltage might be given, as follows from equation (2), by attributing it to a change in the ψ_1-potential. It is seen from columns 3 and 4 of Table 1 that, in the case of the Cl′, Br′ and J′

anions, one must insert into equation (2) before ψ_1 an empirical coefficient equal to *ca.* 0,6.

Since the solutions investigated were not dilute, one cannot expect a quantitative agreement of the experimental data with equation (2) which was derived for dilute solutions, assuming that the laws of ideal solutions can be applied to the ions in the double layer.

Moreover, it is not quite correct to transfer the values of the ψ_1-potential, found from the shift of φ_{max} to much more negative potentials at which $\Delta\eta$ was determined. Only in the case of KJ is the electro-capillary maximum situated in the region of the $\eta - \lg i$ curves where overvoltage measurements are possible.

In the derivation of equations (1) and (2) it is assumed that the influence of the ψ_1-potential increases the hydrogen ion concentration in the surface layer according to the Boltzmann distribution law. In our case such a computation, particularly for KJ in which case the ψ_1-potential is large, would lead to concentrations which have no physical meaning. One may imagine that the electrostatic attraction of adsorbed anions creates conditions for hydrogen ions present in the surface layer which are similar to conditions which exist in concentrated aqueous solutions of the corresponding acids. In the latter case the increase in the reactivity of the hydrogen ion is mainly due not to an increase in its concentration, but to partial dehydration. It is evident that under these conditions equations (1) and (2) may have only a semi-quantitative meaning.

Summary

1. Two methods for measuring the overvoltage on a mercury cathode are described.

2. The hydrogen overvoltage on mercury and the electrocapillary curves for acidified solutions of Na_2SO_4, KCl, KBr, KJ and $[N(C_4H_9)_4]_2SO_4$ were determined.

3. It was found that, in qualitative agreement with **Frumkin's** theory of the dependence of the overvoltage on the ψ_1-potential, (potential at the distance of one ionic radius from the metal surface) surface active anions decrease the hydrogen overvoltage while surface active cations increase it.

4. The magnitude of the overvoltage change amounts to from 0,5 to 0,7 of the shift of the electro-capillary maximum for the same solutions, referring it to the position of the maximum fo a solution of an inactive electrolyte (*e. g.*, Na_2SO_4).

We take this opportunity to express our deep gratitude to Prof. A. Frumkin for suggesting the problem and for rendering valuable advice which aided us in carrying out this work.

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