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Abstract

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ELECTROREDUCTION OF ANIONS AND ADSORPTION PHENOMENA ON A DROPPING ELECTRODE OF THALLIUM AMALGAM

According to the theory of slow discharge, the difference in the rates of the process at the same electrode potential, in the absence of specific adsorption of the initial substance and the reaction product, arises because of the difference in the values of the ψ_1-potentials, which depend on the position of the p.z.c. (^{1}). When the p.z.c. is shifted in the negative direction, the ψ_1-potentials become more positive, which should lead to an increase in the rate of reduction of anions. As follows from measurements on solid electrodes (^{3}), and also on a dropping electrode of thallium amalgam (^{4}), the p.z.c. of which can be strongly shifted in the negative direction (^{5}), the position of the I, φ-curves for reduction of the anion $S_2O_8^{2-}$ for different cathodes is determined by the sequence of p.z.c. values. The study of the reduction of anions on a thallium amalgam electrode led Delakhey and Kleinerman (^{6}) to the conclusion that, as the Tl content in the amalgam is increased, the observed effect of reaction acceleration is in satisfactory agreement with the theory of slow discharge.

We investigated the electroreduction of the anions $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$ on a dropping electrode made of thallium amalgams with concentrations of 40, 26, 9, and 1%, and of the anion $PtCl_4^{2-}$ on 40% Tl(Hg).* The preparation of the amalgams (no substantial difference was found in experiments with amalgams made from spectrally pure and chemically pure Tl) and their analysis were carried out by the method described in (^{7}). The p.z.c. of 40% Tl(Hg), determined from the minimum on the differential-capacitance curve C in $10^{-2}N$ NaF, proved to be equal to −0.925 V, in agreement with (^{5,7}). For amalgams of other concentrations the p.z.c. values were not determined, and their values from (^{5}) were used. The potentials in this work are given in volts relative to the n.c.e. As follows from the measurements carried out, in accordance with the shift of the p.z.c., the fall of the current on the I, φ-curves of the anions studied is displaced in the negative direction as the Tl content in the amalgam is increased.

The rate of reduction of anions increases when the p.z.c. is shifted in the negative direction. The minimum on the I, φ-curve practically disappears upon addition of $4 \cdot 10^{-3}N$ CsCl to $10^{-3}N$ $K_2S_2O_8$ (whereas on mercury, to eliminate the

Fig. 1. Dependence of the reduction rate of $10^{-3}N$ $K_2S_2O_8$ on the potential on 40% thallium amalgam (1—4) and on Hg (5—8) in the presence of KCl at concentrations: $1, 5$—0; $2, 6$—$10^{-3}N$; $3, 7$—$2 \cdot 10^{-3}N$; $4, 8$—$4 \cdot 10^{-3}N$.

Figure 1: Fig. 1. Dependence of the reduction rate of $10^{-3}N$ $K_2S_2O_8$ on the potential on 40% thallium amalgam (1—4) and on Hg (5—8) in the presence of KCl at concentrations: $1, 5$—0; $2, 6$—$10^{-3}N$; $3, 7$—$2 \cdot 10^{-3}N$; $4, 8$—$4 \cdot 10^{-3}N$.

minimum it is necessary to add $\sim 5 \cdot 10^{-2}N$ CsCl). It also follows from the data obtained that the rate of reduction of $S_2O_8^{2-}$ increases sharply with increasing radius of the background cations. On the other hand, measurement of the C, φ-curves in KCl and CsCl solutions shows an increase in C when K^+ is replaced by Cs^+ at negative φ, as on mercury.

From the comparison shown in Fig. 1 of the reduction curves of $S_2O_8^{2-}$ on 40% Tl(Hg), corrected for concentration polarization according to the Mairman–Bagotsky theory, with the corresponding curves for Hg, it follows that the effect of reaction acceleration upon transition to the amalgam depends strongly on the potential and becomes scarcely noticeable at large φ. On 9% Tl(Hg), the rate of reduction of $S_2O_8^{2-}$ at $\varphi > -1.45$ V practically coincides with the rate of the reaction on mercury. Qualitatively, this phenomenon can be understood if one takes into account the negative adsorption of atoms Tl on the surface of the amalgam at negative φ, as a result of which the concentration of Tl in the surface layer decreases with increasing $-\varphi$, and in the case of amalgams with a Tl concentration $< 10\%$, at larger $-\varphi$, becomes equal to zero (5). Calculation of the curves for the dependence of the surface charge on φ from the data of (7), in comparison with the data for mercury, shows that the charge curves for both electrodes approach one another with increasing $-\varphi$, and for 9% Tl(Hg), beginning from ~ -1.5 V, practically coincide.

An analogous acceleration effect, decreasing with $-\varphi$, is also observed in the reduction on Tl(Hg) of the anions $Fe(CN)_6^{3-}$ and $PtCl_4^{2-}$. The inhibition of the reduction of $PtCl_4^{2-}$ is completely removed in the presence of $1N$ KCl, whereas on mercury under analogous conditions a narrow and deep minimum is preserved.

Fig. 1. Dependence of the reduction rate of $10^{-3}N$ $K_2S_2O_8$ on the potential on 40% thallium amalgam (1—4) and on Hg (5—8) in the presence of KCl at concentrations: $1, 5$—0; $2, 6$—$10^{-3}N$; $3, 7$—$2 \cdot 10^{-3}N$; $4, 8$—$4 \cdot 10^{-3}N$.

Determination of the charge of the reacting particle by the method proposed in (2) on 40% Tl(Hg) gives $n_1 = -2$ in the case of $S_2O_8^{2-}$ and values intermediate

* In measurements on 40% Tl(Hg) it was found that cations of alkali metals are discharged at φ values more negative than on Hg. Apparently, this is connected with a shift of the stationary potential of alkali-metal amalgams in going from Hg to 40% Tl(Hg). This phenomenon was not studied in detail.

between -1 and -2 for the anion $PtCl_4^{2-}$, as on a mercury electrode against a CsCl background.

For quantitative comparison of the obtained data with the theory of slow discharge, it is necessary to know the dependence of ψ_1 on φ and on the background concentration. In the simplest case it may be assumed that $\psi_1 = \psi_0$. The calculation of ψ_0-potentials was carried out using the C, φ-curves for mercury and Tl amalgams obtained in (7). In such a calculation, the influence of the negative adsorption of Tl on ψ_0 is also automatically taken into account, since the latter affects the magnitude of C. The ψ_0 values found were used for calculating the i.t.z. (8), which were compared with the curves for mercury. With quantitative agreement of theory with experiment, coincidence should be observed between curves referring to electrodes made of different metals.

For the anion $S_2O_8^{2-}$, the corrected curves coincide with the mercury curves within 20–25% at negative φ, both for 40% (Fig. 2) and for 9% Tl(Hg). The differences at φ close to the p.z.c. of the amalgams are apparently caused, like the deviations of the Tafel dependences from linearity, by the specific adsorption of the $S_2O_8^{2-}$ anion.

In the reduction of $Fe(CN)_6^{3-}$ and $PtCl_4^{2-}$, the i.t.z. coincide in shape and slope with those obtained on mercury. However, they lie lower than the curves for mercury. This means that in experiment the acceleration of the reduction of $Fe(CN)_6^{3-}$ and $PtCl_4^{2-}$ on going to Tl(Hg) turns out to be somewhat smaller than would be expected for $\psi_1 = \psi_0$. It is possible that, in the case of $PtCl_4^{2-}$, the reason for this is the different adsorption conditions of the reaction product —Pt—on the surface of mercury and of the amalgam.

If it is assumed that the center of charge in the transition state is localized in the inner part of the double layer, then the i.t.z. will be located noticeably below the mercury ones already when the center is situated at distances amounting to ~ 4—5% of the thickness of the compact layer. Thus, re-

results of comparing theory with experiment, as does the determination of a (8), depend to a high degree on assumptions concerning the position of the center of the activated complex in the compact layer. On the other hand, when the center of charge is moved beyond the outer Helmholtz plane into the bulk of the solution to distances up to ~ 1 Å, no appreciable violation of the conclusion on agreement between theory and experiment occurs*.

Fig. 2. Reversible half-wave potentials of $10^{-3}N$ $K_2S_2O_8$ in the presence of KCl: $2 \cdot 10^{-3}N$ (1) and $4 \cdot 10^{-3}N$ (2) on Hg and 0 (3), $10^{-3}N$ (4), $2 \cdot 10^{-3}N$ (5), and $4 \cdot 10^{-3}N$ (6) on 40% Tl amalgam

Thus, if one assumes, in accordance with the theory of the retarded discharge, that the reversible half-wave potentials for different electrodes should coincide, then it may be concluded that, at negative φ, the center of charge during reduction of anions must be located close to the outer Helmholtz plane or at small distances from it in the diffuse layer. We also studied the influence of the organic cations $[(C_4H_9)_4N]^+$, $[(C_5H_{11})_4N]^+$, and $[(C_6H_{13})_4N]^+$ on the reduction of $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, and $PtCl_4^{2-}$ on thallium amalgam; the regularities were completely analogous to those found earlier on mercury (9). From kinetic measurements on 40% Tl(Hg), however, it followed that the potential region of adsorption of cations, despite the shift of the p.z.c. in the negative direction, remains approximately the same as on mercury (9). To confirm this, measurements were made of C, φ-curves in $10^{-2}N$ Na_2SO_4 with various additions of organic cations. In addition, in order to study the influence of the nature of the electrode on the adsorption of organic substances, C, φ-curves were measured in $0.1N$ KCl containing various concentrations of n-$C_6H_{13}OH$, whose desorption is observed at less negative potentials than for organic cations (Fig. 3). The potentials of the desorption peaks φ_d and the corresponding surface charges ε_d in solutions without additions of organic substances are presented in Table 1.

Table 1

Background	Adsorbed substance	Concentration	Hg $-\varphi_d$	Hg $-\varepsilon_d$	40% Tl(Hg) $-\varphi_d$	40% Tl(Hg) $-\varepsilon_d$
$0.1N$ KCl	n-$C_6H_{13}OH$	$5 \cdot 10^{-3}M$	1.0	9.75	1.18	6.9
$0.1N$ KCl	n-$C_6H_{13}OH$	$10^{-2}M$	1.09	11.20	1.24	8.4
$0.1N$ KCl	n-$C_6H_{13}OH$	saturated	1.32	14.90	1.45	13.2
$10^{-2}N$ Na_2SO_4	$[(C_4H_9)_4N]^+$	$10^{-4}N$	1.75	21.0	1.80	20.55
$10^{-2}N$ Na_2SO_4	$[(C_4H_9)_4N]^+$	$10^{-3}N$	1.80	21.95	1.85	21.45
$10^{-2}N$ Na_2SO_4	$[(C_5H_{11})_4N]^+$	$10^{-4}N$	1.75	21.0	1.81	20.6
$10^{-2}N$ Na_2SO_4	$[(C_5H_{11})_4N]^+$	$10^{-3}N$	1.82	22.35	1.87	21.85
$10^{-2}N$ Na_2SO_4	$[(C_6H_{13})_4N]^+$	$10^{-4}N$	1.79	21.7	1.84	21.25

The data obtained show that φ_d shifts in the negative direction much less than the p.z.c. The same result follows from measurements of electrocapillary curves in the presence of i-$C_5H_{11}OH$ (5) and was

* In the reduction of $Fe(CN)_6^{3-}$, when the center is moved away from the electrode surface, the agreement of the corrected curves with the mercury curves improves and, at the same time, their straightening occurs (8). However, further investigation is required to interpret the result obtained.

Fig. 13. Curves of differential capacitance on a mercury dropping electrode (B) and on a dropping electrode of 40% Tl(Hg) (A) in 0.1 N KCl solution (1) and in the presence of n-C6H13OH at concentrations: 2—10^-3 N; 3—3.5 • 10^-3 N; 4—5 • 10^-3 N; 5—10^-2 N; 6—saturated solution

Figure 2: Fig. 13. Curves of differential capacitance on a mercury dropping electrode (B) and on a dropping electrode of 40% Tl(Hg) (A) in 0.1 N KCl solution (1) and in the presence of n-C6H13OH at concentrations: 2—10^-3 N; 3—3.5 • 10^-3 N; 4—5 • 10^-3 N; 5—10^-2 N; 6—saturated solution

observed for a mixture of thymol, β-naphthol, and diphenylamine (10). This phenomenon can be explained by a decrease in the adsorption energy of organic substances on going to 40% Tl(Hg). This effect is indicated by the considerably smaller decrease in C near the p.z.c. in the presence of n-$C_6H_{13}OH$ on the amalgam than in the case of mercury, the difference being especially clearly expressed for small concentrations of additives. A consequence of this is also the considerably larger values of ε_d for mercury.

In the adsorption of organic cations, φ_d have more negative values, at which considerable negative adsorption of Tl is observed. Therefore ε_d on Tl(Hg) practically coincide with ε_d for mercury.

Negative adsorption of Tl is also the reason why the φ at which the values of C in 0.1 N KBr and KJ coincide with the values of C in 0.1 N KCl are, on 40% Tl(Hg), respectively ~ -1.30 V and ~ -1.45 V, i.e., are shifted, compared with the mercury electrode, in the negative direction by 350 mV in the first case and by 250 mV in the second, with a shift of the p.z.c. by 450 mV.

Fig. 13. Curves of differential capacitance on a mercury dropping electrode (**B**) and on a dropping electrode of 40% Tl(Hg) (**A**) in 0.1 N KCl solution (**1**) and in the presence of n-$C_6H_{13}OH$ at concentrations: **2** -10^{-3} N; **3** $-3.5 \cdot 10^{-3}$ N; **4** $-5 \cdot 10^{-3}$ N; **5** -10^{-2} N; **6** –saturated solution.

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