

ELECTROLYTIC REDUCTION OF ANIONS AND ADSORPTION ON A THALLIUM AMALGAM DROP ELECTRODE

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According to the theory of slowed down discharge, the difference in the rates of the process at a given potential is due to the difference in the values of ψ_1 -potentials (provided there is no specific adsorption of the initial material or reaction products). The values of the ψ_1 -potentials depend, in turn, on the position of the zero charge point (ZCP) [1]. When the ZCP is displaced toward negative values the ψ_1 -potentials become more positive and this leads to a greater rate of reduction of anions. Measurements with solid electrodes [3] and also with thallium amalgam drop electrodes [4], whose ZCP can be considerably displaced to the negative side [5], show that the position of I, φ reduction curves of the $(S_2O_8)^{2-}$ anion for different cathodes is determined by their respective ZCP. Delahay and Kleinerman [6] have studied the reduction of anions on a thallium amalgam electrode and showed that the observed acceleration of the reaction resulting from an increase of Tl in the amalgam is in good agreement with the theory of slowed down discharge.

We have investigated the reduction of $(S_2O_8)^{2-}$ and $[Fe(CN)_6]^{3-}$ anions on thallium amalgam drop electrodes containing 40, 26, 9, and 1% Tl and the reduction of the $(PtCl_4)^{2-}$ anion on a 40% Tl(Hg) electrode*. The amalgams were prepared and analyzed by the method described in [7]. Amalgams prepared with spectrally and chemically pure Tl gave almost identical results. In agreement with the results published in [5] and [7], the ZCP of 40% Tl(Hg) determined from the minimum on the curve of differential capacitance, C , in a 10^{-2} N NaF solution was found to be -0.925 V. We did not determine the ZCP for the amalgams of the other concentrations; we took their values from [5]. The values of the potentials are given in volts with respect to a normal calomel electrode. Measurements show that the drop of the current on the I, φ curves for the anions investigated is displaced toward negative values with increasing concentrations of Tl in the amalgam, corresponding to the values of the ZCP.

The rate of reduction of the anions increases when the ZCP shifts toward more negative values. When a $4 \cdot 10^{-3}$ N solution of CsCl is added to a 10^{-3} N solution of $K_2S_2O_8$ the minimum on the I, φ curve practically disappears. In the case of mercury it is necessary to add $\sim 5 \cdot 10^{-2}$ N solution of CsCl to make the minimum disappear. The results obtained show also that the rate of reduction of $(S_2O_8)^{2-}$ increases sharply with increasing radii of the background cations. On the other hand, measurements of C, φ curves in KCl and CsCl solutions show that C is also higher in KCl than in CsCl at negative φ , as in the case of mercury.

We have represented in Fig. 1 reduction curves of $(S_2O_8)^{2-}$ on 40% Tl(Hg) and on Hg (these curves were corrected for the concentration polarization according to the Meiman-Bagotskii theory). The figure shows that the increased rate of the reaction on the amalgam as compared to mercury depends largely on the potential and becomes insignificant when φ is large. When $\varphi > -1.45$ V the rates of reduction of $(S_2O_8)^{2-}$ on mercury and on 9% Tl(Hg) are almost the same. We can explain this result qualitatively if we note that at negative φ the Tl atoms are adsorbed negatively at the surface of the amalgam. As the result of this adsorption the concentration of Tl in the surface layer decreases with increasing $-\varphi$ and, in the case of an amalgam containing <10% Tl, becomes zero when $-\varphi$ is large [5]. A comparison of the surface charge variation with φ , calculated on the basis of data in [7], for amalgam

*It was shown experimentally that the deposition potential of metals is more negative on 40% Tl(Hg) than on Hg. This is apparently due to the difference of the steady potentials of amalgams of alkaline metals on these two electrodes. This phenomenon was not investigated in detail.

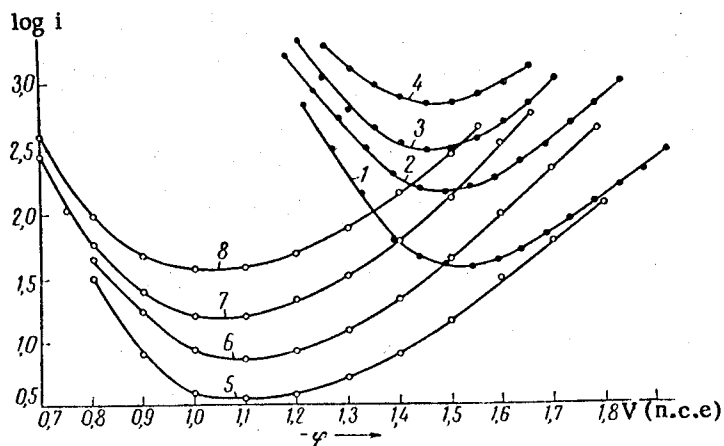


Fig. 1. Dependence of the reduction rate of 10^{-3} N $K_2S_2O_8$ on the potential in the case of 40% Tl(Hg) (1-4) and Hg (5-8) in the presence of KCl in different concentrations: 1, 5) 0; 2, 6) 10^{-3} N; 3, 7) $2 \cdot 10^{-3}$ N; 4, 8) $4 \cdot 10^{-3}$ N.

Background	Adsorbing substance		Hg		40% Tl(Hg)	
			$-\varphi_d$	$-\varepsilon_d$	$-\varphi_d$	$-\varepsilon_d$
0.1 N KCl	n-C ₆ H ₁₃ OH	5 · 10 ⁻³ M	1.0	9.75	1.18	6.9
		10 ⁻² M	1.09	11.20	1.24	8.4
		Saturated	1.32	14.90	1.45	13.2
10 ⁻² N Na ₂ SO ₄	[(C ₄ H ₉) ₄ N] ⁺	10 ⁻⁴ N	1.75	21.0	1.80	20.55
		10 ⁻³ N	1.80	21.95	1.85	21.45
	[C ₅ H ₁₁) ₄ N] ⁺	10 ⁻⁴ N	1.75	21.0	1.81	20.6
		10 ⁻³ N	1.82	22.35	1.87	21.85
	[(C ₆ H ₁₃) ₄ N] ⁺	10 ⁻³ N	1.82	22.35	1.87	21.85
		10 ⁻⁴ N	1.79	21.7	1.84	21.25

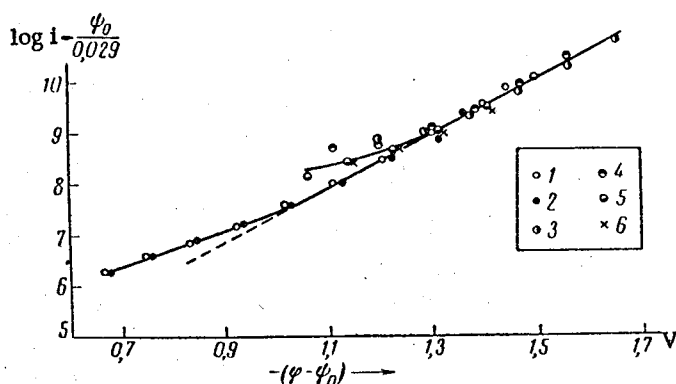


Fig. 2. Corrected reduction curves of 10^{-3} N $K_2S_2O_8$ in the presence of KCl on Hg: 1) $2 \cdot 10^{-3}$ N, 2) $4 \cdot 10^{-3}$ N; and on 40% Tl amalgam: 3) 0, 4) 10^{-3} N, 5) $2 \cdot 10^{-3}$ N, 6) $4 \cdot 10^{-3}$ N.

electrodes with the variation for mercury electrodes shows that the curves approach each other with increasing $-\varphi$ and practically coincide when $\varphi \sim -1.5$ V in the case of the 9% Tl(Hg) electrode.

The rates of reduction of $[Fe(CN)_6]^{3-}$ and $(PtCl_4)^{2-}$ are also higher on Tl(Hg) and increase with decreasing $-\varphi$. The slowing down of the reduction of $(PtCl_4)^{2-}$ on Tl(Hg) is completely eliminated in the presence of 1 N KCl, while on mercury under identical conditions a rather narrow and deep minimum is preserved. The charge of the reacting

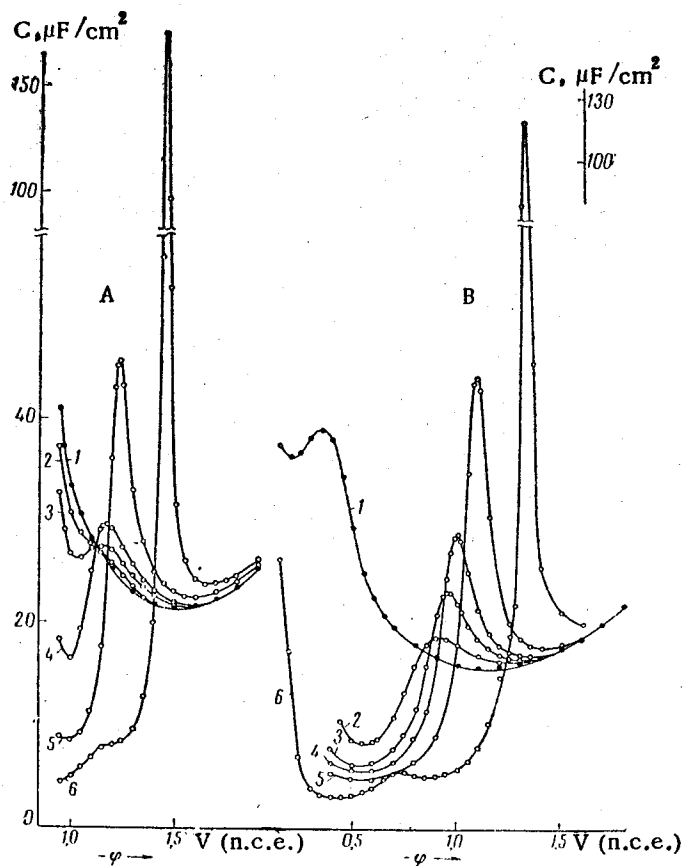


Fig. 3. Curves of differential capacitance on a mercury drop electrode (B) and on 40% Tl(Hg) drop electrode (A) in a 0.1 N KCl solution (1) and in the presence of $n\text{-C}_6\text{H}_{13}\text{OH}$ in the following concentrations: 2) 10^{-3} N; 3) $3.5 \cdot 10^{-3}$ N; 4) $5 \cdot 10^{-3}$ N; 5) 10^{-2} N; 6) saturated solution.

particle measured by the method proposed in [2] gave $n_1 = -2$ for $(\text{S}_2\text{O}_8)^{2-}$ and $-2 < n < -1$ for $(\text{PtCl}_4)^{2-}$ both on a 40% Tl(Hg) and a mercury electrode with a CsCl background.

To compare quantitatively the results obtained with those given by the theory of slowed down discharge it is necessary to know the dependence of ψ_1 on φ and on the concentration of the background. In the simplest case one can assume that $\psi_1 = \psi_0$. We have calculated the ψ_0 -potential on the basis of the C, φ curves obtained in [7] for mercury and Tl amalgam. In this calculation the effect of the negative adsorption of Tl on ψ_0 is taken into account automatically, since this adsorption affects the value of C . From the values of ψ_0 we calculated the real charge points [8] and compared them with the curves for mercury. If the theoretical results are in quantitative agreement with the experimental results, the curves relative to electrodes of different metals must coincide.

The corrected curves for the $(\text{S}_2\text{O}_8)^{2-}$ anion are within 20-25% of the mercury curves at negative φ for both 40% (Fig. 2) and 9% Tl(Hg). At values of φ close to the ZCP of the amalgams the difference is apparently due (as in the case of Tafel relationships) to the deviation from linearity due to the specific adsorption of the $(\text{S}_2\text{O}_8)^{2-}$ anion.

In the case of the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ and $(\text{PtCl}_4)^{2-}$ the shape and the slope of the corrected curves are the same as those obtained on mercury but are below them. This means that the increased reduction rate on thallium amalgam as compared to that on mercury is somewhat less than one would expect if $\psi_1 = \psi_0$. In the case of $(\text{PtCl}_4)^{2-}$ this discrepancy is possible due to the different conditions of adsorption of the reaction products of Pt on the mercury and amalgam surfaces.

If we assume that the center of the charge in the transitional state is localized in the inner part of the double layer, then the corrected curves should be considerably below the mercury curves when the center is at a distance of $\sim 4-5\%$ of the thickness of the dense layer. Thus, the results of comparison between the theory and the experiment as well as the values of α [8] depend to a great extent on the assumed position of the center of the activated complex in the dense layer. On the other hand, if the center of the charge is assumed to be beyond the outer Helmholtz plane within the solution at a distance of ~ 1 A, the agreement with the theory is preserved.* Thus, if on the basis of the theory of slowed down discharge we assume that the corrected curves for different electrodes must coincide, we may conclude that during the reduction of anions the center of charge must be close to the outer Helmholtz plane or at a small distance from it in the diffusion layer when φ is negative. We have also investigated the effect of organic cations $[\text{C}_4(\text{H}_9)_4\text{N}]^+$, $[(\text{C}_5\text{H}_{11})_4\text{N}]^+$, and $[(\text{C}_6\text{H}_{13})_4\text{N}]^+$ on the reduction of $(\text{S}_2\text{O}_8)^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, and $(\text{PtCl}_4)^{2-}$ on thallium amalgam. It was found that the results are completely analogous to those obtained on mercury [9]. However, measurements on 40% Tl(Hg) showed that in spite of the displacement of the ZCP toward negative values the region of cation adsorption potentials remains almost the same as in the case of mercury [9]. To confirm this result we determined the C, φ curves in a 10^{-2} N Na_2SO_4 solution to which different organic cations were added. Also, to determine the effect of the nature of the electrode on the adsorption of organic substances, we determined the C, φ curves for a 0.1 N KCl solution containing different amounts of *n*- $\text{C}_6\text{H}_{13}\text{OH}$, which is desorbed at less negative potentials than the organic cations (Fig. 3). The potentials of desorption peaks φ_d and the corresponding surface charges ε_d in solutions not containing organic substances are represented in the table.

The results obtained show that the values of φ_d are much less displaced toward negative values than the ZCP. Electrocapillary curves obtained in the presence of *i*- $\text{C}_5\text{H}_{11}\text{OH}$ [5] indicate the same result, which was also noted in the case of a mixture of thymol, β -naphthol and diphenylamine [10]. This phenomenon can be explained by the lower adsorption energy of organic substances in the case of 40% Tl(Hg) electrodes. The fact that in the presence of *n*- $\text{C}_6\text{H}_{13}\text{OH}$ the value of C in the vicinity of the ZCP decreases much less on the amalgam than on mercury also indicates this effect; the difference is particularly clear when the concentrations of the organic compounds are low. Consequently, the values of ε_d on mercury are also considerably higher.

The adsorption of organic cations leads to more negative values of φ_d , at which considerable negative adsorption of Tl occurs. Therefore ε_d on Tl(Hg) is practically the same as ε_d on mercury.

Negative adsorption of Tl is also the cause of the fact that the values of φ at which the values of C in 0.1 N KBr and KI are the same as those of C in 0.1 N KCl on 40% Tl(Hg) are respectively ~ -1.30 V and ~ -1.45 V, i.e., with respect to mercury they are displaced toward negative values by 350 mV in the first case and 250 mV in the second, while the ZCP is displaced by 450 mV.

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*In the case of reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ the corrected curves become straighter and are in better agreement with the mercury curves when the center is further away from the surface of the electrode [8]. However, the interpretation of the results needs further study.