

layer and a neutral region of the diffusion layer. The distribution of the field and of matter is qualitatively the same as for a uni-univalent electrolyte.

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SHAPE OF THE CURRENT-TIME CURVES IN THE NEIGHBOURHOOD OF POLARO- GRAPHIC MAXIMA

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In work on polarographic maxima little attention has been paid to analysing the current-time curves. Nevertheless, the shape of the $I-t$ curves may serve as a criterion for the recognition of polarographic maxima, which are sometimes difficult to identify in other ways, especially in the case of organic compounds.

According to the theory propounded by Frumkin and his collaborators^{1,2}, polarographic maxima are produced by tangential movements of the mercury, which agitate the solution and increase the diffusion current. Surface-active substances, being adsorbed on the electrode, tend to inhibit these movements, thus suppressing the maxima. The dependence of the instantaneous current on time at constant potential is represented by the equation $I = kt^\sigma$. The exponent σ depends on the nature of the slow stage and on time. With a stationary electrode, σ has the values -0.5 for purely concentration polarisation, and zero in the case of kinetic limitations. With a dropping electrode, the surface grows in proportion to $t^{0.67}$, and hence $\sigma = 0.17$ † and 0.67 for processes whose rates are limited by diffusion and reaction kinetics respectively.

If the supply of reducible substance to the electrode and the electrode reaction take place at comparable rates, σ has intermediate values, and decreases with time. In the case of kinetic limitations, the current at the electrode is independent of the rate of diffusion and movements of the mercury drop should have no effect at all on the value of σ . In the case of processes which are restricted by diffusion, mixing of the solution as a result of movements of the mercury drop should lead either to a complete or partial elimination of diffusion restrictions (if the reaction velocity constant is not very large) or to the establishment of an almost steady state, in which the concentration of reducible substance in the layer adjacent to the electrode changes little with time (if the rate constant is sufficiently large).

In both the first and the second cases movements of the mercury should result in an increase in σ : i. e. the inequality $-0.5 \leq \sigma \leq 0$ should hold for a stationary electrode, while in the case of a dropping electrode $0.17 \leq \sigma \leq 0.67$. Hence

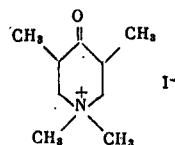
† This value is slightly changed after introducing a correction for spherical diffusion³.

the value of σ should fall after the cessation of tangential movements of the mercury. Thus when polarographic maxima occur, the variation of σ with potential should pass through a maximum at the potentials of most vigorous movement of the mercury. It has been stated³ that the curve relating σ with potential should pass through a maximum also in the case of partly reversible processes. If these two cases are to be distinguished, the current I_∞ must be calculated which would pass through the system at potentials corresponding to the maximum on the $\sigma-\varphi$ curve if the exchange current were infinite, while the ratio of the rate constants for the forward and reverse reactions remained as before. Such a calculation is feasible^{3,8} if the values of I and σ are known at the appropriate electrode potentials. For a partly reversible process at the potential of a maximum on the $\sigma-\varphi$ curve, $I_\infty < I_d$, where I_d is the limiting diffusion current; I_∞ increases smoothly with rise in potential, tending to the value of I_d . The value of I_∞ passes through a maximum in the region where tangential movements of the mercury surface take place, since I and σ increase owing to mixing of the solution; perhaps also $I_\infty > I_d$.

The present work was undertaken with the aim of verifying the above ideas.

The dropping mercury electrode employed had the following characteristics: $m = 0.17 \text{ mg sec}^{-1}$ (with a mercury column 340 mm high) and a drop time $\tau = 17 \text{ sec}$ at a potential of -1.6 V (relative to the saturated calomel electrode, s.c.e.) in 0.1 N KCl; an electrode in the form of a hanging mercury drop having a surface of 0.02 cm², as described in Ref. 4, was also used. The $I-t$ curves were recorded by means of a TsLA oscillographic polarograph modified to operate with a three-electrode set-up and "on the first drop". The instrument maintained the potential of the working electrode constant to within 2-3 mV.

Below are illustrated the curves for the reduction of 1,1,3,5-tetramethyl-4-oxopiperidinium iodide:



The usual polarogram of this compound has a maximum at -1.85 V. Before the potential of the start of the polarographic maximum (-1.74 V s.c.e.) and after the potential of the maximum (-1.94 V), the form of the $I-t$ curve obtained at a hanging mercury drop corresponds to diffusion processes with a value of σ close to -0.5 (Fig. 1). The $I-t$ curve obtained at potentials of the polarographic maximum is illustrated in Fig. 2, from which it is seen that the current falls to a steady-state value, but then increases again; this can only be explained by a decrease in concentration polarisation caused by movements of the surface of the mercury drop. It follows also from Fig. 2 that, in the case of an organic compound, the situation is more complicated than had been expected, surface movement of the mercury drop sometimes arising and sometimes being damped down. The cause of the damping is the adsorption of products of the electrode reaction on the mercury. An investigation of the movement of mercury by a suspended particle method gave a picture coinciding in all details with the results obtained from the $I-t$ curves. The polarogram of benzyl chloride in 40% methanol passes through a maximum whose magnitude is little affected by the height of the mercury

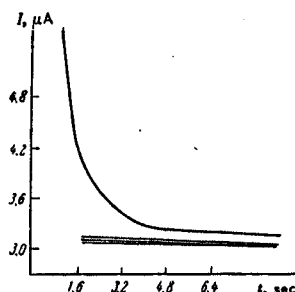


Fig. 1. Current-time curve for a solution containing 10^{-3} M 1,1,3,5-tetramethyl-4-oxopiperidinium iodide + borate buffer of pH 7.5 at a potential of -1.6 V (s.c.e.).

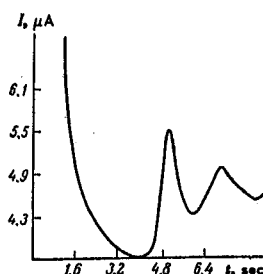


Fig. 2. Current-time curve for 1,1,3,5-tetramethyl-4-oxopiperidinium iodide at -1.85 V.

column but is proportional to the concentration of the reducible substance. The maximum disappears in the presence of surface-active cations (Fig. 3). For this solution, the dependence of σ on potential and time obtained at the dropping mercury electrode differs markedly from the theoretical relation³: with rise in potential, σ increases, reaches a maximum in the neighbourhood of the maximum on the polarogram, and then decreases somewhat. The value of σ varies non-monotonically during the life of the drop.

Examination of the $I-t$ curves corresponding to maxima on the polarogram [of benzyl chloride? (Ed. of Translation)] and on the $\sigma-\varphi$ curve also revealed a considerable "succession effect", the current at the second drop being lower than at the first. This well-known phenomenon is usually explained by impoverishment of the solution in the vicinity of the electrode as a result of electrolysis at the preceding drop, and can be observed only at currents which are sufficiently close to diffusion currents. In this case, however, judging from the value of σ (≥ 0.6) and the dependence of wave height on the pressure of the mercury column, the current is much smaller than the diffusion current.

All the above phenomena can be readily explained on the hypothesis that the maximum on the polarogram of benzyl chloride is due to tangential movements of the mercury, the intensity of which changes with time.

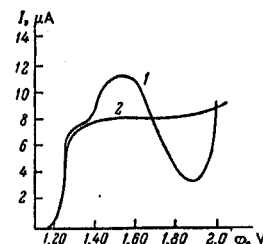


Fig. 3. Polarograms of benzyl chloride (0.00314 M) in solutions containing also 20% of methanol + 0.08 N sodium tetraborate with and without tetramethylammonium bromide: 1) none; 2) 0.26 N.

Consideration of the $I-t$ curves for benzyl chloride indicates further that there are tangential movements of the mercury along the whole polarogram, from the maximum to the minimum. Actually, our calculated values of I_{∞} considerably exceed the values obtained experimentally for I_d (from the second, diffusion wave of benzyl chloride, which appears in the presence of caesium ions⁵).

We have also used the suspended particle method in the case of benzyl chloride. Tangential movements of the mercury were observed from a potential of -1.5 V, in full agreement with the results of the $I-t$ curves. These movements became more vigorous with increase in the negative potential, continuing right to $\varphi = -1.9$ V.

Relations are simpler in the case of the maxima observed in the presence of substances whose reduction products are unable to block the electrode surface. As has been shown in Ref. 6, for example, the $I-t$ curves obtained at the potential of the polarographic maximum of the Cd^{2+} ion with a dropping electrode correspond to $\sigma = 0.25$. This is appreciably greater than the value (0.197) observed in the absence of a maximum, as should be the case from the above considerations. The authors of the paper⁶ remark that the value obtained for σ is inexplicable on the basis of the Ilkovič theory of polarographic maxima⁷, which predicts $\sigma = 0.33$ at the potential of such a maximum. In the light of the above considerations, it is readily seen that this value of σ can be explained by the hydrodynamic theory of polarographic maxima.

SUMMARY

1. It has been confirmed experimentally that the presence of a polarographic maximum can be determined from an analysis of current-time curves.
2. The exponent of σ for the $I-t$ curves passes through a maximum in the region of a polarographic maximum.
3. The complications which may result from the adsorption of the reduction products of organic compounds are indicated.

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TABLE 1. Heat of reaction of sodium selenite with cadmium chloride at 25°.

Wt. of Na_2SeO_3 , g	Wt. of water, g	Wt. of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, g	Rise in temp. (corr.)		Correction for radiation, %		Voltage, V	Current, A	Duration of current, sec	Heat capacity of system, cal deg ⁻¹	Heat of reaction, kcal mole ⁻¹ CdSeO_3
			during reaction Δt_1	during determination of heat capacity Δt_2	during reaction	during determination of heat capacity					
3.1198	325.00	4.1190	0.3698	0.3770	1.98	0.80	2.427	1.522	111.8	261.71	5.37
3.1204	325.00	4.1200	0.3632	0.3330	0.32	1.21	2.462	1.525	99.2	267.30	5.38
3.1203	325.00	4.1200	0.3668	0.3685	0.32	0.94	2.484	1.532	107.4	264.99	5.39
3.1194	325.00	4.1198	0.3661	0.3468	0.51	1.08	2.409	1.499	107.6	267.64	5.43
3.1198	325.00	4.1200	0.3591	0.3260	0.52	1.24	2.405	1.515	102.6	274.03	5.45

Mean 5.40 ± 0.03

HEAT OF FORMATION OF CADMIUM SELENITE

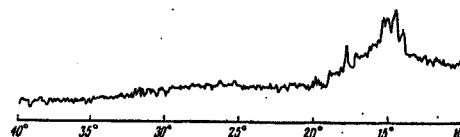
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No-one has previously determined the heat of formation of cadmium selenite, which is of interest in connection with the practical application of CdSeO_3 in the production of phosphors and pigments based on cadmium selenide^{1,2}.

The standard heat of formation of cadmium selenite from the elements has been determined in the present work. Measurements were made in an isothermal calorimeter of the heat of reaction of sodium selenite with cadmium chloride in stoichiometric proportions. An aqueous solution of cadmium chloride (dilution 1:1000) was introduced into the calorimetric vessel, and the crystalline salt Na_2SeO_3 into a tube in amount such that its resulting solution in the calorimeter would be remote from saturation.

At the start of the main period the tube was crushed with a glass rod, when the cadmium chloride reacted with the sodium selenite. The heat capacity of the system was determined electrically at the end of each experiment. The conversion factor from electrical to thermal units was 1 cal = 4.1840 abs. J. As usual, radiation was corrected for by means of the Regnault-Pfaundler-Usov formula. The correction varied from 0.3 to 2.0%. The rise in temperature was measured with a thermometer having a range of 3°. A 1° division on the thermometer scale corresponded to 0.703°C. Results are given in Table 1 (with the thermochemical sign convention).

Analysis of the precipitate of cadmium selenite formed in the calorimeter gave 46.52% Cd and 32.41% Se⁴⁺; calculated for CdSeO_3 , 46.96% and 32.97% respectively. The cadmium was determined by titration with a solution of Trilon B in the presence of the indicator chromogen black ET-OO,³ and Se⁴⁺ by the bromate-arsenite method⁴. The accompanying diagram shows the diffraction pattern of the cadmium selenite precipitate, recorded on a URS-50I diffractometer with ionisation recording and copper radiation filtered through nickel. Specimens for examination were prepared by compressing the powder into a special cell. The rate of movement of the counter was 2° min⁻¹, and that of the paper strip 10 mm min⁻¹. The diagram shows that the precipitate of cadmium selenite obtained in the calorimeter was amorphous.



Diffraction pattern of CdSeO_3 precipitate obtained in calorimeter (glancing angles along horizontal axis, intensities along vertical axis).

Calculation of the standard heat of formation of cadmium selenite from the elements requires a knowledge of the corresponding quantity for Na_2SeO_3 (cryst.). The value recommended⁵ for ΔH_{298}° of Na_2SeO_3 (aq., 1:400) is -236.6 kcal mole⁻¹, obtained from data⁶ for the neutralisation of selenous acid with caustic soda. In order to determine ΔH_{298}° for crystalline sodium selenite, we have measured in the same calorimeter the heat of dissolution of Na_2SeO_3 (cryst.) in water to yield a solution of concentration 1:400. The results are given in Table 2.

Combination of the resulting value (-7.05 kcal mole⁻¹ on the thermodynamic sign convention) with ΔH_{298}° for Na_2SeO_3 (aq., 1:400) gives the heat of formation of Na_2SeO_3 (cryst.) as $\Delta H_{298}^\circ = -229.55$ kcal mole⁻¹. Summation according to Hess's law of the heats of formation

TABLE 2. Heat of dissolution of Na_2SeO_3 in water (dilution 1:400) at 25°.

Wt. of Na_2SeO_3 , g	Wt. of water, g	Rise in temp. (corr.)		Correction for radiation, %		Voltage, V	Current, A	Duration of current, sec	Heat capacity of system, cal deg ⁻¹	Heat of dissolution of Na_2SeO_3 , kcal mole ⁻¹
		during dissolution Δt_1	during determination of heat capacity Δt_2	during dissolution	during determination of heat capacity					
7.8000	325.00	1.1944	0.5607	0.12	2.45	2.958	1.826	114.8	264.24	7.00
7.8000	325.00	1.2074	0.5920	0.28	3.21	2.964	1.823	120.0	261.69	7.01
7.8014	325.00	1.1956	0.5669	0.63	2.80	2.951	1.810	118.6	266.99	7.08
7.8018	325.00	1.1680	0.8992	1.71	4.13	3.026	1.774	102.6	274.76	7.10

Mean 7.05 ± 0.05