Gases were analyzed by mass spectrometry. Solutions were analyzed qualitatively by distillation of the sample solution either with or without neutralization of the sulfuric acid, and examination of the distillate using vapor phase chromatography. Formaldehyde was determined by precipitation with 5,5-dimethyl-1,3-cyclohexanedione.

Characteristics of Anodic Currents at Dropping Amalgam Electrodes

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Anodic polarograms at dropping amalgam electrodes exhibit two apparently different types of anomalies on the negative and positive sides of the electrocapillary maximum (e.c.m.), respectively. In 0.1 M supporting electrolyte solutions, current–potential curves of amalgams which are oxidized on the negative side of e.c.m. exhibit a maximum, the current decreasing abruptly at a potential near e.c.m. As the potential is made further positive, current gradually increases again instead of giving a diffusion current plateau. Streaming was found to occur on both sides of e.c.m., in the downward direction on the negative side and in the upward direction on the positive side. At amalgam electrodes which give an anodic wave on the positive side of e.c.m., no maximum appears, but the limiting current is considerably greater than the true diffusion current and increases gradually as the potential is shifted toward more positive values. Streaming occurs in the upward direction at these electrodes. Experimental evidence is presented, showing that despite the considerable difference in appearance both types of anomalies (termed negative maximum and positive exaltation) can essentially be accounted for in terms of the factors which are considered responsible for the occurrence of the so-called maxima of the first kind. The contribution of the "Spüleffekt" also cannot be ignored for the positive exaltation. In the presence of a sufficient amount of a suitable maximum suppressor, neither the positive exaltation nor the negative maximum appears and the polarogram becomes normal in appearance. However, analysis of current–time curves reveals that the "Spüleffekt" prevails even in the presence of maximum suppressors, and current becomes diffusion-controlled only when the rate of amalgam flow m is smaller than about 0.5 mg. sec.$^{-1}$. Under these conditions current–time curves closely follow the original Ilkovic equation rather than the von Stackelberg–Toome equation.

Cathodic maxima at the dropping mercury electrode have been studied extensively by several groups of investigators and thorough, critical discussions of their characteristics have appeared in recent years.[1,2] On the other hand, only fragmentary descriptions are found in the literature of characteristics of anodic maxima at dropping amalgam electrodes. Furman and Cooper[3] reported that sharp anodic maxima occur at dropping cadmium and zinc amalgam electrodes in dilute solutions of potassium chloride, while no maxima occur at some amalgams in certain media. Heyrovsky[4] observed a vigorous streaming which occurs in the downward direction at potentials of the maximum current at cadmium and zinc amalgam electrodes. He also states that no maximum nor streaming occurs at dropping amalgam electrodes of bismuth, copper, lead, and tin. We confirmed the occurrence of sharp maxima and streaming at cadmium and zinc amalgam electrodes, but contrary to Heyrovsky's statement, we found that at the dropping copper amalgam electrode weak upward streaming takes place and that the limiting current decreases considerably upon addition of surface-active substances.[5] Recently Schupp, Youness, and Watters[6] studied the dependence of anodic limiting currents at a dropping copper amalgam electrode on the capillary characteristics in the absence of surface-active substances and found that the limiting current constant decreases with decreasing value of $m^{2/3}t^{1/6}$. They attribute this to stirring within the amalgam drop caused by the flow of amalgam into the amalgam drop (Spüleffekt).[7,8]

It was the purpose of the present investigation to study systematically effects of various factors on acute maxima observed with dropping amalgam electrodes which yield waves at the negative side of the electrocapillary maximum (e.c.m.) and on exaltation of limiting currents at the positive side of the e.c.m. Experiments are described to throw light on the cause of the two apparently different types of anomalies.

A study was also made of the characteristics of current–time curves during the lifetime of a single amalgam

(1) M. von Stackelberg and R. Doppelfeld, "Advances in Polarography," Vol. 1, I. S. Longmuir, Ed., Pergamon Press, New York, N. Y., 1960, pp. 68–104.

(2) V. G. Levich, "Physicochemical Hydrodynamics," translated by Scripta Technica, Inc., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(3) N. H. Furman and W. C. Cooper, *J. Am. Chem. Soc.*, 72, 5667 (1950).

(4) J. Heyrovsky, *Z. physik. Chem.* (Leipzig), 7 (1958).

(5) I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, 83, 47 (1961).

(6) O. E. Schupp, III, T. Youness, and J. I. Watters, *ibid.*, 84, 505 (1962).

(7) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, 54, 51 (1950).

(8) M. von Stackelberg and V. Toome, *ibid.*, 58, 226 (1954).

Table I. Characteristics of Capillaries Used

Fig. no.	Capillary no.	h, cm.	m, mg. sec.$^{-1}$	t, sec.	Remarks
2, 3	1	37	...	6.1	Sargent "6–12 sec."; t measured with pure Hg in 0.1 M HClO$_4$ at open circuit
4, 5A, 5B	2	49	1.310	5.5	Sargent "6–12 sec."; measured with 2 mM Cu(Hg) in 0.1 M HClO$_4$ at open circuit
5C	3	50	...	3.2	Sargent "2–5 sec."; measured with 2 mM Cu-(Hg) in 0.1 M HClO$_4$ at open circuit
6, 7, 8 (except curves 6 and 7)	4	40	0.472	15.3	Sargent "6–12 sec." (50 μ^b); measured with 2 mM Cd(Hg) in 0.1 M KCl containing 0.05% PAA at −0.2 v.
		60	0.701	10.0	
		80	0.944^a	7.4	
		100	1.187	5.9	
		120	1.416^a	4.9	
8 (curve 6)	5	61	1.834	8.2	Fabricated (114 μ^b); measured with 2 mM Cd-(Hg) in 0.1 M KCl containing 0.01% gelatin at −0.2 v.
8 (curve 7)	6	64	1.943	15.9	Fabricated (240 μ^b); measured with 2 mM Cd(Hg) in 0.1 M KCl containing 0.01% gelatin at −0.2 v.
9	7	40	0.367	15.9	Sargent "6–12 sec."; measured with 1 mM Cu(Hg) in 0.1 M HClO$_4$ containing 0.01% sodium dodecyl sulfate at +0.15 v.
		60	0.559	10.8	
		80	0.734^a	8.2	
		100	0.926	6.6	
		120	1.118^a	5.4	

^{a} Estimated by extrapolation or interpolation. ^{b} Diameter of orifice determined by the drop-weight method: G. S. Smith, *Trans. Faraday Soc.*, **47**, 63 (1951).

drop. In the presence of a suitable surface-active substance, the instantaneous diffusion current at a dropping amalgam electrode with suitable capillary characteristics, according to von Stackelberg and Toome,[8] follows the equation

$$i = 708nCD^{1/2}m^{2/3}t^{1/6}(1 - 39D^{1/2}m^{-1/3}t^{1/6}) \quad (1)$$

To the contrary, we found that current–time curves at both copper and cadmium amalgam electrodes follow the original Ilkovic equation rather than eq. 1, provided that the rate of amalgam flow is sufficiently slow and the "Spüleffekt" is absent.

After finishing this manuscript we became acquainted with a recent paper by Kůta and Smoler,[9] who studied anodic maxima at dropping zinc and cadmium amalgam electrodes. Their interpretation of negative maxima is in essential agreement with ours. These authors do not mention current exaltation at the positive side of the e.c.m., an observation made at copper amalgam, which we reported several years ago[5] and which prompted the present study. The conclusion of Kůta and Smoler that, in the absence of the "Spüleffekt," the Koutecky equation holds is in direct variance with our results. In the limiting current region the Koutecky equation becomes identical with eq. 1.

Experimental

Chemicals. Potassium chloride was ignited at 700° to remove surface-active impurities. All other chemicals were used without purification. C.P. perchloric acid was tested for possible surface-active impurities by comparing polarograms obtained at a dropping copper amalgam electrode in purified and unpurified perchloric acid, the purification having been performed according to the direction given by Feldberg, Enke, and Bricker,[10] by boiling a mixture of 150 ml. of 70%

perchloric acid and 50 ml. of concentrated nitric acid to 100 ml. No difference was found between polarograms with solutions of the original and purified acid, indicating that the C.P. perchloric acid used did not contain significant amounts of organic impurities. Polyacrylamide (PAM 75) was obtained from American Cyanamid Co., and gelatin was a U.S.P. grade.

Electrodes. All amalgams were prepared by electrolysis of dilute perchloric acid containing known amounts of appropriate salts, while stirring the mercury by passing in pure nitrogen. Except for the quantitative experiments with copper amalgam electrodes, a simple electrolysis cell–dropping amalgam electrode assembly, similar to the one described by Delahay[11] was used. The anode in the preparation of amalgams was a platinum spiral, which was placed in a compartment separated by a sintered glass disk from the half-cell in which the amalgam was prepared. This simple apparatus, however, was not suitable for purposes of obtaining accurate and reproducible measurements, particularly with copper amalgams. In the electrolysis cell the amalgam is in direct contact with Tygon tube connections, through which air was found to diffuse slowly to oxidize the amalgam, resulting in a gradual decrease in limiting current. In order to overcome this difficulty, the arrangement illustrated in Figure 1 was used in quantitative experiments carried out with copper amalgam. In this apparatus direct contact of amalgam with Tygon tubing was eliminated by sealing with vacuum cement a polarographic capillary to the lower end of the amalgam reservoir A. The air inside the entire apparatus was first replaced with pure nitrogen by repeating several times evacuation and introduction of nitrogen through stopcocks B and C. The amalgam, prepared in a separate electrolysis cell,

(8) S. W. Feldberg, C. G. Enke, and C. E. Bricker, *J. Electrochem. Soc.*, **110**, 826 (1963).

(9) J. Kůta and I. Smoler, *Collection Czech. Chem. Commun.*, **28**, 2874 (1963).

(10) S. W. Feldberg, C. G. Enke, and C. E. Bricker, *J. Electrochem. Soc.*, **110**, 826 (1963).

(11) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 353.
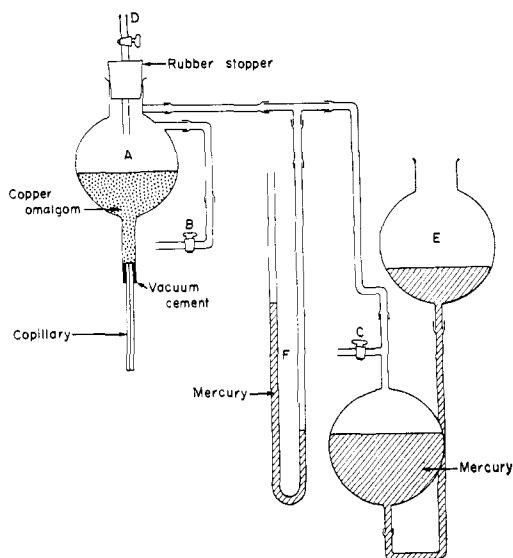
Figure 1. Dropping copper amalgam electrode.

Figure 2. Negative maxima: (A) 2 mM lead amalgam in 0.1 M NaOH; (B) 2 mM cadmium amalgam in 0.1 M KCl; (C) 2 mM zinc amalgam in 0.1 M NaClO$_4$ (curves 1, without PAA; curves 2, with 0.01% PAA (capillary 1).

was then introduced under air-free conditions into reservoir A through D. While nitrogen was kept passing over the amalgam in A, the rubber stopper D was quickly replaced with another stopper through which a platinum wire had been inserted to serve as the lead. The rate of amalgam flow through the capillary was controlled by varying the pressure in the system by raising or lowering the mercury reservoir E. The pressure in the system was read on the manometer F. When the apparatus was not in use, nitrogen was continuously kept passing over the amalgam surface from B to C.

The electrolysis for the preparation of amalgam was continued for a sufficiently long time to assure that the metal ions in the electrolysis solution were reduced quantitatively. In the case of copper amalgam, the completion of electrolysis was confirmed by testing the electrolysis solution for copper ions by the dithizone method. The concentration of amalgam was calculated from the weight of mercury taken and the amount of metal ions added to the electrolysis solution.

Several different capillaries were used in the experiments. Their characteristics are listed in Table I.

The reference electrode was a saturated calomel electrode in all experiments.

Measurements. Polarograms were recorded with appropriate damping with a Leeds and Northrup electrochemograph Type E or a Sargent polarograph Model XXI. All current–potential curves were constructed from original polarograms by plotting middle points of current oscillations against potential.

Current–time curves were recorded in terms of the potential drop across a 100- or 1000-ohm resistance inserted in series with the cell circuit by using a Sanborn single channel recorder Model 151-100A combined with a stabilized d.c. preamplifier Model 151-1800 and a driver amplifier and power supply Model 150-200B/400.

Experiments for current–time curve analysis were carried out at 25°, while polarograms were taken at ambient temperature (24–27°).

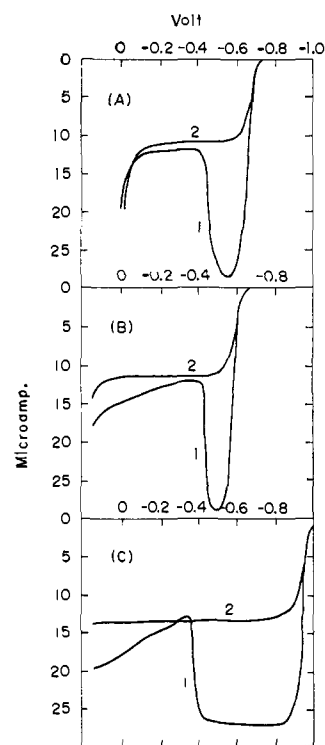*Observation of Streaming.* Streaming around the amalgam drop was observed through a low-power microscope. Fine active charcoal powder was suspended in the solution.

Experimental Results

Effect of Maximum Suppressor. Anodic current–potential curves obtained at various dropping amalgam electrodes in the absence and presence of 0.01% polyacrylamide (PAA) are compared in Figures 2 and 3. In the absence of PAA, acute maxima appeared at lead and cadmium amalgam electrodes in 0.1 M solutions of sodium hydroxide and potassium chloride, respectively. With zinc amalgam in 0.1 M sodium perchlorate a very flat maximum between -0.9 and -0.5 v. was observed (Figure 2C). With these three amalgams the current suddenly exhibited a sharp drop in the potential range between about -0.4 and -0.5 v., which is close to the potential of e.c.m. of pure mercury. In the potential range where these maxima appeared, extremely rapid streaming of the aqueous solution was observed in the direction from the neck to the bottom of the amalgam drop. After the break of the maximum at both cadmium and zinc amalgam electrodes, the limiting current gradually increased as the potential was shifted in the positive direction, as can be seen in Figures 2B and 2C. A rather weak streaming from the bottom to the neck of the drop was observed at potentials more positive than that at e.c.m.

At the bismuth, copper, and lead amalgam electrodes in 0.1 M perchloric acid (see Figure 3) no maximum appeared, but the limiting current was much greater in the absence than in the presence of PAA and increased gradually as the potential was shifted in the positive direction. A weak upward streaming was observed also at these electrodes.
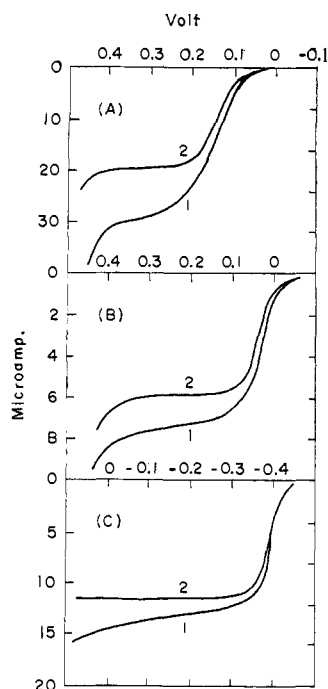
Figure 3. Positive exaltation: (A) 2 mM bismuth amalgam in 0.1 M HClO₄; (B) 1 mM copper amalgam in 0.1 M HClO₄; (C) 2 mM lead amalgam in 0.1 M HClO₄ (curves 1, without PAA; curves 2, with 0.01% PAA; capillary 1).
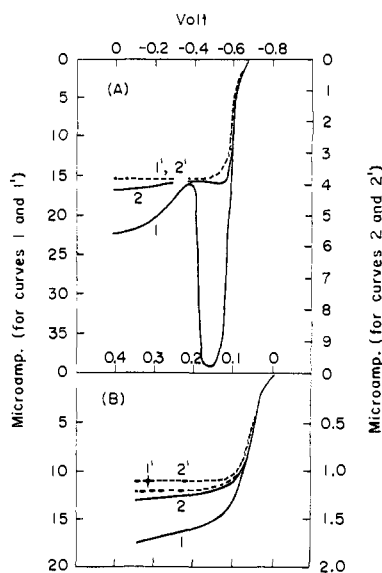

Figure 4. Effect of amalgam concentration: (A) cadmium amalgam in 0.1 M KCl: curve 1, 2 mM without PAA; curve 2, 0.5 mM without PAA; curves 1' and 2', with 0.01% PAA. (B) Copper amalgam in 0.1 M HClO₄: curve 1, 2 mM without PAA; curve 2, 0.2 mM without PAA; curves 1' and 2', with 0.01% PAA (currents corrected for residual; right-hand ordinate for curves 2 and 2'; capillary 2).

We shall call the two different types of anomalies negative maximum and positive exaltation. It is seen from Figures 2 and 3 that both negative maximum and positive exaltation are suppressed by the addition of 0.01% PAA.

Effect of Amalgam Concentration. The steep negative maximum at the 2 mM cadmium amalgam electrode in 0.1 M potassium chloride virtually vanished when the amalgam concentration was decreased to 0.5
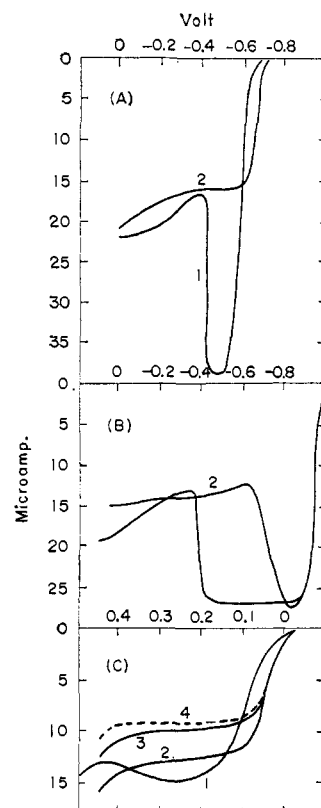

Figure 5. Effect of supporting electrolyte concentration: (A) 2 mM cadmium amalgam in 0.1 M (curve 1) and 1 M (curve 2) KCl (capillary 1); (B) 2 mM zinc amalgam in 0.1 M (curve 1) and 1 M (curve 2) NaClO₄ (capillary 2); (C) 2 mM copper amalgam in 0.01 M (curve 1), 0.1 M (curve 2), and 1 M (curve 3) HClO₄ (curve 4, 1 M HClO₄ plus 0.01% PAA; capillary 3).

mM as shown in Figure 4A. The polarograms obtained with the cadmium amalgam in 0.1 M perchloric acid were of similar appearance as those in the potassium chloride solution, except that the height of the negative maximum was about two-thirds of that in 0.1 M potassium chloride.

The relative magnitude of positive exaltation at both cadmium and copper amalgam electrodes also decreased considerably when the amalgam concentration was decreased from 2 mM to 0.5 mM and 0.2 mM, respectively, as shown in Figure 4A and B.

Effect of Supporting Electrolyte Concentration. The steep negative maximum at the 2 mM cadmium amalgam electrode in 0.1 M potassium chloride completely vanished when the supporting electrolyte concentration was increased to 1 M. The positive exaltation at the same electrode also tended to decrease with increasing supporting electrolyte concentration, but the effect was much less pronounced than that on the negative maximum. The results are presented in Figure 5A. The negative maximum at the zinc amalgam electrode in 0.1 M sodium perchlorate became acute upon increasing the perchlorate concentration to 1 M, no "maximum plateau" being observed (see Figure 5B).

The limiting current at the copper amalgam electrode was found to decrease to a significant extent with increasing concentration of perchloric acid, as illustrated in Figure 5C. The current–potential curve obtained in 4 M perchloric acid was practically the same as that obtained in 1 M. The displacement of the current–
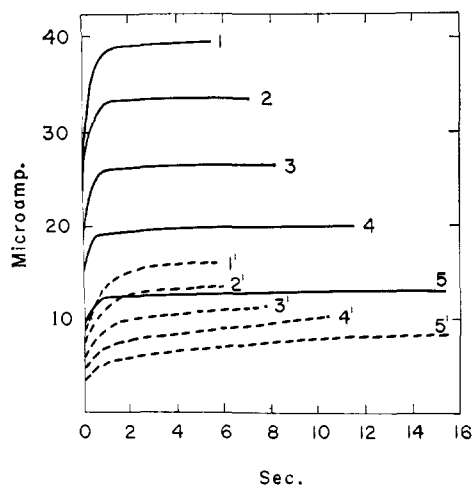
Figure 6. Current–time curves at 2 mM cadmium amalgam electrode at -0.50 v. in 0.1 M KCl with (curves·1'–5') and without (curves 1–5) 0.05% PAA: $h = 120$ cm. for curves 1 and 1', 100 cm. for curves 2 and 2', 80 cm. for curves 3 and 3', 60 cm. for curves 4 and 4', and 40 cm. for curves 5 and 5' (capillary 4).
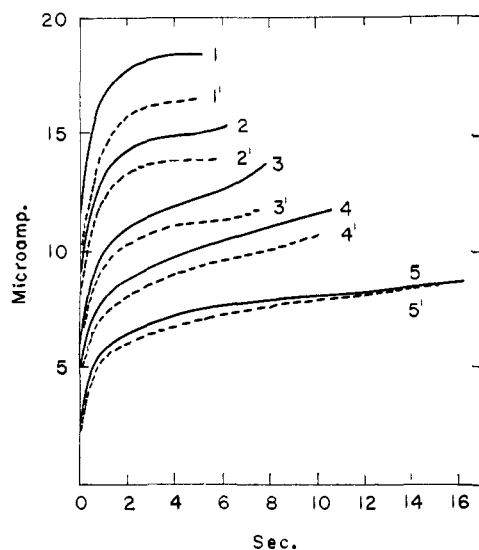

Figure 7. Current–time curves at 2 mM cadmium amalgam electrode at -0.20 v. (other conditions are the same as for Figure 6).

Figure 8. Analysis of current–time curves at 2 mM cadmium amalgam electrode at -0.2 v.: curves 1–5 obtained from curves 1'–5' in Figure 7; curve 6 obtained with capillary 5 in 0.1 M KCl containing 0.01% gelatin; curve 7 obtained with capillary 6 in the same solution. The dashed line was calculated by using von Stackelberg and Toome's equation and their D value.

Figure 9. Analysis of current–time curves at 0.889 mM copper amalgam electrode at $+0.15$ v.: solution, 0.1 M HClO$_4$ plus 0.01% sodium dodecyl sulfate; capillary 7, $h = 120$ cm. for curve 1, 100 cm. for curve 2, 80 cm. for curve 3, 60 cm. for curve 4, and 40 cm. for curve 5.

potential curve in 0.01 M perchloric acid toward positive potentials is due to the effect of iR drop. The limiting current in the presence of 0.01% PAA was essentially independent of perchloric acid concentration in the range of 0.01 to 4 M.

Effect of Amalgam Pressure. For both negative maximum and positive exaltation, the ratio of currents in the absence of maximum suppressor to that in its presence was found to decrease considerably as the pressure on the amalgam drop is decreased, *i.e.*, as the rate of flow of amalgam m is decreased and the drop time t is increased. The results obtained with cadmium amalgam in 0.1 M potassium chloride are illustrated in Figure 6 by current–time curves taken at -0.5 v. (corresponding to the apex of the maximum). It was found that 0.01% PAA was not sufficient to suppress the streaming completely, particularly at fast dropping rates, and the current–time curves showed a small peak at the early stages of drop growth. For
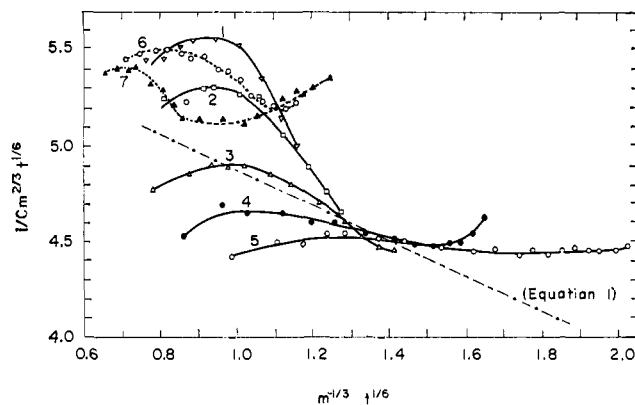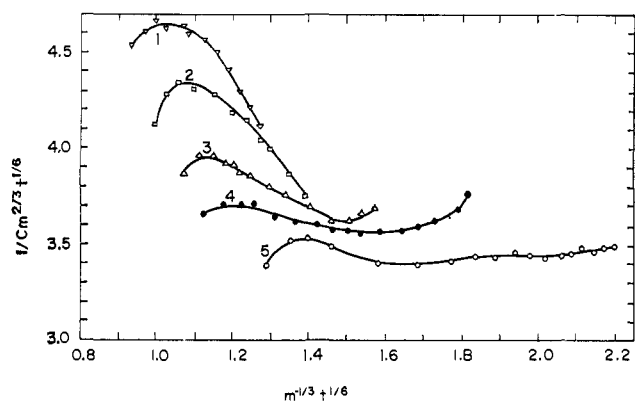
this reason the concentration of PAA was increased to 0.05%. The ratios of current at the end of drop life in the absence of PAA to that in the presence of 0.05% PAA were 2.47, 2.50, 2.29, 1.90, and 1.53 at $h = 120$, 100, 80, 60, and 40 cm., respectively.

The current–time curves taken at -0.2 v. at various pressures at the same electrode are reproduced in Figure 7. It is readily seen that the current exaltation at this potential also decreases with decreasing pressure. At $h = 40$ cm. the current–time curves in the absence and presence of PAA practically overlapped.

The current–time curves obtained with copper amalgam in 0.1 M perchloric acid in the presence and absence of 0.01% sodium dodecyl sulfate exhibited essentially the same shape as the curves shown in Figure 7.

Analysis of Current–Time Curves Obtained in the Presence of Maximum Suppressor. The von Stackelberg–Toome equation (eq. 1) predicts that a plot of $i/Cm^{2/3}t^{1/6}$ vs. $m^{-1/3}t^{1/6}$ should yield a straight line with a slope of $-708 \times 39nD$. The current–time curves 1–5 in Figure 7 and those obtained with copper amalgam were analyzed accordingly. The plots are shown in Figures 8 (curves 1 to 5) and 9. The predicted linear

plot was not found, the plot tending to become horizontal as the amalgam pressure was decreased, indicating that the current–time curve approaches the original Ilkovic equation as the dropping rate is made smaller. Curves 6 and 7 in Figure 8 were obtained from the current–time curves taken in the presence of 0.01 % gelatin using capillaries with larger orifice. The significance of these results is discussed in the next section.

On cathodic reduction waves at the dropping mercury electrode an effect of depletion of electroactive species is observed.[12,13] The limiting current at the first drop is appreciably greater than that observed with succeeding drops, because the solution near the electrode is becoming depleted of electroactive substance during the growth of the first drop, this impoverishment giving rise to a smaller current at the next and succeeding drops. As expected, and in agreement with von Stackelberg and Toome,[8] no such depletion effect was observed in anodic oxidation of dropping amalgam electrodes.

Discussion

Absence of Maximum Suppressor. The interpretations presented below for both negative maximum and positive exaltation were inspired chiefly by the recent paper on cathodic maxima by von Stackelberg and Doppelfeld.[1]

We shall first consider the negative amalgam maxima. Following the above authors, a basic assumption is made that the current density at the neck of the amalgam drop hanging at the end of a capillary is smaller than that at the bottom portion of the drop because of the shielding effect of the base of the capillary. In anodic oxidation at potentials on the negative side of e.c.m., this shielding effect on current distribution should bring about a more negative potential of the amalgam against the surrounding solution and hence a smaller interfacial tension at the neck than at the bottom of the amalgam drop. Thus, the streaming accompanied by negative anodic maxima is anticipated to proceed from the neck to the bottom (the opposite direction from that observed with negative cathodic maxima), which was actually found to be the case. As far as the effects of concentrations of amalgam and supporting electrolyte are concerned, the discussion given by von Stackelberg and Doppelfeld[1] regarding the effects of corresponding factors on *positive* cathodic maxima are directly applicable. According to these authors, if the electrocapillary curve can be approximated as a simple parabola, current i on a cathodic maximum is given by

$$i\alpha\sqrt{\nu} \propto \sqrt{\Delta\psi z} \qquad (2)$$

where ν is the velocity of streaming, $\Delta\psi$ is the potential difference between the neck and the bottom, and z is the specific mobility of the drop surface defined by Frumkin and Levich (cited in ref. 1)

$$z = \frac{q}{2\eta + 3\eta' + q^2/\kappa} \qquad (3)$$

where q is the average charge density on the drop surface, κ is the specific conductance of the solution, and

η and η' are the viscosities of the solution and mercury, respectively. Since z is independent of amalgam concentration if the amalgam is sufficiently dilute and does not affect the viscosity, the effect of amalgam concentration on the magnitude of a negative amalgam maximum should be entirely due to its effect on $\Delta\psi$. In view of the relation

$$\Delta\psi = R\Delta i \qquad (4)$$

where R is the resistance in the aqueous solution between the neck and the bottom of the amalgam drop, and Δi is the difference in current between the two regions, it is anticipated that $\Delta\psi$ is smaller at smaller amalgam concentrations because Δi becomes smaller. The observed effect of amalgam concentration on negative amalgam maxima (Figure 4A) is thus in qualitative accord with relation 2.

The concentration of supporting electrolyte, on the other hand, affects both z and $\Delta\psi$. However, in the potential range near e.c.m., z can be regarded as being independent of supporting electrolyte concentration because q is small near e.c.m. and the term q^2/κ in eq. 3 can be neglected, and also because q does not vary greatly with supporting electrolyte concentration near e.c.m. This is demonstrated by the z *vs.* potential curves in Figure 2 of ref. 3. On the other hand, $\Delta\psi$ is expected to decrease with increasing electrolyte concentration because R decreases (eq. 4). Thus, because the negative maximum at the cadmium amalgam electrode occurs in a potential range near e.c.m. (Figure 5A), the effect of supporting electrolyte concentration on this maximum may be attributed solely to its effect on $\Delta\psi$.

Zinc amalgam is oxidized at potentials considerably more negative than that at e.c.m., and therefore the magnitude of z at these potentials is considerably affected by supporting electrolyte concentration. As shown by von Stackelberg and Doppelfeld[1] and in agreement with eq. 3, z increases with increasing electrolyte concentration at a constant potential, the effect becoming greater as the potential becomes more removed from that at e.c.m. Qualitatively this explains the fact that the flat negative maximum of zinc amalgam in 0.1 M sodium perchlorate becomes acute in 1 M solution, as the streaming becomes less pronounced upon approaching e.c.m. (Figure 5B). No further attempt was made to interpret the variation of maximum current with potential because $\Delta\psi$ cannot be calculated theoretically as a function of potential.

As in the case of cathodic maxima of the first kind,[14] the magnitude of negative amalgam maxima becomes smaller, the slower the rate of flow of amalgam (Figure 6). This can be accounted for by considering the motion inside the amalgam drop and its effect on $\Delta\psi$. As already mentioned, the shielding effect brings about a current density difference between the neck and the bottom of the drop, *i.e.*, a smaller current density at the neck than at the bottom. In the case of negative amalgam maxima, this corresponds to a larger concentration of metal on the amalgam surface at the neck than at the bottom. The downward streaming of the aqueous solution around the drop causes the amalgam on the drop surface to flow in the same direction, as

(12) W. Hans and W. Henne, *Naturwissenschaften*, **40**, 524 (1953).
(13) J. M. Markowitz and P. J. Elving, *J. Am. Chem. Soc.*, **81**, 3518 (1959).

(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, p. 160.

is shown schematically in Figure 10A. Thus, once the streaming is started by the shielding effect, this mode of amalgam flow supplies fresh amalgam from the capillary directly to the neck area. It appears that this situation not only maintains but enhances the concentration difference between the neck and the bottom and hence $\Delta\psi$. When the rate of amalgam flow is made smaller, the rate of supply of fresh amalgam to the neck area is decreased, and consequently this results in a decrease in $\Delta\psi$.

The positive exaltation is quite different in appearance from the negative maximum. It more or less resembles the so-called maximum of the second kind in that the exaltation extends over a wide potential range. However, the possibility that the positive exaltation is a maximum of the second kind is ruled out for the following three reasons. (1) With maxima of the second kind, streaming velocity and hence current attain a maximum value at the potential of e.c.m. and decrease as the potential is further removed from e.c.m., whereas the current with positive amalgam exaltation was found to increase with increasing positive potential. (2) Maxima of the second kind become greater with increasing supporting electrolyte concentration, whereas the opposite result was found with positive amalgam exaltation. (3) Maxima of the second kind are independent of the concentration of electroactive species, whereas the positive amalgam exaltation was found to become smaller with decreasing amalgam concentration. The characteristics of maxima of the second kind mentioned above have been studied thoroughly by Russian workers and are now well understood.[2] On the other hand, if it is assumed that the positive exaltation is of the same nature as maxima of the first kind, the observed effect of concentrations of amalgam and supporting electrolyte can be understood qualitatively by similar reasoning as presented for the negative amalgam maxima. The direction of streaming observed is also consistent with this assumption. On the positive side of e.c.m., a smaller current density at the neck of the drop brought about by the shielding effect corresponds to a less positive potential and hence a larger surface tension. Thus, the direction of streaming is expected to be from the bottom toward the neck, which was actually found to be the case. However, under otherwise identical conditions, the velocity of streaming and the magnitude of accompanying anomalous current are appreciably smaller in the potential range of the positive exaltation than at potentials where negative maxima occur. This can be understood by considering the mode of flow within the amalgam drop and its effect on $\Delta\psi$. In view of the direction of streaming observed in the vicinity of the drop surface, the motion inside the amalgam drop is considered to proceed in the manner shown in Figure 10B. Fresh amalgam flowing out of the capillary will flow to the bottom area from where it flows along the surface toward the neck. In the process of this flow from the bottom to the neck, the amalgam will become progressively more oxidized, giving rise to a larger metal concentration at the drop surface near the bottom than around the neck. On the other hand, the shielding effect results in a larger surface concentration of metal at the neck than at the bottom. Thus, the flow of amalgam tends to neutralize the concentration differ-
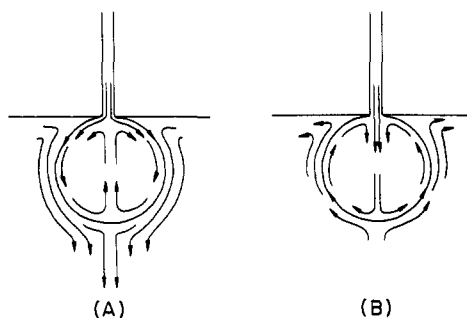

(A)   (B)

Figure 10. Streaming at dropping amalgam electrode: (A) negative maximum, (B) positive exaltation.

ence and hence to decrease $\Delta\psi$ brought about by the shielding effect. As a result of these two opposing effects there is much weaker streaming accompanying a positive exaltation than a negative maximum.

When the rate of amalgam flow, m, is increased by increasing the amalgam pressure, fresh amalgam will reach the bottom area at a greater speed and tend to keep the metal concentration greater around this part. Consequently, $\Delta\psi$ is expected to become smaller at larger m. Actually, however, the positive exaltation tends to be enhanced at larger m and smaller t. This indicates that the "Spüleffekt" also becomes more pronounced with increasing m. A more detailed interpretation of the situation cannot be offered at present. The dependence of current on potential is also difficult to interpret because the variation of $\Delta\psi$ with potential cannot be predicted.

Presence of Maximum Suppressor. The results illustrated in Figures 8 and 9 indicate that eq. 1 does not hold for any of the curves. von Stackelberg and Toome[5] state that eq. 1 holds if the capillary has a drop time of 7 to 25 sec. and a diameter of 38 to 100 μ (corresponding drop weight mt being 4.5 to 12 mg.), and if the pressure is greater than 50 cm. The capillaries used in the experiments for Figure 8 (curves 1 to 5) and 9 were Sargent "6–12 sec." capillaries, and had a diameter of about 50 μ. Curves 3 and 4 in these figures were obtained from current–time curves taken within the range of experimental conditions specified by von Stackelberg and Toome. These authors analyzed current–time curves obtained with 10 mM cadmium amalgam in 0.1 M potassium chloride containing 0.01% gelatin. It is possible that this high amalgam concentration accounts for the difference in results obtained by von Stackelberg and by us. In order to confirm that the difference between their results and ours is not due to the maximum suppressor, we ran a few experiments with 0.01% gelatin. The results obtained were the same as those obtained in the presence of 0.05% PAA, and the plot of $i/Cm^{2/3}t^{1/6}$ vs. $m^{-1/3}t^{1/6}$ showed exactly the same characteristics with both maximum suppressors. Curve 6 in Figure 8 was obtained with a capillary which had approximately the same diameter (114 μ) as the one used by von Stackelberg and Toome (100 μ) in their experimental tests of eq. 1. None of our experimental data fitted this equation, while at slow dropping rates $i/Cm^{2/3}t^{1/6}$ was found to become nearly constant, which is the situation anticipated from the original Ilkovic equation. This is the more remarkable in view of the fact that

cathodic current–time curves follow neither the original Ilkovic equation nor the modified equation of the type of eq. 1 with a plus sign replacing the minus sign, even for the first drop, and hence in the absence of the depletion effect.[15] Our results also do not agree with those of Kůta and Smoler, who, from the "average" slope of log i–log t plots conclude that in the absence of the "Spüleffekt" the Koutecky equation holds. However, this equation (see eq. 1) does not predict a straight line for such a plot. On the other hand, at slow dropping rates we found, in accordance with the Ilkovic equation, a straight-line relation. For example, the current–time curve corresponding to curve 5 of Figure 9 gave a linear log i–log t plot within the time range of 0.7 to 15.9 sec., with a slope of 0.177. This value compares favorably with the value of $^1/_6$ (0.167) given in the simple Ilkovic equation.

It is of interest to note that the capillaries used to obtain curves 5 and 7 in Figure 8 had practically the same drop time (15.3 and 15.9 sec.), but their m values were considerably different (0.742 and 1.943 mg. sec.$^{-1}$). These results clearly indicate that, for dropping amalgam oxidations, it is the flow rate m and not the drop time t that is responsible for the deviation from the Ilkovic equation. Thus, there is little doubt that the greater deviation at higher flow rates is due to the "Spüleffekt."

The diffusion coefficient of copper in mercury calculated from the value of $i/Cm^{2/3}t^{1/6} = 3.45$, where i is the maximal current at the moment the drop falls, at

(15) J. M. Los and D. W. Murray, "Advances in Polarography," ref. 1, Vol. 2, p. 408.

$h = 40$ cm. (curve 5 in Figure 9) by using the original Ilkovic equation, is equal to 5.95×10^{-6} cm.^{2} sec.$^{-1}$. Furman and Cooper[3] reported the value of 1.06×10^{-5} cm.^{2} sec.$^{-2}$, but this value must be too high because they used capillaries with short drop times (1.4–5.0 sec.) and large m values (1.1–1.4 mg. sec.$^{-1}$) and did not consider the "Spüleffekt." The diffusion coefficient calculated from the value of $i_d(\text{av.})/Cm^{2/3} \cdot t^{1/6} = 3.55$ reported by Schupp, Youness, and Watters[6] by using the Ilkovic equation becomes equal to 8.55×10^{-6} cm.^{2} sec.$^{-1}$. Apparently this value is also too high because the characteristics of their capillary ($m = 0.636$ mg. sec.$^{-1}$, $t = 11.10$ sec.) do not assure complete absence of the "Spüleffekt." The diffusion coefficient of cadmium in mercury calculated from $i/Cm^{2/3}t^{1/6} = 4.45$ at $h = 40$ cm. (curve 5 in Figure 8) is equal to 9.80×10^{-6} cm.^{2} sec.$^{-1}$ as compared to the value 1.68×10^{-5} cm.^{2} sec.$^{-1}$ reported by von Stackelberg and Toome[8] and 1.520×10^{-5} cm.^{2} sec.$^{-1}$ chosen by Furman and Cooper.[3]

In conclusion it may be stated that the extent of stirring decreases with decreasing m, decreasing amalgam concentration, increasing supporting electrolyte concentration, and presence of a suitable surface-active substance. For studies of anodic dropping amalgam electrode reactions, it is recommended to eliminate stirring effects by using a capillary with an m value not greater than 0.5 mg. sec.$^{-1}$, by working with very dilute amalgams, and by adding supporting electrolyte in large concentration and a suitable surfactant which does not affect adversely the rate of the electrode reaction.

The Thermodynamics of Ionization of Cyanocarbon Acids

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The relationship between acid strength and heats and entropies of ionization in water of five cyanocarbon acids whose pK covers the range 11 to −6 has been investigated. The heats of ionization of four of the acids [malononitrile, p-(tricyanovinyl)phenyldicyanomethane, methyl dicyanoacetate, and bis(tricyanovinyl)amine] were measured in the present work. The first one was determined calorimetrically and the others from a spectroscopic study of the temperature dependence of the protonation equilibria in sulfuric acid solutions. The latter two acids required acidity function techniques. A method was used for the determination of $\Delta H°$ that is based on a simple relation between the heat of ionization in a given acid solution and the temperature derivative of the indicator ratio. This heat is extrapolated by the overlap technique to estimate $\Delta H°$. The entropies were calculated from $\Delta H°$ and pK. The temperature dependence of the pK of p-nitroaniline has also been redetermined by spectroscopic methods and used along with activity coefficient data to extrapolate ΔH for p-(tricyanovinyl)phenyldicyanomethane to dilute solution. It was found that most of the variation of pK with structure for the cyanocarbon acids comes through variation of $\Delta H°$. The entropies are rather small in absolute value ranging from $\sim −7$ to ~ 0 e.u. The correlation with the entropies of other acid ionizations is also discussed.

Introduction

One of the more interesting aspects of the study of the relationship between molecular structure and equilibria is the relation between structure and acid strength. According to a simplified picture, variations in acid strength from variations in structure should result from variations of the vapor phase ionic dissociation free energy of the H–A bond (or stability of the anion) and variations in the difference in free energy of hydration of the anion and the neutral molecule. The bond dissociation (or anion stabilization) free energy should be primarily an enthalpy effect, the changes in intramolecular entropy being rather small. According to the Born model, in aqueous solution, the hydration