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Millicoulometry. IV. The Anomalous Wave in Polarograms of Solutions of High Ionic Strength

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The anomalous wave occurring after a normal reduction wave in polarograms of solutions of high ionic strength has been studied by millicoulometric techniques. Contrary to previously suggested theories, it is due neither to the reduction of an abnormally large amount of the reducible material brought to the surface of the dropping electrode by stirring, nor to the electroreduction of water. It is attributed to an increase in the energy required to maintain the electrical double layer around the drop by overcoming the disordering effect of water or anions liberated at the drop surface when metal ions are reduced.

Introduction

Orlemann and Kolthoff[1] first described the anomalous wave observed at potentials more negative than about −0.9 v. *vs.* S.C.E. in polarograms of solutions of high ionic strength (above about 0.5). The wave is found only after a normal reduction wave: it does not appear in the c.–v. curve of the supporting electrolyte alone, nor does it appear in polarograms secured with a stationary mercury microcathode. Orlemann and Kolthoff ascribed it to the catalytic electroreduction of water (whence the name "water wave") and supported this interpretation by showing that the expected hydrogen-ion wave was suppressed when traces of acid were added to a solution giving the anomalous wave.

More recently Kryukova[2–4] proposed that the anomalous wave is due to stirring of the solution near the mercury drop, and termed the phenomenon a "maximum of the second kind." This is presumed to be due to the tangential motion of the mercury as it emerges from the capillary, whereas the familiar "maximum of the first kind" is attributed to the non-uniform charge density on the drop surface. In either case there results a flow of the solution past the drop surface, so that more of the reducible ion reaches the electrode than could do so under the influence of the diffusion gradient in a quiet solution, and complete concentration polarization of the electrode is effectively prevented. An excellent review of this theory has been published by von Stackelberg.[5] It should be mentioned that Orlemann and Kolthoff[1] were unable to observe microscopically any stirring around the electrode at potentials along the anomalous wave, though this is easily done when dealing with a "maximum of the first kind."

The operational difference between the two interpretations is this: while they agree that the excess current is due to an electroreduction process, Orlemann and Kolthoff assume that the reaction $H_2O + e^- = {}^1/_2H_2 + OH^-$ takes place in addition to the reduction of the metal ion, whereas Kryukova asserts that the anomalous current is due solely to the reduction of an abnormally large amount of metal ion. Thus, if Orlemann and Kolthoff are correct, the electrolysis of a solution at a potential on the anomalous wave will consume more electricity than can be accounted for on the basis of the amount of metal deposited, and this excess will result in a corresponding increase in the hydroxyl-ion concentration of the solution. On the other hand, Kryukova's interpretation demands that the amount of electricity consumed be exactly one faraday per equivalent of metal deposited.

This communication describes the results of experiments which were performed in an attempt to permit a definitive choice between these two alternatives. Rather unexpectedly, it was found that neither is correct: there is no change in the composition of the solution which can be quantitatively correlated with the amount of electricity represented by the anomalous wave.

Experimental

The millicoulometer and the general technique of performing millicoulometric electrolyses,[6] and the micro H-cell[7] have been described elsewhere. The sensitivity of the millicoulometer was checked at several points by the procedure used previously[8] and was found to have changed by less than 0.1% in 15 months.

Diffusion currents were measured by reading the deflections on the visual scale of a calibrated Sargent–Heyrovsky Model XII polarograph. All measurements were made at 25.00 ± 0.02°. A Beckman Model G *p*H meter was used for the *p*H measurements.

Thallous chloride was twice recrystallized from water; all other chemicals were ordinary reagent grade.

Solutions were prepared by the following procedure: a clean dry calibrated 10-ml. volumetric flask was weighed, then the desired amount of indifferent salt was added and the flask was reweighed. A known volume of a standard solution of the reducible metal ion was added from a calibrated volumetric pipet, and the solution was diluted to the mark and weighed again. Thus both the molarity of the supporting electrolyte and the number of micromoles of reducible ion contained in each g. of the solution were accurately known. At the same time a nearly equally concentrated (±10%) solution of the indifferent salt alone was prepared to permit the measurement of the residual current.

About 0.8 g. of this solution, accurately weighed by difference, was transferred to the micro-cell and deaerated; then it was electrolyzed at a potential on the plateau of the normal wave of the reducible ion until at least 30% of the ion had been deposited. This usually required about an hour. The diffusion current, the millicoulometer register and the clock were read near the middle and again at the end of this period, so that two values of *n* (the number of faradays required for the reduction of one mole of metal ion) for the normal wave could be calculated.

The number of micromoles of reducible ion remaining at the end of this electrolysis could be calculated from the amount originally added to the cell and the ratio of the in-

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[1] E. F. Orlemann and I. M. Kolthoff, This Journal, **64**, 833 (1942).

[2] T. A. Kryukova and B. N. Kabanov, *J. Gen. Chem.* (*U. S. S. R.*), **15**, 294 (1945); *C. A.*, **40**, 3345 (1946).

[3] T. A. Kryukova, *J. Gen. Chem.* (*U. S. S. R.*), **21**, 365 (1947); *C. A.*, **41**, 6160 (1947).

[4] T. A. Kryukova, *Zavodskaya Lab.*, **14**, 511 (1948); *C. A.*, **43**, 4971 (1949).

[5] M. v. Stackelberg, *Fortschr. Chem. Forsch.*, **2**, 229 (1951).

[6] S. Bogan, L. Meites, E. Peters and J. M. Sturtevant, This Journal, **73**, 1584 (1951).

[7] T. Meites and L. Meites, *Anal. Chem.*, **23**, 1893 (1951).

[8] L. Meites, *ibid.*, **24**, 1057 (1952).

itial and final diffusion currents. The applied potential was then changed to a value near the peak of the anomalous wave and the electrolysis was resumed. An immediate measurement of the current at this new potential allowed the calculation of the ratio of the total current (including the anomalous current, but corrected for the separately determined residual current) to the diffusion current of the normal wave. This ratio is henceforth designated as R. The electrolysis was continued for another hour or so in exactly the same way as the electrolysis on the plateau of the normal wave. These data provided information on both the apparent value of n at potentials along the anomalous wave and the current ratio R. Table I shows the data secured in a typical experiment.

TABLE I

MILLICOULOMETRIC ELECTROLYSIS OF CADMIUM(II) IN 2.5F POTASSIUM THIOCYANATE

0.798 g. of a 2.51 F potassium thiocyanate solution initially containing 1.436 micromoles of cadmium(II) was electrolyzed at −1.00 v. *vs.* S.C.E., then at −1.50 v. The blank counting rate of the millicoulometer, including the contribution from the residual current, was 0.2920 count/sec. at −1.00 v. and 0.2969 count/sec. at −1.50 v.

Time, sec.	Net counts	Mean sensitivity, μF_y/count	μF_y used	Current, arbitrary units*		Micromoles reduced	n
				−1.0 v.	−1.5 v.		
Electrolysis at −1.00 v.							
0	0	....	0	81.0	..	0	...
2070	1609	4.690×10^{-4}	0.755	59.8	..	0.376	2.00_6
3596	2168	4.631	1.004	52.6	..	0.503	1.99_6
Electrolysis at −1.50 v.							
0	0	....	0	(52.6)	70.7	0	...
2718	1372	4.599	0.631	39.4	..	0.234	2.69_7
4595	2109	4.584	.967	32.4	44.3	.358	2.70_0

* Corrected for the residual current

$$n_2/n_1 = 2.69_9/2.00_1 = 1.34_9;\ \overline{R} = 1.35_5$$

This procedure had the advantage of avoiding the necessity of weighing out and deaerating a second portion of the solution, and served to eliminate the effects on n_2/n_1, the ratio of the values of n for the two waves, of any uncertainties in the amount of reducible ion originally taken. That these uncertainties could not in any case have been very great is shown by the fact that the experimental value of n_1 always agreed with the theoretical value for the reduction of the ion in question to within ±0.5%. This accuracy is very much better than the ±3% claimed by Bogan, Meites, Peters and Sturtevant.[6] This improvement is partly due to the avoidance in this work of measurements made before a considerable fraction of the metal ion had been deposited, but most of it is due to the much more accurate calibration data secured since their paper was published. The accuracy and precision of the millicoulometric data now appear to be substantially identical with those of the polarographic measurements themselves.

It might be mentioned that the number of counts recorded during each interval was converted into the number of microfaradays consumed by the use of the calibration figure corresponding to the mean net counting rate during that interval.

Data and Discussion

Table II shows the data secured in electrolyses of solutions of cadmium, cupric and thallous ions in a number of supporting electrolytes. It is evident from this table that the percentage increase in current along the anomalous wave is exactly equal to the percentage increase in the amount of electricity which flows through the cell during the reduction of one micromole of metal ion. If the anomalous current were due solely to the reduction of excess metal ion, as Kryukova proposes, the value of n would remain unchanged. If the anomalous current were due partly to the reduction of excess metal ion, and partly to some other cause, n_2/n_1 would be greater than 1 but less than R: the fraction of the anomalous current due to the reduction of excess metal ion could be calculated as

$$1 - \{[(n_2/n_1) - 1]/(R - 1)\}$$

TABLE II

RESULTS OF MILLICOULOMETRIC ELECTROLYSES

Reducible ion	Supporting electrolyte	n_2/n_1	$\overline{R}$
Cd(II)	1.5 F KCl	$2.30_3/2.00_2 = 1.15_0$	1.14_6
	3.5 F KCl	$2.61_6/1.99_2 = 1.31_3$	1.31_9
	1.3 F KSCN	$2.18_0/2.00_4 = 1.08_8$	1.07_2
	2.5 F KSCN	$2.69_9/2.00_1 = 1.34_9$	1.35_5
	5.2 F KSCN	$2.96_9/1.99_5 = 1.48_8$	1.49_5
Cu(II)	1.2 F KCl	$2.08_8/1.99_7 = 1.04_6$	1.03_7
	2.3 F KCl	$2.64_2/2.00_7 = 1.31_6$	1.33_0
	4.0 F $NaNO_3$	$2.52_0/2.00_3 = 1.25_8$	1.26_9
	1.3 F KSCN	$2.10_4/1.99_1 = 1.05_7$	1.04_9
	5.2 F KSCN	$3.06_9/2.00_4 = 1.53_1$	1.52_2
Tl(I)	3.5 F KCl	$1.13_0/1.00_0 = 1.13_0$	1.13_4
	3.9 F $NaNO_3$	$1.70_0/1.00_3 = 1.69_5$	1.70_3
	1.3 F KSCN	$1.07_7/0.99_5 = 1.08_2$	1.07_0
	2.6 F KSCN	$1.26_0/0.99_9 = 1.26_1$	1.26_1
	5.3 F KSCN	$1.41_3/1.00_2 = 1.41_0$	1.40_6

Mean $\overline{R}/(n_2/n_1) = 0.999 \pm 0.006$.

The present data, however, show that this quantity is equal to zero. That is, at potentials along the anomalous wave the reducible ion is brought to the electrode surface solely under the influence of the normal diffusion gradient. More precisely, the mean fraction of the anomalous current due to reduction of excess metal ion, including the data of all fifteen electrolyses, is −4.2%: of course this method of calculation greatly magnifies the effects of the experimental errors.

Although the data thus far secured appeared to support the interpretation of Orlemann and Kolthoff, it seemed difficult to reconcile the evidence with the supposed production of hydroxyl ions at the surface of the electrode. The difficulty may be illustrated by recalling the work of Lingane and Niedrach[9] on the polarography of lead(II)–tellurium(IV) solutions. In alkaline solutions the lead and tellurite (reduction to the −2 state) waves are individually well defined. But the addition of lead(II) to a tellurite solution does not increase the total current, for the −2 tellurium produced at the electrode surface diffuses outward and reacts with inwardly diffusing lead ions to form insoluble PbTe, which cannot be reduced. The authors remark that ". . . the (lead) cannot contribute to the total diffusion current until its flux at the electrode (proportional to $CD^{1/2}$) exceeds the flux of +4 tellurium." The assumed situation in the present case differs slightly from this, because a rate constant is presumed to be involved, but it is evident that if hydroxyl ion is produced at the electrode surface, cadmium or cupric hydroxide should precipitate in the diffusion layer. Thus the reduction of the water should not increase the total current until the amount of hydroxyl ion formed is greater than that required to react with all of the inwardly dif-

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(9) J. J. Lingane and L. W. Niedrach, THIS JOURNAL, 71, 196 (1949).

fusing metal ion. Since thallous ion does not form an insoluble hydroxide, considerably different phenomena should be observed in its polarograms, but actually the effect is very similar to those found with the other ions.

To provide a conclusive test of the "water wave" hypothesis, therefore, a number of experiments were performed which may be illustrated by the following typical example. A portion of the same solution used in the experiment of Table I was placed in a large H-cell with a fritted glass gas dispersion cylinder,[10] and a rapid stream of hydrogen was passed through it for 20 minutes to remove dissolved carbon dioxide. Its *p*H was then found to be 6.0_3. Another portion of the solution, weighing 2.673 g. (2.40 ml.), was placed in the micro-cell, deaerated, and electrolyzed in the usual manner for 26 hours at -1.50 v. *vs.* S.C.E. At the end of this time the amount of cadmium ion present in the solution was found to have decreased from 4.81 to 0.03 micromole, and the millicoulometer readings, after correction for the residual current, showed that 12.96 microfaradays of electricity had passed through the cell. Of these, $2(4.81 - 0.03) = 9.56$ had been consumed by the reduction of cadmium, so that the remaining 3.40 microfaradays had been consumed by the anomalous process. The *p*H of the solution after this electrolysis was found to be 6.3_7.

This change in *p*H—the largest of any observed in these experiments—is probably not far removed from the error of measurement of the *p*H of a small volume of completely unbuffered solution. Even taking it at its face value, however, and assuming for simplicity that the *p*H meter reading under these conditions gives $-\log [H^+]$ directly, one calculates that 5×10^{-4} micromole of hydrogen ion had been removed (or an equal amount of hydroxyl ion had been liberated) per ml. of solution. This corresponds to the production of 1.2×10^{-3} micromole of hydroxyl ion in the whole solution, which in turn represents only 0.0012 microfaraday. This is negligibly small in comparison with the 3.40 microfaraday which had to be accounted for, a conclusion confirmed by the results of all the other experiments performed.

Consequently the anomalous current is not due to the reduction of excess metal ion, it does not correspond to the reduction of water or hydrogen ion, and there is no appreciable amount of any other substance present which could be reduced at these potentials. Therefore it very probably represents an increase in the condenser current, which is the current required to establish and maintain the electrical double layer around the drop. Let us examine some of the details and consequences of this hypothesis.

In the absence of any reducible ion, the condenser current must be only large enough to effect a partial separation of the cations and anions in the vicinity of the drop, and to maintain the resulting arrangement against the effects of Brownian motion and of the growth of the drop. Suppose, however, that the solution also contains a reducible ion which forms an aquo-complex: its reduction will liberate water at the electrode surface. This tends to disrupt the semi-ordered structure of cations and water molecules around the drop,[11] and the condenser current must increase. A similar explanation would apply if the reducible ion forms a complex with the anion of the supporting electrolyte instead of with water, except that the effect of liberating anions in the predominantly cationic portion of the double layer would be expected to be greater than the effect of liberating water. The data of Table II do, in fact, show that the anomalous current with thallous ion in chloride and thiocyanate media (in which only aquo-complexes are formed) is appreciably less than with cadmium or cupric ions, which form complexes with these anions. Since the amount of water (or anion) liberated at the drop surface is clearly proportional to the amount of metal reduced, it is reasonable that the anomalous current should be proportional to the diffusion current.[12]

The fact that the anomalous current is not observed at low concentrations of supporting electrolyte is probably due to a lower degree of order in the cation-water structure in the double layer in the dilute solutions. At higher concentrations, however, the interionic distances become much smaller and the structure would become more rigid, so that more energy would be required to maintain it. At extremely high ionic strengths the tetrahedral structure of water itself breaks down, and in addition the decreasing activity of water should cause the reducible ions to be less highly hydrated and thus to liberate less water when the central metal atom is reduced.

Consequently one would expect the anomalous current to pass through a maximum and then decrease again as the supporting electrolyte concentration is increased. Polarograms of lead(II) in sodium hydroxide solutions of various concentrations between 0.25 and 16 *F* were recorded, and the ratios of the maximum anomalous current to the diffusion current of biplumbite ion are given in Table III. The relative value of the anomalous current is greatest in about 3 *F* NaOH. Although the same phenomenon would be predicted in other cases, the ionic strength at the peak of the curve would doubtless differ from this value with other reducible ions and other indifferent salts.

TABLE III

THE ANOMALOUS WAVE WITH LEAD(II) IN SODIUM HYDROXIDE MEDIA

The concentration of lead(II) was 1.3 m*M*. On open circuit in 0.25 *F* sodium hydroxide $m^{2/3}t^{1/6}$ was 2.75 mg.$^{2/3}$ sec.$^{-1/2}$ and *t* was 2.09 sec.

[NaOH], *F*	0.25	0.52	0.78	1.31	2.04	2.8	3.8
i_{max}/i_d	1.00	1.07	1.20	1.32	1.40	1.45	1.41

[NaOH], *F*	4.9	5.8	6.9	9.0	10.6	12.0	15.9
i_{max}/i_d	1.35	1.32	1.29	1.21	1.08	1.00	1.00

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(10) L. Meites and T. Meites, *Anal. Chem.*, **23**, 1194 (1951).

(11) Orlemann and Kolthoff found marked differences in the magnitudes of the anomalous currents secured with (aquo-)thallous ion in various alkali and alkaline earth chlorides, but with a given cation little or no effect resulted from substituting nitrate or hydroxide for chloride. This is in line with the interpretation offered here, for at such negative potentials as these the properties of the electrical double layer are determined solely by the identity and concentration of the *cation* of the supporting electrolyte.[12]

(12) D. C. Grahame, E. M. Coffin and J. I. Cummings, ONR Project No. NR-051-150, Technical Report No. 2, August, 1950.

Unfortunately, there appears to exist no method by which the degree of what might be termed the "quasi-crystalline structure" of these concentrated electrolyte solutions can be evaluated. Observations of their Raman spectra and temperatures of maximum density indicate an increasing degree of derangement of the tetrahedral structure of water with increasing salt concentration, and show that both the cation and anion exert marked effects on its extent, but they are unable to give any information about the orderliness of the arrangement of the ions even in the bulk of the solution, let alone the considerably more complicated arrangement which must prevail in the neighborhood of the drop.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Effect of Substituents on the Protolytic Constants of Anilinium Type Protolytes[1a,b]

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The protolytic reaction constant of *o*-, *m*- and *p*-nitroanilinium ions, *o*-, *m*- and *p*-chloroanilinium ions, *o*-, *m*- and *p*-methylanilinium ions, *m*- and *p*-fluoroanilinium ions, *p*-dimethylaminoazobenzene and *m*-nitro-*p*-methylanilinium ions have been determined by a colorimetric method in the solvents water, anhydrous methanol and anhydrous ethanol. The effect of small amounts of water on the protolytic constants in anhydrous methanol has been determined. The relative order of the protolytic constants in the various solvents is discussed on a structural basis and comparisons made with the phenol and benzoic acid series. The Hammett relationship is expanded to include the ortho position. Comparisons between calculations of the protolytic constant by means of electrostatic considerations are made with the observed data, and the validity of the Sarmousakis theory with respect to both substituents and solvent is evaluated.

Many data concerning the equilibrium constants of reactions between the anilinium ions and the various hydroxylic solvents have accumulated in the literature. Since a fairly complete series of these protolytic reactions has not been studied by a single investigator using a single method (especially in anhydrous solvents), this investigation was begun to provide an internally consistent set of equilibrium constants for such reactions. This set of internally consistent data leads to some correlation between the structural features of the molecules and the relative magnitudes of the equilibrium constants of the reactions involving these molecules.

The structurally related protolytes investigated were the anilinium ion and various substituted anilinium ions: the *o*-, *m*- and *p*-chloro-; the *o*-, *m*- and *p*-nitro-; the *o*-, *m*- and *p*-methyl-; the *m*- and *p*-fluoro-; the *m*-nitro-*p*-methyl-; and *p*-dimethylaminoazobenzene (butter yellow, hereinafter abbreviated BY).

The equilibria studied may be represented by

$$\mathrm{A_1 + B_2 \rightleftarrows A_2 + B_1} \qquad (1)$$

where the essential structural difference between A and B is a proton.

When B_2 is the solvent S, eq. 1 becomes

$$\mathrm{A^+ + S \rightleftarrows SH^+ + B} \qquad (2)$$

where A^+ represents an anilinium ion and SH^+ represents the solvated proton. Therefore

$$K_S = (C_{SH^+}/C_S)\cdot(C_B/C_{A^+}) \qquad (3)$$

where K_S is the concentration protolysis constant. Limiting values obtained at infinite dilution are designated by superscript zero, *e.g.*, K_S^0.

The conventional protolysis constant is

$$K_C = K_S C_S \qquad (4)$$

When, in eq. 1, A_1 is the indicator A_i, then

$$K_{A_iB} = (C_{B_i}/C_{A_i})\cdot(C_A/C_B) \qquad (5)$$

The evaluation of this equilibrium constant is, experimentally, a matter of determining the concentrations at equilibrium of the various species involved. Here the ratio C_{B_i}/C_{A_i} was determined from colorimetric measurements.

For the protolytic reaction between the substituted anilinium ions and aniline eq. 1 becomes

$$\mathrm{A_x + B_o \rightleftarrows A_o + B_x} \qquad (6)$$

where the subscript o refers to aniline and the subscript x refers to the substituted aniline. Therefore, the protolytic constant is

$$K_{A_xB_o} = (B_x/A_x)\cdot(A_o/B_o) \qquad (7)$$

in which the solvent is implicit in species solvation.

The advantages of using the ratio of the protolysis constants, $K_{A_xB_o}$, rather than the conventional protolysis constants, are: (1) the elimination of the need to know autoprotolysis constants when comparing with the data of different investigators; (2) its lower sensitivity (of $K_{A_xB_o}$) to small changes in the medium and (3) its emphasis on substituent effects.

Experimental

Procedure.—The indicator used at the start of the investigation was butter yellow (BY), whose acid–base forms are the same charge type as anilinium–aniline. This proved satisfactory in water and methanol but not in ethanol. The indicator *m*-nitro-*p*-methylaniline was used in ethanol.

The determination of the protolytic constant, K_{A_iB}, involved (1) the fixing of the buffer ratio A/B and (2) the measurement, spectrophotometrically, of the ratio B_i/A_i. When Beer's law obtained, the ratio B_i/A_i was determined by the relationship

$$\text{Fraction } A_i = -\frac{\log(I_r/I_x) - \log(I_r/I_{B_i})}{\log(I_r/I_{B_i}) - \log(I_r/I_{A_i})} \qquad (8)$$

where I denotes the light intensity transmitted through the

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(1) (a) In order to avoid the semantic difficulties inherent in the terms *acid* and *base*, Brönsted terminology will be used throughout. (b) This paper was extracted from the dissertation presented by C. Arne Arenberg to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952.