Post Adsorption Wave of Cuprous Thiocyanate in Polarograms of Dilute Thiocyanate Solutions Containing Copper(II)[1]

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In dilute (<0.1 M) thiocyanate solutions, copper(II) yields three waves at the dropping mercury electrode. From the dependence of the wave height on copper concentration and on the height of the mercury reservoir, the third wave is attributed to the reduction of an adsorbed monomolecular layer of cuprous thiocyanate. This interpretation is supported by the shape of electrocapillary curves, variation of half-wave potentials with concentrations of copper and thiocyanate and current–potential curves obtained at the rotated dropping mercury electrode.

In connection with a study of the effect of surface-active substances on copper(II) waves at the conventional and the rotated dropping mercury electrodes, we determined current–potential curves of copper(II) in solutions containing various concentrations of thiocyanate. Although it has been reported[2,3] that copper(II) yields two waves when the concentration of thiocyanate is smaller than 0.1 M, we observed an additional wave which has the characteristics of a so-called "postwave" which is observed when the oxidized form of an electroactive species is strongly adsorbed on the mercury surface. This paper deals with a study of the characteristics of the third wave, which appears to be the result of the reduction of an adsorbed layer of cuprous thiocyanate.

In more concentrated solutions of thiocyanate (>0.5 M) the current–potential curves of copper (II) are more involved and there is no agreement in the literature on their interpretation.[3-5] No adsorption wave is observed in such media presumably because copper(I) remains in solution in the form of complex ions. The polarography of copper(II) in concentrated thiocyanate solutions will be discussed in a subsequent paper.

Experimental

Materials.—Potassium thiocyanate, perchloric acid, sodium perchlorate and cupric perchlorate were C.P. grade and used without further purification. The copper content of the stock solution of cupric perchlorate was determined iodometrically. A small amount of C.P. chloroform, washed twice with dilute perchloric acid and with water, was added into the electrolysis cell to prevent the reduction of copper(II) in the bulk of the solution by mercury in the presence of thiocyanate. Polyacrylamide (PAM 75, obtained from American Cyanamid Co., New York) was used as maximum suppressor.

Electrodes.—Both a conventional dropping mercury electrode (d.m.e.) and a rotated dropping mercury electrode (r.d.m.e.) (210 r.p.m.) were used. A saturated calomel electrode was the reference electrode in all experiments.

Measurements.—Current–potential curves were recorded with a Sargent Polarograph Model XXI. Currents for the wave analysis were measured by operating the instrument manually. All current values given in tables have been corrected for residual currents. Experiments were carried out in a thermostat maintained at 25 ± 0.1°.

Experimental Results

Stability of Cupric Thiocyanate Solutions.—

Philips and Bramley[6] reported that cupric thio-

cyanate is gradually reduced to cuprous thiocyanate in the presence of excess potassium thiocyanate. Kitson[7] found that the yellow color of cupric thiocyanate complex can be made the basis for the colorimetric determination of copper(II) only when a suitable holding oxidant, e.g. potassium persulfate, is added to prevent the reduction of copper(II). Podchinova and Onosova[8] found that the reduction of copper(II) can be prevented by the addition of nitric acid. On the contrary, Meites[3] mentions that copper(II) is not reduced by excess potassium thiocyanate.

We studied the stability of copper(II) thiocyanate solutions by comparing polarograms obtained with freshly prepared solutions and with aged solutions. In 0.1 M potassium thiocyanate a considerable decrease in current was observed after aging either in a nitrogen or oxygen atmosphere both in the presence and absence of polyacrylamide (PAA). In experiments which yielded curves 1 and 1′ in Fig. 1, a weighed amount of solid potassium thiocyanate was added to a deaerated solution in the polarographic cell which contained copper or copper and PAA immediately before taking polarograms. In aged solutions which yielded curves 2 and 3, turbidity caused by precipitated cuprous thiocyanate was observed. It also was found that in 0.1 M potassium thiocyanate an additional wave appeared at about −1.4 volts (not shown in Fig. 1) whose height was negligibly small in fresh solutions but increased considerably when the solution was aged. This wave is not due to the reduction of species containing copper, and details will be described elsewhere in connection with a discussion of the polarography of copper in more concentrated thiocyanate solutions.

When the thiocyanate concentration was decreased to 0.01 and 0.1 M sodium perchlorate or perchloric acid was added as additional supporting electrolyte, no change in current or in shape of current–potential curves was observed on overnight standing. The polarograms had the same shape as curve 1 in Fig. 1 in the presence of 0.01 % PAA and as curve 1′ in the absence of the surface-active substance. Identical curves were obtained with sodium perchlorate and with perchloric acid as supporting electrolytes. In order to avoid complications resulting from unstability of copper(II) thiocyanate solutions, the concentration of thiocyanate was kept equal to 0.01 M.

(1) This investigation was supported by a research grant from the National Science Foundation.

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, p. 494.

(3) L. Meites, THIS JOURNAL, 73, 4479 (1951).

(4) E. L. Colichman, ibid., 72, 4036 (1950).

(5) I. A. Korshnov and N. I. Malyugina, Zhur. Obshchei Khim., 20, 1399 (1951); C A., 45, 1456 (1951).

(6) J. C. Philips and A. Bramley, J. Chem. Soc., London, 109, 597 (1916).

(7) R. G. Kitson, Anal. Chem., 22, 664 (1950).

(8) V. N. Podchinova and S. P. Onosova, Zhur. Anal. Khim., 13, 533 (1958).

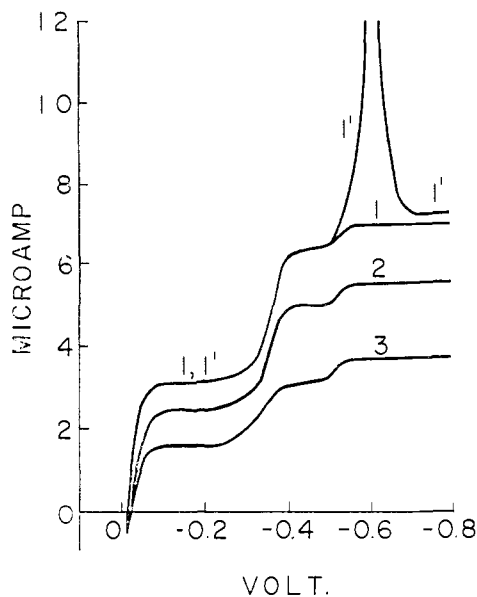Fig. 1.—Effect of aging in 0.1 M KCNS which was 9.94 × 10^{-4} M in Cu(II), (d.m.e., $h = 82$ cm.) 1, fresh, with 0.01% polyacrylamide (PAA); 1', fresh, no PAA; 2, aged overnight, with PAA; 3, aged two days, with PAA.

It is seen in Fig. 1 that the total current on the plateau of the third wave is somewhat greater in the absence than in the presence of PAA. The difference must be attributed to a slight streaming of the solution, remaining even after the maximum has been passed when no surface-active substance is present. With other surface-active substances than PAA, e.g., 0.006 % thymol, the same total diffusion current was observed as with PAA.

The total diffusion current observed in the presence of 0.01 M potassium thiocyanate and 0.1 M perchlorate or perchloric acid was found equal to the diffusion current in the absence of thiocyanate. Thus the total diffusion current in 0.01 M potassium thiocyanate corresponds to the reduction of copper(II) to copper metal.

Characteristics of Current–Potential Curves.— It is noteworthy that in the absence of PAA a maximum is absent on the first and the second waves, while a sharp maximum appears on the third wave (Fig. 1). Polarograms at the r.d.m.e. also do not exhibit on the first two waves maxima of the second kind, which are usually observed at the r.d.m.e. in the absence of maximum suppressors.[9] The heights of the first two waves in Fig. 2 are the same in the absence and in the presence of 0.01 % PAA, but the height of the third wave is much smaller with PAA present than in its absence. Electrocapillary curves obtained at the d.m.e. in the presence and absence of thiocyanate and copper(II) clearly show that the addition of copper(II) in thiocyanate solution causes a significant decrease of interfacial tension at potentials corresponding to the first two waves (see Fig. 3). These results tend to indicate that cuprous thiocyanate produced as a result of the reduction of copper(II) is adsorbed on the surface of mercury drops. At the potential where the third wave attains a limiting value all copper(II) reaching
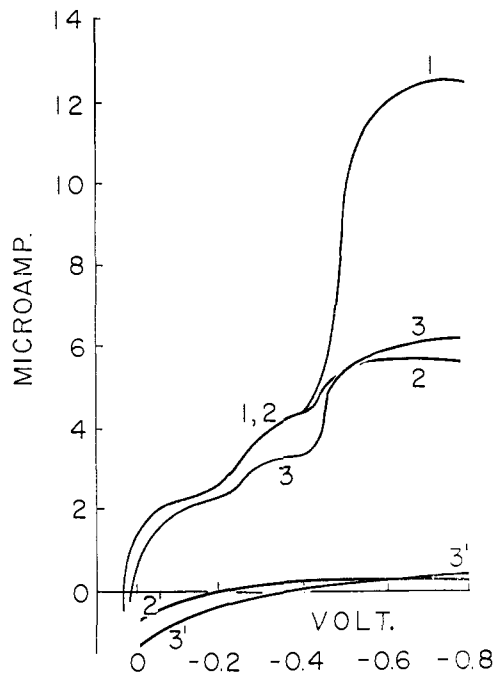
(9) W. Stricks and I. M. Kolthoff, This Journal, **78**, 2085 (1956).

Fig. 2.—Current–potential curves at r.d.m.e. (210 r.p.m.) in 9.94 × 10^{-5} M Cu(II), 0.1 M in HClO$_4$ and 0.01 M in KCNS: 1, no PAA, $h = 41.5$ cm.; 2, 0.01% PAA, $h = 41.5$ cm.; 3, 0.01% PAA, $h = 81.5$ cm.; 2', 3', residual for 2 and 3.

the electrode surface must be reduced directly to copper metal and cuprous thiocyanate is no longer formed. The formation of copper(I) thiocyanate complexes need not be considered in dilute thiocyanate solutions.

The proportionality between current at the d.m.e. and copper concentration was examined at various potentials with solutions containing 0.1 M perchloric acid and 0.01 M potassium thiocyanate in the presence of 0.01 % PAA. Results are shown in Table I, in which values of $i/Ct^{1/6}$ are tabulated instead of i/C because the droptime varies considerably with potential and slightly with copper concentration. It is clear that proportionality holds at −0.1 volt (first diffusion current) and at −0.8 volt (total current) but fails to hold on the plateau of the second wave. The constancy of $i/Cm^{1/2}t^{1/6}$ values at the two different heights of the mercury reservoir at −0.1 and at −0.8 volt shows that the current on the plateau of the first wave and the total current are both diffusion controlled. The average value of $i/Ct^{1/6}$ or $i/Cm^{1/2}t^{1/6}$ at −0.8 volt was found to be double the value at −0.1 volt, indicating that copper(I) is formed on the first wave, which begins to be reduced further to copper metal at the potential where the second wave starts. Since the solubility of cuprous thiocyanate is very small (the solubility product[10] is of the order 10^{-14}), cuprous ions formed at the surface of the mercury drops are expected to precipitate quantitatively at potentials on the first wave.

The last column of Table I shows that the height of the third wave at a given mercury pressure is con-

(10) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants," Part II. The Chemical Society, London. 1958.

TABLE I

PROPORTIONALITY BETWEEN CURRENT AND COPPER CONCENTRATION AT D.M.E. AT VARIOUS POTENTIALS IN SOLUTIONS 0.1 M IN HClO$_4$, 0.01 M IN KCNS AND 0.01 % IN POLYACRYLAMIDE

(m = 1.122 mg./sec. at h = 44 cm., 2.124 mg./sec. at h = 82 cm.)

h, cm.	C, mM	$i(\mu a.)$	-0.1 v. t(sec.)	$i/Ct^{1/6}$	$i(\mu a.)$	-0.38 v. t(sec.)	$i/Ct^{1/6}$	$i(\mu a.)$	-0.8 v. t(sec.)	$i/Ct^{1/6}$	$\dfrac{i(-0.8\text{ v.})-}{i(-0.38\text{ v.})}=i_a$
	1.99	4.73	5.72	1.78	9.60	6.53	3.53	9.84	6.53	3.62	0.24
	0.994	2.42	5.74	1.81	4.68	6.63	3.43	4.93	6.50	3.63	.25
44	.795	1.98	5.79	1.86	3.74	6.66	3.43	4.06	6.51	3.74	.32
	.397	0.98	5.87	1.84	1.72	6.65	3.16	2.01	6.51	3.71	.29
	.199	0.47	5.89	1.76	0.68	6.54	2.50	0.97	6.52	3.57	.29
			Av.	1.81					Av.	3.65	Av. 0.28
			$i/Cm^{2/3}t^{1/6}=1.68$						$i/Cm^{2/3}t^{1/6}=3.38$		$i_a/h=0.0066$
	1.99	6.70	3.02	2.80	13.50	3.42	5.53	14.00	3.49	5.71	0.50
	0.994	3.35	3.03	2.80	6.47	3.49	5.28	6.93	3.49	5.66	.46
82	.795	2.72	3.06	2.84	5.07	3.50	5.18	5.57	3.48	5.69	.50
	.397	1.31	3.11	2.73	2.21	3.49	4.52	2.74	3.48	5.61	.53
	.199	0.64	3.09	2.66	0.77	3.45	3.15	1.31	3.48	5.35	.54
			Av.	2.77					Av.	5.60	Av. 0.51
			$i/Cm^{2/3}t^{1/6}=1.68$						$i/Cm^{2/3}t^{1/6}=3.39$		$i_a/h=0.0062$

stant with varying copper concentration and is directly proportional to the height of the mercury column. When the copper concentration is decreased below 2×10^{-4} M (curve 4 in Fig. 4), the second wave disappears and the height of the th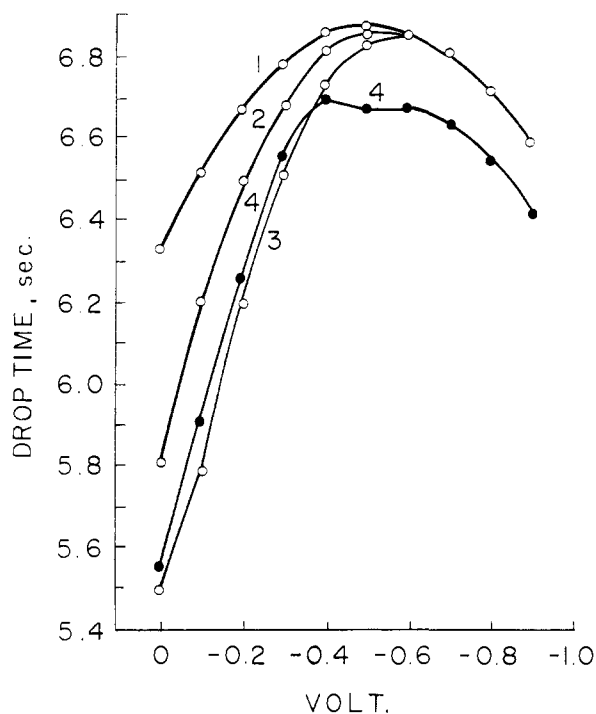ird wave becomes smaller than the constant height observed at higher copper concentrations. These characteristics of the third wave are typical of those of a postwave which is observed when the oxidized form of an electroactive species is adsorbed on dropping mercury. The difference in potential for the reduction of adsorbed cuprous thiocyanate (the third wave) and for the reduction of unadsorbed

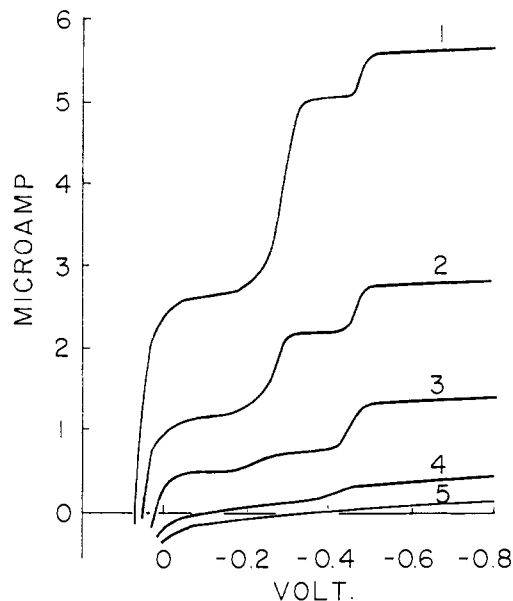cuprous thiocyanate (the second wave) should correspond to the energy involved in the adsorption process.[11]

Fig. 4.—Effect of copper concentration in 0.1 M HClO$_4$, 0.01 M KCNS and 0.01% PAA (d.m.e., h = 82 cm.): 1, 7.95 × 10^{-4} M; 2, 3.97 × 10^{-4} M; 3, 1.99 × 10^{-4} M; 4, 4.97 × 10^{-5} M; 5, no copper. Not corrected for residual current.

The polarograms at the r.d.m.e. become similar to those at the d.m.e. when maxima of the second kind appearing on the third wave are suppressed by the addition of PAA (see Fig. 2). As shown in Table II, the height of the third wave at the r.d.m.e. was found again to be proportional to the height of the mercury reservoir. From Table II and Fig. 2 it appears that the total limiting current measured at −0.8 volt is considerably greater than twice the limiting current of the first wave measured at −0.1 volt. This is attributed to the much greater effect

Fig. 3.—Electrocapillary curves (d.m.e., h = 44 cm.): 1, 0.1 M HClO$_4$; 2, 0.1 M HClO$_4$ + 0.01 M KCNS; 3, 2 + 4 × 10^{-4} M Cu(ClO$_4$)$_2$; 4, 3 + 0.01% PAA.

served at higher copper concentrations. These characteristics of the third wave are typical of those of a postwave which is observed when the oxidized form of an electroactive species is adsorbed on dropping mercury. The difference in potential for the reduction of adsorbed cuprous thiocyanate (the third wave) and for the reduction of unadsorbed

(11) R. Brdicka, Z. Elektrochem., **48**, 278 (1942).

TABLE II

Variation of Current with Height of Mercury at r.d.m.e. (210 r.p.m.) in a Solution 9.94×10^{-5} M in Cu(II), 0.1 M in HClO$_4$, 0.01 M in KCNS and 0.01% in Polyacrylamide

(m = 8.47, 12.58, 16.54 mg./sec. at h = 41.5, 61.5, 81.5 cm.)

h, cm.	$i(\mu a.)$ −0.1 v.	$t(sec.)$ −0.1 v.	$i/t^{1/2}$	$i(\mu a.)$ −0.38 v.	$t(sec.)$ −0.38 v.	$i(\mu a.)$ −0.8 v.	$t(sec.)$ −0.8 v.	$i/t^{1/2}$	r^a	$i(-0.8\text{ v.}) - i(-0.38\text{ v.}) = i_a$	i_a/h
41.5	2.64	4.47	1.25	4.34	4.95	5.48	4.74	2.58	2.06	1.14	0.0275
61.5	2.70	3.14	1.52	3.84	3.38	5.66	3.25	3.14	2.07	1.82	.0296
81.5	2.74	2.40	1.77	3.44	2.56	5.80	2.50	3.67	2.07	2.36	.0286

^{a} $r = (i/t^{1/2} \text{ at } -0.8 \text{ v.})/(i/t^{1/2} \text{ at } -0.1 \text{ v.})$.

of drop time on the limiting current at the r.d.m.e. ($\sim t^{1/2}$) than at the d.m.e. ($\sim t^{1/6}$).[12] When corrections are made for the drop time effect, the ratio of limiting currents at the two potentials becomes equal to 2.06 to 2.07 (see Table II). This small deviation from the ratio 2.00 must be attributed to the fact that the limiting current at the r.d.m.e. is not exactly proportional to $t^{1/2}$, the exponent usually being greater than $1/2$ because of the deformation of mercury drops from a spherical shape.[12]

Discussion

A general theoretical treatment of adsorption waves (prewave and postwave) at the d.m.e. was first described by Brdicka,[11] who derived the expression for the average limiting current of an adsorption wave i_a

$$i_a = 0.85 n F z m^{2/3} t^{1/3} \tag{1}$$

in which i_a is expressed in amperes, z is the maximum number of adsorbed moles per cm.², m is the rate of mercury flow in g./sec., t is the drop time in sec., and n and F have their usual significance. Using the data at the d.m.e. given in Table I, we find z = 5.9×10^{-10} mole/cm.² at h = 44 cm. and 5.7×10^{-10} mole/cm.² at h = 82 cm. Taking the average of these two values and multiplying by the Avogadro number, z becomes equal to 3.5×10^{14} molecules/cm.² Thus, assuming that cuprous thiocyanate forms a monomolecular layer, the area covered by one adsorbed molecule of CuCNS becomes equal to 30 Å.², which appears to be a reasonable value. The crystal structure or the size of cuprous thiocyanate could not be found in the literature.

The height of adsorption waves at the r.d.m.e. should also be directly proportional to the maximum number of moles of adsorbed species, and equation 1 is expected to be valid both at the d.m.e. and at the r.d.m.e. The value of z calculated by using the data at the r.d.m.e. given in Table II becomes equal to 5.7×10^{-10}, 6.2×10^{-10} and 6.1×10^{-10} mole/cm.² at values of h = 41.5, 61.5 and 81.5 cm., respectively. The average value of z, 6.0×10^{-10} mole/cm.², is in good agreement with the value 5.8×10^{-10} mole/cm.² calculated from results at the d.m.e.

A comparison of i_a values at the d.m.e. and at the r.d.m.e. shows that the adsorption current at the r.d.m.e. is about four to five times greater than that at the d.m.e. The difference is simply due to the greater value of m at the r.d.m.e. It is also interesting to note that the dependence of the adsorption current on the height of the mercury reservoir at the r.d.m.e. is quite different from that of a mass

(12) Y. Okinaka and I. M. Kolthoff, This Journal, 79, 3326 (1957).

transfer controlled limiting current, a kinetic current, and a catalytic current, all of which are practically independent of the height of the mercury reservoir.[12,13]
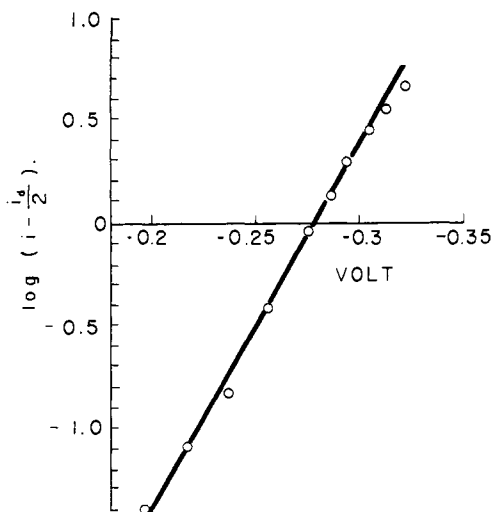

Fig. 5.—Analysis of the second wave obtained with 2 × 10^{-3} M Cu(II) in solution 0.1 M in HClO$_4$, 0.01 M in KCNS and 0.01% in PAA (d.m.e., h = 44 cm.).

Characteristics of the Various Waves. First Wave.—Thiocyanate depolarizes the d.m.e. anodically and the zero current potential is a typical mixed potential[14] where the anodic current caused by the oxidation of mercury to mercury thiocyanate is equal to the cathodic current caused by the electro-reduction of copper(II) to copper(I). Mercury in dilute thiocyanate reduces copper(II) quantitatively to copper(I); thus the shape of the first wave corresponds to the beginning of the dissolution wave of mercury in dilute thiocyanate. At the first diffusion current plateau all the copper (II) is reduced to copper(I) which is precipitated quantitatively at the mercury surface in the form of CuCNS.

Second Wave.—This wave corresponds to the reduction of copper(I) to copper amalgam

$$CuCNS(solid) \rightleftharpoons Cu^+ + CNS^- \tag{2}$$

$$Cu^+ + e^- + Hg \rightleftharpoons Cu(Hg) \tag{3}$$
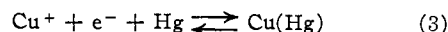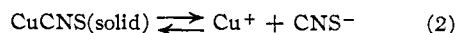
Assuming that solubility equilibrium is established rapidly and that reaction 3 is reversible at the d.m.e. under our experimental conditions, the potential on the second wave should be given by

(13) Y. Okinaka and I. M. Kolthoff, ibid., 82, 324 (1960).

(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 119.

TABLE III

VARIATION OF HALF-WAVE POTENTIALS OF THE SECOND AND THE THIRD WAVES WITH COPPER CONCENTRATION AT D.M.E. IN SOLUTIONS 0.1 M IN HClO$_4$, 0.01 M IN KCNS AND 0.01% IN POLYACRYLAMIDE

h, cm.	C, mM	i_d,[a] μa.	$(E_{1/2})_{II}$ v.	$\Delta(E_{1/2})_{II}$ obsd.	$\Delta(E_{1/2})_{II}$ calcd.	$(E_{1/2})_{III}$ v.	$\Delta(E_{1/2})_{III}$ obsd.	$\Delta(E_{1/2})_{III}$ calcd.
	1.99	9.84	−0.309			−0.492		
				0.018	0.019		0.016	0.018
	0.994	4.93	− .291			− .476		
44				.022	.028		.017	.025
	.397	2.01	− .269			− .459		
				.027	.033		.024	.031
	.199	0.97	− .242			− .435		
	1.99	14.00	−0.303			−0.484		
				0.014	0.020		0.020	0.019
	0.994	6.93	− .289			− .474		
82				.028	.032		.018	.027
	.397	2.74	− .261			− .456		
				.030	.047		.012	.026
	.199	1.31	− .231			− .444		

[a] Measured at −0.8 volt.

$$E = E^0 - \frac{RT}{F} \ln \frac{C_a^0 f_a}{a_{Hg}[Cu^+]^0 f_{Cu^+}} \quad (4)$$

where E^0 is the standard potential of the cuprous ion–copper amalgam electrode, a_{Hg} is the activity of mercury in the amalgam, C_a^0 is the concentration of the amalgam formed on the surface of the mercury drops, $[Cu^+]^0$ is the concentration of cuprous ions at the mercury surface, and the f terms are the corresponding activity coefficients. Since the amalgam formed is very dilute, a_{Hg} can be regarded as a constant. C_a^0 is directly proportional to current corrected for the diffusion current corresponding to the reduction of copper(II) to copper(I) and can be expressed by

$$C_a^0 = \frac{i - \frac{i_d}{2}}{k_a} \quad (5)$$

where i_d is the total diffusion current measured at e.g. −0.8 volt, and k_a is a proportionality factor. In view of the small solubility of cuprous thiocyanate, it can be assumed that in the entire potential range on the second wave solid cuprous thiocyanate is present in equilibrium with cuprous and thiocyanate ions. This assumption should hold except when the concentration of copper(II) ions in the bulk of the solution is smaller than the concentration where the second wave disappears. Thus we can write

$$[Cu^+]^0 = \frac{K_{sp}}{[CNS^-]} \cdot \frac{1}{f_{Cu^+} f_{CNS^-}} \quad (6)$$

where K_{sp} is the solubility product of cuprous thiocyanate, and $[CNS^-]$ is the concentration of thiocyanate ions in the bulk of the solution, which can be regarded as being equal to its concentration at the electrode surface so long as a sufficient excess is present. From 4, 5 and 6 we obtain

$$E = E' - \frac{RT}{F} \ln \left(i - \frac{i_d}{2}\right) - \frac{RT}{F} \ln [CNS]^- \quad (7)$$

where

$$E' = E^0 - \frac{RT}{F} \ln \frac{f_a f_{CNS^-}}{a_{Hg} k_a K_{sp}} = \text{Constant} \quad (8)$$

Equation 7 predicts that a plot of E vs. log$[i - (i_d/2)]$ on the second wave should yield a straight line with a slope of 0.059 volt at 25° at constant

thiocyanate concentration. The second wave obtained with a solution 2×10^{-3} M in copper(II), 0.1 M in perchloric acid, 0.01 M in potassium thiocyanate aud 0.01 % PAA was analyzed in this manner. As shown in Fig. 5, the plot yielded a straight line with a slope of 0.055 volt, which is in satisfactory agreement with the theoretical value.

At the half-wave potential of the second wave, $(E_{1/2})_{II}$, we have

$$i = [(3i_d/2) - i_a]/2 \quad (9)$$

It follows from 7 and 9 that

$$(E_{1/2})_{II} = E_{II}'' - \frac{RT}{F} \ln \left(\frac{i_d}{2} - i_a\right) - \frac{RT}{F} \ln[CNS^-] \quad (10)$$

where $E_{II}'' = E' - (RT/F) \ln (1/2) = $ constant. According to this expression the half-wave potential of the second wave at constant thiocyanate concentration is dependent on i_d and hence on the concentration of copper(II). The shift of half-wave potential is given by

$$\Delta(E_{1/2})_{II} = -0.059 \lambda \log[(i_d/2) - i_a] \text{ at } 25° \quad (11)$$

In Table III the shift of half-wave potential observed is compared with calculated values, showing the essential validity of equation 11.

Equation 10 also predicts that the half-wave potential of the second wave should be shifted by 0.059 volt in the negative direction with a tenfold increase in thiocyanate concentration. The half-wave potential of the second wave observed with 10^{-3} M copper(II) in 0.01 M potassium thiocyanate containing 0.1 M perchloric acid was −0.290 volt, while the value found in 0.1 M potassium thiocyanate (freshly prepared) was −0.355 volt. The observed difference of 0.065 volt is in approximate agreement with the theoretical value of 0.059 volt.

Third Wave.—Considering that the height of the third wave corresponds to the reduction of a monolayer of adsorbed cuprous thiocyanate, solid unadsorbed cuprous thiocyanate is absent at potentials on the third wave. It may be assumed that the following equilibrium is established at the electrode surface on the third wave

$$\text{CuCNS (adsorbed)} \rightleftarrows \text{Cu}^+ + \text{CNS}^- \quad (12)$$
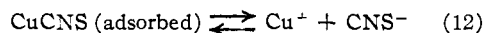
Then the concentration of cuprous ions at the electrode surface is given by

$$[\text{Cu}^+]^0 = \frac{Ka_{ad}}{[\text{CNS}^-]f_{\text{Cu}^+}f_{\text{CNS}^-}} \quad (13)$$

where K and a_{ad} are, respectively, the dissociation constant and the activity of adsorbed cuprous thiocyanate. Relations 4 and 5 should be valid both on the second and the third waves, and hence from 4, 5 and 13 we obtain

$$E = E^0 - \frac{RT}{F} \ln \frac{f_a f_{\text{CNS}^-}}{a_{\text{Hg}}k_a Ka_{ad}} - \frac{RT}{F} \ln \left(i - \frac{i_d}{2} \right) - \frac{RT}{F} \ln [\text{CNS}^-] \quad (14)$$

In this expression a_{ad} varies with potential along the third wave. Therefore, the third wave cannot be analyzed simply by plotting E vs. $\log[i - (i_d/2)]$.

At the half-wave potential, however, a_{ad} should be constant and independent of copper(II) concentration, corresponding to a half coverage of the mercury surface. The current at the half-wave potential $(E_{1/2})_{III}$ is given by

$$i = i_d - (i_a/2) \quad (15)$$

From 14 and 15 we obtain

$$(E_{1/2})_{III} = E_{III}'' - \frac{RT}{F} \ln (i_d - i_a) - \frac{RT}{F} \ln [\text{CNS}^-] \quad (16)$$

where

$$E_{III}'' = E^0 - \frac{RT}{F} \ln \frac{f_a f_{\text{CNS}^-}}{2a_{\text{Hg}}k_a Ka_{ad}} = \text{Constant} \quad (17)$$

The shift of half-wave potential of the third wave with i_d and hence with copper concentration is then given by

$$\Delta(E_{1/2})_{III} = -0.059 \, \Delta \log(i_d - i_a) \quad (18)$$

Observed and calculated values of $\Delta(E_{1/2})_{III}$ are compared in Table III. The agreement was only approximate. It is predicted from eq. 16 that the half-wave potential of the third wave should be shifted by 0.059 volt in the negative direction with a tenfold increase in thiocyanate concentration. The half-wave potentials of the third waves observed with 10^{-3} M copper(II) in 0.01 and 0.1 M potassium thiocyanate were -0.485 and -0.540 volt, respectively. The difference of 0.055 volt is in satisfactory agreement with the theoretical value.

The Acidity and Complexes of Peroxydiphosphoric Acid[1]

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The third and fourth acid dissociation constants of peroxydiphosphoric acid were measured at 25° by pH titrations of the tetramethylammonium salt with hydrochloric acid at a series of ionic strengths. Extrapolation to infinite dilution yielded the values $K_3 = 6.6 \pm 0.3 \times 10^{-6}$ and $K_4 = 2.1 \pm 0.1 \times 10^{-8}$. Approximate values for the first and second acid dissociation constants, which could not be obtained from the pH titration, were estimated from the trend observed in other tetravalent acids of similar structure to be $K_1 \cong 2$ and $K_2 \cong 3 \times 10^{-1}$. Formation constants for complex ions of peroxydiphosphate ion and the cations—Li$^+$, Na$^+$, K$^+$ and Mg^{+2}—were measured at 25° and unit ionic strength by the pH lowering technique and compared with known constants for pyrophosphate. Structural implications are discussed.

Introduction

Although peroxydiphosphoric acid, $H_4P_2O_8$, and its salts have been known for many years,[3] they have received little attention compared with other oxyacids of phosphorus and with the peroxyacids of other elements, such as sulfur. The present investigation of the acid dissociation constants of $H_4P_2O_8$ was carried out as part of a general study of the aqueous chemistry of this acid and its salts.[1] During the course of the measurements, it was found that aqueous peroxydiphosphate ion forms complex ions with alkali metal cations similar to those which have been reported for pyrophosphate.[4] It was, therefore, necessary to carry out the measurement of the acid dissociation constants in the absence of alkali metal ions. The tetramethylammonium salt was employed, and negligible complexing was assumed for this large cation.

(1) Abstracted from the Ph.D. Thesis submitted by M. M. C. at Brown University, 1960. Presented in part before the Division of Physical Chemistry at the 135th American Chemical Society Meeting, Boston, Mass., April, 1959.

(2) Monsanto Fellow 1958–1959.

(3) J. Schmidlin and P. Massini, Ber., 43, 1162 (1910).

(4) S. M. Lambert and J. I. Watters, This Journal, 79, 4262, 5606 (1957).

Peroxydiphosphate ion, $P_2O_8^{-4}$, is quite stable in neutral or basic solution at room temperature but undergoes rapid hydrolysis to form peroxymonophosphoric acid in acidic solution

$$H_4P_2O_8 + H_2O \longrightarrow H_3PO_5 + H_3PO_4$$
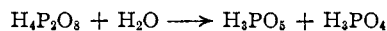
The titrations were, therefore, carried out by adding acid to the salt form in order to minimize the hydrolysis.

Experimental

Impure $K_4P_2O_8$ was prepared electrolytically by the method of Fichter and Gutzwiller[5] and purified by conversion to crystalline $Li_4P_2O_8 \cdot 4H_2O$ according to the procedure of Chulski.[6] After two recrystallizations from water-methanol, a product was obtained which was 99.5% pure, as determined by iodometric titration for total active oxygen and by gravimetric determination of total phosphorus by precipitation of phosphate with magnesia mixture. The lithium peroxydiphosphate was converted to the tetramethylammonium salt by ion exchange using a column containing a ten-fold excess of Dowex 50-x4, 100–200 mesh cation exchange resin. The ion exchange procedure was shown in separate experiments to result in no measurable decomposition of the peroxide. The tetramethylammonium chloride used to charge the column and to adjust the ionic strength during the titrations was either the East-

(5) F. Fichter and G. Gutzwiller, Helv. Chim. Acta, 11, 323 (1928).

(6) T. Chulski, Ph.D. Thesis, Michigan State University, 1953.