as to indicate strong bonding through the oxygen atom. The two bands found for $SnCl_4 \cdot 2SeOCl_2$ indicate strong bonding again through the oxygen atom; but this compound is somewhat weaker than $TiCl_4 \cdot 2SeOCl_2$, in agreement with the observation that the latter can be sublimed whereas the former cannot. The band at 835 cm.$^{-1}$ is weak, the major peak coming at 947 cm.$^{-1}$. The latter frequency is characteristic of liquid $SeOCl_2$. $SeOCl_2$ dissolved in $SnCl_4$ exhibits only one band which is but slightly shifted from the standard frequency, from which we can conclude that very little interaction between the components of the solution takes place. However, it appears that $SeOCl_2$ interacts strongly with $TiCl_4$ when the latter is used as solvent for the former.

In the liquid systems it is to be noted that the intensity of the most strongly shifted band (the one we postulate as being due to donor–acceptor interaction) is reduced relative to the intensities of other bands observed in the order $POCl_3$–$TiCl_4$, $POCl_3$–$SnCl_4$, $SeOCl_2$–$SnCl_4$, a strongly shifted band being absent in the last system. The order follows the degree of donor–acceptor action postulated in Table I. It is possible that similar spectral studies could be used to measure the degree of association of molecular complexes in the liquid state.

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CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Effects of Surface Active Substances on Polarographic Waves of Copper(II) Ions[1]

BY I. M. KOLTHOFF AND Y. OKINAKA

RECEIVED NOVEMBER 17, 1958

A study has been made of the effects of anionic, non-ionic and cationic surface-active substances on the polarographic waves of copper(II) ions in non-acidified and acidified solutions. The reduction of copper(II) ions in 0.1 *M* perchloric acid is irreversible but is made more reversible by the presence of anionic surface-active substances. Non-ionic and cationic surface-active substances distort the copper wave, the effect of cationic substances being much greater than that of non-ionic substances. With several uncharged and cationic substances two waves are observed, the first wave being kinetic in nature both in acidified and non-acidified solutions. The kinetic current in acidified solutions is controlled by the rate of penetration of aquo-copper(II) ions (penetration current) through the adsorbed film of surface-active substance in accordance with Frumkin's theory. In non-acidified solutions or in fluoride buffers of *p*H 4.5 to 5 containing Triton X-100, a kinetic current is observed which is much larger than that in acidified solutions. This current is the sum of the penetration current of aquo-copper(II) ions and a kinetic current attributed to a two electron reduction of $CuOH^+$, the formation of which at the electrode surface is controlled by the rate of the reaction $Cu^{+2} + OH^- \rightarrow CuOH^+$. It appears that the rate of this reaction is dependent upon the nature of the surface-active substance present in the system.

Surface-active substances (denoted as SAS) usually employed to eliminate maxima on polarographic waves often cause undesirable effects such as suppression of a diffusion current, shift of a half-wave potential, splitting of a wave into two or more waves or a combination of these effects. No general interpretation is found in the literature, although several examples of these effects are described. Lingane[2] was the first to describe the effect of gelatin on the copper wave in solutions acidified with sulfuric acid, but no interpretation was given. Tanford[3] reported that the copper wave becomes increasingly more distorted with decreasing *p*H in the presence of serum or egg albumin and interpreted this result in terms of an electrostatic repulsion between copper ions and positively charged protein molecules at low *p*H values. Kivalo[4] also studied the same phenomenon but attributed the greater distortion at lower *p*H to a stronger adsorption of the protein molecules on the mercury surface at lower *p*H values. Effects of other SAS's on the copper wave also have been described by several authors,[5] but no systematic studies are described on the effect of charge type of an SAS on the appearance of the current-potential curves in acidified and non-acidified media.

In the present paper results of such a study are described and discussed. The experiments were carried out in the presence of sufficiently large amounts of SAS to assure complete coverage of the mercury surface by the adsorbed substance from the beginning of the drop formation, so that the effect of adsorption kinetics on polarograms need not be considered.

Experimental

Materials.—Reagent grade sodium perchlorate was recrystallized twice from conductivity water, dried first in a vacuum desiccator and finally in an oven at 110°. Other chemicals were used without further purification. The copper content of the stock solution of copper perchlorate was determined iodometrically. A stock stolution of dodecylamine perchlorate was prepared by dissolving 0.5 gram of Armeen 12D (Armour and Co.)[6] in 100 ml. of a standard perchloric acid containing the equivalent amount of the acid. The *p*H of this solution was found to be equal to 6. Sodium dodecyl sulfate was a product of Proctor and Gamble Co. Igepon AP Extra (fatty alkyl ester sulfonates) was obtained from General Dyestuff Corporation. Samples of

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[1] This investigation was supported by a research grant from the National Science Foundation.

[2] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 584 (1943).

[3] C. Tanford, THIS JOURNAL, **74**, 6036 (1952).

[4] P. Kivalo, *Suomen Kemistilehti*, **30**, 88 (1957).

[5] (a) M. A. Loshkarev and A. A. Krjukova, *Zhur. Fiz. Khim.*, **23**, 209 (1949); *Doklady Akad. Nauk SSSR*, **72**, 919 (1950); *Zhur. Fiz. Khim.*, **26**, 737 (1952); (b) E. L. Colichman, THIS JOURNAL, **72**, 4038 (1950); (c) A. P. Martirosyan and T. A. Krjukova, *Zhur. Fiz. Khim.*, **28**, 851 (1953); (d) M. Dratovsky and M. Ebert, *Chim. Listy*, **48**, 498 (1954); (e) P. Zuman, *Chem. Zvesti*, **8**, 789 (1954); (f) W. Kemula and E. Weronski, in "Proceedings of the Polarographic Conference in Warsaw," Panstwowe Wydawnictwo Naukowe, Warsaw, 1957, p. 219.

[6] Dodecylamine 95%, tetradecylamine 3%, decylamine 2%: average molecular weight, 185.

Tritons[7] of various molecular weights were obtained from Rohm and Haas Co. Solutions of all these SAS's were prepared by dissolution in water. Deaeration was done by passing pure Linde nitrogen. Experiments were carried out at 25° unless otherwise noted.

Electrode.—The dropping mercury electrode had these characteristics in 0.1 M sodium perchlorate: m = 1.32 mg./sec., t = 5.06 sec. (open circuit) at h = 51.5 cm.

Measurements.—Average current-potential curves were recorded by using a Sargent Polarograph Model XXI or a Leeds and Northrup Electrochemograph Type E. Average currents for the wave analysis were measured manually. Maximum currents were measured with the Leeds and Northrup instrument without damping and also by operating it manually.

Experimental Results

Wave Characteristics in the Absence of SAS.—Figure 1 shows current–potential curves and their conventional analysis of 2.83 × 10^{-4} M copper perchlorate in 0.1 M sodium perchlorate (1 and 1′) and in 0.1 M perchloric acid (2 and 2′). A maximum was absent at this small concentration of copper. The half-wave potentials were +0.029 volt and −0.007 volt *vs.* SCE in sodium perchlorate and in perchloric acid solutions, respectively. The logarithmic plots clearly indicate that the wave in the sodium perchlorate solution is close to reversible, while that in the perchloric acid solution is irreversible. The slope of the straight portion of line 1′ is 0.035 as compared to the theoretical value 0.030 for a reversible reduction involving two electrons.

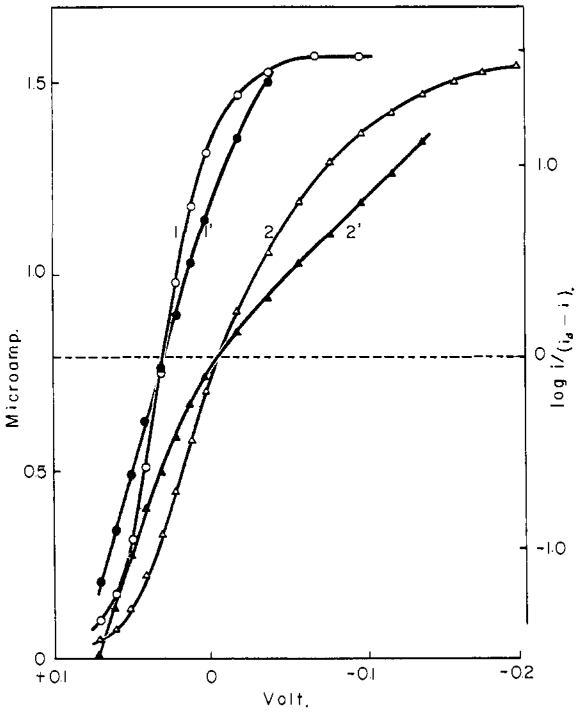

Fig. 1.—Current-potential curves (1, 2) and their analysis (1′, 2′) in the absence of SAS: (1, 1′), 0.1 M sodium perchlorate; (2, 2′), 0.1 M perchloric acid. Concentration of copper perchlorate, 2.83 × 10^{-4} M, h = 51.5 cm.

Effect of Anionic SAS's.—Experiments with solutions of 1.13 × 10^{-3} copper perchlorate in 0.1 M perchloric acid in the presence of various concentrations of sodium dodecyl sulfate showed that the maximum was completely eliminated by the addition of 0.0001% of this substance, and that with further increase of its concentration the wave became increasingly steep, while the half-wave potential was shifted to more positive potentials. Results obtained in the presence of 0.1% of sodium dodecyl sulfate in 0.1 M perchloric acid are shown in Fig. 2. The logarithmic plot yields a perfectly straight line with a slope of 0.032. The half-wave potential was +0.027 volt. Similar results were obtained also in 0.1 M sodium perchlorate, the half-wave potential being equal to +0.020 volt. Igepon AP Extra also was found to make the copper wave more reversible.

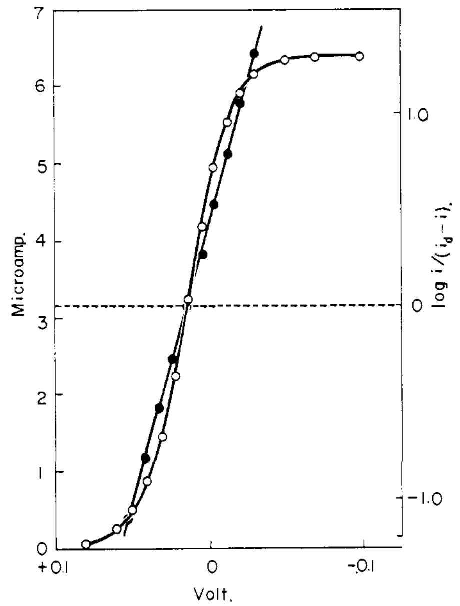

Fig. 2.—Current-potential curve and its analysis of 1.13 × 10^{-3} M copper perchlorate in 0.1 M perchloric acid in the presence of 0.1% sodium dodecyl sulfate, h = 51.5 cm.

Effect of Non-ionic SAS's.—Figure 3 shows current–potential curves obtained at two different heights of the mercury column in the presence of 0.05% Triton X-100 in 0.1 M sodium perchlorate

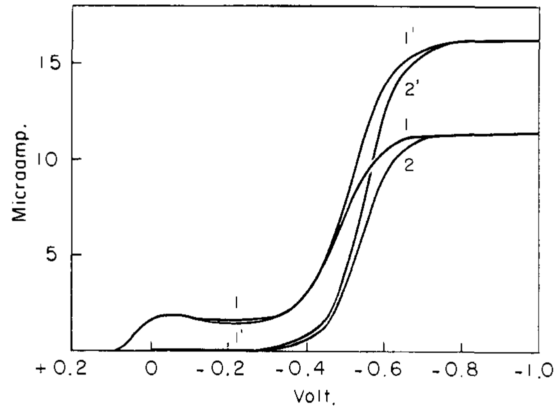

Fig. 3.—Current-potential curves 2.27 × 10^{-3} M copper perchlorate in the presence of 0.05% Triton X-100 at h = 44 cm. (1, 2) and 82 cm. (1′, 2′): (1, 1′), 0.1 M sodium perchlorate; (2, 2′), 0.1 M perchloric acid.

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[7] $C_8H_{17}(C_6H_4)(OCH_2CH_2)_nOH$, n = 5 for X-45, 9 to 10 for X-100, 20 for X-205, 30 for X-305.

(1,1′) and in 0.1 *M* perchloric acid (2,2′). The presence of 1% Triton X-100 gave practically the same results. It is seen from Fig. 3 that the height of the first wave in 0.1 *M* sodium perchlorate is virtually independent of the height of mercury, indicating that the first wave is typically kinetic. In 0.1 *M* perchloric acid solution the first wave is negligibly small as compared to the total wave height (0.046 microampere at −0.2 volt, 11.4 microamperes at −0.9 volt). The total current at potentials more negative than −0.8 volt was found to be diffusion-controlled both in sodium perchlorate and perchloric acid solutions.

The effect of Triton X-305 is much smaller than that of Triton X-100, as shown in Fig. 4. The first wave in 0.1 *M* sodium perchlorate (curves 1 and 1′) was found to be so large that it is almost diffusion-controlled, while that in 0.1 *M* perchloric acid (curves 2 and 2′) was independent of the height of mercury.

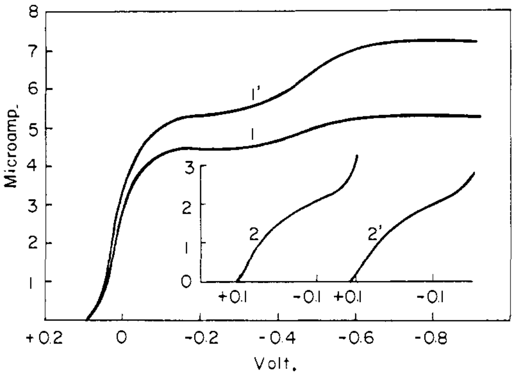

Fig. 4.—Current–potential curves in the presence of 0.1% Triton X305 at h = 44 cm. (1, 2) and 82 cm. (1′, 2′): (1, 1′), 1.07×10^{-3} *M* copper perchlorate in 0.1 *M* sodium perchlorate; (2, 2′), 1.07×10^{-2} *M* copper perchlorate in 0.1 *M* perchloric acid.

The height of the first wave in perchloric acid solution appears to be proportional to the copper concentration both in the presence of Triton X-100 and X-305 (Fig. 5).

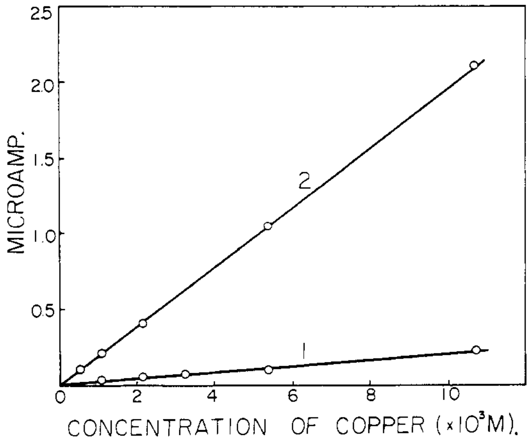

Fig. 5.—Current *vs.* concentration of copper in 0.1 *M* perchloric acid: (1), 0.1% Triton X-100 at −0.2 volt *vs.* SCE; (2), 0.1% Triton X-305 at −0.1 volt *vs.* SCE, h = 44 cm.

The dependence of the height of the first wave on the copper concentration in the sodium perchlorate solution in the presence of 0.1% Triton X-100 is shown by curve 1 in Fig. 6. The current is not proportional to the copper concentration but approximately proportional to the square root of the total copper concentration (curve 1′ in Fig. 6). In a fluoride buffer of pH 4.5, in which copper is known to form a complex only to a negligibly small extent,[8] the current–potential curve in the presence of 0.1% Triton has the same appearance as in the sodium perchlorate solution, but the height of the first wave is proportional to the copper concentration (line 2 in Fig. 6). These results strongly suggest that the kinetic current observed in sodium perchlorate solutions or in fluoride buffers is controlled by the rate of a chemical reaction involving hydrogen or hydroxyl ions.

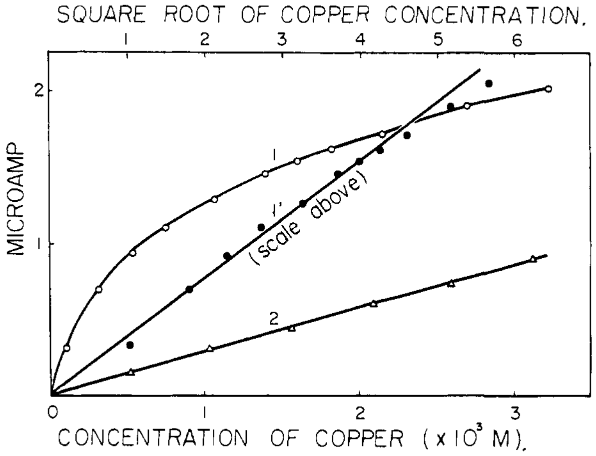

Fig. 6.—Current at −0.2 volt *vs.* concentration of copper (1, 2) and *vs.* square root of copper concentration (1′) in the presence of 0.1% Triton X-100: (1, 1′), 0.1 *M* sodium perchlorate; (2), 0.04 *M* sodium perchlorate and 0.06 *M* sodium fluoride. pH adjusted to 4.5 with perchloric acid, h = 44 cm.

The effects of temperature on the first wave in a sodium perchlorate solution and in a fluoride buffer both in the presence of 0.1% Triton X-100 are reproduced in Fig. 7. The temperature coefficient is much greater in the fluoride buffer than in the unbuffered sodium perchlorate solution.

From Fig. 8 it is evident that the effect of large concentrations of various Tritons on current–potential curves in sodium perchlorate solutions increases with decreasing molecular weight of the SAS.

Observations were made on the effect of concentration of sodium perchlorate in the presence of 0.1% Triton X-100. With increasing salt concentration the height of the first wave increased; for example, with solutions of 2.27×10^{-4} *M* copper in 0.01, 0.1 and 1 *M* sodium perchlorate, currents at −0.15 volt at h = 51.5 cm. were 0.32, 0.62 and 0.74 microampere, respectively. It also was found that the second wave was shifted to more negative potentials with increasing concentration of sodium perchlorate. No explanation of these ef-

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[8] P. W. West, J. Dean and E. J. Breda, *Collection Czechoslov. Chem. Comm.*, **13**, 1 (1948).

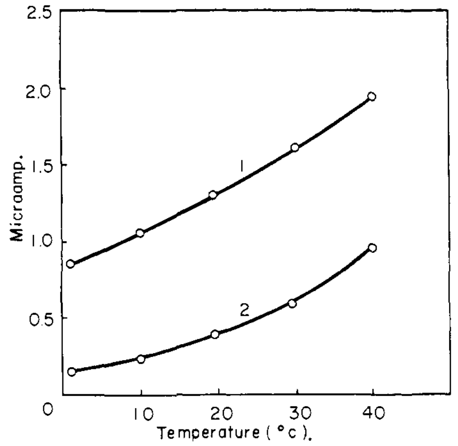

Fig. 7.—Effect of temperature on current at −0.2 volt in the presence of 0.1% Triton X-100: (1), 1.04×10^{-3} *M* copper in 0.1 *M* sodium perchlorate; (2), 2.08×10^{-3} *M* copper in 0.04 *M* sodium perchlorate plus 0.06 *M* sodium fluoride; *p*H 4.5, *h* = 44 cm.

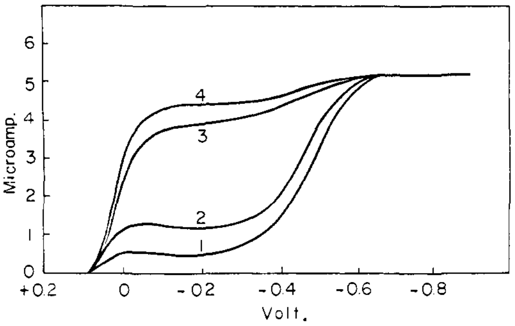

Fig. 8.—Current–potential curves of 1.04×10^{-3} *M* copper perchlorate in 0.1 *M* sodium perchlorate in the presence of (1) 0.03% Triton X-45 (saturated); (2) 0.1% Triton X-100; (3) 0.17% Triton X-205; (4) 0.24% Triton X-305; *h* = 44 cm.

fects of electrolyte concentration can be offered at present.

Effect of Cationic SAS's.—Current–potential curves obtained in the presence of 0.01% dodecylamine perchlorate in 0.1 *M* sodium perchlorate and in 0.1 *M* perchloric acid are shown in Fig. 9. The first wave in the sodium perchlorate solution is much smaller than that observed in the presence of Tritons. In the perchloric acid solution the first wave is entirely absent. The half-wave potential of the second wave is *ca.* −1.0 volt as compared to *ca.* −0.5 volt observed in the presence of Triton X-100. These results indicate that dodecylamine perchlorate is much more effective in distorting the copper waves than are the Tritons.

Discussion

Acidified Solutions (0.1 *M* Perchloric Acid).—In the absence of SAS the reduction of copper(II) in perchloric acid is not reversible (Fig. 1). The plot of log $i/(i_d - i)$ *vs.* E of an irreversible wave yields either a straight line or a curve. It was shown by Delahay[9] that when the rate of an electrode reaction is slow but not slow enough to increase the overvoltage more than about $0.12/n_a$ volt, (n_a being the number of electrons involved in the rate-determining step), the logarithmic plot yields a curve because the rate of the backward reaction (oxidation) plays a part. Such a wave is called by him "quasi-reversible" as distinguished from a totally irreversible wave in which the overvoltage is greater than about $0.12/n_a$ volt and the backward reaction is negligible. The logarithmic plot of such a wave yields a straight line. It appears that the copper wave in 0.1 *M* perchloric acid is quasi-reversible. The only reducible species in such an acid solution is aquo-copper ion (denoted as Cu^{+2}), and its reduction must be quasi-reversible.

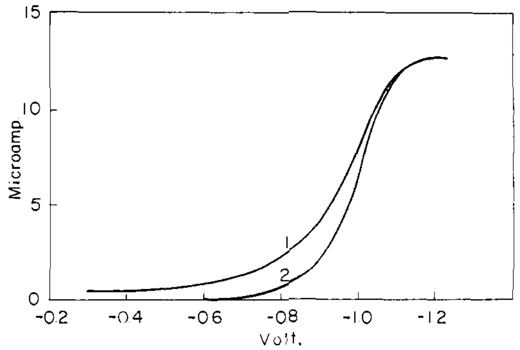

Fig. 9.—Current–potential curves of 2.27×10^{-3} *M* copper perchlorate in the presence of 0.01% dodecylamine perchlorate: (1), 0.1 *M* sodium perchlorate; (2), 0.1 *M* perchloric acid; *h* = 51.5 cm.

One of the most interesting results in this paper is that anionic SAS's make the copper wave more reversible in contrast to the distorting effect exerted by non-ionic and cationic SAS's. The striking difference in this respect between anionic and cationic SAS's hitherto has not been reported in the literature; it can be understood on the basis of the theory of Frumkin. According to Frumkin's theory of electrostatic effects,[10] the rate of an electrode reaction is determined by (1) the potential ψ_1 where the center of the reacting particles is located, which is not equal to the electrode potential φ (with reference to the null-charge potential), and (2) the concentration of the reacting species at this point. On the basis of these assumptions, the electrode potential φ is expressed by the equation

$$\varphi = \frac{RT}{\alpha n_a F}(\ln i + \ln k + \ln C) + (1 - z/\alpha n_a)\,\psi_1 \quad (1)$$

where α is the transfer coefficient, i the cathodic current density, k a constant, C the bulk concentration of the reacting species and z the valence of the reacting species taken with its sign. Assuming that α is not varied by the presence of SAS, the shift of electrode potential $\Delta\varphi$ corresponding to the shift $\Delta\psi_1$ at a constant current density is given by

$$\Delta\varphi = (1 - z/\alpha n_a)\Delta\psi_1 \quad (2)$$

The adsorption of an anion like dodecyl sulfate shifts the ψ_1 potential to a more negative value, and hence $\Delta\psi_1 < 0$. For copper $z = +2$, $n_a = 1$ or 2 and generally $0 < \alpha < 1$. Therefore, $(1 - z/\alpha n_a) < 0$ and hence $\Delta\varphi > 0$, indicating that at a

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(9) P. Delahay, THIS JOURNAL, **75**, 1430 (1953).

(10) (a) A. N. Frumkin, *Zhur. Fiz. Khim.*, **24**, 244 (1950); (b) *Doklady Akad. Nauk SSSR*, **85**, 373 (1952); (c) *Z. Elektrochem.*, **59**, 807 (1955); (d) *Nova Acta Leopoldina*, **19**, 132 (1957).

given current density the electrode potential in the presence of adsorbed anionic substances is more positive than in their absence. In other words, the overvoltage decreases under such conditions. Thus the theory is in qualitative accord with our experimental results. More quantitative comparison cannot be made at present because the ψ_1 potential is unknown.

It should be made clear at this point that the "electrostatic" theory of Frumkin is concerned with the variation of the effective potential as a result of adsorption or uneven distribution of components of the solution in the double layer at the electrode–solution interface but not with a direct electrostatic interaction between reducible ion and charged adsorbed substance to aid migration of the ion. Kivalo[4] states that electrostatic effects should be nullified to a great extent in a medium containing a high concentration of inert electrolyte, as is evidenced by the fact that the migration current is suppressed already by small additions of inert electrolyte. However, it must be realized that the migration effect is not related directly to the electrostatic effect in the sense of Frumkin. Gelatin, egg albumin and serum albumin used by Tanford[3] and Kivalo[4] are positively charged in acid solutions, while they are negatively charged in neutral solutions. Therefore, their results that these proteins distort the copper wave only at low *p*H can be expected on the basis of the theory of Frumkin and need not be attributed to a stronger adsorption of proteins in acid than in neutral medium at the mercury–solution interface.[4]

All non-ionic SAS's tested so far distort the copper wave in acid solutions. In the presence of Triton X-100 or X-305 in perchloric acid solutions, two waves appear, the first wave being kinetic in nature and very small in comparison with the second wave. It is not plausible that the first kinetic wave is controlled by a chemical reaction preceding the electrode reaction, because Cu^{+2} ions are considered to be the only species present in the acid solution. According to Frumkin,[10b,d] the penetration of the reacting particles into the adsorbed layer proceeds as the rate-determining step in certain cases. On the basis of this assumption he explained the appearance of a kinetic limiting current (called "penetration current") observed by Losew[11] in the discharge of cadmium ions on a cadmium amalgam electrode in the presence of tetrabutylammonium ions.[10d] In agreement with Frumkin, the kinetic current of copper in acid solutions containing Tritons is attributed to the slow penetration of Cu^{+2} ions through the adsorbed film. As may be expected, the penetration current is proportional to the copper concentration (Fig. 5). The experimental result that the penetration current is greater with Triton X-305 than with Triton X-100 (Figs. 3, 4 and 5) appears to indicate that the adsorbed film of Triton X-305 is more loosely packed than that of Triton X-100.

The potential range at which the second wave occurs is not related to a desorption of Tritons. At the rotated dropping mercury electrode,[12] we found that the desorption of Triton X-100 at a concentration of 0.05% begins at about -1.6 volt which is far more negative than the potential at which the second wave begins to rise (about -0.4 volt). Apparently, at potentials more negative than that at which the second wave starts, electrons acquire enough energy to combine with copper ions on the solution side of the adsorbed layer. With further increasing negative potential the rate of reduction of Cu^{+2} ions increases so much that it finally exceeds the rate of diffusion, and consequently the current becomes diffusion-controlled.

The second wave obtained by measuring maximum currents at the end of the drop life in a solution containing 2.27×10^{-3} *M* copper, 0.1 *M* perchloric acid and 0.05% Triton X-100 was analyzed according to Koutecky's polarographic method for the evaluation of kinetic parameters.[13] Correction for the limiting current of the first wave was not made, because it was negligibly small. Using the Ilkovic equation for the diffusion current, the diffusion coefficient of the copper ion was estimated to be 8.5×10^{-6} cm.²/sec. At two different heights of mercury (44 and 82 cm.) the plots of log k (k being the formal rate constant for the reduction of the copper ion) *vs.* E yielded straight lines, as shown in Fig. 10. From these lines the rate constant k_0 at $E = 0$ *vs.* NHE and αn_a were found to be 2.7×10^{-6} cm./sec. and 0.59, respectively. From the value of k_0 the rate constant k_s at the standard potential, -0.003 volt *vs.* NCE,[14] of the copper(II)–copper amalgam couple was calculated to be 4.4×10^{-9} cm./sec. The half-wave potentials at $h = 44$ and 82 cm. were -0.503 and -0.516 volt *vs.* SCE, respectively, the difference of 13 millivolts being in good agreement with the calculated difference of 14 millivolts. (For the calculation of the shift of half-wave potential with height of mercury, see reference 13.) This result indicates that the second wave is completely irreversible, that the corresponding electrode reaction involves a single rate-determining step and that the appearance of the wave is not related to a desorption or a change in extent of adsorption of the SAS.

With dodecylamine perchlorate as SAS in 0.1 *M* perchloric acid solution, only one wave appeared (Fig. 9), indiating that Cu^{+2} ions do not penetrate the adsorbed layer of this substance. In this connection, it is of interest to mention that the diffusion current of mercury(II) ions in dilute nitric acid was found to decrease considerably in the presence of dodecylamine perchlorate, giving a minimum at about -0.5 volt, while Triton X-100 did not affect the reduction wave of mercury ions. These results also appear to indicate the very compact nature of the film of dodecylamine cation. This cationic SAS shifts the copper wave to more negative potentials than the Tritons do. Qualitatively, the effect is accounted for again in terms of Frumkin's theory of electrostatic effects. The adsorption of cationic substances shifts the ψ_1 po-

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(11) W. W. Losew, *Doklady Akad. Nauk SSSR*, **107**, 432 (1956).

(12) I. M. Kolthoff and Y. Okinaka, *Anal. Chim. Acta*, **18**, 83 (1958).

(13) See, for example, P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter 4; "Instrumental Analysis," the Macmillan Co., New York, N. Y., 1957, Chapters 4 and 15.

(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, p. 227.

tential to more positive values, and consequently $\Delta\psi_1 > 0$ and hence $\Delta\varphi < 0$, indicating that the overvoltage is increased by the adsorption of cationic SAS's.

Non-acidified Solutions.—It is striking that in the absence of SAS the copper wave in the sodium perchlorate solution approaches reversibility much more closely than that in 0.1 *M* perchloric acid (Fig. 1). Considering the fact that inorganic cations are not adsorbed on positively charged mercury surface,[15] it is not to be expected that the rate of reduction of the aquo-copper ion will be different in the presence of hydrogen than of sodium ions. Various experimental observations indicate that the faster reduction in non-acidified solutions than in the presence of an excess hydrogen ions must be due to a reduction of the $CuOH^+$ ion rather than of aquo-copper ions. The wave in non-acidified solution must be kinetic in nature, since the concentration of $CuOH^+$ in the bulk of the sodium perchlorate solution is only of the order of a per cent. of that of Cu^{+2} even at a total copper concentration as low as 10^{-4} *M*.[16]

The above interpretation of the role of the $CuOH^+$ ion also accounts for the observations in the presence of 0.05% Triton X-100 in non-acidified solutions where two waves are observed (Fig. 3), the first one being kinetic in nature. Apparently the adsorbed film interferes with the rate of formation of the $CuOH^+$ at the surface of the electrode. The dependence of the kinetic current on the copper concentration in the sodium perchlorate solution and in the fluoride buffer (Fig. 6) indicates that the reaction controlling the rate of formation of $CuOH^+$ must be

$$Cu^{+2} + OH^- \longrightarrow CuOH^+ \qquad (3)$$

and not the protolysis reaction

$$Cu^{+2} + H_2O \longrightarrow CuOH^+ + H^+ \qquad (4)$$

If reaction 4 were rate determining, the rate of formation of $CuOH^+$ and hence the height of the kinetic wave would be directly proportional to $[Cu^{+2}]$ and independent of *p*H. On the other hand, in terms of reaction 3 the rate of formation of $CuOH^+$ is proportional to $[Cu^{+2}][OH^-]$. In unbuffered solutions, it is found that

$$[Cu^{+2}][OH^-] = [Cu^{+2}]K_w/[H^+] = [Cu^{+2}]K_w/\sqrt{K_h[Cu^{+2}]} = K\sqrt{[Cu^{+2}]}$$

where K_h is the protolysis constant for reaction 4 and $K = K_w/\sqrt{K_h}$. Since $[Cu^{+2}]$ is practically equal to the total copper concentration, the rate of formation of $CuOH^+$ should be proportional to the square root of the total copper concentration. Indeed the experimental result in the sodium perchlorate solution is in fair agreement with this interpretation (Fig. 6). In a given buffer solution, $[OH^-]$ is constant, and accordingly the rate of formation of $CuOH^+$ is expected to be proportional to $[Cu^{+2}]$. This was found to be true in the fluoride buffer (Fig. 6). In view of the fact that there is a small penetration current of Cu^{+2} observed in acid solutions, it is considered that there will be a contribution of the same order of magnitude of the penetration current of Cu^{+2} in non-acidified solutions. Thus the kinetic current in non-acidified solutions in the presence of Triton X-100 will actually be a sum of the current controlled by the rate of formation of $CuOH^+$ and the penetration current of Cu^{+2}. The height of the kinetic wave was found to decrease with decreasing *p*H of the buffers. However, because of the contribution of the penetration current, the decrease of the kinetic current was less than corresponded to the increase of the hydrogen ion concentration.

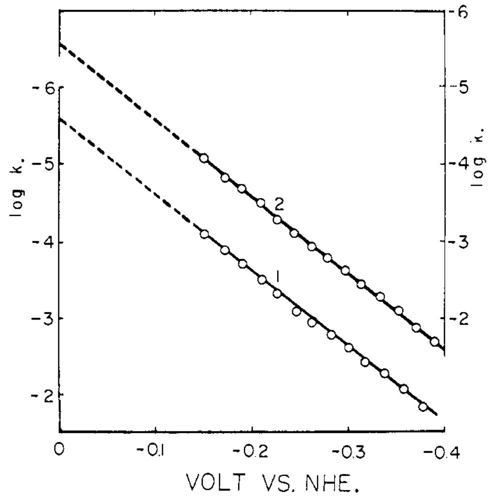

Fig. 10.—log *k* *vs.* *E:* 2.27×10^{-3} *M* copper perchlorate in 0.1 *M* perchloric acid in the presence of 0.05% Triton X-100; (1), *h* = 44 cm.; (2), *h* = 82 cm.

The effect of temperature on the kinetic current (Fig. 7) lends support to the interpretation that this current is controlled by the rate of a chemical reaction. The current at −0.2 volt in the fluoride buffer was increased about 1.5 times with a ten degree increase in temperature. This is the order of magnitude of the temperature coefficient of the rate of a chemical reaction. The increase of the kinetic current with temperature in the sodium perchlorate solution was only about 20% per ten degrees. The difference is attributed to the fact that the increase of $[OH^-]$ with temperature in the unbuffered solution is much smaller than that in the buffer solution. In a fluoride buffer the effect of a change in temperature upon the hydrogen ion concentration is very small, and $[OH^-]$ increases in proportion to the increase of K_w with temperature. On the other hand, in an unbuffered solution containing pure copper perchlorate the increase of $[OH^-]$ with temperature is much less than in the buffered solution.

The fact that the first wave in non-acidified solutions in the presence of Triton X-100 appears at the same potential as the wave in its absence indicates that the electrode reaction proper is not affected by the presence of the adsorbed film. The second wave appears at the same potential both in non-acidified and acidified solutions, indicating that the second wave in non-acidified

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[15] D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

[16] The protolysis constant for the reaction $Cu^{+2} + H_2O \rightleftarrows CuOH^+ + H^+$ has been reported to be of the order of *ca.* 10^{-8} at zero ionic strength: J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants. Part II. Inorganic Ligands," The Chemical Society, London, 1958, p. 15.

solutions is due to the irreversible reduction of Cu^{+2}.

Apparently, the rate of formation of $CuOH^+$ is affected by the presence of an adsorbed film. Experimental results with various Tritons of different molecular weights[7] (Fig. 8) show that the effectiveness in decreasing the rate of formation of $CuOH^+$ decreases with increasing molecular weight. The half-wave potential of the second wave is shifted to slightly more negative values with decreasing molecular weight. In view of the fact that the solubility of Tritons in water increases with increasing molecular weight, it is considered that the adsorbed layer of Tritons of higher molecular weight is less compact and is more hydrated. Apparently the compactness of the adsorbed layer greatly affects the rate of formation of $CuOH^+$ and the rate of electron transfer through the adsorbed layer, as well as the rate of penetration of Cu^{+2} ions (compare the height of the first waves in presence of Triton X-100 and X-305, Figs. 3, 4 and 8).

The small kinetic current in the presence of dodecylamine cations in the sodium perchlorate solution (Fig. 9) is also attributed to the slow formation of $CuOH^+$. Apparently, the film of dodecylamine perchlorate is of a more compact nature than that of Tritons, and the kinetic current in the presence of the former is much smaller than that in the presence of Tritons.

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MINNEAPOLIS, MINNESOTA

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Equilibrium Polymerization of ϵ-Caprolactam

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A theory applicable to the equilibrium polymerization of ϵ-caprolactam in presence of water is presented and compared with experimental results. The agreement is excellent for low water concentrations. A single formula is developed correlating the initiator concentration (between 0.1 and 1.0 moles/kg.) with the number average degree of polymerization for the temperature range investigated, and the ΔH^0 values for the initiation and propagation steps are given.

I. Introduction

It was pointed out previously[1,2] that certain types of equilibrium polymerization could be described by the sets of equations

$$XY + M \rightleftharpoons XMY \qquad K = \frac{[XMY]}{[XY][M]} \tag{1}$$

$$XMY + M \rightleftharpoons XM_2Y \qquad K_3 = \frac{[XM_2Y]}{[XMY][M]} \tag{2}$$

$$XM_2Y + M \rightleftharpoons XM_3Y \qquad K_3 = \frac{[XM_3Y]}{[XM_2Y][M]} \tag{3}$$

$$XM_nY + M \rightleftharpoons XM_{n+1}Y \qquad K_3 = \frac{[XM_{n+1}Y]}{[XM_nY][M]} \tag{4}$$

Where XY (subsequently to be written as X) is the initiator (which can be both ionic or non-ionic), M is the monomer and K and K_3 the equilibrium constants for initiation and propagation, respectively. These equations were shown to yield the following results in terms of experimentally determinable quantities[1]

$$\bar{P}_n = \frac{1}{1 - K_3[M]} \tag{5}$$

$$[M_0] = [M](1 + K[X]\bar{P}_n{}^2) \tag{6}$$

$$[X_0] = [X](1 + K[M]\bar{P}_n) \tag{7}$$

$$\bar{P}_n = \frac{[M_0] - [M]}{[X_0] - [X]} \tag{8}$$

Where P_n (subsequently to be written as P) is the number average degree of polymerization, [M] is the equilibrium concentration of monomer and $[X_0]$ and $[M_0]$ the initial concentration of initiator and monomer, respectively.

It has been known for a long time that conversion of ϵ-caprolactam (CL) into products of the Nylon 6 polyamide type leads to a state of equilibrium with definite amounts of the initial components. This equilibrium system has been widely investigated in the past, and data describing it are available in the literature. Here an attempt is made to represent the data obtained by two sources[3,4] over a sufficiently wide range of variables (temperature and initiator concentration) in terms of the theory outlined above in equations 1 through 8.

II. Treatment of Data

The experimental data available in the literature are of the type: a known mole ratio m of H_2O to CL is charged in a vessel; the vessel is brought to a definite temperature and polymerization is carried out to equilibrium. When equilibrium is reached, the value of P and [M] are determined.

We shall use the concentration units of moles/kilogram; we use this rather than moles/liter because there is a density change when CL converts to polymer.

It is necessary to be able to compute $[M_0]$ and [X] from the initial mole ratio m. This is accomplished as indicated

$$[X_0] = \frac{1000m}{18m + 113} \tag{9a}$$

$$[M_0] = [M_{00}] - \frac{[M_{00}]}{[X_{00}]}[X_0] = 8.85 - 0.1594[X_0] \tag{9b}$$

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(1) A. V. Tobolsky, *J. Poly. Sci.*, **25**, 220 (1957).

(2) A. V. Tobolsky, *ibid.*, **31**, 122 (1958).

(3) F. Wiloth, *Z. Physik. Chem.*, *N. F.*, **4**, 66 (1955).

(4) P. F. Van Velden, G. M. Van Der Want, D. Heikens, Ch. A. Kruissink, P. H. Hermans, A. J. Staveman, *Recueil*, **74**, 1376 (1955).