In the case of potassium hexacyanomanganate(III), it was found that the cadmium salt of the complex could be completely precipitated by addition of a slight excess of cadmium sulfate solution. After centrifugation, the radiocyanide was precipitated as silver cyanide from the supernatant. The conversion to zinc cyanide was then made in the usual manner. This separation was found applicable to several other systems, namely, potassium hexacyanocobaltate(III), potassium hexacyanochromate(III), potassiumhexacyanoferrate(III), potassium hexacyanoferrate(II) and potassium tetracyanopalladate(II).

It was found possible to effect the separation of radiocyanide from solutions containing it and potassium tetracyanomercurate(II) by the direct precipitation of zinc radiocyanide and this method was first employed. As exchange appeared to take place instantaneously, it was considered desirable to devise a second procedure which would also be applicable to solutions containing mercuric cyanide rather than the ion, $Hg(CN)_4^{-2}$. A separation was achieved by precipitating silver radiocyanide from solution, then converting to zinc cyanide according to the usual procedure.

The separation of radiocyanide from potassium tetracyanonickelate(II) was accomplished by adding $0.05f$ lead nitrate to precipitate lead radiocyanide. After centrifuging, the lead cyanide was freed from insoluble impurities (probably a trace of lead tetracyanonickelate(II)) by dissolving it in hot water and recentrifuging. The radiocyanide in the supernatant was then converted to zinc radiocyanide for the specific activity determination. The results indicated complete and instantaneous exchange and it therefore would have been desirable to have tested another separation procedure. To date, however, all attempts in this direction were unsuccessful.

Following the observation that cyanate was produced in solutions containing free cyanide and potassium hexacyanoferrate(III) (refer under "Experimental Results"), it was thought necessary to determine whether or not there was any exchange between cyanate and radiocyanide. The separation was accomplished by direct precipitation of zinc radiocyanide.

Summary

The exchange of radiocyanide with the following complexes was studied at *p*H *ca.* 10: potassium tetracyanonickelate(II), potassium tetracyanopalladate(II), potassium tetracyanomercurate(II), potassium hexacyanomanganate(III), potassium hexacyanochromate(III), potassium hexacyanoferrate(II) and (III), potassium hexacyanocobaltate(III), and potassium octocyanomolybdate(IV). Exchange was observed to be immeasurably rapid with the di- and tetracyanides, fast but measurable in the case of potassium hexacyanomanganate(III) and negligible for the other complexes. The exchange of potassium octocyanomolybdate(IV) was found to be strongly photocatalyzed. Exchange of potassium hexacyanoferrate(II), and possibly of potassium hexacyanochromate(III), was induced in acid solution, *i. e.*, at *p*H 2–4. This pattern of exchange data supports the viewpoint that over-all thermodynamic instability constants are misleading in predicting exchange. The postulate of decreasing exchange rate with increasing coördination number is in qualitative agreement with the results.

LOS ANGELES, CALIFORNIA RECEIVED FEBRUARY 4, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

Determination and Significance of Polarographic Critical Micelle Concentrations

BY EUGENE L. COLICHMAN[1]

The suppression of maxima, by the use of small quantities of gelatin, agar, various dyes, and other less commonly used materials, is well known in polarographic investigations. Kolthoff and Lingane[2] discuss the characteristics and elimination of maxima in polarography and point out the inadequacies in the adsorption theories[3,4] used to explain the phenomena. It has been shown that in practical work the suppressive action of gelatin on the diffusion current must be taken into account when using concentrations greater than about 0.01 per cent.[5,6] In the present investigation, it was found that even smaller quantities of gelatin and other colloidal agents can influence diffusion currents and half wave potentials.

In studying the significance of the polarographically determined critical micelle concentrations, cadmium, manganese(II), and copper(II) systems in neutral, acidic, and basic supporting electrolytes were investigated in the presence of non-reducible colloidal materials.

The polarographic micelle point (P.M.P.) is shown here to be identical with the classical critical micelle concentration (C.M.C.) as determined by an already accepted procedure,[7,8] namely, surface tension–concentration curves. Furthermore, this concentration seems to be equal to the concentration of colloidal agent just sufficient to suppress maxima, the maximum suppression point (M.S.P.).

Experimental

The polarographic apparatus and procedure used in this investigation has been described in detail elsewhere.[9] Determinations were made at 25.0 ± 0.1°. Special care was taken to ensure complete removal of adsorbed colloidal materials in the polarographic cell by washing thoroughly with alcohol and water between each polarographic deter-

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[1] Department of Chemistry, University of Portland, Portland, Oregon.

[2] Kolthoff and Lingane, "Polarography," Chap. 8, Interscience Publishers, New York, N. Y., 1946.

[3] Heyrovsky, "Actualités scientifiques et industrielles," No. 90, Paris, 1934.

[4] Ilkovic, *Collection Czechoslov. Chem. Commun.*, **8**, 13 (1936).

[5] Ilkovic, ref. 4, p. 122.

[6] Lingane, *Anal. Chem.*, **15**, 583 (1943).

[7] Early results: (a) Lottermoser and Puschel, *Kolloid Z.*, **63**, 175 (1933); (b) Powney and Addison, *Trans. Far. Soc.*, **33**, 1243 (1937).

[8] Miles and Shedlovsky, *J. Phys. Chem.*, **48**, 57 (1944).

[9] Meites and Meites, *Anal. Chem.*, in press.

TABLE I

CRITICAL MICELLE CONCENTRATIONS OF COLLOIDAL AGENTS

Substance	Supporting electrolyte	Reducible ion	P. M. P., %	Function changing	Surface tension C. M. C.
Gelatin[b]	1.0 *M* KNO_3	Cd^{+2}	6.0×10^{-3}	$E_{1/2}$	3.0×10^{-3} %
	1.0 *M* HNO_3	Cd^{+2}	3.8×10^{-3} 1.2×10^{-2}	$E_{1/2}$ and i_d	
	0.7 *M* $HClO_4$	Cd^{+2}	7.2×10^{-3} 2.4×10^{-2}	$E_{1/2}$ and i_d	
	1.0 *M* KCl	Mn^{+2}	6.3×10^{-3}	$E_{1/2}$	3.0×10^{-3} %
	1.0 *M* KSCN	Mn^{+2}	3.0×10^{-3}	$E_{1/2}$	
	5.0 *M* NH_3–0.1 *M* NH_4Cl	Mn^{+2}	3.5×10^{-3} 5.5×10^{-3a}	$E_{1/2}$ and i_d	
Triton[c] X-100	1.0 *M* KCl	Mn^{+2}	1.5×10^{-3}	$E_{1/2}$	2.2×10^{-3} %
	1.0 *M* KNO_3	Cd^{+2}	2.5×10^{-3}	$E_{1/2}$ and i_d	2.2×10^{-3} %
	1.0 *M* HNO_3	Cd^{+2}	1.8×10^{-3}	$E_{1/2}$ and i_d	
	0.7 *M* $HClO_4$	Cd^{+2}	1.6×10^{-3} 3.7×10^{-3}	$E_{1/2}$ and i_d	
	5.0 *M* NH_3–0.1 *M* NH_4Cl	$Cd(NH_3)_4^{+2}$	2.0×10^{-3}	$E_{1/2}$	
			M		
Lauryltrimethylammonium bromide	1.0 *M* KCl	Mn^{+2}	3.2×10^{-4} 5.3×10^{-4a}	$E_{1/2}$	4.0×10^{-4} *M*
Cetyltrimethylammonium bromide	1.0 *M* KCl	Cd^{+2}	7.4×10^{-5} 3.5×10^{-4}	$E_{1/2}$	6.0×10^{-5} *M* 2.0×10^{-4} *M*
	1.0 *M* KNO_3	Cd^{+2}	6.5×10^{-5} 2.3×10^{-4}	$E_{1/2}$ and i_d	
	5.0 *M* NH_3–0.1 *M* NH_4Cl	$Cd(NH_3)_4^{+2}$	8.0×10^{-5}	$E_{1/2}$	

[a] Where i_m/i_d equals unity. [b] Solutions prepared fresh just before use by dissolving gelatin at about 80°. [c] Using reported mol. wt. of 600, av. molarity of P. M. P. and C. M. C. is 3.3×10^{-5} *M*.

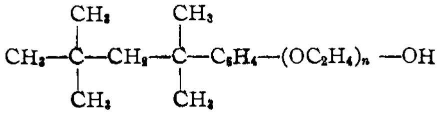
mination. Soaking the cell with a saturated potassium chloride solution usually removed the last traces of surface active material. The agar–KCl plug was changed frequently.

A Beckman Quartz Spectrophotometer, Model DU, with 1-cm. quartz cells was used in the ultraviolet absorption investigation.

A Cenco–DuNouy Interfacial Tensiometer, #70540, was used in making the surface tension measurements.

Lauryl- and Cetyltrimethylammonium Bromides.—Quaternary salts were prepared by refluxing lauryl and cetyl bromides (Eastman Kodak Co. White Label) with fifty per cent. excess quantities of alcoholic trimethylamine, until a test portion showed complete solubility in water. Salts obtained were recrystallized twice from distilled water, and then dried in a vacuum desiccator over sulfuric acid.

Gelatin was "Bacto" acid hydrolyzed[10] (Difco Laboratories). Triton X-100 (Rohm and Haas Co.) is 100% active and has the general formula



$$CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-C_6H_4-(OC_2H_4)_n-OH$$

The average molecular weight is reported[11] to be approximately 600. All other chemicals used were reagent grade.

Results and Discussion

The polarographic critical micelle concentrations (P.M.P.) presented in Tables I and II have been determined from the original polarograms by a graphical method of plotting $E_{1/2}$ or i_d (corrected for dilution) *vs.* log *C*. The P.M.P. in these graphs is taken as that minimum concentration where the linear relationship first shows a sharp break or discontinuity. P.M.P. data on the colloidal materials employed here are not comparable with previous C.M.C.'s reported due to the high ionic strengths of the solutions. Previous results[12] show that the C.M.C. for a given colloidal agent is considerably lower[13] when salt is present.

Surface tension measurements by the DuNouy ring method have been made on all the colloidal agents in 1.0 *M* potassium chloride so that critical micelle concentrations determined by this accepted procedure could be compared with the polarographically determined results. These surface tension C.M.C.'s included in Table I and shown graphically, Fig. 1, substantiate the identical nature of the polarographic micelle point (P.M.P.) and the classical critical micelle concentration.

The very low value found for the C.M.C. of Triton X-100 is considerably less than that reported previously.[11b] This is not due to differences in the ionic strengths of the solutions since surface tension measurements on Triton X-100 in pure water showed substantially the same C.M.C. as that found in 1.0 *M* potassium chloride.

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[10] Sheppard, Houck and Dittmar, *J. Phys. Chem.*, **46**, 158 (1942), show this variety of gelatin to have an isoelectric point, *p*H 7-9; it will behave as a cationic active material up to about *p*H 8, and anionic above *p*H 8.

[11] (a) Marsden and McBain, *J. Phys. Colloid Chem.*, **52**, 110 (1948); (b) Gonick and McBain, THIS JOURNAL, **69**, 334 (1947).

[12] Corrin and Harkins, THIS JOURNAL, **69**, 679, 683 (1947).

[13] For example, Kolthoff and Stricks, *J. Phys. Colloid Chem.*, **52**, 915 (1948), and **53**, 424 (1949), found C.M.C.'s approximately ten-fold lower for sodium and potassium laurate in 1.0 *M* sodium chloride and in 1.0 *M* potassium hydroxide.

TABLE II

MAXIMA SUPPRESSION POINTS OF COLLOIDAL AGENTS

Substance	Supporting electrolyte	Reducible ion	$E_{d.e.}$ *vs.* S. C. E., v. at M. S. P.	M. S. P., %	P. M. P., %	Function changing
Gelatin	1.0 *M* KNO_3	Cu^{+2}	+0.01	4.5×10^{-3}	None	None
	1.0 *M* HNO_3	Cu^{+2}	0.00	5.9×10^{-3}	6.5×10^{-3}	$E_{1/2}$ and i_d
					1.7×10^{-2}	
	0.7 *M* $HClO_4$	Cu^{+2}	+0.01	5.2×10^{-3}	6.0×10^{-3}	$E_{1/2}$ and i_d
					2.0×10^{-2}	
	5.0 *M* NH_3–0.1 *M* NH_4Cl	$Cu(NH_3)_4^{+2}$	−0.28 Cu(II) −0.56 Cu(I)	5.8×10^{-3}	6.4×10^{-3}	$E_{1/2}$
	5.0 *M* NH_3–0.1 *M* NH_4Cl	$Cd(NH_3)_4^{+2}$	−0.83	5.5×10^{-3}	3.5×10^{-3}	$E_{1/2}$ and i_d
	1.0 *M* KOH	$Cu(OH)_4^{-2}$	−0.39 Cu(II) −0.49 Cu(I)	2.8×10^{-3}	3.2×10^{-3}	i_d
	1.0 *M* KSCN	$Cu(SCN)_4^{-2}$	−0.52 Cu(II)	6.0×10^{-3}	7.2×10^{-3}	$E_{1/2}$ and i_d
			−1.48 Cu(I)		2.8×10^{-2}	Cu(I) only
Triton X-100	1.0 *M* KNO_3	Cu^{+2}	0.00	2.0×10^{-3}	2.0×10^{-3}	$E_{1/2}$ and i_d
	1.0 *M* HNO_3	Cu^{+2}	0.00	1.9×10^{-3}	2.2×10^{-3}	$E_{1/2}$ and i_d
	0.7 *M* $HClO_4$	Cu^{+2}	+0.01	1.5×10^{-3}	2.0×10^{-3}	$E_{1/2}$ and i_d
	5.0 *M* NH_3–0.1 *M* NH_4Cl	$Cu(NH_3)_4^{+2}$	−0.28 Cu(II) −0.56 Cu(I)	1.6×10^{-3}	1.8×10^{-3}	$E_{1/2}$ and i_d
	1.0 *M* KOH	$Cu(OH)_4^{-2}$	−0.40 Cu(II) −0.51 Cu(I)	1.8×10^{-3}	2.0×10^{-3}	$E_{1/2}$ and i_d
	1.0 *M* KSCN	$Cu(SCN)_4^{-2}$	−0.52 Cu(II)	1.6×10^{-3}	1.8×10^{-3}	$E_{1/2}$ and i_d
			−1.48 Cu(I)			Cu(I) only
				M	*M*	
Lauryltrimethylammonium bromide	1.0 *M* KNO_3	Cu^{+2}	0.00	9.3×10^{-5}	9.3×10^{-5}	$E_{1/2}$ and i_d
					3.8×10^{-4}	
	1.0 *M* HNO_3	Cu^{+2}	0.00	8.7×10^{-5}	9.5×10^{-5}	
					6.0×10^{-4}	$E_{1/2}$ and i_d
	1.0 *M* KCl	Mn^{+2}	−1.52	5.3×10^{-4}	3.2×10^{-4}	$E_{1/2}$
	5.0 *M* NH_3–0.1 *M* NH_4Cl	$Cu(NH_3)_4^{+2}$	−0.26 Cu(II) −0.63 Cu(I)	4.0×10^{-4}	3.0×10^{-4}	$E_{1/2}$ and i_d
	1.0 *M* KOH	$Cu(OH)_4^{-2}$	−0.39 Cu(II)	3.0×10^{-5}	3.5×10^{-5}	i_d
			−0.50 Cu(I)		3.8×10^{-4}	
Cetyltrimethylammonium bromide	1.0 *M* KNO_3	Cu^{+2}	0.00	8.0×10^{-5}	7.4×10^{-5}	$E_{1/2}$ and i_d
					4.2×10^{-4}	
	1.0 *M* HNO_3	Cu^{+2}	0.00	7.5×10^{-5}	7.0×10^{-5}	
					3.8×10^{-4}	$E_{1/2}$ and i_d
	5.0 *M* NH_3–0.1 *M* NH_4Cl	$Cu(NH_3)_4^{+2}$	−0.28 Cu(II)	7.3×10^{-5}	8.0×10^{-5}	
			−0.56 Cu(I)		1.5×10^{-4}	$E_{1/2}$ and i_d
	1.0 *M* KOH	$Cu(OH)_4^{-2}$	−0.43 Cu(II)	1.7×10^{-5}	2.1×10^{-5}	i_d
			−0.53 Cu(I)		1.3×10^{-4}	$E_{1/2}$ and i_d

No quantitative date on gelatin are available for comparison. Micelle formation in solution has been reported frequently. The increase in conductance known to result when high field strengths[14,15] and frequencies[16] are applied to agar and gum arabic solutions substantiates micelle formation by polydispersed non-homogeneous proteins.

Complex formation between the cationic quaternary salts and inorganic cations is not very likely. However, the possibility of complex ion formation between gelatin and the inorganic reducible cations bears consideration in view of the prevalence of such phenomena in the literature. Recent results on the binding of both organic and inorganic ions by proteins[17] and metal ion–protein complexes[18] certainly justifies the existence of many ion–protein complexes. It should be pointed out, however, that the latest results cited were obtained with monodispersed homogeneous proteins (*e. g.*, bovine serum albumin) and will not necessarily be the same with a polydispersed non-homogeneous material like gelatin. The known micellar formation of gelatin is probably due to aggregation of the lower molecular weight fractions present as a result of partial hydrolysis. In the case of gelatin, it is quite possible, however, that complex ion formation plays some part in the phenomena observed.

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(14) Schiele, *Physik. Z.*, **34**, 60 (1933).

(15) Malch and Hartley, *Z. physik. Chem.*, **A170**, 321 (1934).

(16) Schmid and Larsen, *Z. Elektrochem.*, **44**, 651 (1938).

(17) (a) Longsworth and Jacobsen, *J. Phys. Colloid Chem.*, **53**, 126 (1949); (b) Klotz, *et al.*, THIS JOURNAL, **68**, 1486, 2299 (1946); (c) Scatchard and Black, *ibid.*, **68**, 88 (1946).

(18) Klotz and Curme, *ibid.*, **70**, 939 (1948).

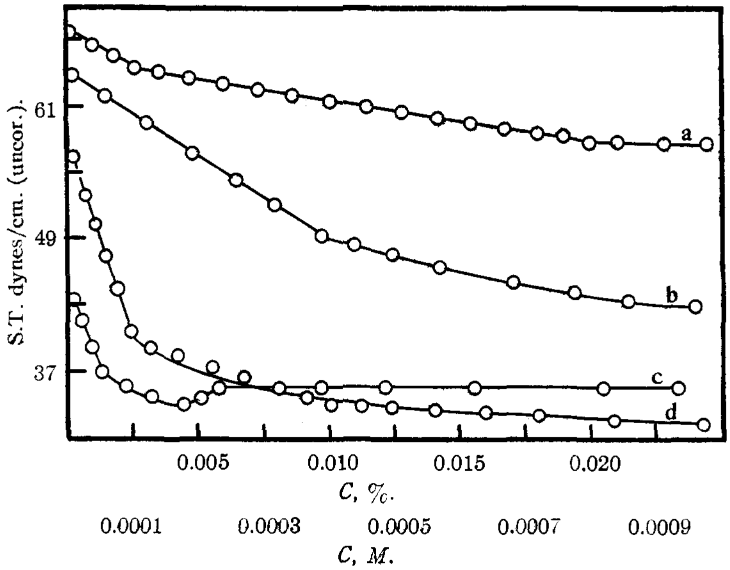

Fig. 1.—Surface tension–concentration curves of colloidal agents in 1 *M* KCl: (a) gelatin; (b) lauryltrimethylammonium bromide; (c) cetyltrimethylammonium bromide; (d) Triton X-100.

The absorption spectra of various cadmium and manganese systems in the presence of the highest concentration of colloidal material employed polarographically were examined relative to the same systems in the absence of Cd^{+2} or Mn^{+2} over the range 2500–3200 Å. It was necessary to lower the supporting electrolyte concentration to 1/20 of the value employed in the polarographic investigation due to high absorption capacity. Cupric ion solutions were examined similarly in the visible region of the spectra. Negligible differences in absorption between the two comparison solutions was taken as indicative of little or no complex formation.

That complex ion formation alone will not explain all the results is seen further on consideration of the graphical method of analysis of the polarographic data. Sharp discontinuities or breaks in either $E_{1/2}$ or i_d (diffusion current corrected for dilution) *vs.* log *C* curves would not be obtained if complex ion formation were the predominate and only phenomena. Furthermore, it is certainly more than coincidental that the P.M.P. and M.S.P. values obtained from polarographic results coincide with C.M.C. values obtained by the classical surface tension method (Fig. 1).

It should be pointed out that the complex ion phenomenon observed[17–18] on pure proteins is not comparable or inconsistent with the results reported here on known micelle forming agents. Gelatin's micelle forming ability is influenced perhaps by its known complex formation with inorganic cations.

The maximum suppression point (M.S.P.) of a given suppressor is defined and obtained as follows: values of i_m/i_d (ratio of diffusion current at maximum and when suppressed) are plotted *vs.* log *C* and extrapolated, from the straight line relationship obtained, to complete suppression (where i_m/i_d is unity).

The results, obtained by the above method and compiled in Table II, seem to indicate that the maximum suppression point (M.S.P.) for a given colloidal agent is identical with its critical micelle concentration.

Although most of the systems dealt with here involve "positive maxima," some data on "negative maxima" have also been obtained. The results here with strongly surface-active materials will not confirm the rule of Heyrovsky and Dillinger.[19]

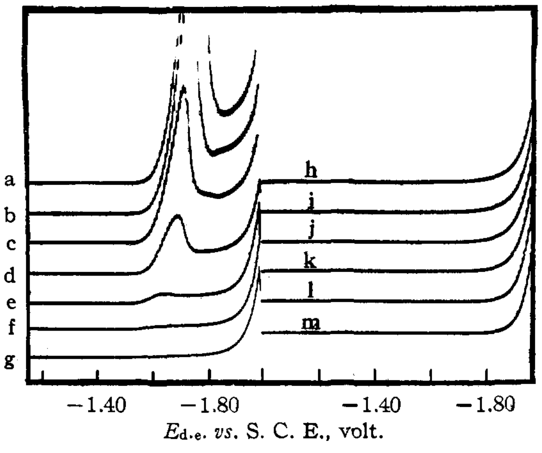

Fig. 2.—Typical polarogram, effect of gelatin on 0.004 *M* +2 manganese in 5 *M* ammonia–0.1 *M* ammonium chloride, % × 10^3: (a) 0, (b) 0.95, (c) 1.88, (d) 2.76, (e) 4.44, (f) 6.01, (g) 7.48, (h) 8.86, (i) 10.1, (j) 17.7, (k) 25.0, (l) 39.0, (m) 71.0.

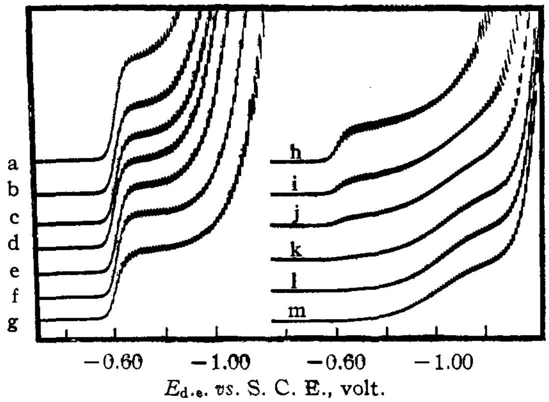

Fig. 3.—Typical polarogram, effect of triton X-100 on 0.004 *M* cadmium in 1 *M* nitric acid, % × 10^3: (a) 0, (b) 0.27, (c) 0.53, (d) 0.79, (e) 1.05, (f) 1.55, (g) 2.02, (h) 2.94, (i) 4.21, (j) 5.73, (k) 10.0, (l) 18.1, (m) 36.5.

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(19) Heyrovsky and Dillinger, *Collection Czechoslov. Chem. Commun.*, **2**, 626 (1930).

Highly surface-active cationic, anionic, and nonionic species suppress maxima at all voltages irrespective of whether these maxima are "positive" or "negative." It should be pointed out that the adsorptive power of the colloidal agents used is very much greater than that of the non surface-active ions present in the supporting electrolyte and the species being reduced. Therefore, it is not surprising that the sign rule of Heyrovsky is not applicable here. At a concentration of colloidal agent equal to or greater than the M.S.P. value, non surface-active ions probably have been desorbed completely from the surface of the mercury drop. Under these conditions, adsorption and depolarization by the reducible ion no longer occurs; thus no maximum is observed in the *c.-v.* curve.

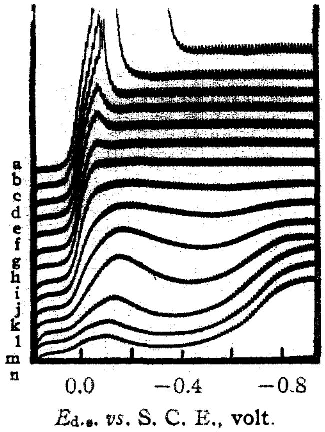

Fig. 4.—Typical polarogram of 0.004 *M* Cu(II) in 1 *M* potassium nitrate, effect of triton X-100, *C*, % × 10^3: (a) 0, (b) 0.27, (c) 0.53, (d) 0.79, (e) 1.05, (f) 1.55, (g) 2.02, (h) 2.94, (i) 4.21, (j) 5.73, (k) 10.0, (l) 18.2, (m) 36.7, (n) 53.0.

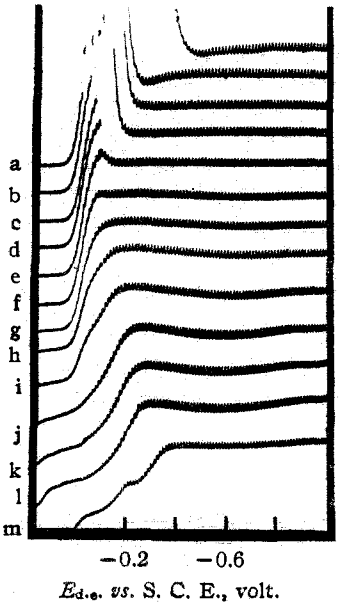

Fig. 5.—Typical polarogram of 0.004 *M* Cu(II) in 1 *M* potassium nitrate, effect of lauryltrimethylammonium bromide, *M* × 10^4: (a) 0, (b) 0.13, (c) 0.26, (d) 0.39, (e) 0.52, (f) 0.71, (g) 0.93, (h) 1.3, (i) 1.8, (j) 3.9, (k) 5.9, (l) 9.8, (m) 10.4.

The various sample polarograms reproduced (Figs. 2–10) have been chosen to show pictorially some of the many manifestations of the colloidal action found. Pronounced effects are obtained if maxima suppressors are employed at concentrations greater than those corresponding to their M.S.P. values.

Figure 2 illustrates that maxima suppression can destroy polarographic waves completely.

In Fig. 3, a new wave appears at −1.010 v. when Triton is approximately 0.005%; it is completely formed at approximately 0.04%, simultaneous with the complete disappearance of the first wave.

A comparison of Figs. 4 and 5 shows the specific influence that the colloidal agent can have on the reducible species in the same supporting electrolyte.

Comparing Figs. 5 and 6, it is seen that in nitric acid, Cu(II) is reduced stepwise at around 0.0004 *M* concentration of the quaternary salt while in potassium nitrate the colloidal agent concentration has to be increased to about 0.001 *M* before the same phenomenon is observed.

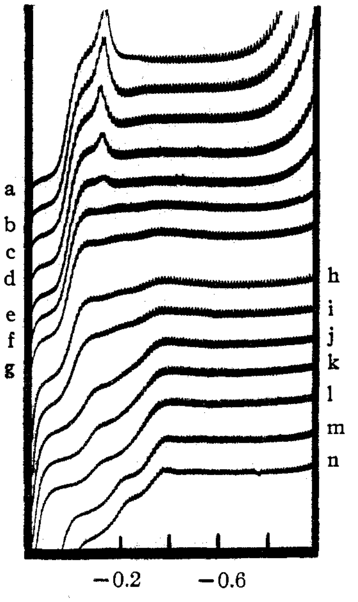

Fig. 6.—Typical polarogram of 0.004 *M* Cu(II) in 1 *M* nitric acid, effect of lauryltrimethylammonium bromide, *M* × 10^4: (a) 0, (b) 0.13, (c) 0.26, (d) 0.39, (e) 0.52, (f) 0.71, (g) 0.93, (h) 1.3, (i) 1.8, (j) 3.9, (k) 5.9, (l) 9.8, (m) 10.4, (n) 16.3.

The influence of both acid and base on the colloidal properties of Triton X-100 is seen in Figs. 7 and 8. The abrupt shift in half-wave potential

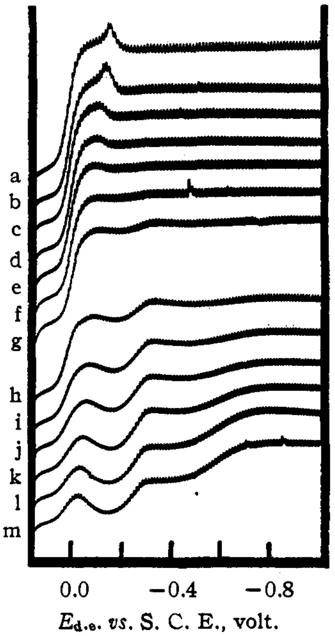

Fig. 7.—Typical polarogram of 0.004 *M* Cu(II) in 0.7 *M* perchloric acid, effect of triton X-100, *C*, % × 10^3: (a) 0, (b) 0.30, (c) 0.60, (d) 0.90, (e) 1.2, (f) 1.8, (g) 2.4, (h) 2.9, (i) 4.1, (j) 5.6, (k) 10.0, (l) 18.0, (m) 37.0.

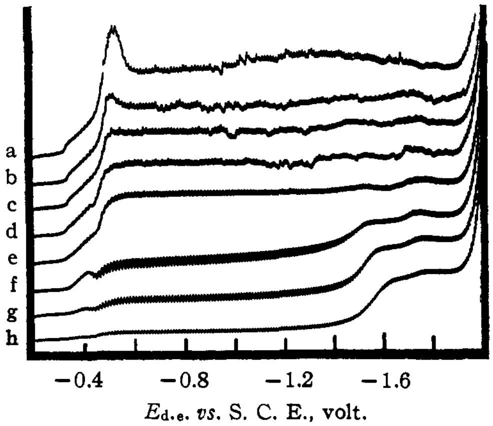

Fig. 8.—Typical polarogram of 0.002 *M* Cu(II) in 1 *M* potassium hydroxide, effect of triton X-100, *C*, % × 10^3: (a) 0, (b) 0.3, (c) 0.6, (d) 1.2, (e) 1.8, (f) 2.8, (g) 3.7, (h) 5.9.

at the M.S.P. value (around 2 × 10^{-3}%), seen in Fig. 8, shows how the supporting electrolyte can promote or aid the colloidal phenomena. These results are especially significant since Triton, a non-ionic compound, is completely inert in either acidic or basic solutions.

In Fig. 9, it is seen that the very active colloidal agent, cetyltrimethylammonium bromide, causes the ordinary stepwise, reduction of cupric ion to proceed completely in one step from Cu(II) to Cu(Hg). Gelatin did not bring about the same effect.

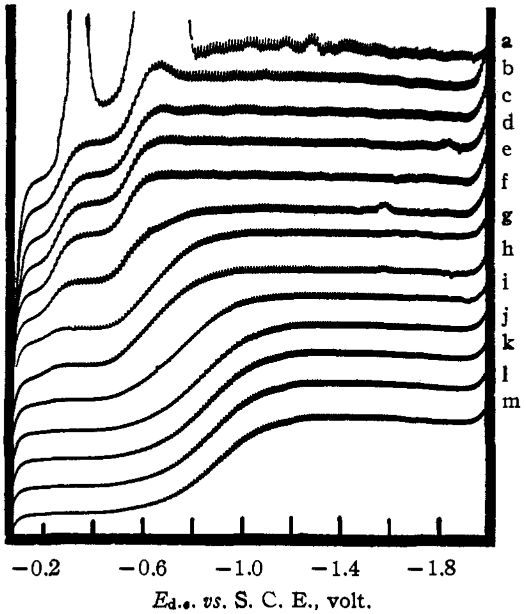

Fig. 9.—Typical polarogram of 0.004 *M* Cu(II) in 5 *M* ammonia–0.1 *M* ammonium chloride, effect of cetyltrimethylammonium bromide, *M* × 10^4: (a) 0, (b) 0.11, (c) 0.21, (d) 0.40, (e) 0.75, (f) 1.1, (g) 2.0, (h) 2.8, (i) 4.0, (j) 6.5, (k) 10.0, (l) 18.0, (m) 36.0.

Figure 10 shows the influence of gelatin on the Cu(I) to Cu(Hg) wave and substantiates the half-wave potentials as: −0.52 v. and −1.48 v. for the two-step reduction of Cu(II). These values are in severe disagreement with the values reported[20] previously for Cu(II) in 0.1 *M* potassium thiocyanate, namely: −0.02 v. and −0.39 v.

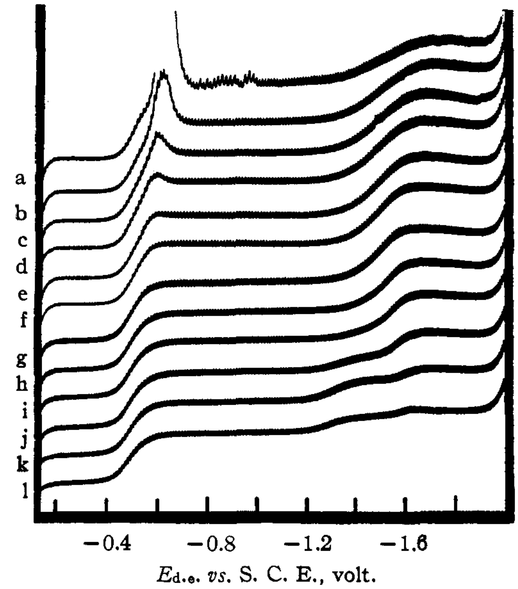

Fig. 10.—Typical polarogram of 0.004 *M* Cu(II) in 1 *M* potassium thiocyanate, effect of gelatin; *C*, % × 10^3: (a) 0, (b) 0.96, (c) 1.88, (d) 2.76, (e) 4.44, (f) 6.01, (g) 8.86, (h) 16.6, (i) 24.2, (j) 38.6, (k) 58.6, (l) 88.5.

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[20] Ref. 8, p. 279.

The new values are not due to impurities as evidenced by determinations at slightly higher concentrations of the same copper salt solution. In each case the height of both the Cu(II) and Cu(I) waves were equal.

The results here show that in any polarographic determination involving maxima, the influence of even exceedingly small concentrations of maxima suppressors should be known or tested. In general a concentration of maximum suppressor equal to the M.S.P. value is sufficient and any concentration above this value is likely to alter the half-wave potential and/or diffusion current. Conclusions reached in two recent investigations[21] do not seem warranted on the basis of the polarographic evidence presented here.

Cetyltrimethylammonium bromide and Triton X-100 are available commercially. Since their stock solutions do not decompose as do gelatin and agar, these materials are suggested as desirable suppressors in polarographic investigations.

Acknowledgment.—The author wishes to express his appreciation to Dr. L. Meites for the use of his polarographic equipment.

Summary

The critical concentration for micelle formation is shown to be identical with the concentration necessary to suppress maxima (M.S.P.). The great adsorptivity of the colloidal agents at concentrations corresponding to their M.S.P. values seems to account for the ability to suppress maxima by displacing the less actively adsorbed non-surface-active ions from the mercury drop surface.

Concentrations of maxima suppressors greater than the M.S.P. values can influence polarographic properties. Specific influences have been noted and discussed.

During the main investigation half-wave potential values for the two step reduction of Cu(II) in potassium thiocyanate, in severe disagreement with those previously reported, were noted.

NEW HAVEN, CONN. RECEIVED JUNE 15, 1949

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[21] (a) Buckley and Taylor, *J. Res. Natl. Bureau Standards*, **34**, 97(1945); (b) Coe and Rogers, THIS JOURNAL, **70**, 3276 (1948); (c) see published correspondence in this regard: Meites and Colichman, *Anal. Chem.*, **21**, 758 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Spectra of Some 2,4-Dinitrophenylhydrazones[1]

BY H. HARRY SZMANT AND HENRY J. PLANINSEK

The color of the 2,4-dinitrophenylhydrazones (DNPH) is thought[2,3] to be an indication of the degree of unsaturation present in the parent carbonyl compound. Since the characteristic behavior associated with unsaturation in organic compounds is caused by the presence of readily excited η electrons, it was of interest to us to observe a curious gradation of color in the DNPH of the *p*-acetyl derivatives of phenyl sulfide, sulfoxide and sulfone which were prepared in the course of another investigation.[4] In this paper we wish to report the results of the study of the absorption spectra in the ultraviolet and visible range of the above mentioned and several reference compounds.

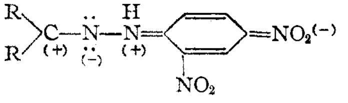
Experimental and Results

The DNPH were prepared by the customary method.[5] The compounds required repeated crystallizations until a constant melting point was obtained; toluene was the most favorable solvent from the viewpoint of solubility. In order to remove traces of toluene occluded in the crystals, the final products were recrystallized once from ethanol. It is probable that the low melting points of the DNPH as they are first obtained are due to the existence of geometrical isomers rather than to the presence of impurities (or starting materials). It can thus be assumed that repeated crystallizations simply serve to isolate the higher melting isomer.

The physical and spectral data are summarized in Table I. The absorption spectra reproduced in Figs. 1 and 2 were determined by means of a Beckman DU spectrophotometer using solutions containing approximately 10 mg. of the compound per liter of 95% ethanol.

Discussion

Braude and Jones[3] pointed out that the absorption spectrum of the DNPH of a carbonyl compound is more useful for the interpretation of the electronic nature of a given structure than that of the parent carbonyl compound. This is presumably the result of the polarizing effect of the 2,4-dinitrophenyl portion of the molecule on the residue of the carbonyl compound. This polarizing force dampens the various resonance possibilities in the carbonyl compound and causes an adjustment of the electron distribution around the polarized carbon-nitrogen double bond (I). In the DNPH of a simple ketone such



(I)

as acetone the maximum of 2,4-dinitrophenylhydrazine (352 mμ)[3] is displaced toward the visible (360 mμ).[2]

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[1] Presented in part before the Organic Division of the American Chemical Society, San Francisco, Calif., April, 1949.

[2] Roberts and Green, THIS JOURNAL, **68**, 214 (1946).

[3] Braude and Jones, *J. Chem. Soc.*, 498 (1945).

[4] Szmant and Palopoli, THIS JOURNAL, **72**, 1757 (1950).

[5] Shriner and Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.