[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, AND THE SCHOOL OF CHEMISTRY UNIVERSITY OF MINNESOTA]

The Induced Reduction at the Dropping Mercury Electrode of Colloidal Silver Bromide by Dicyanide Argentate(I) Ion

BY RICHARD C. BOWERS AND I. M. KOLTHOFF

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The dicyanide argentate(I) ion, in the absence of an excess of cyanide, produces a composite polarographic wave consisting of both an anodic and cathodic region. The cathodic wave results from the reduction of the complex ion to silver (amalgam) and cyanide ion and involves one electron. At potentials more positive than about −0.30 v. (*vs.* S.C.E.), the cyanide formed by the reduction gives rise to an anodic wave involving two electrons for the formation of mercuric cyanide. The observed anodic wave yields diffusion currents corresponding to the difference of the diffusion currents of the above two waves. In the presence of the dicyanide argentate(I) ion, colloidal silver bromide is kinetically reduced at the dropping mercury electrode. The complex ion is regenerated by a reaction between the cyanide formed by reduction and the colloidal silver bromide. The data are treated on the basis of the reaction layer concept as well as of the more rigorous treatment given by Delahay.[10] The value of the pseudo rate constant, which contains a term converting the molecular silver bromide concentration into a surface area, calculated by the two methods are in good agreement, an average value of 800 liters mole^{-1} sec.$^{-1}$ at 25° being derived.

Introduction

During the course of an investigation of the aging of colloidal silver bromide, it was found that the limiting reduction current of dicyanide argentate(I) ion at the dropping mercury electrode is increased markedly in the presence of colloidal silver bromide. This is attributed to an induced reduction of the colloidal silver bromide as a result of the occurrence of the following "chain reaction"

$$Ag(CN)_2^- + Hg + e \longrightarrow Ag(Hg) + 2CN^- \quad (1a)$$

$$AgBr_{(colloidal)} + 2CN^- \longrightarrow Ag(CN)_2^- + Br^- \quad (1b)$$

Many examples of kinetic currents have been reported in the literature,[1] however, to the authors' knowledge, this is the first example involving a heterogeneous chemical reaction. The present paper gives the results of a kinetic study of this induced reduction of silver bromide. In this connection, more detailed information on the polarographic behavior of dicyanide argentate(I) ion, first described by Saniger,[2] was desired.

Experimental

Potassium Dicyanide Argentate(I) Solutions.—Fresh stock solutions of this reagent were prepared daily from a 0.1000 *M* silver nitrate (reagent grade) and a 0.05 *M* potassium cyanide (C.P. grade) solution. The potassium cyanide was standardized with the silver nitrate solution by the method of Liebig and Deniges[3] and equivalent amounts of each solution mixed so that no excess cyanide would be present.

Colloidal Silver Bromide.—Fresh colloidal silver bromide was prepared by adding 10 ml. of 0.1000 *M* silver nitrate to 35 ml. of 0.03214 *M* potassium bromide, contained in a 50 or 100-ml. volumetric flask and diluting the solution to the mark. A dialyzed colloid was prepared by adding 200 ml. of 0.100 *M* silver nitrate to 700 ml. of 0.03214 *M* potassium bromide. After dialyzing for 40 hr., the colloid was diluted to one liter and the amount of solid silver bromide determined gravimetrically in an aliquot.

Solutions for Study of Induced Reduction of Silver Bromide.—These were prepared from stock potassium dicyanide argentate(I) and colloidal silver bromide solutions plus sufficient potassium nitrate to give a resultant concentration of 0.05 *M* in this electrolyte. Higher concentrations of supporting electrolyte could not be employed because of a slow flocculation of the colloid. In order to keep the effect of aging of silver bromide[4] to a minimum, the mixture of fresh colloid with dicyanide argentate was studied polarographically immediately after preparation. All solutions were deaerated with Linde H. P. nitrogen and maintained at 25 ± 0.1°.

Apparatus.—The capillaries employed in the construction of the dropping mercury electrode were all treated with silicone before use. If this was not done, a gradual increase in drop time was observed with continual usage in the presence of the colloid.

Current–potential curves were measured using either a Sargent Model XXI polarograph or a manual polarograph similar to that described by Lingane.[5]

Results and Discussion

Polarographic Behavior of the Dicyanide Argentate(I) Ion in the Absence of Colloidal Silver Bromide.—The dicyanide argentate(I) ion, in the absence of an excess of cyanide, was found to yield a composite polarographic wave having both an anodic and cathodic region. As reported by Saniger,[2] with solutions 5×10^{-4} *M* and less in $Ag(CN)_2^-$, the wave is well defined but at higher concentrations a maximum is observed on the cathodic portion of the wave (Fig. 1). The cathodic and anodic limiting currents are equal in magnitude and directly proportional to the concentration of the dicyanide argentate(I) ion. The cathodic reaction is represented by

$$Ag(CN)_2^- + Hg + e \longrightarrow Ag(Hg) + 2CN^- \quad (2)$$

The cyanide ion formed gives rise to an anodic current according to the reaction

$$Hg + 2CN^- \longrightarrow Hg(CN)_2 + 2e \quad (3)$$

and the anodic wave observed corresponds to the sum of reactions 2 and 3 and is represented by the over-all reaction

$$Ag(CN)_2^- + 2Hg \longrightarrow Ag(Hg) + Hg(CN)_2 + e \quad (4)$$

The height of the cathodic part of the composite wave is equal to that of the anodic part as would be predicted from equations 2 and 4. This composite wave is unique in its kind as the cathodic part corresponds to quite a different reaction than the anodic part. The zero current potential is a typical mixed potential.[6] The cathodic wave can-

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[1] See for example, P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter 5.

[2] E. B. Saniger, *Rec. trav. chim.*, **44**, 549 (1925).

[3] See I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p. 282.

[4] I. M. Kolthoff and R. C. Bowers, THIS JOURNAL, **76**, 1503 (1954).

[5] J. J. Lingane, *Anal. Chem.*, **21**, 47 (1947).

[6] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed. Interscience Publishers, Inc., New York, N. Y., 1952, p. 116.

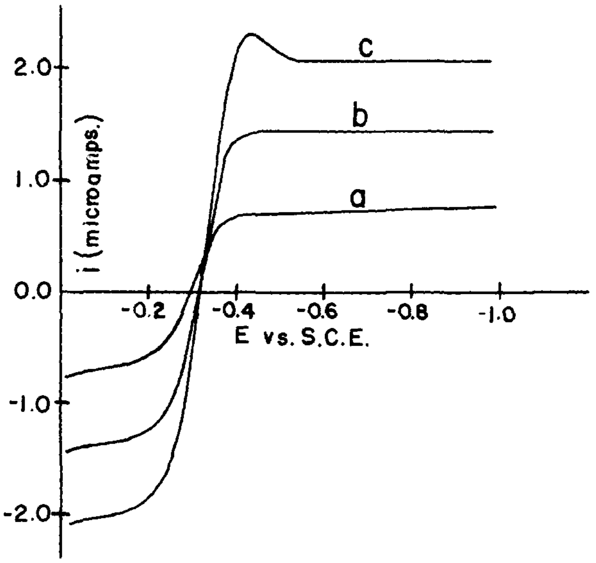

Fig. 1.—Polarographic waves of the dicyanide argentate(I) ion; supporting electrolyte 0.05 M KNO_3 and 0.0025 M KBr: (a) 2.04×10^{-4} M; (b) 4.09×10^{-4} M; (c) 6.13×10^{-4} M.

not appear at a more positive potential because of the simultaneous occurrence of anodic reaction 3. It is planned to study the composite wave in well buffered solutions. For our purposes some characteristics of the composite wave are summarized in Table I.

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF THE DICYANIDE ARGENTATE(I) ION

(Supporting electrolyte 0.05 M in potassium nitrate and 0.0025 M in potassium bromide)

$C_{(AgCN)_2^-}$ (mM)	$(i_d)_c{}^c$	$-(i_d)_a{}^c$	$I = \frac{i_d}{Cm^{2/3}t^{1/6}}$	$-E_{1/2}$ vs. S.C.E.
0.0658[b]	0.31	0.31	2.20	0.272
.102[a]	.33	.32	2.24	.282
.161[b]	.80	.80	2.32	.295
.204[a]	.68	.67	2.34	.300
.307[a]	1.00	1.00	2.29	.306
.312[b]	1.54	1.54	2.30	.309
.409[a]	1.37	1.34	2.34	.317
.511[a]	1.70	1.64	2.30	.319
.588[b]	2.85	2.87	2.28	.325
.613[a]	2.06	2.06	2.36	...
1.05[b]	5.06	5.15	2.27	.336

[a] t = 5.19 sec.; m = 1.126 mg./sec. [b] t = 4.62 sec.; m = 2.140 mg./sec. [c] Corrected for residual current.

From the average value of 2.29 for the diffusion current constant, the diffusion coefficient of dicyanide argentate(I) ion is calculated to be 1.42×10^{-5} cm.^{2}/sec. The half-wave potential (zero current potential) is dependent upon the concentration of $Ag(CN)_2^-$ and varies between −0.27 and −0.34 volt *vs.* S.C.E. This is in agreement with Saniger[2] who observed a half-wave potential of about −0.30 volt *vs.* S.C.E.

Polarographic Behavior of Colloidal Silver Bromide in the Absence of the Dicyanide Argentate(I) Ion.—Colloidal silver bromide, containing an excess of alkali bromide, shows a peculiar and poorly reproducible behavior at the dropping mercury electrode. When the silver bromide concentration in a freshly prepared suspension is greater than about 5×10^{-3} M, a reduction wave is observed which starts at about −0.10 volt *vs.* S.C.E. The resulting current-potential curves are essentially straight lines of a slope governed by the iR drop (Fig. 2). The current increases to a maximum and then drops abruptly to zero. However, the potential at maximum current and this current are not well reproducible. Recently Micka[7] has reported a similar depolarizaion of the dropping mercury electrode in stirred suspensions of freshly precipitated metal sulfides and other precipitates.

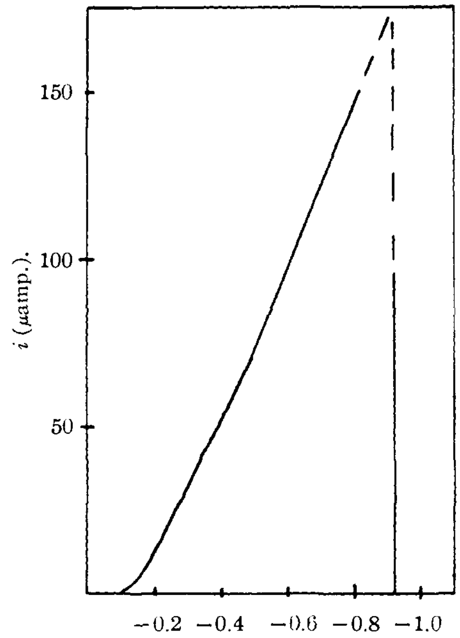

Fig. 2.—Depolarization of dropping mercury electrode in 0.020 M colloidal silver bromide. (Potential not corrected for iR drop.)

The abrupt drop of the current occurs at a potential (corrected for iR) close to that at the electrocapillary maximum. The excess of bromide in the silver bromide sol displaces the isoelectric point to more negative potentials. A film formation of silver bromide, upon collision of the negative colloid with the surface of the dropping mercury, will be facilitated by a positive charge of the mercury. Apparently, only extremely small particles can cause the formation of a film. An aged silver bromide sol of the same concentration as a fresh sol did not depolarize cathodically the dropping mercury electrode. In this connection, it is of interest to mention that a platinum wire electrode becomes coated with a film of silver bromide when it is placed into a silver bromide sol.[8] Addition of a surface-active substance like gelatin prevents this coating. We find that the presence of such negatively charged surface-active substances as wool violet 6BN and sodium dodecane sulfate prevents the cathodic depolarization of the dropping mer-

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[7] K. Micka, *Chem. Listy*, **49**, 1144 (1955); **51**, 223 (1957); *Collection Czechoslov. Communs.*, **22**, 1400 (1957).

[8] I. M. Kolthoff and J. T. Stock, *The Analyst*, **80**, 860 (1955).

cury in a silver bromide sol. The effect of positively charged surface-active substances could not be tested because of the flocculation of the colloid.

Induced Reduction of Colloidal Silver Bromide in the Presence of the Dicyanide Argentate(I) Ion.—The enhancement of the cathodic limiting current of the dicyanide argentate(I) ion in the presence of colloidal silver bromide is attributed to the regeneration of $Ag(CN)_2^-$ at the electrode surface according to reaction scheme 1. The induced current is kinetic in nature and its magnitude is expected to be a function of the rate of the regeneration reaction. This in turn will be a function of the cyanide ion concentration at the electrode surface and of the magnitude of the surface of silver bromide available in the reaction layer. Thus the induced current is expected to depend on the particle size and number of particles. Assuming that the diffusion coefficients of the cyanide ion and the dicyanide argentate(I) ion are equal, the concentration of the cyanide, formed according to equation 1a, at the surface of the electrode should be equal to double the bulk concentration of dicyanide argentate. The order in cyanide ion of the heterogeneous reaction will thus be reflected by the dependence of the kinetic current on the dicyanide argentate(I) ion concentration in the body of the solution.

At low concentrations of $Ag(CN)_2^-$ (less than 1×10^{-4} M), the kinetic current is very nearly directly proportional to the bulk concentration of this species. For example, with a 0.0192 M fresh silver bromide sol, 0.0166, 0.0331, 0.0659 and 0.0981 millimolar in dicyanide argentate(I) ion, the values found for $i_k/[Ag(CN)_2^-]_b$ were 76, 81, 85 and 76, respectively. However, a considerable deviation from linearity is observed at higher concentrations of $Ag(CN)_2^-$ (Fig. 3). In order to eliminate the cathodic depolarization of the mercury by the higher concentrations of fresh silver bromide sol (curve a), the solutions were made up to contain 0.04 mg./ml. wool violet 6BN. The results at concentrations of less than 10^{-4} M suggest that the rate of dissolution of the colloid (reaction 1b) is first order in cyanide ion concentration, the deviation at larger concentrations arising from a depletion of the colloid at the electrode surface.

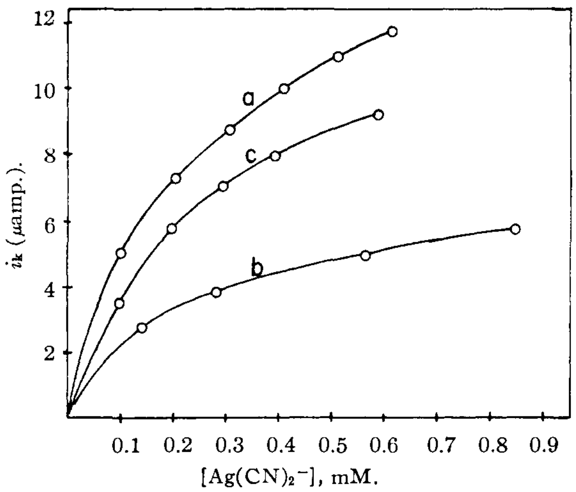

Fig. 3.—Dependence of kinetic current on the concentration of dicyanide argentate(I) ion: (a) fresh colloid, $[AgBr]_b = 0.0196$ M, 0.04 mg./ml. wool violet; (b) fresh colloid, $[AgBr]_b = 0.00250$ M, no wool violet; (c) dialyzed colloid, $[AgBr]_b = 0.0189$ M, no wool violet.

Brdicka and K. Wiesner[9] were the first to give a treatment of a kinetic current involving a chemical reaction in a homogeneous medium. Their treatment is based on the concept of a reaction layer in which the chemical reaction is assumed to take place. More exact treatments of kinetic currents arising from regeneration reactions have been given by Delahay and Stiehl[10] and Koutecky.[11] The former authors adapted a treatment of the boundary value problem for linear diffusion to the dropping mercury electrode whereas the latter solved the boundary value problem for spherical diffusion at the dropping mercury electrode. In both of these treatments the concentration at the electrode surface of the species undergoing an induced reduction can be taken equal to its bulk concentration. In our case, the more rigorous equations cannot be applied except at very low concentrations of $Ag(CN)_2^-$, since a depletion of the colloid at higher concentrations is observed.

Empirically, it has been found that the dependence of the kinetic current upon the $Ag(CN)_2^-$ concentration can be expressed very nearly by

$$\frac{[Ag(CN)_2^-]_b}{i_k} = \frac{1}{\alpha} + \frac{[Ag(CN)_2^-]_b}{\beta} \qquad (5)$$

the subscript b denoting bulk concentration. Typical plots of $[Ag(CN)_2^-]_b/i_k$ *vs.* $[Ag(CN)_2^-]_b$ are shown in Fig. 4.

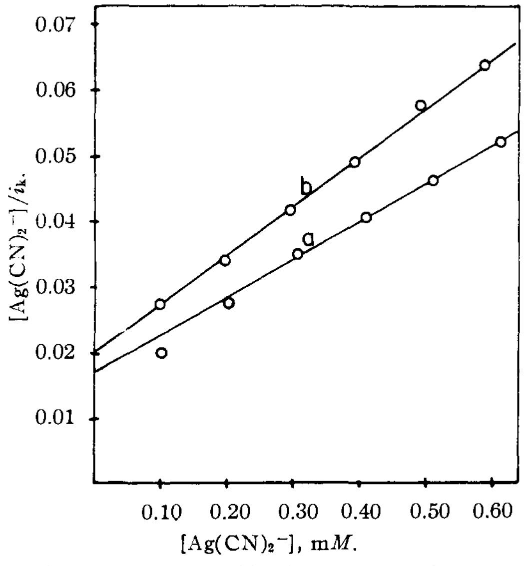

Fig. 4.—Dependence of kinetic current on the concentration of dicyanide argentate(I) ion according to equation 5: (a) fresh colloid, $[AgBr]_b = 0.0196$ M, 0.04 mg./ml. wool violet; (b) dialyzed colloid, $[AgBr]_b = 0.0189$ M, no wool violet.

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[9] R. Brdicka and K. Wiesner, *Collection Czechoslov Chem. Communs.*, **12**, 39 (1949).

[10] P. Delahay and G. L. Stiehl, THIS JOURNAL, **74**, 3500 (1952).

[11] J. Koutecky, *Chem. Listy*, **47**, 9 (1953); *Collection Czechoslov. Chem. Communs.*, **18**, 311 (1953).

These plots allow an extrapolation of $[\mathrm{Ag(CN)_2^-}]_b/\bar{i}_k$ to infinite dilution where the more rigorous treatments are valid. According to Delahay's treatment, at large values of k_zC_z, the time average catalytic current at infinite dilution becomes

$$\bar{i}_k = 753nm^{2/3}\tau^{2/3}D^{1/2}C_A\,(2k_zC_z)^{1/2} \quad (6)$$

where the current is in microamp., n is the number of electrons involved in the electrode reaction, m is the rate of flow of mercury in mg./sec., τ is the drop time in seconds, D is the diffusion coefficient of the dicyanide argentate(I) ion in cm.^{2}/sec., C_A is the bulk concentration of $\mathrm{Ag(CN)_2^-}$ in mmoles/l., C_z is the bulk molar concentration of suspended silver bromide and k_z is the pseudo rate constant. This implies that the value of k_z derived from experimental data includes a proportionality constant which is expected to be different for different sols. Equation 6 differs from the one given by Delahay[10] by the factor square root of two. This term arises in our case because two cyanide ions are formed from the reduction of one dicyanide argentate(I) ion. In the reaction scheme considered by Delahay there was a one to one ratio of reduced to oxidized species.

Since equation 6 is valid at infinite dilution, the value of α (determined by graphical extrapolation) can be expressed by

$$\alpha = 1065m^{2/3}\tau^{2/3}D^{1/2}(k_zC_z)^{1/2} \quad (7)$$

The form of equation 5 is also in accord with a treatment based on the reaction layer concept. In this treatment it is assumed that a preferential complete dissolution of individual particles of silver bromide occurs. Thus there is a decrease in the number of colloid particles rather than in the size of the particles. This dissolution may involve the smallest particles only. Furthermore it is probable that the rate of replenishment of the colloid *via* diffusion from the bulk of the solution is slow and this will be neglected. Under these conditions, the instantaneous concentration of the colloid in the reaction layer is given by

$$C_z = C^0_z - \frac{\int_0^t i_k\mathrm{d}t}{nFA\mu \times 10^3} \quad (8)$$

where C_z^0 is the bulk concentration of the silver bromide colloid expressed in moles/liter, A is the area of the mercury drop, μ is the reaction layer thickness and i_k the instantaneous current. Actually we have used the average current in the calculations. Although this approximation introduces an error, the calculated rate constants are of the correct order of magnitude. Application of the reaction layer concept then yields

$$i_k = 2FA\mu k_z[\mathrm{Ag(CN)_2^-}]_b\left[C^0_z - \frac{\bar{i}_k t}{FA\mu \times 10^3}\right] \quad (9)$$

and the time average current is

$$\bar{i}_k = 2F\bar{A}\mu k_z[\mathrm{Ag(CN)_2^-}]_b\left[C^0_z - \frac{k_z[\mathrm{Ag(CN)_2^-}]_b\tau\bar{i}_k}{10^{+3}}\right] \quad (10)$$

Rearrangement of equation 10 then yields

$$\frac{[\mathrm{Ag(CN)_2^-}]_b}{\bar{i}_k} = \frac{1}{2F\bar{A}\mu k_zC_z^0} - \frac{[\mathrm{Ag(CN)_2^-}]_b\tau}{2F\bar{A}\mu \times 10^{+3}C_z^0} \quad (11)$$

A comparison of equations 5 and 11 indicates that

$$\alpha = 2F\bar{A}\mu k_zC^0_z \quad (12)$$

$$\beta = 2F\bar{A}\mu \times 10^3C^0_z/\tau \quad (13)$$

and

$$k_z = \alpha \times 10^3/\beta\tau \quad (14)$$

Values of α and β obtained from the plots of $[\mathrm{Ag(CN)_2^-}]_b/\bar{i}_k$ *vs.* $[\mathrm{Ag(CN)_2^-}]_b$ as well as values of k_z calculated by the two different methods are given in Table II.

TABLE II

VALUES OF α, β AND k_z

System	m	τ	α	β	k_z (l./mole sec.) Eq. 14	Eq. 7
Fresh colloid (0.04 mg./ml. W. V.)	1.126	5.10	60.3	17.1	690	1130
Fresh colloid (no W. V.)	2.17	4.08	24.4	8.13	740	810
Dialyzed colloid (no W. V.)	1.126	5.10	51.0	12.9	780	840

The values of the pseudo rate constant from the two different treatments are in good agreement, especially in view of the approximations involved in the reaction layer concept treatment.

A comparison of equation 6 to the fundamental reaction layer concept equation 9, gives for the reaction layer thickness

$$\mu = 1.08 \times 10^{-2}\sqrt{D/k_zC_z} \quad (15)$$

The value of μ can also be calculated from the value of β (equation 13). A comparison of the reaction layer thickness calculated by the two different equations is shown in Table III.

TABLE III

System	[AgBr] (moles/l.)	μ (cm.) Eq. 13	Eq. 15[a]
Fresh colloid	0.0196	1.4×10^{-5}	0.87×10^{-5}
Fresh colloid	.00250	3.1×10^{-5}	2.9×10^{-5}
Dialyzed colloid	.0189	1.1×10^{-5}	1.0×10^{-5}

[a] k_z from Delahay's treatment used in calculation.

In the plot of $[\mathrm{Ag(CN)_2^-}]_b/\bar{i}_k$ *vs.* $[\mathrm{Sg(CN)_2^-}]_b$ in Fig. 4, the first point obtained with the fresh colloid (curve a) deviates slightly from the straight line. This may be due to the inherent inadequacy of the reaction layer concept or to the assumptions made in the derivation of equation 10. However, in view of the excellent straight line plot of the data obtained with the dialyzed colloid, it is felt that the deviation observed with the fresh colloid may be due to a very rapid Ostwald ripening of the fresh colloid in the presence of $\mathrm{Ag(CN)_2^-}$ during the period in which the experiments were run.[4] This explanation becomes more plausible when it is realized that the experiments were carried out by adding increasing amounts of $\mathrm{Ag(CN)_2^-}$ to the colloid, such that a considerable aging must have occurred before the measurements at the higher concentrations were made.

The value of the pseudo rate constant k_z obtained for the fresh colloid, is expected to be considerably larger than that for the dialyzed colloid because of the larger specific surface of the former. This was not observed however. Due to the aging which occurs, the particles in the fresh colloid may actually have grown almost to their ultimate size during the period of deaeration and current measurement. In particular this is expected in the case of the more dilute colloid system since fairly large concentrations of $Ag(CN)_2^-$ were employed in these experiments. In the experiments with the more concentrated fresh colloid, a small amount of wool violet was added. This dye is adsorbed on the surface of the colloid particles thereby decreasing the magnitude of the surface available for the reaction. This would also be expected to lead to smaller values for k_z. Saturation of the surface with wool violet eliminates completely the kinetic current. This effect is illustrated in Table IV.

TABLE IV

EFFECT OF WOOL VIOLET 6BN ON THE KINETIC CURRENT

0.0198 M AgBr; 0.204×10^{-3} M $Ag(CN)_2^-$

Added wool violet (mg./ml.)	i_k (μamp.)
0.020	7.88
.040	7.55
.100	5.70
.200	0.30
.400	0.00

At a level of 0.04 mg./ml. wool violet, the effect is small but not insignificant and would account in part for the unexpected agreement of the values of k_z for the more concentrated fresh colloid and the dialyzed colloid.

It is of interest to calculate an approximate value for the heterogeneous rate constant from the derived value of the pseudo rate constant and the specific surface of the dialyzed colloid. The experimentally derived rate constant is related to the heterogeneous rate constant k_h by the equation

$$1000k_z = k_hA \qquad (16)$$

Kolthoff and Bowers[4] found, from radioactive bromide exchange experiments, that 5% of the silver bromide in a dialyzed colloid is present in the surface. Using this value and taking the thickness of one layer of silver bromide as 2.9 Å., values of 5.1×10^7 cm.^{2}/mole for the surface area of the dialyzed colloid and 1.6×10^{-2} cm./sec. for the heterogeneous rate constant are obtained.

Dependence of the Kinetic Current on the Height of Mercury.—At low ratios of dicyanide argentate-(I) to colloidal silver bromide, the kinetic current was found to be independent of the head of mercury. However, as the ratio was increased, a large dependence was observed. Since α, according to either the reaction layer concept or the more rigorous equation, is independent of h whereas β, according to the assumptions made in the derivation of equation 10, is directly proportional to the height of mercury, these observations are in qualitative agreement with the theory presented. Values of β, as a function of h, can be calculated from the currents obtained at various heights of mercury by making use of equation 5 and assuming α to be constant. When this was done and plots of log h *vs.* log β made, straight lines having the slopes indicated in Table V were obtained.

TABLE V

VALUES OF Δ LOG h/Δ LOG β

System	$[Ag(CN)_2^-]$ (mmoles/l.)	[AgBr] (moles/l.)	α	$\frac{\Delta \log h}{\Delta \log \beta}$
Fresh colloid	0.307	0.0196	60.3	0.95
Fresh colloid	.565	.00250	24.4	1.10
Dialyzed colloid	.588	.0189	51.0	0.97

These results are in good agreement with the assumptions made in the derivation of equation 10.

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MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Voltammetric Membrane Electrodes. II. Current–Potential Curves of Reversible and Irreversible Electrode Processes[1]

BY RICHARD C. BOWERS AND ARTHUR M. WILSON[2]

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Current–potential curves for reversible and irreversible electrode processes, at the voltammetric mercury membrane electrode (V.M.M.E.), are quantitatively interpreted by assuming that a linear concentration gradient is established fairly rapidly within the membrane diffusion layer. Experimental results for the reduction of thallous and nickel ion and for the reduction and oxidation of the *p*-benzoquinone–hydroquinone couple are given. The criteria of reversibility at membrane electrodes are discussed.

Introduction

In a previous publication,[3] it was pointed out that the limiting currents observed at a voltammetric membrane electrode indicate that the membrane provides a well-defined diffusion layer when the electrode is placed in a stirred solution. Due to the finite thickness of the membrane, a linear concentration gradient within the membrane is established fairly rapidly. Current–potential curve equations derived on the basis of the Nernst diffusion layer concept[4] are therefore expected to be quantitatively obeyed at this type electrode. The present paper presents a theoretical treatment, based on this concept; and an experimental study of current–potential curves for reversible and irreversible processes occurring at the voltammetric mercury membrane electrode (V.M.M.E.).

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(1) Based on the dissertation of Arthur M. Wilson in partial fulfillment of the requirements for the Doctor of Philosophy, 1958.

(2) Toni-Gillette Fellow, 1956–1957; Du Pont Teaching Fellow; 1957–1958.

(3) R. C. Bowers and A. M. Wilson, THIS JOURNAL, **80**, 2968 (1958).

(4) W. Nernst, *Z. physik. Chem.*, **47**, 52 (1904).