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

Studies on Aging and Coprecipitation. XLV. The Irreversible Flocculation of Colloidal Silver Bromide and the Aging in the Flocculated State[1]

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The specific surface of the particles during flocculation of freshly prepared silver bromide colloid decreases very markedly (about 10 times). The flocculation of a few weeks old dialyzed colloidal silver bromide suspension is accompanied by a considerably smaller decrease of the specific surface. Cementing of the particles in the floc occurs, but no subsequent fusion. Under the experimental conditions there was no indication of Ostwald ripening during and after the flocculation of fresh and aged (dialyzed) colloidal solutions. Exchange between radioactive bromide and freshly flocculated silver bromide is very rapid and highly heterogeneous. The extent of this exchange decreases upon aging of the flocs and is considerably greater in flocs prepared from fresh colloids than in those prepared from aged dialyzed colloids. The decrease in the specific surface in flocs from fresh and dialyzed colloids and also the rate of exchange with r.a. bromide are accounted for by the Schottky defects. The primary particles of a fresh colloid are so small that Schottky defects extend throughout the particles; they account for the great thermal mobility of silver bromide in the fresh floc, resulting in cementing and fusion of the particles. In the dialyzed colloid the Schottky defects extend only to about six surface layers; upon flocculation cementing but no fusion of particles occur. Electron micrographs substantiate the interpretation of the irreversible flocculation of colloidal silver bromide.

In a previous paper[2] it was found that flocculation of a freshly prepared silver bromide colloidal suspension is accompanied by a tremendous decrease of the adsorption of wool violet of the order of 20 times. If no "aging" took place upon flocculation the wool violet adsorption, which is proportional to the specific surface, should be the same as before flocculation. It is shown in the present paper that the decrease in specific surface during flocculation is due to a cementing and fusing together of the primary particles, the flocculation of silver bromide being an irreversible process.

Experimental

The "aging" during and after flocculation of fresh, aged and of dialyzed colloidal suspensions has been studied by similar techniques as have been applied previously.[2] For a detailed description of some modifications of these techniques reference is made to the thesis of the junior author.[3] The methods of preparation of the colloidal suspensions have been reported.[2] After addition of flocculating agent, the suspension was aged by allowing it either to be shaken, stirred or to stand. In a few experiments, the flocculated silver bromide was centrifuged for a few minutes, the supernatant liquid poured off and the precipitate washed several times with the aging medium to be used before being suspended in it. In some instances (aging in alcohol and benzene) the aging medium was removed by suitable washing before the adsorption of wool violet was determined.

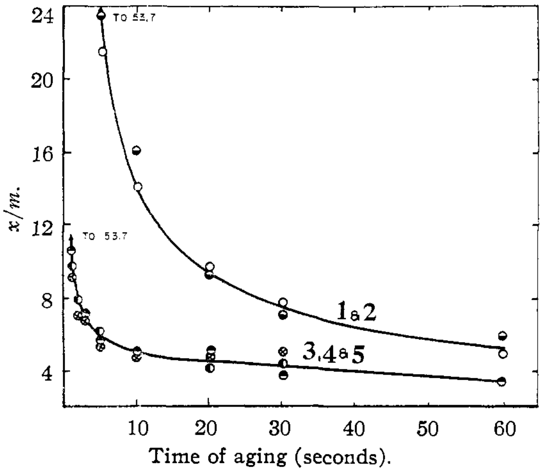

Fig. 1.—Effect of KCN and KBr concentration on aging after flocculation of fresh (1 minute old) silver bromide colloid; flocculated with KNO_3: 1, 0.00227 *M* in KBr, 0.100 *M* in KNO_3 -○-; 2, 0.00227 *M* in KBr, 1.0×10^{-4} *M* in KCN, 0.100 *M* in KNO_3 -◒-; 3, 0.00227 *M* in KBr, 0.118 *M* in KNO_3 -◓-; 4, 0.00227 *M* in KBr, 1.0×10^{-4} *M* in KCN, 0.118 *M* in KNO_3 -⊗-; 5, 0.0224 *M* in KBr, 0.118 *M* in KNO_3 -◐-.

It was found desirable to determine the extent of aging during the first few seconds after adding flocculating agent. This was accomplished by adding the flocculating agent and the wool violet or r.a. bromide solutions by means of calibrated hypodermic syringes. The suspensions were continually stirred during these operations by means of a motor driven glass stirring rod rotating at 700 r.p.m.

Results

A. Change of Specific Surface (Wool Violet Absorption).—Effects of bromide concentration, small concentrations of cyanide and other factors on change of specific surface after flocculation are described below.

(a) **Fresh Colloid.**—The change of specific surface as measured by wool violet adsorption was determined during the first 60 seconds after the addition of flocculating electrolyte. The results are shown in Fig. 1. The bromide concentration and presence of cyanide have no effect on the decrease in specific surface after flocculation. The decrease of specific surface upon longer periods of aging (not shown in Fig. 1) was relatively small and practically the same in 0.1 and 0.2 *M* potassium nitrate. Also shaking promoted the aging only slightly. For example, in 0.2 *M* potassium nitrate, x/m (adsorbed wool violet in mg./g.) was 3.0 after 5 minutes, 1.7 after 1 hour, 0.7 after 1 day and 0.5 after 7 days.

(b) **Preaged Dialyzed Colloid.**—This colloid was prepared by method II[2] and was 2 weeks old when flocculated. x/m was 11.4 mg. wool violet per gram prior to flocculation. The adsorption of wool violet during the first few minutes after flocculation is given in Fig. 2. For comparison, results obtained with a freshly prepared colloid are given in curve 1. Similar curves during the first 24 hours after flocculation are given in Fig. 3.

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(1) This investigation was supported by a research grant from the Office of Ordnance Research.

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

(3) R. C. Bowers, Ph.D. Thesis, University of Minnesota, 1953.

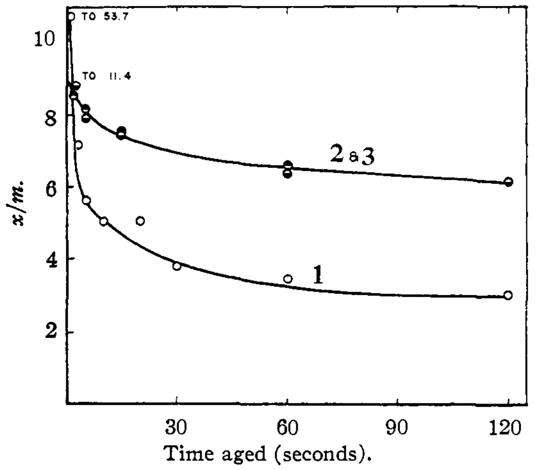

Fig. 2.—Decrease in specific surface during the first two minutes after flocculation. Suspensions were 0.150 *M* in KNO_3, 0.0023 *M* in KBr: 1, fresh colloid -○-; 2, dialyzed colloid 2 weeks old -◒-; 3, as 2 but 1.0 × 10^{-4} *M* in KCN -◓-.

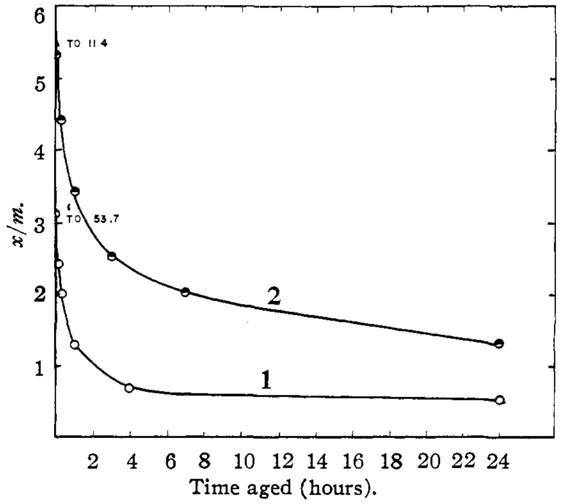

Fig. 3.—Decrease in specific surface during 24 hours after flocculation. Suspensions were 0.150 *M* in KNO_3, 0.0023 *M* in KBr: 1, fresh colloid -○-; 2, dialyzed colloid 2 weeks old -◓-; identical results as shown in curve 2 obtained when dialyzed colloid was made 1.0 × 10^{-4} *M* in KCN.

Shaking of the suspensions promoted the aging as compared to standing, the least aging being found when the precipitate was allowed to stand after centrifuging. The effects are relatively small but reproducible and are illustrated in Fig. 4, where some results obtained after flocculation of a dialyzed, two days old colloid are given.

A comparison was made of the rate of decrease of specific surface of a flocculated 2-days old dialyzed colloid when the floc was allowed to stand in different aging media. Immediately after flocculation the suspension was centrifuged, the supernatant liquid poured off and the precipitate washed twice with the proper aging medium. Results are given in Fig. 5.

Experiments were also carried out in benzene as an aging medium. After aging, the benzene was poured off, the precipitate washed twice with absolute ethanol, once with water and then the wool violet adsorption determined. Adsorption equilibrium was attained extremely slowly after this treatment of the precipitate; apparently benzene is adsorbed on the precipitate and is very slowly replaced by dye. After 27 hours of shaking, equilibrium appeared to have been established. No apparent change of specific surface was observed after allowing the flocculated silver bromide to stand 3 days in benzene.

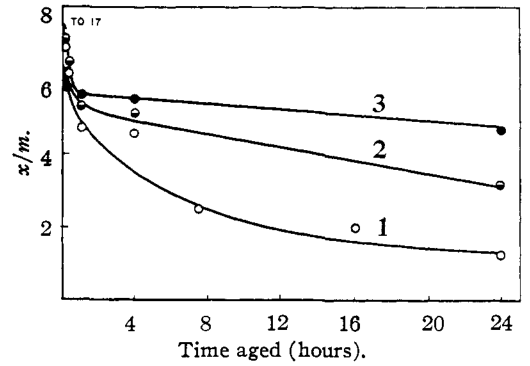

Fig. 4.—Decrease in specific surface of dialyzed 2-day old colloid after flocculation with KNO_3: 1, shaken; 2, standing; 3, centrifuged.

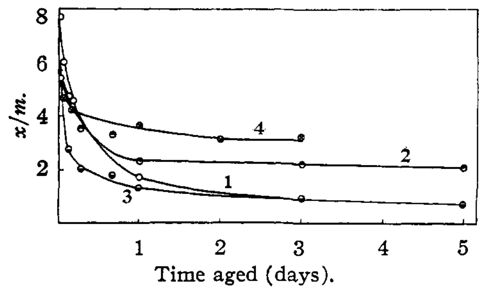

Fig. 5.—Decrease in specific surface of dialyzed 2-day old colloid after flocculation: 1, aged in mother liquor, 0.22 *M* in KNO_3, 0.00225 *M* in KBr; 2, aged in pure water; 3, aged in absolute ethanol, 0.0025 *M* in KBr; 4, aged in absolute ethanol, no KBr present.

B. Exchange Experiments with Radioactive Bromide.—Colloidal suspensions of silver bromide were prepared by both methods I and II.[2] Those prepared by method I were flocculated one minute after their formation with potassium nitrate (final concentration 0.120 *M*) and aged with shaking for various periods of time before the r.a. bromide experiments were made. The penetration of r.a. bromide was also determined after flocculating 50-ml. samples of 2-weeks old dialyzed colloid with potassium nitrate (final concentration 0.116 *M*) and aging with shaking. Exchange experiments were also made in the presence of wool violet to determine the percentage surface of some of the flocculated precipitates of silver bromide while one experiment was run to determine the effect of solvent (ethanol *vs.* water) on the extent of the exchange between r.a. bromide and flocculated silver bromide.

(a) Fresh Colloid.—Some representative results are given in Fig. 6.

The heterogeneous distribution of the bromide

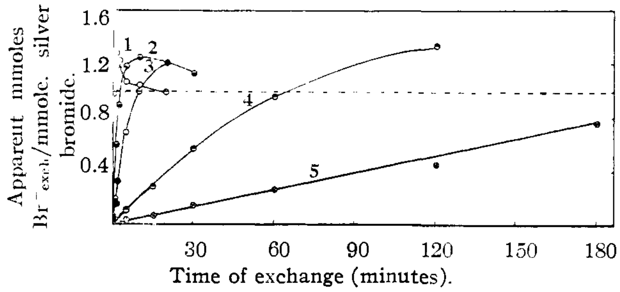

Fig. 6.—Exchange between r.a. bromide and flocculated silver bromide (from fresh colloid): 1, 5 seconds; 2, 15 seconds; 3, 1 minute; 4, 15 minutes; 5, 1 hour after flocculation.

between solution and the fresh floc (1 minute or less after flocculation) is quite evident from the maxima in curves 1, 2 and 3. With the fresh floc (curve 1) 100% apparent exchange was attained upon longer shaking after the maximum was observed. A small concentration of cyanide had no effect on the rate of exchange as illustrated in Fig. 7. When the experiment was repeated using a precipitate one hour after flocculation, again no effect of cyanide was observed. Increasing the bromide concentration decreased the observed rate of exchange. The effect is mainly apparent and due to a less heterogeneous primary distribution than at lower bromide concentrations. Partly the effect is explained by an increased rate of aging of the precipitate at higher bromide concentrations.

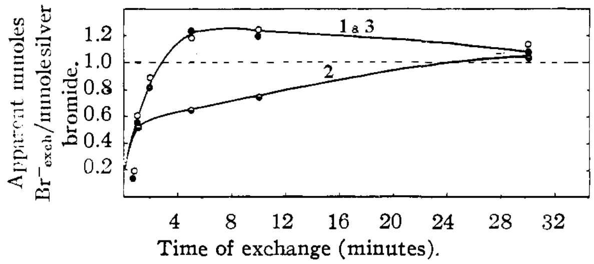

Fig. 7.—Effect of KCN and concentration of KBr on rate of penetration of r.a. bromide into flocculated silver bromide (from fresh colloid) 15 seconds after flocculation: 1, 0.00227 *M* in KBr; 2, 0.0205 *M* in KBr; 3, 0.00227 *M* in KBr, 1.0 × 10^{-4} *M* in KCN.

The specific surface was measured by determining the equilibrium distribution of r.a. bromide on a wool violet coated precipitate 1 and 60 minutes after flocculation. The extrapolated value for the precipitate 1 minute after flocculation corresponded to 2.0% and of the 60 minutes old precipitate to 1.2% surface.

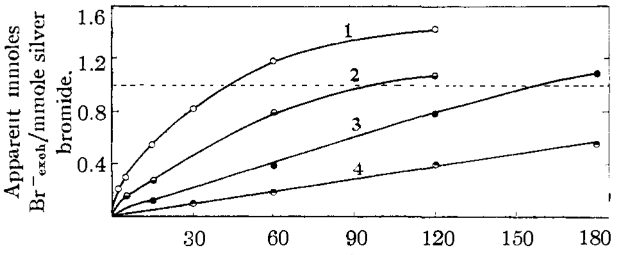

Fig. 8.—Exchange between r.a. bromide and flocculated silver bromide (from 2-week old dialyzed colloid): 1, 15 seconds; 2, 1 minute; 3, 15 minutes; 4, 1 hour after flocculation.

(b) **Dialyzed Colloid (2 Weeks Old).**—Some results of exchange experiments are given in Fig. 8. Experiments carried out in the presence of 10^{-4} *M* cyanide again had no effect on the rate of penetration. An increase of the bromide concentration in the supernatant liquid again decreased the rate of apparent exchange as had been found with flocs prepared from fresh colloid.

The rate of exchange was compared in aqueous and ethanol media. The colloid was flocculated, centrifuged and the supernatant liquid poured off. The precipitate was then shaken with a 0.018 *M* r.a. bromide solution either in water or in 91% ethanol. In both experiments, the precipitate was 15 minutes old after flocculation and the same amounts of precipitate and solution were used. As is seen from Fig. 9, the rate of apparent exchange is much greater in alcohol than in water.

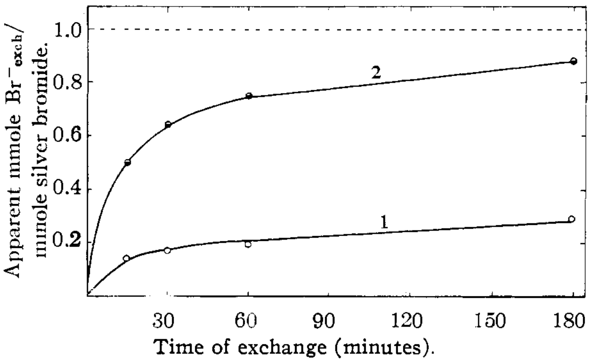

Fig. 9.—Exchange between r.a. bromide and flocculated silver bromide (from 2-weeks old dialyzed colloid) 15 minutes after flocculation: 1, in water; 2, in ethanol.

The specific surface of the freshly flocculated precipitates was determined by the r.a. method in the presence of wool violet. By extrapolation it was found that 1 minute after flocculation 2.7% of the precipitate consisted of surface.

C. **Electron Micrographs.**—Figure 10 is a picture of the particles present 10 seconds after flocculation of a fresh colloid. In addition to agglomerates, primary particles are still recognizable. These primary particles disappear rapidly while the size of the flocs increases on aging, as is evident from Fig. 11.

For comparison with the flocculated particles, the size of the primary particles in a 3 weeks old (dialyzed) colloid is shown in Fig. 12. Many primary particles are still recognizable in the fresh floc prepared from dialyzed 2 weeks old colloid (Figs. 13 and 14).

The size of the individual particles, making up the agglomerate increases upon further aging—as is seen from a comparison of Figs. 13 and 15.

Discussion

When a freshly prepared colloidal suspension of silver bromide is flocculated the specific surface (expressed in mg. wool violet adsorbed per gram of silver bromide) was found to decrease from about 54 to about 5.0 (10 seconds after flocculation), or by a

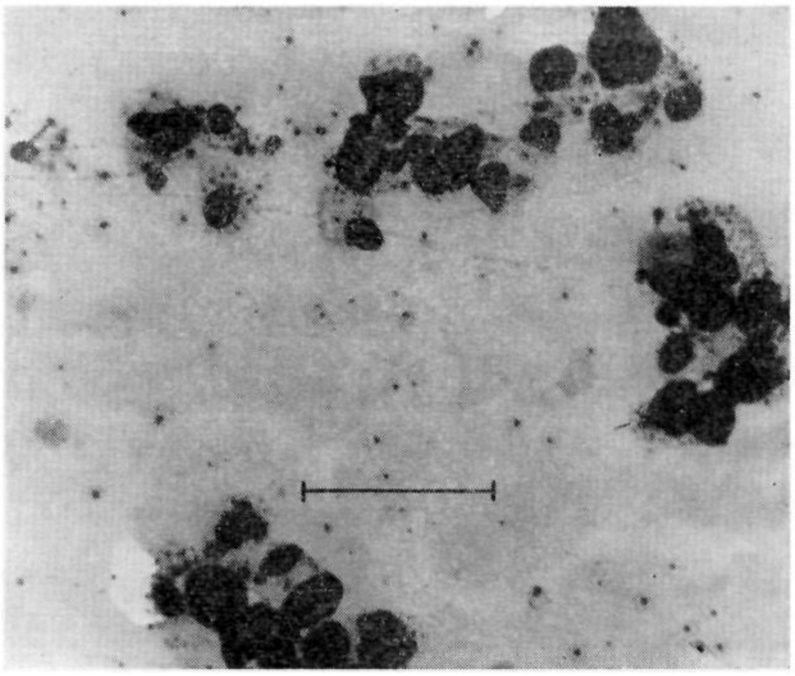

Fig. 10.—Agglomerates and primary particles present in flocculated silver bromide (from fresh colloid) 10 seconds after the addition of electrolyte. The diameters of the non-flocculated primary particles are from less than 0.02 to 0.1 μ. The agglomerates are about 0.3 μ and larger; x/m = 5.0, × 27800.

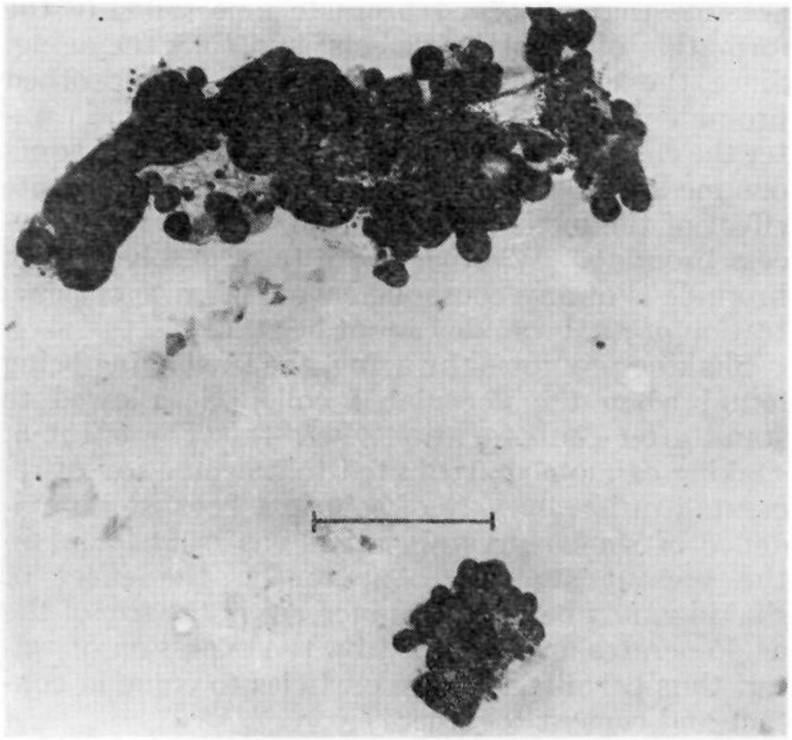

Fig. 11.—Agglomerates present 2 minutes after flocculation of fresh silver bromide colloid. The size of the flocs vary from about 1 μ to several microns. A large amount of cementing together is evidenced; x/m = 3.0, × 23600.

factor of 10. On the other hand with the preaged dialyzed colloid the change was from 11.4 to 7.7 or a factor of only 1.5. This rapid decrease of the specific surface upon flocculation of a fresh colloid cannot be attributed to an extremely rapid Ostwald ripening or to recrystallization in liquid films around the particles, because such recrystallization cannot be expected to occur with this great speed. Moreover, the electron micrographs (Fig. 10) still show many primary particles in the fresh floc.

The flocculation of colloidal silver bromide is an irreversible process. In a previous paper[2] we have postulated that Schottky defects extend throughout the small particles of a fresh colloid, but only to 5 or 6 layers beyond the surface in aged dialyzed colloids. These Schottky defects account for the great thermal mobility of silver bromide even at room temperature and thus for the rapid exchange with r.a. bromide. Because of the high thermal mobility, the particles in a floc of a fresh colloid rapidly cement together by means of a surface fusion, and upon further aging a more or less complete fusion of the particles occurs while the primary particles disappear (Fig. 11). Immediately after flocculation of the tiny particles there is a very large number of Schottky defects in the cemented particles which accounts for the very rapid exchange with r.a. bromide (Fig. 6). After 15 minutes of aging, when fusion has taken place and the number of Schottky defects has greatly decreased, the rate of r.a. exchange has similarly decreased. It appears that aging in the flocculated state under experimental conditions as described in this paper is due to thermal effects and not partly to recrystallization by way of a liquid phase as Kolthoff and O'Brien[4] postulated. As a matter of fact cyanide, which greatly promotes Ostwald ripening,[2] had no effect on the rate of decrease of surface during flocculation or on the rate of penetration of r.a. bromide and rate of aging soon after flocculation.

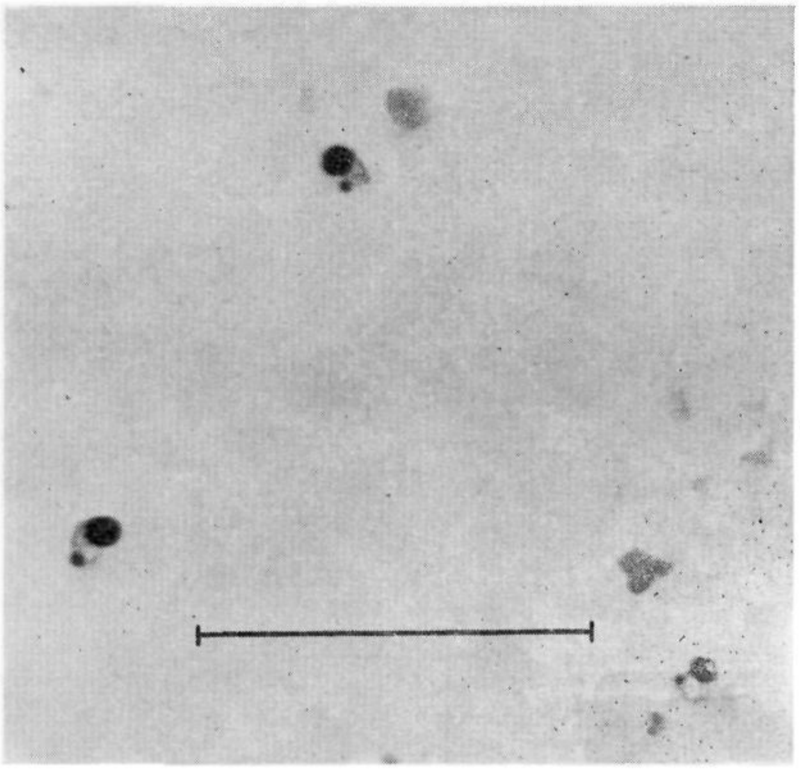

Fig. 12.—Particles present in 3 week old dialyzed colloid of silver bromide. Diameters of the particles are about 0.1 μ × 49000.

Upon flocculation of the preaged dialyzed colloid, the particles of which have a very small "hard" core practically without Schottky defects, a rapid cementing occurs but no complete fusion on further aging of the floc. Figure 15 shows some primary particles still recognizable as such in the floc. The r.a. exchange is highly heterogeneous and occurs mainly in the outer layers containing Schottky defects. On further aging the relative number of these defect decreases and the rate of penetration of r.a. bromide also decreases slowly (Fig. 8). Again cyanide has no effect on the rate of decrease of surface (Figs. 2 and 3) or on the rate of penetration of r.a. bromide. The above interpretation also

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[4] I. M. Kolthoff and A. S. O'Brien, THIS JOURNAL, **61**, 3414 (1939).

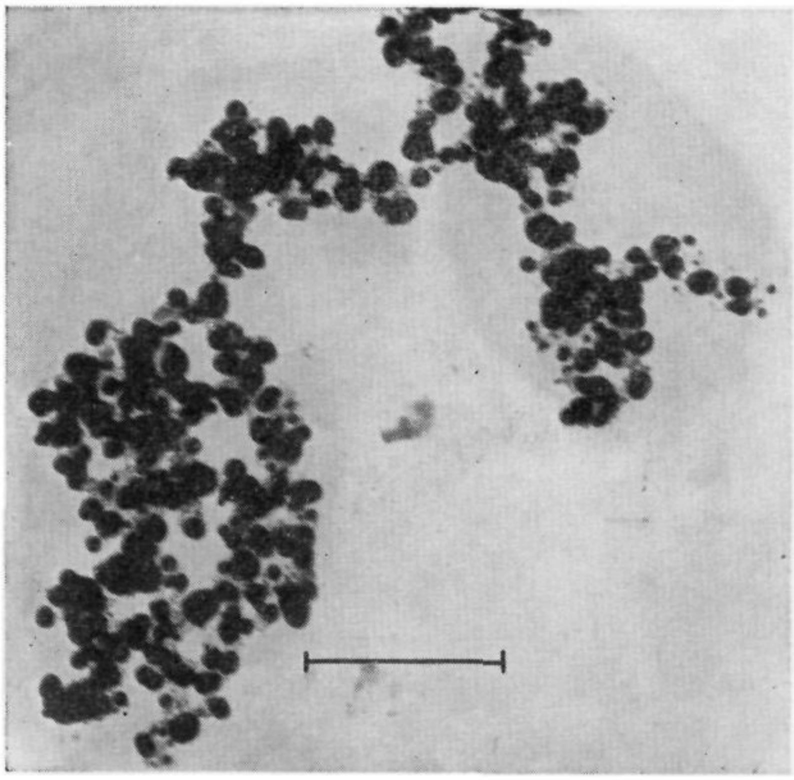

Fig. 13.—Agglomerate present in flocculated silver bromide (from 3-week old dialyzed colloid) 10 seconds after flocculation. The size of the particles in the floc is 0.1 μ and larger; x/m = 7.7, ×25400.

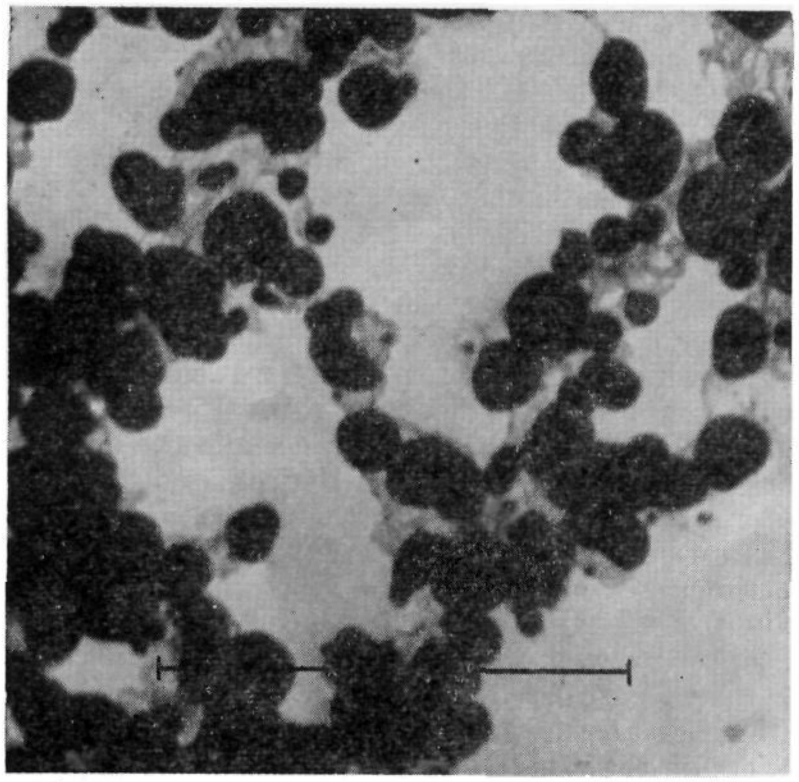

Fig. 14.—An enlarged section of agglomerates similar to that shown in Fig. 13. The particles in the floc are from 0.1 to 0.2 micron in diameter, ×60300.

accounts for the experimental fact that the rate of penetration of r.a. bromide is considerably greater in a fresh floc from a fresh colloid than from an aged dialyzed colloid, even though the specific surface of the former is about two-thirds or less of that of the latter.

An excess of bromide increases the rate of decrease of the specific surface in aqueous and alcoholic media, the effect being considerably greater in alcohol than in water. On the other hand the aging is less in alcohol than in water in the absence of bromide (Fig. 5). Also the rate of exchange with r.a. bromide (excess bromide present) was found to be considerably greater in alcoholic than in aqueous medium (Fig. 9). Quite generally, an excess of bromide was found to promote the aging. It seems possible that adsorbed bromide ions promote the formation of Schottky defects[2] and thus the aging. Since the energy of desolvation of the adsorbed bromide ions is much smaller in alcohol than in water the effect is much greater in alcohol than in aqueous medium. In line with this is that an opposite effect of the medium is found in the absence of excess bromide. Whether the rate of desolvation of bromide is of any consequence on the rate of penetration of r.a. bromide cannot be stated.

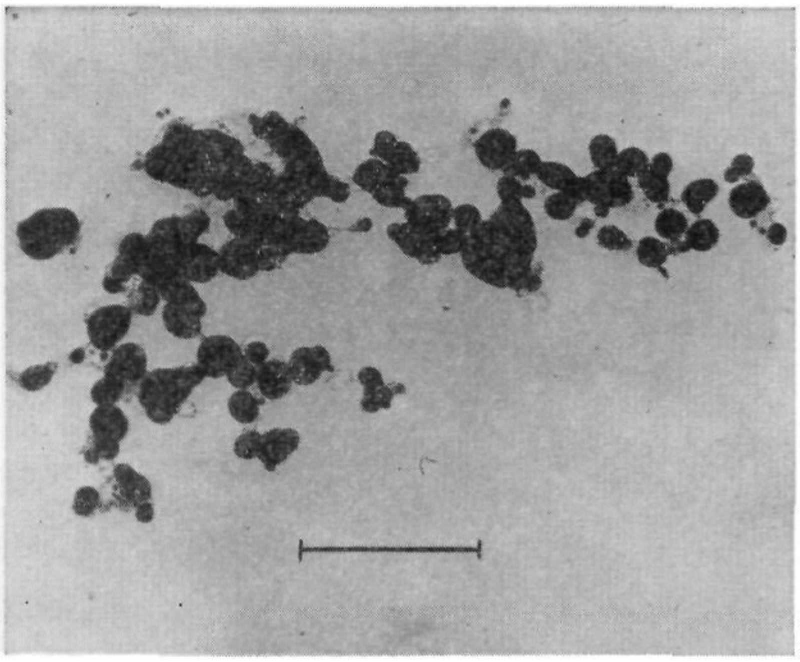

Fig. 15.—Agglomerate present in flocculated silver bromide (from 3-week old dialyzed colloid) 2 minutes after flocculation. The particles in the floc are from 0.1 to 0.4 μ in diameter; x/m = 6.1, ×25600.

Shaking promotes the aging, the least aging being found when the flocculated colloid is allowed to stand after centrifugation (Fig. 4). The effect of shaking cannot be attributed to a promotion of recrystallization by way of solution, because no evidence of such recrystallization has been found in the present studies. Apparently, the effect of shaking must be due to an increase in the size of the agglomerates accompanied by the expulsion of water, thus permitting more particles to come in contact and cement together.

The indication that adsorbed benzene prevents the aging of flocculated colloids deserves further study.

In the above, reasons have been given why the flocculation of colloidal silver bromide is an irreversible process. If it were possible to eliminate the Schottky defects from the particles, the thermal mobility would be greatly decreased and the flocculation process might become more or less reversible. Since cadmium bromide forms mixed crystals with silver bromide, the cadmium ions taking the place of silver ions, it was thought possible that cadmium bromide added to a silver bromide colloid might fill many of the Schottky holes and thus make peptization of the floc possible. Preliminary experiments were carried out with a fresh colloid, one portion of which was flocculated with calcium bromide and another with cadmium bromide. Results of wool violet adsorption indicated that the specific surface of the fresh floc obtained with cadmium bromide was much smaller than the specific surface in the colloidal state but the decrease was not nearly as pronounced as upon flocculation with calcium bromide of the same concentration. Also, upon removal of the supernatant liquid and shaking with dilute potassium bromide no peptization was observed when flocculated with calcium bromide, but some peptization occurred when flocculated with cadmium bromide. The possibility of making the flocculation partly or entirely reversible by elimination of Schottky defects is being further studied.

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MINNEAPOLIS, MINNESOTA

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

Formation and Properties of Various Mercuric Mercapto Thioglycolates Formed in Reactions between Mercuric Mercury and Thioglycolic Acid

BY W. STRICKS, I. M. KOLTHOFF AND A. HEYNDRICKX

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Reactions of thioglycolic acid (TSH) with mercuric mercury have been studied polarographically and compared with similar reactions of cysteine and glutathione reported previously. In the absence of chloride thioglycolic acid can form at least two compounds with mercury: $Hg(TS)_2$ and slightly soluble $Hg_2(TS)_2$ in which one mercury is bound firmly as mercaptide. In the presence of much chloride the formation of $Hg_2(TS)_2$ is suppressed by the complex $HgCl_4^{=}$. The apparent dissociation constants of three charge types of the mercuric mercapto thioglycolate were calculated from e.m.f. measurements. The charge of the carboxyl group was found to have little effect on the stability of the mercaptides. From the values of the dissociation constants at 12 and 25° the heats and entropies of formation were calculated. A comparison of the data obtained with thioglycolic acid, cysteine and glutathione indicates that the stability of the mercuric mercaptides of the three thiol compounds is determined almost entirely by the strength of the mercury–sulfur bonds; and that the uncharged amino group and the charged or uncharged carboxyl groups have little effect on the stability.

For an interpretation of some of the results obtained in a recent study[1] of the reactions between cysteine and reduced glutathione with mercuric mercury it appeared desirable to carry out a similar study with a compound containing only sulfhydryl and carboxyl as reactive groups. The present paper deals with a study of the thioglycolic acid (TSH)–mercuric system at varying *p*H and temperatures. Polarographically it is shown that mercury can form at least two reaction products with thioglycolic acid. Apparent dissociation constants, heats and entropies of formation of the mercapto mercuric thioglycolates have been calculated from e.m.f. measurements. The results are compared with those obtained with cysteine[1] and glutathione.[1]

Materials.—A "pure" product of thioglycolic acid from Eimer and Amend was purified and analyzed by methods described previously.[2] Stock solutions of the acid (0.01 and 0.2 *M*) were prepared with air-free water. Only freshly prepared solutions of the acid were used. All other stock solutions and chemicals were the same as used before.[1]

Experimental Methods.—The experimental details for the determination of current voltage curves, e.m.f. and *p*H measurements were identical with those given previously.[1] The characteristics of the capillary used in the present polarographic work were: $m = 2.17$ mg. sec.$^{-1}$; $t = 3.91$ sec. (open circuit); $m^{2/3}t^{1/6} = 2.104$ mg.$^{2/3}$ sec.$^{-1/2}$; $h = 60$ cm.

Dissociation constants of the mercuric mercaptides of thioglycolic acid were calculated from e.m.f. measurements of mercury metal in equilibrium with mercuric mercaptides in the presence of a large excess of uncomplexed acid. Under these conditions all the mercury in the solution is in the mercuric form. Mercurous thioglycolate is unstable and readily disproportionates into mercury metal and the mercuric compound.

Polarographic Measurements.—Air-free 10^{-3} *M* TSH solutions in the absence and presence of chloride ion were titrated with 0.05 *M* mercuric solutions and complete polarograms were taken after each addition of mercury. The polarographic behavior of thioglycolic acid[2] and of its mercuric mercaptide is similar to that of cysteine[3] and glutathione.[4] For this reason polarograms are not presented in this paper. The diffusion currents (corrected for residual current and change in volume) of the various compounds present in the course of a titration were plotted against the volume of mercury solution added. An example of such a plot obtained with a solution at *p*H 5.57 in the absence of chloride is given in Fig. 1. Analogous to cysteine and glutathione the anodic diffusion current of TSH is found to disappear when TSH and mercury are present in a mole ratio 2:1. At this point only the reduction wave of mercury in the slightly dissociated mercaptide $Hg(TS)_2$ is observed

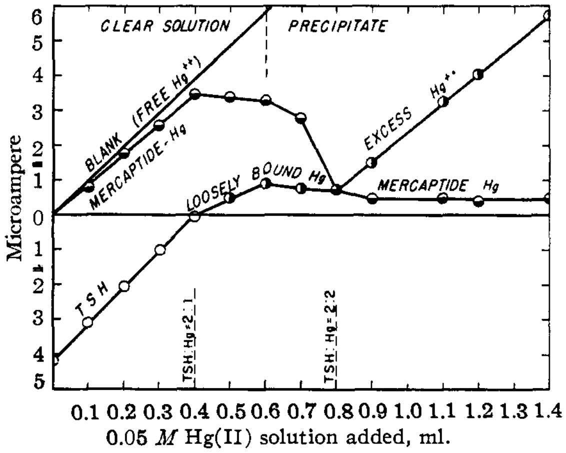

Fig. 1.—Titration of 40 ml. of 10^{-3} *M* thioglycolic acid (acetate buffer, 0.1 *M* KNO_3, 2.5 × 10^{-3}% gelatin, *p*H 5.57) with 0.05 *M* mercuric acetate. Plot of diffusion current *versus* ml. Hg(II) solution added: ⊙,◑, i_d, measured at −0.1 v.; ⊖, i_d, measured at −065. v.

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[1] W. Stricks and I. M. Kolthoff, THIS JOURNAL, **75**, 5673 (1953).

[2] D. L. Leussing and I. M. Kolthoff, *J. Electrochem. Soc.*, **100**, 334 (1953).

[3] I. M. Kolthoff and C. Barnum, THIS JOURNAL, **62**, 306 (1940).

[4] W. Stricks and I. M. Kolthoff, *ibid.*, **74**, 4646 (1952).