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Adsorption in Photographic Development. I. On the Non-Adsorption of Organic Developers to Metallic Silver

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Adsorption theories of photographic development have been proposed by W. D. Bancroft,[1] by S. E. Sheppard[2] and by A. J. Rabinovitch.[3] Bancroft did not specify any definite mechanism for the adsorption of the reducing agent, but laid stress on the reduction of adsorption to peptization. However, and the point is important, he suggested that "If the reducing agent is adsorbed much more strongly by exposed silver bromide than by unexposed silver bromide, the former will develop more rapidly than the latter, and we shall get a negative. If the reducing agent is adsorbed more strongly to unexposed than to exposed silver bromide, we shall get a positive. If there is not much difference in the adsorptions, we shall have exposed and unexposed silver bromide developing at so nearly the same rate that we get a more or less uniform fogging." As Bancroft pointed out, failing independent proof, the theory remains an assumption or interpretation *ad hoc.* He considered, however, that some experimental support to the hypothesis was given by experiments indicating a peptization of latent image (or of exposed silver bromide) by acid solutions of certain developing agents (elon, hydrazine, *p*-aminophenol and hydroquinone).

Sheppard[2] suggested that the essential feature of the adsorption was the formation of a definite chemical combination of the reducer with the silver cation of the silver halide, followed by an internal decomposition of this to metallic silver and oxidation product, this decomposition being catalyzed by the latent image silver. As an example of the type of reaction there was instanced the catalysis of the autoreduction of the silver sulfite complex by colloidal silver.[4]

The difficulty of direct experimental investigation under developing conditions (alkaline for organic reducers) is evidently in the separation of the adsorption from the reduction. P. Wulff and K. Seidl[3] attacked the problem by substituting for the organic reducer a meta-substituted body of otherwise similar type, which does not develop, *viz.*, resorcinol (*m*-dihydroxybenzene). Their experiments indicated that in alkaline solution this substance is adsorbed to silver bromide. Apart from certain inadequate controls (*p*H stabilization), it is difficult to appraise the support for the adsorption hypothesis, precisely because resorcinol is not a developer. A few years later, A. J. Rabinovitch and S. S. Peisakhovitch[3] published a paper describing experiments supposed to support a different form of adsorption theory, to wit, that the reducer in development is adsorbed to the *silver* of the latent image, and that these adsorbed developer molecules reduce silver ions (presumably from solution).

The procedure used by them was to mix the silver sol and hydroquinone and to determine the concentration of the latter before and after ultrafiltration. The concentrations of both the sol and hydroquinone were determined prior to the mixing; after mixing, the iodimetric titration gave an estimation of both colloidal silver and hydroquinone. The amount of hydroquinone in the mixture was then obtained by difference. Portions of the mixture were ultra-filtered through collodion membranes and the filtrate titrated iodimetrically for hydroquinone. The difference in the hydroquinone value before and after filtration Rabinovitch called "adsorbed" hydroquinone.

This conclusion would be correct, providing no reaction occurred that would change the hydroquinone chemically during the process. Actually they found 77% of their original hydroquinone escaping analytical detection even before ultrafiltration. No attempt was made to correct or prevent this loss; instead they merely claimed it to be oxidized, giving no attention to the fact that if oxidation occurred before ultra-filtration, it could very likely occur during ultra-filtration, which is a time-consuming operation.

In a sample calculation they showed that the silver sol–hydroquinone mixture contained only 23% of the original hydroquinone before, and

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[1] W. D. Bancroft, presented at the American Chem. Soc. meeting, Rochester, N. Y., 1913; *Trans. Faraday Soc.*, **19**, 252 (1923).

[2] S. E. Sheppard, *Phot. J.*, **43**, 136 (1919); S. E. Sheppard and G. Meyer, *ibid.*, **44**, 17 (1920).

[3] A. J. Rabinovitch and S. S. Peisakhovitch, *Z. wiss. Phot.*, **33**, 94 (1934).

[4] S. E. Sheppard, *Phot. J.*, **59**, 135 (1919); T. H. James, THIS JOURNAL, **62**, 3411 (1940).

5.5% after, ultra-filtration; thus, 17.5% was adsorbed.

In planning the present investigation, the importance of preventing any chemical change in the developer was greatly stressed. Besides performing the experiments in an oxygen-free atmosphere, great care was exercised in preparing a silver oxide-free silver sol.

Experimental

Solutions: Silver Sol.—It appeared indispensable to have a sol free from ionic silver, because of the ability of silver ions to oxidize organic developers in the presence of colloidal silver; a method was devised in which the sol could be made in gelatin solution, this solution allowed to gelate, and then thoroughly washed free from silver ions and reducing agent. Six grams of ash-free, desensitized gelatin is soaked in 100 ml. of distilled water for fifteen minutes. This is heated on a steam-bath until the gelatin is completely dissolved and then to 90° over a low flame. At this temperature is added slowly, with mechanical agitation, 5 g. of pure dextrose (E. K. Co. Chemical no. 84) and heating is continued to 96–97°. After the flame has been removed and the temperature has fallen to exactly 95°, there is added to the agitated solution 45 ml. of a solution containing 4 g. of silver nitrate and 4 ml. of concentrated ammonia. This solution is added by pouring as quickly as possible from a beaker. The temperature of the resulting mixture falls to about 75°. Agitation is continued for one and one-half minutes, after which the now deep-red solution is cooled quickly in a brine-bath to 40°, while stirring with the thermometer. Mechanical agitation is then resumed and the resulting sol is allowed to cool to room temperature during two hours. It is then placed in the refrigerator to gelate.

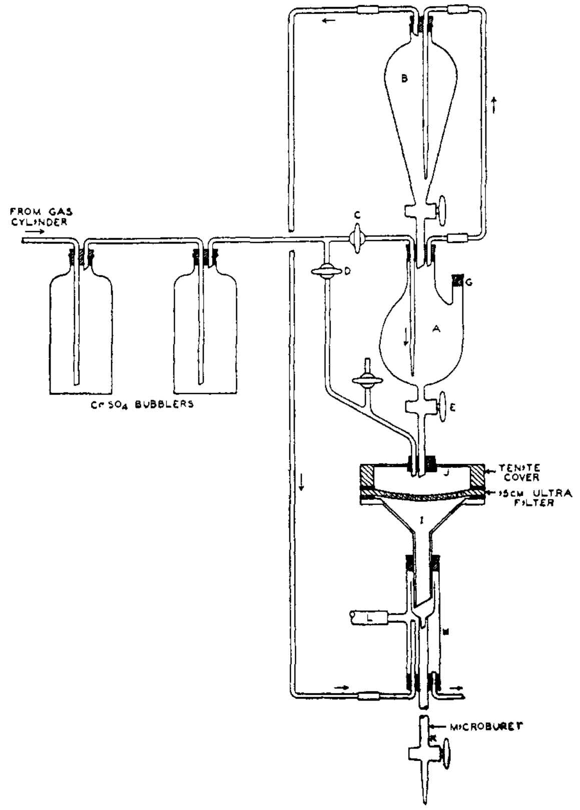

Fig. 1.

The sol which has become a firm jelly is "noodled" and placed in 2 liters of ice-cold water and mechanically stirred for thirty minutes. The water is then drained off through a coarse piece of cloth and the noodled sol again suspended in 2 liters of fresh ice-cold water. The washing is repeated until 50 ml. of the wash water no longer shows any reduction with 5 ml. of Fehling solution. Ten to fifteen washings usually are required. The washed sol is melted and diluted so that it will contain 1.6–1.7 g. of silver per liter.

Analysis of Silver Sol.—The metallic silver content of the sol is determined by adding an excess of the standard iodine solution and back-titrating the excess.[5] The total silver content is determined by boiling with dilute nitric acid and titrating with a standard thiocyanate solution. Agreement in both titrations is proof of the absence of ionic silver.

Particle Size.—The particle size of the silver sol was estimated from photographs made by Mr. A. L. Schoen, of these Laboratories, with an electron microscope at 25,000 × magnification on enlarged prints at further open magnification of 82,000 × and 90,000 × magnification (*i. e.*, between 3 and 4 times enlarged). Micrometer readings were made of about 100 images and gave an average diameter of 20 mμ, with a range between 10 and 40 mμ. Ultramicroscopic examination showed the particles to be amicroscopic.

Borate Buffer.—The 0.4 *M* borate–nitrate buffer is prepared by dissolving 0.4 mole of boric acid and 0.4 mole of potassium nitrate in water and diluting to one liter. To 750 ml. of this solution are added 275 ml. of 0.5 *N* sodium hydroxide and 225 ml. of water. The *p*H of this solution is approximately 9.

Other Solutions.—Reagent quality chemicals were used in preparing the 0.01 *N* hydroquinone, 0.01 *N* elon (N-methyl *p*-aminophenol sulfate), 0.01 *N* iodine (containing 48 g. of potassium iodide per liter), 0.01 *N* sodium thiosulfate, and 0.06 *N* potassium iodate. The hydroquinone and elon solutions were freshly prepared for each experiment in cooled boiled water.

Apparatus.—A satisfactory apparatus for the complete removal and exclusion of oxygen during the course of the experiment was constructed according to the diagram of Fig. 1. Flask A is the bulb of a 500-ml. Kjeldahl flask to which is sealed the stopcock E and side-neck G; flask B is a 500-ml. pear-shaped separatory funnel. Flasks A and B are tightly joined by means of a rubber stopper. Suitable glass tube connections are made for the passage of oxygen-free hydrogen, first through the solution in flask A and then through the solution of flask B before entering the chamber H to maintain an inert atmosphere therein.

The ultra-filter I is fitted with a Tenite cover J to effect a pressure filtering aid instead of a vacuum. A rubber stopper is placed in an inverted tapered hole through the center of the cover to adapt flask A to the ultra-filter and also to carry an inlet tube to the filtering chamber for the

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(5) E. Einecke, *Z. anal. Chem.*, **89**, 90 (1932).

hydrogen gas. A 10-ml. buret is used to catch the filtrate and also to serve as a convenient way of measuring the sample for analysis. The chamber H provides an oxygen-free connection between the buret and the filter; the atmosphere is being maintained inert by the slow stream of purified hydrogen coming from flask B. A suction at L firmly holds the collodion membrane in position while the cover J is tightly clamped down.

Hydrogen gas from commercial cylinders is purified by bubbling it through fritted glass plates immersed in 0.3 *N* chromous sulfate solution.[6] By manipulating stopcocks C and D, one stream of hydrogen can be made to serve for both the pressure and for the maintenance of an inert atmosphere in the apparatus. A hydrogen pressure of one atmosphere is used for filtration; stopcock C regulates the pressure in the apparatus so that the bubbling rate is 40–50 bubbles per minute.

Procedure.—To 100 ml. of the silver sol containing 1.690 g. of silver per liter is added 25.00 ml. of the borate–nitrate buffer. One hundred milliliters of the mixture now containing (100/125) × 1.690 or 1.352 g. of silver per liter, is transferred by means of a pipet to flask B. In flask A is placed 150 ml. of the 0.01 *N* organic developer. The air in the rest of the apparatus is displaced by the purified hydrogen, and the gas is then bubbled through the solutions for fifteen to seventeen hours. At the end of this time 50 ml. of the organic developer is removed with a pipet through the small side-neck, precautions being taken to avoid any diffusion of air into the flask during the withdrawal.[7] The sol in flask B is run slowly into flask A while the bubbling hydrogen provides sufficient agitation for quick homogeneity. One-half hour is allowed for attainment of equilibrium, during which time the filter apparatus is assembled and flushed free of oxygen below and above the collodion membrane before filtration is attempted.

Approximately 30 ml. of the mixture is run into the filter and filtered; more of the mixture is added as needed. When 50 ml. of the filtrate has been removed, the succeeding 10-ml. portions are analyzed for hydroquinone until three successive portions check.

Analytical Methods.—The solutions used in the analytical determinations are standardized at the time of each experiment. The thiosulfate solution is standardized against potassium iodate. The standard sodium thiosulfate is used to standardize the iodine solution. The actual concentration of the organic developer is determined after the hydrogen bubbling treatment, by iodimetrically titrating portions of the 50-ml. sample from the bulk of the solution of flask A. The standardization of the solutions and actual determinations of the organic developers are done in an acetate buffer.[8]

Results

The concentrations of the sol and organic developers were chosen as such in order to approximate those used by Rabinovitch. Also, all of the experiments were performed under as nearly as possible identical conditions. The importance of running control or "blank" experiments was realized for determining the consumption of the organic developer, as well as to account for any other small loss of the developer in the course of the experiment. Two such control experiments were used, the first being one to account for any retention of the organic developer by the gelatin or membrane; and the second being one to account for consumption of iodine by silver particles in the ultra-filtrate. The second of these blanks was found to be insignificant, while the first had considerable importance, as appears in the results.

The results of the adsorption of hydroquinone and N-methyl-*p*-aminophenol sulfate (elon) are tabulated in Table I. For convenience, the results are based on the number of milli-equivalents (m. e.) per liter of the 1:1 mixture by volume of the sol and organic developer.

Columns 3 and 4 show the distribution of the organic developer before and after ultra-filtration for both the actual experiments and for the blanks. The developer lost during filtration is given in Columns 5 and 6; also in Column 6 the average percentage loss is given. The figure of Column 7 represents the average value of Column 6 corrected for the experimental blank. The last column contains the value of the total developer accounted for; it is the difference between the figures of Column 7 and 100.

Discussion

The average of several experiments shows a recovery of 99.56% hydroquinone and 99.77% elon in the ultra-filtrate. Since these values are within the limits of experimental error, it is evident that colloidal metallic silver does not exhibit an appreciable adsorptive affinity for either hydroquinone or elon.

The small losses of 0.44% hydroquinone and 0.23% elon obtained in the ultra-filtration process are in marked contrast to the 17.5% reported by Rabinovitch, *et al.* It is felt that they obtained this high value because no attempt was made to prevent oxidation of the hydroquinone during the slow filtration process. The need of preventing oxidation seemed evident from their observation that a 77% loss in the hydroquinone occurred shortly after mixing the developer and silver sol prior to the ultra-filtration.

The absence of adsorption of the developing

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[6] H. W. Stone, THIS JOURNAL, **58**, 1591 (1936); *Ind. Eng. Chem., Anal. Ed.*, **8**, 188 (1936).

[7] The solution removed is used for determining the concentration of the organic developer. This was thought to be more strictly correct than to analyze it before the hydrogen gas treatment.

[8] I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 452.

TABLE I

1 Expt.	2 Concn. of Ag. m. e./l.	3 Concn. of developer at start, m. e./l.	4 Concn. of developer in filtrate, m. e./l.	5 Developer missing in filtrate, m. e./l.	6 Developer missing in filtrate, %		7 Developer unaccounted for, %	8 Developer accounted for, %
			Hydroquinone–Silver Sol					
1	6.260	5.059	4.942	0.117	2.31	2.03 Av.	0.44	99.56
2	6.260	5.080	4.993	.087	1.73			
3	6.260	5.082	4.977	.105	2.06			
4	0.00	5.060	4.974	.086	1.70	1.59		
5	0.00	5.054	4.979	.075	1.48			
			Elon–Silver Sol					
1	6.260	5.091	4.988	0.103	2.02	2.01 Av.	0.23	99.77
2	6.260	5.093	4.991	.102	2.00			
3	0.00	5.117	5.026	.091	1.78	1.78		

agent to metallic silver (and this in alkaline media as present in development of silver halide emulsions) is an argument against recent theories of development based on Gurney and Mott's[9] theory of the photographic process. These writers extended their theory of the photolysis of silver halide, and of latent-image formation, to development.

It was suggested that in development the primary event is the approach of a reducer ion or molecule to the metallic silver nucleus, to which the reducer donates an electron

$$R^- + [Ag] \longrightarrow R + [Ag]^-$$

The negatively charged silver nucleus is then supposed to attract to it: (i) in "chemical" development, interstitial silver ions of the silver halide lattice, and (ii) in "physical" development, silver ions from solution. The silver ions thus attracted are then neutralized by the excess electrons of the silver, and the reaction proceeds over the silver surface.

A similar mechanism was postulated by Frank-Kamenetzky,[10] based on Rabinovitch's theory of developer adsorption to silver. It is evident that the present results contradict his hypothesis.

The theory of photographic development has undergone a radical transformation through the investigations of T. H. James.[11] He has demonstrated the critical importance of the potential barrier at the surface of the silver bromide grain, primarily as formed by adsorbed bromide ions, and secondly by gelatin, dyes and the like. He has shown that the magnitude of the "induction period" in development is essentially determined by the sign and magnitude (0, 1, 2, 3. . .) of the charge on the reducing ion.

The adsorption theory of development, as a general proposition, can be restated on this basis in James' conclusion, "The chemical reaction itself must take place beyond the potential barrier, and hence be localized at or very near the surface of the grain." Within this, *i. e.*, within the barrier represented by the electrokinetic potential, the adsorption proper could be (i) of reducing ion to silver metal (ii) to silver halide (iii) of silver ion to silver metal. The first of these appears excluded by the results presented. As regards the second, the conditions are similar to those for the adsorption of dyes.[12] For most developers having negatively charged ions, adsorption will be both kinetically impeded, as brought out by James, by the potential barrier, and thermodynamically minimized by the excess bromide-ion layer for pAg > 6. Hence, the most probable adsorption feature is that of silver ions to silver metal. Indirect evidence for this has been given by James[13] in his studies on the mechanism of development. Since, at the points of formation of latent image, there are breaks in the potential barrier, reducer ions[14] can penetrate here, and after adsorbing to the silver ions of the latent-image nuclei, the complex can undergo internal reduction–oxidation with formation of metallic silver. The importance of the resonance structure of the reducer for this autoreduction of the silver complex has been indicated by James and Weissberger.[15]

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(9) R. W. Gurney and N. F. Mott, *Proc. Roy. Soc.* (London), **164**, 151 (1938); J. W. Webb and C. H. Evans, *J. Opt. Soc. Am.*, **28**, 249 (1938).

(10) D. A. Frank-Kamenetzky, *Acta Physicochim.*, *U. R. S. S.*, **12**, 13 (1940).

(11) T. H. James, *J. Phys. Chem.*, **43**, 701 (1939); **44**, 42 (1940); THIS JOURNAL, **62**, 3411 (1940).

(12) S. E. Sheppard, R. H. Lambert and R. L. Keenan, *J. Phys. Chem.*, **36**, 174 (1932); S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **7**, 265, 426 (1939).

(13) T. H. James, THIS JOURNAL, **61**, 648 (1939); **62**, 530 (1940).

(14) Also, of course, neutral reducing molecules such as *p*-phenylenediamine.

(15) E. C. Armstrong, T. H. James and A. Weissberger, THIS JOURNAL, **63**, 182 (1941).

To what extent the silver ions adsorbed to the nuclei are directly derived from migrant silver ions of the silver halide crystal, or from the contiguous solution, is not yet clear, and must await further researches. Also, the direct determination of silver-ion adsorption to metallic silver and to silver sulfide is under investigation as a further phase of the present work, and also the direct determination of the adsorption of gelatin to silver halide. Incidentally, later experiments have shown that under the conditions studied in the foregoing experiments no adsorption of developer was found on silver sulfide.

Summary

1. A method is described for the determination of the adsorption of organic reducing substances to metallic (colloid) silver in an oxygen-free atmosphere.

2. Under these conditions no adsorption of hydroquinone or of methyl-*p*-aminophenol was observed greater than accountable by the error of experiment, of the order of ~0.3 per cent.

3. It is concluded that the evidence adduced by A. J. Rabinovitch in support of the hypothesis of adsorption to metallic silver is unreliable.

4. Experiments under the same conditions with silver sulfide failed to show any adsorption of these developers.

5. The bearing of the results on the theory of photographic development is discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of Pyrimidine and Purine Derivatives of Cystamine and of a New Type of Thiazolidinopyrimidine[1]

BY ALAN HART NATHAN AND MARSTON TAYLOR BOGERT

Following up the investigations on the synthesis of some new pyrimidines and uric acids from cystamine, by Mills and Bogert,[2] the classical Traube method[3] was utilized for the preparation of the desired iminobarbituric acid (IX) by condensation of *bis*-(β-ureidoethyl) disulfide (V) with cyanoacetic acid and acetic anhydride to the corresponding cyanoacetyl derivative (VIII), and cyclization of the latter by treatment with aqueous alkali.

Baum[4] has reported that, in the cyclization of cyanoacetylurea and of its derivatives, very small amounts of alkali suffice to bring this about, but that there is apt to be a simultaneous competing hydrolytic action. This hydrolysis occurs most easily with cyanoacetylurea itself, less readily with N-alkyl derivatives, and not to any appreciable extent with N,N′-disubstituted ureas. In our experiments, concentrated sodium hydroxide effected the cyclization of the ureido compound (VIII) to the iminobarbituryl derivative (IX), but weaker alkalies, *e. g.*, sodium bicarbonate and ammonium hydroxide, were found to be equally effective and therefore were used, to diminish the risk of hydrolysis.

By the action of sodium or isoamyl nitrite on (IX), an isonitroso group was introduced in position 5, and the resultant iminovioluric acid (X) was reduced by sodium hydrosulfite in ammoniacal solution, following the procedure of Hepner and Frenkenberg[5] to the corresponding diaminouracil (XI). Fused with urea at 170–180°, by the Gabriel and Colman method,[6] the uric acid derivative (XII) was obtained.

The reduction of this disulfide (XII) to the corresponding mercaptan, with immediate or subsequent cyclization to a thiazolidinouric acid, has not yet been accomplished.

Mills and Bogert[2] synthesized a *bis*-(β-[uric acid ethyl]) disulfide, in which it was not determined whether the $—SCH_2CH_2—$ group was attached to the uric acid nucleus at position 1 or position 3. Since the compound (XII) described in the present paper carries its $—SCH_2CH_2—$ group in position 3, and is not identical with the Mills and Bogert product, it follows that the latter is probably the isomer carrying the substitution in position 1. This conclusion is supported also by the fact that the Mills and Bogert uric acid was prepared

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[1] Presented in abstract before the Division of Organic Chemistry, April 10, 1940, at the Cincinnati Meeting of the Am. Chem. Soc.

[2] Mills and Bogert, THIS JOURNAL, **62**, 1173 (1940).

[3] (a) Traube, *Ber.*, **33**, 1371, 3036 (1900); (b) Conrad, *Ann.*, **340**, 310 (1905).

[4] Baum, *Ber.*, **41**, 532 (1908).

[5] Hepner and Frenkenberg, *Helv. Chim. Acta*, **15**, 350, 533 (1932).

[6] Gabriel and Colman, *Ber.*, **34**, 1247 (1901).