[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF RADCLIFFE COLLEGE AND HARVARD UNIVERSITY]

Studies of the Precipitation of Silver Chloride. II. From Silver Nitrate and Hydrochloric Acid

BY CHARLES H. GREENE AND LAWRENCE D. FRIZZELL

In a previous paper[1] the construction and operation of a "photronic nephelometer" for measuring the opalescences of silver chloride suspensions from the moment of precipitation were described. It is the purpose of this paper to present results obtained with this instrument in a study of suspensions produced by mixing dilute solutions of silver nitrate and hydrochloric acid.

In the formation of such suspensions there are two clearly defined stages; an initial very rapid growth in opalescence, followed by a period of slow development to a maximum and subsequent falling off. The relative importance of these stages depends primarily upon the concentration of the precipitating reagent. This phenomenon has also been observed by Kober[2] and Tezak.[3] Our results, however, show more clearly the very rapid nature of the initial stage of the precipitation and in more detail the way in which the opalescence depends upon the concentration of the reagent present in excess.

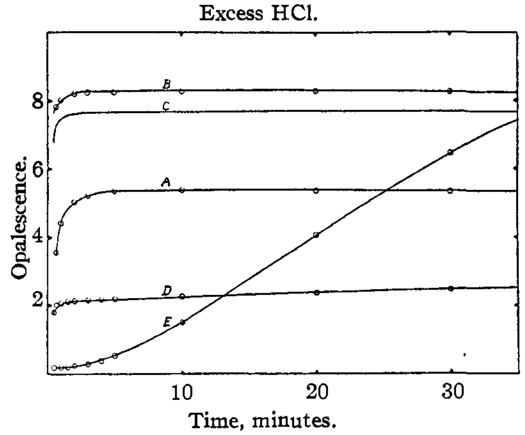

Fig. 1.—The change with time in the opalescence of silver chloride precipitated with an excess of hydrochloric acid (Table I).

Experimental

The preparation of materials and the general mode of carrying out experiments have been described.[1] Briefly, the opalescence produced by adding 10.75 ml. of 0.001 *N* silver nitrate (or hydrochloric acid) from a pipet, to an excess of hydrochloric acid (or silver nitrate) in 300 ml. of solution in a beaker was measured by means of a photronic cell and compared with a ground glass standard. With this volume of solution the final concentration of the silver chloride suspension in the beaker was 3.46×10^{-5} mole per liter. We have called the solution in the beaker, which was always present in excess in these experiments, the "precipitant" and refer to its concentration before the addition of the solution from the pipet as "the initial concentration of precipitant."

The silver nitrate used in some of the present experiments was purified by repeated crystallization in platinum. For the rest of the experiments, mint silver was purified by electrolytic transport. The crystals obtained in this way were dissolved in redistilled nitric acid and the silver nitrate recrystallized from water in order to obtain a neutral solution which would surely be free from traces of chloride. No difference could be traced in the results obtained with these different preparations of silver nitrate.

In Figs. 1 and 2 are presented the results of a series of experiments which illustrate the two stages in the development of opalescence. Curves 1A, 1B, 2A, 2B and 2C represent the mean of a number of separate experiments. Curves 1C, 1D, 1E, 2D and 2E are of individual experiments which are representative of all of the experiments carried out and averaged in Table I. In these curves the opalescence is the ratio of the light scattered by the suspension to the light scattered by the ground glass multiplied by ten.

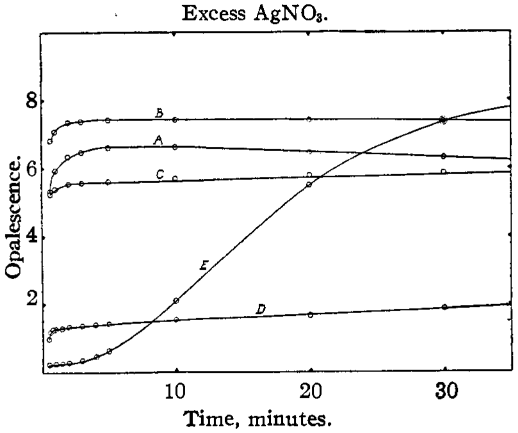

Fig. 2.—The change with time in the opalescence of silver chloride precipitated with an excess of silver nitrate (Table I).

The data presented in Table I will give an idea of the extent of the deviations found between identical experiments in the region of small electrolyte concentration. The data are for the experiments plotted in Figs. 1 and 2 ten minutes after precipitation.

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(1) Greene, THIS JOURNAL, **56**, 1269 (1934).

(2) Kober, *Ind. Eng. Chem.*, **10**, 556 (1918).

(3) Tezak, *Bull. soc. chim. roy. Yougoslav.*, **4**, 137 (1933).

TABLE I

Rate of stirring, 350–380 r. p. m.; Temp., 25.0°; Time of addition, 27 sec.

Curve	No. expts.	Initial concn. of precipitant × 10^4	Opalescence after ten minutes Mean	Mean dev.	Max.	Min.
1A	5	0.50 HCl	5.38	0.60	6.46	3.92
1B	5	1.7 HCl	8.27	.18	8.63	8.10
1C	8	3.3 HCl	7.41	.50	8.65	5.83
1D	7	5.0 HCl	2.16	.97	3.68	0.52
1E	3	10.0 HCl	1.53	.12	1.70	1.38
2A	5	0.50 $AgNO_3$	6.62	.17	6.94	6.39
2B	5	1.0 $AgNO_3$	7.42	.59	8.16	6.42
2C	5	1.7 $AgNO_3$	5.70	.82	6.80	4.39
[a]	6	3.3 $AgNO_3$	5.63	.82	6.67	4.33
2D	6	5.0 $AgNO_3$	2.48	.98	3.88	0.92
2E	3	10.0 $AgNO_3$	2.15	.42	2.77	1.57

[a] These experiments were not plotted in Fig. 2 since on the average they practically coincide with curve 2C.

In an effort to discover the cause of the large deviations apparent in Table I, experiments were carried out in which the rate of stirring, the rate of emptying the pipet and the position of the tip of the pipet were changed. From Table II in which the results of varying these factors are summarized, it is evident that the changes in opalescence caused by large changes in the rate of stirring, etc., are no greater than fortuitous variations between identical experiments. There appears to be some tendency for rapid addition and thorough stirring to produce smaller opalescences in the experiments with 5 × 10^{-4} M precipitant. It is unfortunate that the chance variations in dilute solutions are so large that we cannot draw more definite conclusions concerning the effects of these factors. The variations in opalescence produced by changes in the concentration of precipitant are so large, however, that they stand out clearly in spite of the large experimental error. With higher concentrations of electrolytes than those employed in the experiments discussed in this paper the reproducibility is much better.

TABLE II

Concentration of HCl, 3.3 × 10^{-4} M before precipitation.

No. expts.	Rate of stirring, r. p. m.	Time to empty pipet, sec.	Opalescence (average) Clear 10 min.	Mean dev.	Red 11 min.	Blue 12 min.
8	380	27	7.41	0.50		
3[a]	380	27	7.92	.84		
2	360	300	8.50	.03		
2	360	7	7.68	.08		
13[b]	365	27	7.88	.42	6.53	8.50
4[b]	65	300	7.93	.22	7.81	8.06
6[b]	720	7	7.89	.29	6.45	8.68
Concentration of HCl, 5.0 × 10^{-4} before precipitation						
7	350	27	2.16	0.97	1.59	2.73
19	510	7	1.62	.66	1.26	2.09
Concentration of $AgNO_3$, 5.0 × 10^{-4} before precipitation						
6	350	27	2.48	0.98	1.82	3.15
13	510	7	1.26	.27	1.06	1.73

[a] In these experiments the tip of the pipet was immersed in the solution in the beaker just before delivery.

[b] In these experiments a triple stirrer with stationary baffle blades was employed to provide more rapid mixing. It was removed before the opalescence readings were taken.

The opalescence was found to depend upon the temperature in a way which will be described later, but the suspensions were by no means sensitive enough to variations in the temperature to permit one to ascribe the large experimental errors to chance fluctuations in the thermostat temperature. The effect of illumination was investigated in a few experiments. In all cases the opalescence at a given stage and the development afterward were independent of whether the precipitate had been illumined before or had been produced and kept in complete darkness. Doubling the illumination at the time of precipitation also appeared to have no effect.

Finally, the small opalescences which occur when the concentration of precipitant is 5 × 10^{-4} M or more are not due to supersaturation in the ordinary sense. This was proved by introducing 1 ml. of a fully developed suspension into an experiment like that depicted by curve D, Fig. 1. The normal slow increase in opalescence was not accelerated at all by this "seeding."

In Figs. 3 and 4 opalescence after definite time intervals (indicated by the numbers on the curves) has been plotted against the initial concentration of the reagent present in excess. In drawing the curves in the regions of small concentrations particular weight has been given to the points representing the averaged experiments which have been plotted in Figs. 1 and 2. These points are indicated by the large circles. The small circles represent the results of individual experiments.

Discussion

From Figs. 1 and 2 it appears that excess silver nitrate is qualitatively similar to excess hydrochloric acid in its effect upon the opalescence of a silver chloride precipitate. The chief difference is in the rapid first stage reaction. Here, as the excess of precipitant is increased, the opalescence reaches a maximum at a smaller concentration when silver nitrate is in excess than when hydrochloric acid is in excess. It then drops to a value of about 5.7 and remains roughly constant until the excess of silver nitrate reaches a concentration of 3.3 × 10^{-4} when there is a rapid drop. There appears to be a sort of step in the silver nitrate curve which is not apparent with the hydrochloric acid. This may be seen more clearly in Figs. 3 and 4. Figures 3 and 4 show also how the second stage of slow development in opalescence depends upon the concentration of the excess precipitant. With an excess of 10^{-3} M of either silver ion or chloride ion the opalescence finally reached goes through a maximum as high as that reached in the initial stage with a ten-fold smaller concentration of precipitant.

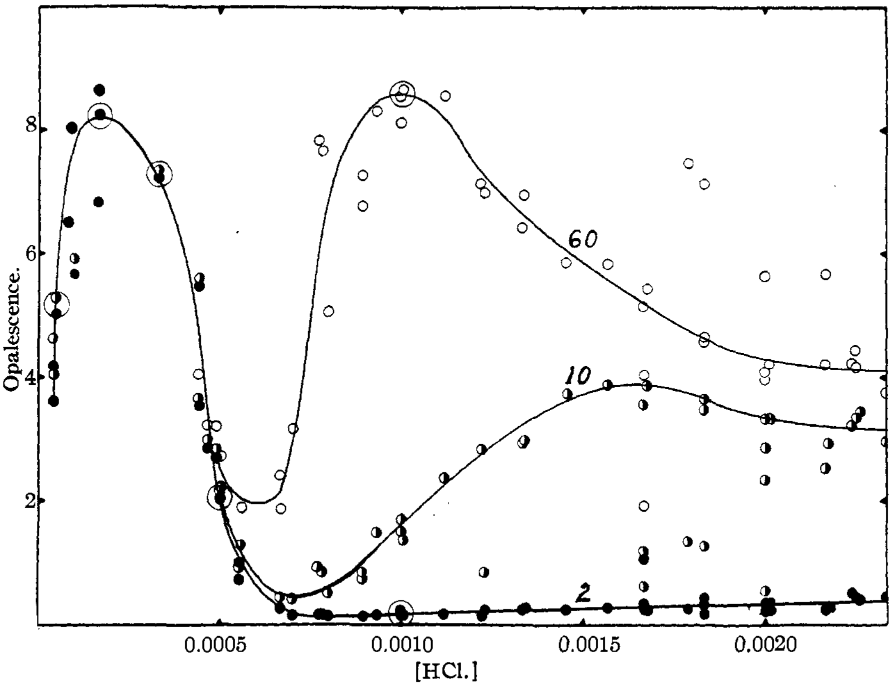

Fig. 3.—*The effect of concentration of precipitant upon the opalescence of silver chloride precipitated with an excess of hydrochloric acid:* ●, *opalescence after two minutes;* ◑, *opalescence after ten minutes;* ○, *opalescence after sixty minutes.*

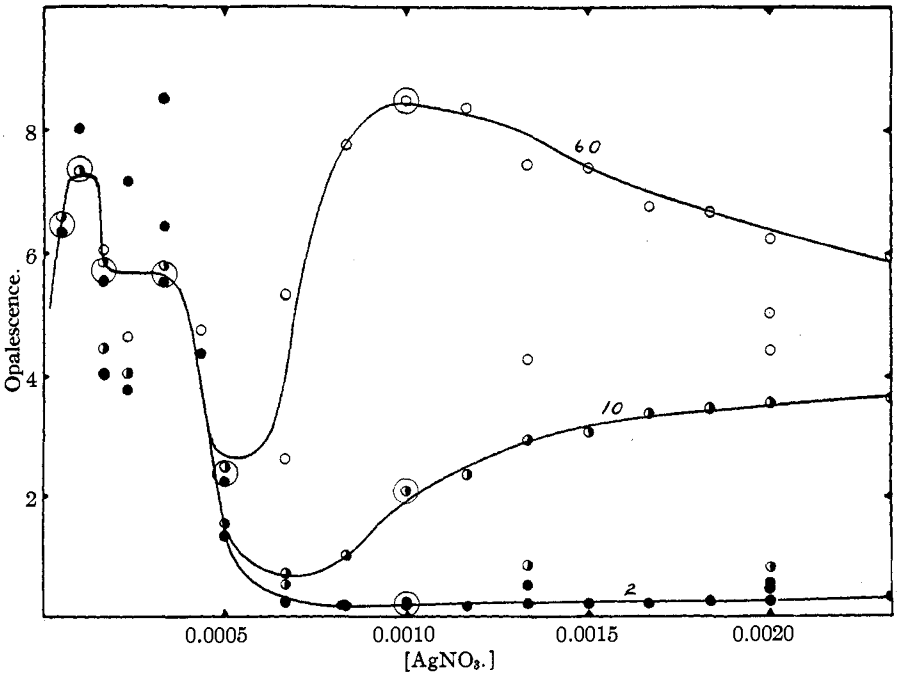

Fig. 4.—The effect of concentration of precipitant upon the opalescence of silver chloride precipitated with an excess of silver nitrate: ●, opalescence after two minutes; ◑, opalescence after ten minutes; ○, opalescence after sixty minutes.

The changes in opalescence which occur in these suspensions of silver chloride may be explained most simply as being due to changes in the size of the silver chloride particles. As the concentration of the reagent present in excess is increased, the size of the particles which crystallize initially from the solution diminishes. This is what one would expect from Von Weimarn's second law of precipitation.[4]

In the more dilute solutions of the precipitant, where relatively large particles are formed, the total surface and consequently the light reflecting power of the particles increases with diminishing particle size. In the more concentrated solutions (above 1.7 × 10^{-4} M) the diameter of the particles initially formed is so small in comparison with the wave length of the light that the conditions of Rayleigh's equation obtain. Consequently, the light scattered instead of increasing with the surface decreases rapidly with diminishing particle size.

The behavior of the rapid first stage of the precipitation reaction is completely explained on this basis. The second stage of slow development, which appears only when there are present particles so small as to be inefficient in reflecting light, may be interpreted as being due to coagulation of the primary silver chloride particles. We postpone a discussion of the second coagulation stage until a later paper in which the effects of other electrolytes may be compared with the effect of excess of precipitant.

Further Experiments

One consequence of this explanation of our results is that the suspensions which scatter light poorly because of the small size of their particles should scatter a larger proportion of blue light than of red in comparison with suspensions composed of larger particles. Qualitatively, the suspensions at the minimum of opalescence with 5.0 × 10^{-4} M precipitant were decidedly bluish in appearance, but it was difficult with the eye to compare the colors of suspensions differing widely in total light reflecting power.

In order to obtain quantitative data the photronic nephelometer was modified so that blue and red glass color filters could be inserted in the illuminating beam at the shutter I.[5] By means of these the color of a suspension could be compared with the ground glass standard. In Table III are given the opalescence values with the color filters for the experiments plotted in Figs. 1 and 2. In columns 5 and 6 of Table II similar color values are given. From Table III it appears that as the excess of precipitant, whether silver or chloride, is increased the suspensions reflect relatively more of the blue and less of the red. This is in accord with the explanation which we propose.

TABLE III

Curve	Initial concn. of precipitant × 10^4	Opalescence (average of a number of expts.) Clear 10 min.	Red 11 min.	Blue 12 min.	$\frac{\text{Blue}}{\text{Red}}$
1A	0.5 HCl	5.38	5.62	5.58	0.99
1B	1.7 HCl	8.27	8.08	8.56	1.06
1D	5.0 HCl	2.16	1.59	2.73	1.72
2A	0.5 $AgNO_3$	6.62	6.64	6.81	1.03
2B	1.0 $AgNO_3$	7.42	6.34	8.14	1.28
2C	1.7 $AgNO_3$	5.70	4.42	6.60	1.49
2D	5.0 $AgNO_3$	2.48	1.82	3.15	1.73

From Table II one would judge that a slowly formed precipitate contains more of the large, red reflecting particles than one formed by more rapid addition of the solution in the pipet.

Further evidence that the changes in opalescence with increasing concentration of precipitant are due to diminishing size of the primary particles of silver chloride is afforded by experiments in which nitric acid was added after the time of precipitation. Figure 5 shows the results of a set of such experiments. The arrow in each case marks the point at which 10 ml. of approximately 2.4 M nitric acid was mixed with the suspension. It is evident that the addition of nitric acid before the maximum of initial opalescence dilutes the suspension and diminishes the opalescence. Beyond the maximum the initial diminution in opalescence due to dilution is soon more than balanced by a growth which it seems possible to interpret only as being due to coagulation of the small primary particles of silver chloride. When the primary particles are large so that the amount of light reflected depends upon the total surface any coalescence of particles would serve only to diminish the opalescence.

The rate of settling of even the coarsest of these suspensions is too slow for convenient study with gravity alone. With a centrifuge, however, further information was obtained about the size of the particles of silver chloride. Suspensions precipitated in the usual manner with an excess of hydrochloric acid, after an initial reading of the opalescence, were divided between two 250-ml.

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[4] Von Weimarn, *Chem. Rev.*, **2**, 217 (1925).

[5] Glasses 590 blue and 243 red manufactured by the Corning Glass Company were used; thickness 2 mm.

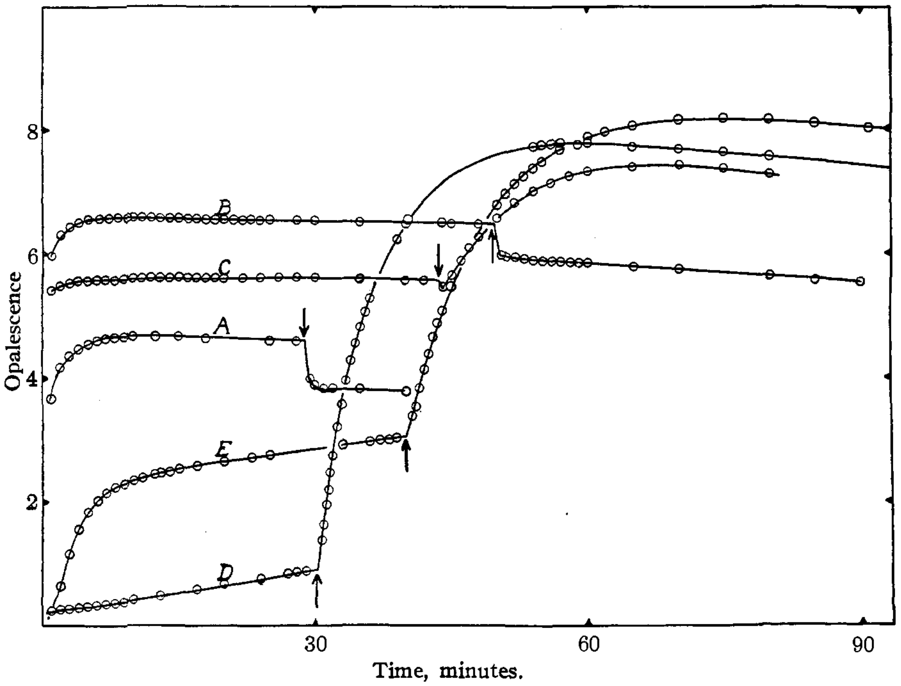

Fig. 5.—The effect of nitric acid upon the opalescence of silver chloride precipitates. The arrows mark the points at which the nitric acid was introduced.

Curve	A	B	C	D	E
Initial concn. HCl × 10^4	0.45	0.89	4.47	6.71	44.7
Concn. HNO_3 × 10^3 (final)	73	72	73	73	73

Pyrex bottles and centrifuged for ten minutes at 1500 r. p. m. The suspensions were then siphoned from the centrifuge bottles, with care to avoid disturbing any precipitate on the bottom, and the opalescence again measured in the original precipitation beaker. In a number of experiments 10 ml. of 2 *M* nitric acid was then added to promote coagulation. It is evident from Table IV, which presents the results of these experiments, that the large opalescences produced by the smallest excesses of hydrochloric acid are almost completely thrown out by this amount of centrifuging.

TABLE IV

The effect of centrifuging for ten minutes at 1500 r. p. m. at an average radius of 13.6 cm.

Concn. of precipitant × 10^4	Opalescence readings Before centrifuging	After centrifuging	After adding 10 ml. of 2 *N* HNO_3 (max.)
0.67 HCl	5.07	0.35	..
.67 HCl	6.24	.80	0.24
1.7 HCl	8.07	1.60	1.36
3.3 HCl	7.76	4.85	4.71
3.3 HCl	7.83	4.49	4.25
3.3 HCl	7.92	4.15	..
6.7 HCl	1.54	1.58	6.46
6.7 HCl	0.29	0.87	5.75
10.0 HCl	.35	1.16[a]	..

[a] On standing the opalescence developed to a maximum of 7.16 without the addition of any coagulating electrolyte.

With increasing concentrations of precipitant the opalescence remaining after centrifuging becomes a larger fraction of the initial opalescence and finally there is actually an increase during the centrifuging. In these suspensions which are too fine grained to be thrown out, the addition of nitric acid after centrifuging results in a rapid increase in opalescence.

These experiments can be utilized to gain some idea of the actual size of the particles. If one assumes that the particles are spheres, all of the same size, and that all those which are thrown against the bottoms of the centrifuge bottles stick and are lost to the suspension, then the fractional decrease in opalescence may be taken as measuring the fraction of the total depth of solution in the bottles from which particles are removed by centrifuging.

In the experiments with 3.3 × 10^{-4} *M* hydrochloric acid the average decrease in opalescence was 42.6%. In the centrifuge the bottoms of the bottles were 17.3 cm. from the center of revolution and the depth of the solution in the bottles was 7.4 cm. Employing Stokes law as applied to the motion of spherical particles through a liquid in a centrifugal field by Svedberg,[6] one finds that the average radius of the particles in the experiments in question was 1.1×10^{-5} cm. In a similar way it appears that for complete settling out of the particles under the given conditions the radius must be greater than 1.8×10^{-5} cm. while in suspensions so fine that fewer than 10% of the particles are thrown out the radius must be less than 0.5×10^{-5} cm.

Finally, even more conclusive evidence that the growth of initial opalescence to a maximum and its subsequent rapid diminution with increasing concentration of precipitant is due to progressive diminution in particle size was obtained by observations upon the suspensions with a slit ultramicroscope. It was plainly evident that the number of particles and the magnitude of the Brownian movement increased greatly as the concentration of precipitant increased in the experiments plotted in Figs. 1 and 2.

Counting the particles in a definite field was difficult because of the rapid Brownian movement. Fairly satisfactory determinations were obtained finally, however, by making a large number of counts at four-second intervals of the number of particles in a small field. The results presented in Table V can be considered to have only roughly quantitative significance. They show clearly, however, that the number of particles per unit volume increases as the excess of precipitant increases.

TABLE V

Concn. of precipitant $\times 10^4$	Opalescence at 30 minutes	Particle number	Diameter $\times 10^5$ cm.
0.50 HCl	5.5	0.17	3.2
1.7 HCl	8.3	.53	2.2
3.3 HCl	8.2	.74	2.0
4.2 HCl	5.0	1.9	1.4
0.5 $AgNO_3$	6.2	0.22	3.0
1.7 $AgNO_3$	5.5	2.1	1.4
3.3 $AgNO_3$	5.8	2.0	1.4
4.2 $AgNO_3$	5.0	2.5	1.3

The numbers given in the third column of Table V represent the average number of particles per single count in one square of the ultramicroscope field. The numbers given in the fourth column indicate the diameter of the particles, again on the assumption that they are spheres of uniform size. With 3.3×10^{-4} *M* hydrochloric acid the radius found in this way is 1.0×10^{-5} cm.

In all cases a greater number of particles resulted with a given excess of silver nitrate than with the same excess of hydrochloric acid. Apparently with excess silver there are a greater number of crystallization centers. One series of experiments was carried out in which a small amount of nitric acid was added to the silver nitrate before precipitation. The concentration of nitric acid was only 3.3×10^{-4} *M* and that of the silver nitrate 1.7×10^{-4}. Table VI shows the effect of this nitric acid upon the opalescence and particle number.

TABLE VI

Number of experiments	5	4
Concentration $AgNO_3$	1.7×10^{-4}	1.7×10^{-4}
Concentration HNO_3	0	3.3×10^{-4}
Opalescence after 30 min.	5.86	7.44
Mean deviation	0.70	0.42
Particle number per square	2.1[a]	0.78
Particle diameter, cm.	1.4×10^{-5}	2.0×10^{-5}

[a] Particle counts were made upon only two of the five suspensions.

It is evident that the number of particles is markedly decreased by the presence of a trace of acid. Some of the nuclei are either dissolved or rendered inactive by the acid.

With concentrations of precipitant greater than 4.2×10^{-4} *M* the number of particles increased very rapidly. It became impossible to make even approximate counts, however, because of the very rapid Brownian movement and because the individual particles were very dim and hard to see.

The phenomena with 10^{-3} *M* precipitant were extremely interesting and afford some insight into the mechanism of coagulation. When first examined with the ultramicroscope two minutes after precipitation, nothing could be seen in these suspensions. After a few minutes a large number of very faint particles became visible. These appeared to grow brighter as time passed without much change in number. After about fifteen minutes asymmetric particles appeared in the suspensions. These looked like pairs of closely joined particles. Indeed one would occasionally see two free particles unite to form a double particle. As time passed the number of double particles increased and particles composed of three, four or even more single ones could be seen. Such compound particles, which appeared very bright in the field of the ultramicroscope, undoubtedly account for a large fraction of the opalescence exhibited by suspensions in this range after coagulation.

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(6) Svedberg, "Colloid Chemistry," 2d ed., Chemical Catalog Co., New York, 1928, p. 148.

There is a peculiar and characteristic difference between the large particles in suspensions coagulated with an excess of hydrochloric acid and those coagulated with an excess of silver nitrate. In the chloride solutions the particles unite to form rods or chains while in the silver solutions irregular spherical clumps are formed.

The Rate of Formation of the Initial Particles.—It is evident from the curves of Figs. 1 and 2 that the time required for the formation of the initial particles is very short. Full opalescence is reached with dilute solutions practically as soon as the solutions can be mixed. It is impossible to measure the rate of such a rapid development of opalescence with the photronic nephelometer because of the time required to mix the solutions and the time required for the sensitive galvanometer to respond.

The curves of Figs. 1 and 2 indicate that the rate of formation of the primary particles is somewhat slower with the very smallest excesses of precipitant, *i. e.*, with concentrations less than 1.7×10^{-4} *M*. Curves A and B in these figures are decidedly more concave toward the time axis than are the curves representing experiments with a larger excess of precipitant. This probably indicates that the rate of crystallization of the last portions of silver chloride is slower in these dilute solutions where the degree of supersaturation is low. Even here, however, at least 70% of the maximum opalescence is reached by the time the pipet is emptied.

Further information was gained by precipitating silver chloride in a flowing system. Silver nitrate and hydrochloric acid, dilute enough so that a high initial opalescence would result, were introduced at the top of a vertical glass tube and the resulting mixture examined under a strong light as it flowed down the tube. In order to diminish the amount of light scattered from the outside the tube was immersed in benzene.

With a rate of flow of 20 cm. per second opalescence could be observed within a fraction of a centimeter of the point at which the solutions mixed. This indicates that particles of visible size are formed in a few hundredths of a second. From this point the opalescence increased markedly for a distance of about 10 cm. and then more slowly for 30 cm. more. Beyond 40 cm., the opalescence was constant as far as the eye could judge and equal to that obtained by refilling the tube with the suspension at rest. It appears then that the maximum steady opalescence requires only two seconds for development in this apparatus. We cannot be sure, however, whether this two seconds represents the time required for the precipitation to take place or the time required for complete mixing of the solutions in the tube. In any case there is no question but that the initial formation of particles of silver chloride is a very rapid process.

In conclusion, we wish to express our appreciation of a grant from the Milton Fund of Harvard University without which much of this work would have been impossible.

Summary

Two distinct stages have been observed in the formation of a precipitate of silver chloride. It has been shown that the rate of development of opalescence depends chiefly upon the concentration of the reagent present in excess and is relatively unaffected by variations in the rate of mixing and the rate of stirring. By measurement of the colors of the suspensions and the coagulating effect of nitric acid upon them it has been shown that their behavior is best explained as being due to progressive diminution in particle size with the increasing supersaturation which results from increased concentrations of precipitant.

Support is lent to this explanation by experiments with a centrifuge and experiments with an ultramicroscope. These experiments also indicate that particles of silver chloride in water first begin to follow Rayleigh's law and show a rapidly diminishing efficiency in scattering visible light when their radius becomes less than 10^{-5} cm.

Experiments with a flowing system indicate that visible particles of silver chloride are formed in the initial stage of the precipitation in a few hundredths of a second and that this stage of the reaction is virtually complete in two seconds or less.

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