In order to explain this behavior we have to recall that the speed of perfection does not depend upon the solubility of the barium sulfate in the *bulk of the solution but in the liquid film around the particles.* The fact that barium ions are more effective in inhibiting the aging than sulfate ions may be explained by the fact that barium ions are more strongly attracted by the barium sulfate lattice than are the sulfate ions. The adsorption of barium nitrate is greater than that of sodium sulfate from solutions of the same concentration.[7] Consequently, the concentration of the barium ions in the liquid film may be much greater than that of sulfate ions, although both are present in the same concentration in the bulk of the solution. Barium ions, therefore, inhibit the aging more than sulfate ions. An effect of the charge of the particles may also have to be considered.

Summary

1. Barium sulfate precipitated at room temperature from 0.1 M barium nitrate and 0.1 M sodium sulfate is highly imperfect. Its speed of perfection decreases in the following order with the composition of the mother liquor: $Ba^{++} = SO_4^{=} > 0.005\ M\ SO_4^{=} > 0.033\ M\ SO_4^{=} > 0.005\ M\ Ba^{++}$.

2. The specific surface of fresh barium sulfate increases slightly upon aging for a day in 0.005 M barium solution, showing conclusively that Ostwald ripening does not play a part. The decrease of the specific surface upon aging in 0.005 M sulfate solution is explained by an agglomeration with a subsequent cementing together of the particles as a result of the recrystallizations occurring in the liquid film around the particles.

3. It is postulated that the speed of perfection depends upon the solubility of the lattice material in the liquid film around the particles. In connection herewith an explanation is offered of the fact that barium sulfate perfects itself much more rapidly in 0.005 M sulfate than in 0.005 M barium solutions.

4. The properties of the fresh barium sulfate have been found to be independent of the way of mixing the 0.1 M precipitating agents.

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[7] *Cf.* S. Mattson, *J. Phys. Chem.*, **32**, 1546 (1928).

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

Studies on Aging of Fresh Precipitates. XX. Aging of Freshly Precipitated Barium Sulfate[1]

BY I. M. KOLTHOFF AND G. E. NOPONEN

In a previous paper[2] the mechanism of the aging in dilute barium and sulfate solutions of barium sulfate, precipitated at room temperature from 0.1 M solutions, has been discussed. In the present paper the effects of various factors affecting the speed of aging are discussed. Regarding the materials used and the methods of analysis the reader is referred to the previous paper.[2]

Aging in 50% Ethanol.—The solubility of barium sulfate is much less in mixtures of water and ethanol than in pure water. Therefore it may be expected that the speed of aging will be reduced considerably when the barium sulfate is allowed to age in a medium of 50% ethanol instead of in water. A similar effect of alcohol has been found on the speed of aging of freshly prepared lead sulfate.[3]

To 25 ml. of 0.11 M barium nitrate was added 25 ml. of 0.1 M sodium sulfate followed immediately by the addition of 50 ml. of absolute ethanol. The resulting suspensions containing an excess of barium were shaken for twenty-four hours at 26 ± 1°, centrifuged and the alcoholic mother liquor poured off. To the barium sulfate left were added 25 ml. of water, 25 ml. of 0.01 M sodium sulfate and 25 ml. of 0.01 M sodium chromate and the suspension shaken for one hour and twenty-four hours, respectively. After one hour of shaking 55.5% of the chromate had disappeared by going into the precipitate; after twenty-four hours, 92.0%. When the barium sulfate was aged for twenty-four hours without the addition of 50 ml. of ethanol and then treated as above 20.9 and 88.4% of chromate were found to be removed after one hour and twenty-four hours of shaking with the chromate–sulfate solution. Comparing the results with those in Table III of the previous paper[2] reveals that only very slight aging had occurred

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[1] From a thesis submitted by G. E. Noponen to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the degree of Doctor of Philosophy, June, 1936.

[2] I. M. Kolthoff and G. E. Noponen, THIS JOURNAL, **60**, 499 (1938).

[3] I. M. Kolthoff and Ch. Rosenblum, *ibid.*, **57**, 597 (1935).

TABLE I

SPEED OF PENETRATION OF CHROMATE IN THE PRESENCE OF WOOL VIOLET

Time of shaking with chromate	15 min.	30 min.	1 hour	4 hours	1 day	2 days	1 week	3 weeks
Chromate in precipitate, % (presence of dye)	3.4	5.1	6.7	10.7	..	17.5	..	19.6
Chromate in precipitate, % (absence of dye)			24.3		36.7[a]		35.2[a]	35.6[a]

[a] Homogeneous distribution of chromate throughout the solid.

TABLE II

SPEED OF PENETRATION OF CHROMATE IN THE PRESENCE OF GELATIN

Time of shaking with chromate	1 hr.	2 hrs.	4 hrs.	21 hrs.	29 hrs.	2 days	7 days	24 days
Chromate in ppt., %; 1 hour old	...	6.5	10.0	16.7	...	19.6	21.3	22.4
Chromate in ppt., %; 24 hours old	0.5	...	0.9	..	1.2	..	1.9	3.1

after shaking the precipitate for twenty-four hours in a medium of 50% ethanol. The above experiments were repeated and the barium sulfate, after shaking for twenty-four hours in a medium of 50% ethanol and centrifuging, was treated with 25 ml. of water, 25 ml. of 0.01 *M* barium nitrate and 50 ml. of wool violet solution containing 1 g. of dye per liter. The suspension was shaken for one hour and then centrifuged. An aliquot part of the centrifugate, after removing the traces of alcohol by evaporation to dryness, was analyzed for dye by the volumetric method. The precipitate adsorbed 34.3 mg. of dye per gram of barium sulfate, whereas a fresh precipitate of barium sulfate was found to adsorb 37.2 mg. of dye per 1 g. under similar conditions. Hence the specific surface of the barium sulfate had hardly changed upon aging in the medium of 50% ethanol.

The above aging experiments were carried out in the presence of an excess of barium (0.0025 *M*) in the supernatant liquid. They were repeated in an identical way in the presence of an excess of sulfate (0.0025 *M*) by adding together 25 ml. of 0.11 *M* sodium sulfate and 25 ml. of 0.1 *M* barium nitrate and 50 ml. of ethanol. Upon subsequent shaking with the sulfate–chromate solution, 50.5% of chromate was found to be removed after one hour of shaking and 89.5% after twenty-four hours. When the fresh precipitate was shaken with the sulfate–chromate mixture 92.2 and 82.7% of chromate were found to be removed after one hour and twenty-four hours, respectively; on the other hand, after aging for twenty-four hours in 0.005 *M* sulfate in water only 2.9 and 4.9%, respectively, were removed. It may be inferred that the barium sulfate after shaking for twenty-four hours in the alcoholic medium has aged less than when shaken for less than one hour in aqueous medium. After aging for twenty-four hours in the medium of 50% ethanol the barium sulfate adsorbed 35.2 mg. of wool violet per gram, whereas the fresh precipitate adsorbed 37.4 mg. per gram and a precipitate aged for twenty-four hours in 0.005 *M* sulfate in water only 13.2 mg. per gram. Hence the specific surface of the barium sulfate had hardly changed upon aging for twenty-four hours in 50% ethanol containing an excess of sulfate.

From these experiments it follows that the speed of the entire aging is considerably less in a medium of 50% ethanol than in water.

Effect of Wool Violet on Speed of Aging.—Kolthoff and Rosenblum[4] have shown that the aging of fresh lead sulfate in the presence of an excess of lead is greatly inhibited by coating the precipitate with wool violet. It was of interest to determine whether the adsorbed wool violet exerted a similar effect upon the aging of barium sulfate in the presence of an excess of sulfate. The following experiments were performed. To 50 ml. of 0.1 *M* sodium sulfate were added 25 ml. of 0.1 *M* barium nitrate and 50 ml. of a wool violet solution containing 1 g. of dye per liter. The suspension was shaken for five minutes and then 25 ml. of 0.1 *M* sodium chromate was added. The mixture was put on the shaker and after various periods of time samples were centrifuged and analyzed for chromate. The presence of the dye did not interfere with the iodometric determination of the chromate. For comparison similar experiments were made in which the 50 ml. of dye was replaced by 50 ml. of water. The results are given in Table I.

Although it is doubtful whether the barium sulfate is covered completely with a layer of the dye in the presence of a relatively large excess of sulfate it is seen readily that the wool violet inhibits the recrystallization process considerably. Even after three weeks of shaking in the presence of dye, the solid phase is not nearly in equilibrium with the solution, whereas in the absence of dye homogeneous distribution is obtained after one to two days of shaking.

Effect of Gelatin on Speed of Aging.—Sven Odén[5] has found that gelatin is strongly adsorbed on barium sulfate. Therefore, it was of interest to study the effect of gelatin upon the speed of aging of barium sulfate.

The gelatin solution was prepared by dissolving 11 g. of Nelson's photographic gelatin in 1 liter of water. To 50 ml. of 0.1 *M* sodium sulfate was added 25 ml. of 0.10 *M* barium nitrate and 25 ml. of 1.1% gelatin solution. The suspension was shaken for one hour and twenty-four hours, respectively. Then 25 ml. of 0.1 *M* sodium chromate was added, and the mixture was again placed on the shaker. After various periods of time samples were removed, centrifuged and analyzed for chromate iodometrically. The gelatin does not interfere with this determination. The results are reported in Table II.

These experiments show conclusively that a pronounced perfection of the barium sulfate occurs when the latter is aged in the presence of gelatin. After one day of aging the speed of penetration of the chromate is extremely slow whereas it is relatively fast when the precipitate has aged for one hour. It is not possible to conclude from these experiments whether the gelatin has any inhibiting

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[4] I. M. Kolthoff and Ch. Rosenblum, THIS JOURNAL, **57**, 607 (1935).

[5] Sven Odén, *Arkiv Kemi, Mineral. Geol.*, **7**, No. 26 (1920).

effect upon the aging. The results of experiments reported in Table II are not comparable with those carried out in the absence of gelatin, because the latter will inhibit the speed of diffusion of the chromate to the surface of the particles and therefore decrease the speed of formation of the mixed crystals. In order to get an idea whether the gelatin has any effect upon the speed of aging of barium sulfate the following experiment was carried out. To 20 ml. of 0.1 *M* sodium sulfate was added 10 ml. of 0.1 *M* barium nitrate. The suspension was shaken for twenty-four hours, then 30 ml. of water, 20 ml. of 1.1% gelatin solution and 10 ml. of 0.1 *M* sodium chromate were added. The suspension was shaken for various periods of time and the solution analyzed for chromate. After one hour of shaking 0.44% of the chromate was found to be removed by the precipitate, after one week 0.45%, after three weeks 0.46%. Apparently, the chromate exchanges only with sulfate on the surface of the barium sulfate, but does not penetrate into the interior of the precipitate after three weeks of shaking. From these experiments and those in Table II one might infer that gelatin has a slight inhibiting effect upon the speed of aging of barium sulfate.

A priori we expected a large effect of the gelatin comparable to that of wool violet. In order to explain the small effect we have to consider the fact that gelatin is strongly hydrated even in the adsorbed state on barium sulfate. Apparently there is enough water around the particles with the adsorbed gelatin to allow recrystallization in the liquid film. On the other hand, it may be expected that gelatin will inhibit the agglomeration and the subsequent cementing together of the particles. More experiments are planned to get a more detailed picture of the effect of gelatin upon the aging.

Effect of Temperature upon the Degree of Perfection of Barium Sulfate.—Experiments were carried out in which barium sulfate was precipitated at room temperature and also at boiling temperature. The perfection of the precipitates was determined by measuring the speed of penetration of lead[2] at room temperature (26 ± 1°) into the fresh precipitates and into the precipitates after digestion at 95° for one hour. To 50 ml. of 0.11 *M* barium nitrate was added at room temperature and at boiling temperature, respectively, 50 ml. of 0.1 *M* sodium sulfate. When precipitated hot the suspension was cooled immediately to room temperature and to both suspensions were added 20 ml. of 0.1 *M* lead nitrate and water to make the volume 250 ml. The mixtures were placed on a shaker, and samples were removed after various periods of time and analyzed for lead. In the aging experiments the suspensions before the addition of lead were digested at 95° for one hour, then cooled to room temperature and further treated as above. The results are given in Table III.

TABLE III

EFFECT OF TEMPERATURE UPON PERFECTION OF BARIUM SULFATE

Conditions of pptn.	Conditions of aging	Percentage of added lead in precipitate after shaking for		
		1 hour	24 hours	1 week
26°	..	21.4	24.4	20.8
Boiling temp.	..	4.0	12.9	16.1
26°	1 hour at 95°	0.9	1.2	2.2
Boiling temp.	1 hour at 95°	1.4	1.7	2.4

The results show that the fresh precipitate formed at boiling temperature is still extremely imperfect. Regarding the speed of mixed crystal formation with lead, it behaves as a precipitate formed at room temperature, which has been aged in the supernatant liquid for a few hours.[2] A comparable small effect of the temperature upon the degree of perfection has been found in the case of lead sulfate.[6] The effect of temperature upon the solubility of both salts, barium and lead sulfate, is relatively small which accounts for the small effect of the temperature of precipitation upon the degree of perfection of the precipitate. In other cases, in which the effect of temperature upon the solubility is more pronounced, the degree of perfection of the precipitate may be expected to be greatly dependent upon the temperature of precipitation.

A precipitate of barium sulfate formed at room temperature and digested for one hour at 95° behaves as a precipitate formed at room temperature and aged for more than a week in the supernatant liquid (compare with Table I in previous paper[2]). When the precipitate is formed at boiling temperature and digested for one hour at 95° it is slightly "fresher" than barium sulfate formed at room temperature and subjected to the same aging. Apparently, the precipitate formed at boiling temperature consists of larger particles and ages less rapidly at 95° than the precipitate formed at room temperature. Independent of the temperature of formation of the barium sulfate digestion at 95° for one hour causes a very pronounced aging. It was investigated whether it would be possible to obtain by digestion at much higher temperatures a precipitate of such a degree of perfection that it would not be subject to further recrystallization when heated in the aqueous mother liquor. For this purpose barium sulfate was prepared by adding 25 ml. of 0.11 *M* barium nitrate to 25 ml. 0.1 *M* sodium sulfate. The suspension was sealed in a Pyrex tube and placed in a Carius oven at 185° for twenty-four hours. At the end of this period, the tube was cooled, opened and 25 ml. of 0.1 *M* lead nitrate was added. The tube was sealed again and heated for twenty-four hours and five days, respectively, at 185°. Then it was opened and the mother liquor analyzed for lead. The results were compared with those in which the precipitate had not been preheated for twenty-four hours at 185° before the addition of lead. In the latter case 13.0% of the added lead was found in the precipitate after heating for twenty-four hours and 12.4% after five days. In case the precipitate was preheated the corresponding figures were 2.2 and 3.4%, respectively. Although the precipitate had become very coarse and relatively perfect by the preheating at 185° it was still subject to further recrystallization as evidenced by the continuous penetration of the lead at 185°. In a previous study[7] it had been found that such a perfected precipitate even allowed the slow penetration of lead at room temperature when shaken with a solution containing barium and lead.

The present study is of an exploratory character only. It is planned to make a more detailed study of the various factors discussed in this paper in the near future.

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(6) I. M. Kolthoff and Ch. Rosenblum, THIS JOURNAL, **57**, 2577 (1935).

(7) I. M. Kolthoff and Wm. M. MacNevin, *ibid.*, **58**, 499 (1936).

Summary

1. Adsorbed wool violet strongly inhibits the aging of barium sulfate.

2. The presence of much gelatin in the aqueous suspension inhibits the aging of barium sulfate only slightly, although it is strongly adsorbed on barium sulfate. This is explained by the hydrophilic character of the adsorbed gelatin.

3. The aging of barium sulfate is strongly inhibited in a medium of 50% ethanol.

4. Precipitates of barium sulfate prepared at boiling temperature are very imperfect. Aging of precipitates at higher temperature promotes the perfection process considerably.

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

Studies on Aging of Fresh Precipitates. XXI. Properties of Barium Sulfate Precipitated from Ammonium Acetate Medium and the Coprecipitation of Lead

BY I. M. KOLTHOFF AND G. E. NOPONEN

A study of the properties of barium sulfate precipitated from ammonium acetate medium is not only of theoretical but also of practical importance in connection with the problem of separating barium and lead, and of the extraction of lead sulfate from the mixed sulfates with ammonium acetate solution.[1] In the present work the coprecipitation of lead with barium sulfate, when the latter is precipitated from a medium containing much ammonium acetate, has been investigated. In a previous study[2] it has been shown that under equilibrium conditions the amount of lead in the solid phase can be calculated from the distribution expression. It should be realized that the value of the distribution constant, K, found previously,[2] decreases considerably when the liquid phase contains much acetate, as the activity coefficient of the lead ions is decreased much more than that of the barium ions as a result of complex formation. But the value of K does not decrease to zero; therefore, it is impossible to have pure barium sulfate in equilibrium with a solution containing lead and ammonium acetate. All one can hope for in analytical work is to find conditions under which the barium sulfate precipitate contains a minimum amount of lead and the solid phase is far removed from the state of equilibrium with the liquid phase.

Experimental

In the following work experiments were carried out under such conditions that the lead, if present alone in the solution, would not precipitate in the form of lead sulfate. In order to know these conditions, the solubility of lead sulfate was determined by shaking pure samples of the salt for three to four hours at room temperature (26 ± 1°) with the solutions containing varying amounts of ammonium acetate and sodium sulfate. The lead content of the saturated solution was found by precipitation as lead chromate from hot acetic acid solution with potassium dichromate and iodimetric determination of the chromate in the precipitate. The results are given in Table I.

TABLE I

SOLUBILITY OF LEAD SULFATE IN AMMONIUM ACETATE–SULFATE SOLUTIONS AT 26 ± 1°

Concn. ammonium acetate, M	Concn. sodium sulfate, M	Concn. of lead, moles/liter
0.6[a]	0.01	0.0052
.6	.005	.0089
1.5	.005	.0288
2	.01	.0390
3	.005	.0697
3	.01	.0692

[a] Solution was also 0.6 M in acetic acid.

Coprecipitation of Lead with Barium Sulfate from Ammonium Acetate Medium.—In the following experiments the concentration of ammonium acetate, after making up to a volume of 100 ml. was 2 M. In the first series the barium sulfate was precipitated by adding the sulfate to a mixture of barium and lead in ammonium acetate, in the second series the barium was added to a mixture of lead and sulfate in ammonium acetate. Series I: to 20 ml. of 0.05 M barium nitrate was added 10 ml. of 0.10 M lead nitrate and 34 ml. of 6 M ammonium acetate. The mixture was shaken while 20 ml. of 0.10 M sodium sulfate was added from a buret in four to five minutes. The volume was then made up to 100 ml. and the suspension placed on a shaker. After various periods of shaking the suspensions were centrifuged and 50 ml. of the centrifugate analyzed for lead by adding 2 to 3 ml. of 6 M acetic acid, heating to the boiling point and adding 10 ml. of 0.05 M

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[1] *Cf.* J. Majdel, *Z. anal. Chem.*, **83**, 36 (1931); F. Feigl and L. Weidenfeld, *ibid.*, **84**, 220 (1931); W. W. Scott and S. M. Alldredge, *Ind. Eng. Chem., Anal. Ed.*, **3**, 32 (1931); J. W. Marden, THIS JOURNAL, **38**, 310 (1916).

[2] I. M. Kolthoff and G. E. Noponen, *ibid.*, **60**, 197 (1938).