the solid and liquid, respectively, $\log_{10} P_{(mm.)} = 9.33902 - (1864.8/T)$; $\log_{10} P_{(mm.)} = 7.744603 - (1453.063/T)$.

2. The triple point of hydrogen cyanide has been calculated to be 658.24°K. or —14.86°C. at a vapor pressure of 131.16 mm. The normal boiling point is 298.75°K. or +25.65°C.

3. The latent heats of sublimation, fusion and evaporation are 316.13, 69.29 and 246.84 calories per gram, respectively.

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THE INFLUENCE OF CITRATES ON THE PRECIPITATION OF BARIUM SULFATE

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In 1858 Spiller[1] reported that in the course of an investigation he attempted to precipitate barium phosphate from a solution containing alum, citric acid, sodium phosphate and ammonia but obtained no precipiate, which led him to investigate the cause of the sulfuric acid and barium salt existing together in the same solution. He concluded that this peculiar condition was due to the formation of a soluble double salt by the citrate. This solution could only be prepared by adding the barium salt to a mixture of the sulfate and citrate and after preparation the barium sulfate could be precipitated in a "peculiar flocculent condition" by barium nitrate in excess, hydrochloric, acetic, tartaric, or oxalic acid or by heating.

A similar case was noted by Scheerer[2] who found that when sodium metaphosphate was treated with hydrochloric acid, barium chloride added and the mixture shaken until the barium metaphosphate dissolved, no precipitate of barium sulfate was formed on the addition of dil. sulfuric acid. Cases[3] have also been found of the simultaneous presence of barium and sulfates in dilute solution, in certain mineral waters.

The influence of citrates on the solubility and precipitation of certain other salts has also been studied[4] by Lea, Warington, Teodossiu and Mains, as well as the influence of different substances on the solubility and precipitation of barium sulfate[5] by Gil-

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[1] Spiller, *J. Chem. Soc.*, [I] **10**, 110 (1858).

[2] Scheerer, *Chem. Gaz.*, **17**, 57 (1859).

[3] Anon., *J. Chem. Soc.*, [I] **25**, 923 (1872). Carles, *J. Pharm.*, [6] **13**, 562 (1901).

[4] Lea, *J. Chem. Soc.*, [I] **27**, 964 (1874). Warington, *ibid.*, **28**, 993 (1875). Teodossiu, *Bull. soc. chim. România*, **3**, 9 (1921); Mains, *J. Assoc. Official Agr. Chem.*, **4**, 235 (1920).

[5] Gilkowsky, *J. Chem. Soc.*, [I] **25**, 1113 (1872). Lucion and Tauber, *Chem.-Ztg.*, **12**, 427, 477 (1888). Fraps, *Am. Chem. J.*, **27**, 288 (1902). Kernot, *Rend. accad. sci. Napoli*, (iii) **15**, 155 (1909). Johnson and Adams, THIS JOURNAL, **33**, 829 (1911). Karaoglanow, *Z. anal. Chem.*, **56**, 225 (1917). Weiser, *J. Phys. Chem.*, **21**, 314 (1917); **23**, 205 (1919).

kowsky, Lucion and Tauber, Fraps, Kernot, Johnson and Adams, Karaoglanow and Weiser.

Colloidal solutions of barium sulfate have also been prepared[6] by Recoura, Feilman, Kato, Von Weimarn and Gengou.

Experimental Part

As the information given by Spiller[1] is not very definite with regard to the concentration of the solutions used, a series of experiments was made to determine the best conditions for the formation of his so-called solution of barium sulfate. One cc. of N sodium sulfate solution was measured into a test-tube, the volume of sodium citrate solution required to give the desired concentration was added, and the mixture diluted to 9 cc., after which 1 cc. of N barium nitrate solution was added. This gave 1.0 milligram equivalent of both barium and sulfate ions or, if the product of the reaction remained in solution, a 0.1 N solution of barium sulfate. The concentration of the sodium citrate was varied from zero to saturation. Even so low a concentration as a 0.02 N solution of sodium citrate showed a slight tendency towards suspending the barium sulfate which precipitated. As the concentration of the sodium citrate was increased the milky barium sulfate suspension gradually cleared, until at 0.2 N concentration of sodium citrate, an apparently true solution was produced—one that was quite clear or very slightly opalescent. The clearest "solution" was obtained when the concentration of the sodium citrate was twice that of the barium sulfate. Higher concentrations of sodium citrate gave clear "solutions" at first but they were not nearly as permanent as those with 0.2 N sodium citrate which remained transparent for 10 to 14 days.

It is worth while to mention the process of formation of this apparent solution of barium sulfate. No change was noticed when the solutions of sodium sulfate and sodium citrate were mixed and diluted; but upon the addition of the barium salt, a gelatinous precipitate of barium citrate separated and in cases where there was a rather large quantity of sodium citrate present, this precipitate was almost sufficient to solidify the contents of the test-tube for a moment. When the mixture was shaken, the gelatinous precipitate changed, with the evolution of a very small amount of heat, to a milky precipitate, apparently of barium sulfate, and within a few moments the milkiness faded into a clear, or slightly opalescent "solution."

These experiments were then repeated with solutions of such concentrations as to give 0.2, 0.3, 0.4, 0.6, 0.8, 1.0 and 1.5 N "solutions" of barium sulfate, and the concentration of sodium citrate was varied in each case

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[6] (a) Recoura, *Compt. rend.*, **146**, 1274 (1908). (b) Feilman, *Trans. Faraday Soc.*, **4**, 175 (1909). (c) Kato, *Mem. Coll. Sci. Eng. Imp. Univ., Kyoto*, **2**, 187 (1909–1910). (d) Von Weimarn, *Kolloid-Z.*, **2**, 76 (1907); **3**, 166 (1908). Bancroft, "Applied Colloid Chem.," McGraw-Hill Book Co., **1921**, p. 163. (e) Gengou, *Z. Kolloidchem.*, **9**, 88 (1911).

from zero to saturation. Finally, saturated solutions of sodium sulfate, barium chloride and sodium citrate were used. The amount of barium sulfate that can be held in this type of "solution" seemed to be limited only by the solubility of the salts used. In all of these experiments it was found that the maximum clearness was obtained with the ratio of the equivalents of sodium citrate and barium sulfate at 2 : 1, although an excess of sodium citrate seemed to have no very detrimental effect. However, with the strong "solutions" of barium sulfate the stability and clearness both decreased with increased concentration.

The effect of varying concentrations of the sodium citrate on the respective concentrations of barium sulfate is shown qualitatively in Fig. 1.

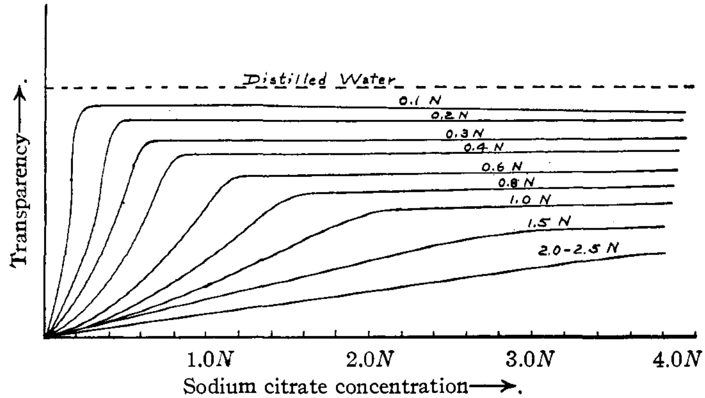

Fig. 1.—Effect of the citrate concentration on the clearness of barium sulfate "solutions" of various concentrations.

Using the concentrations which gave the clearest "solutions" when the barium salt was added last, that is, barium sulfate 0.1 *N* and sodium citrate 0.2 *N*, it was found that this apparent solution of barium sulfate did not form if either the sodium sulfate or sodium citrate was added last.

The assumption was made at the beginning of this investigation that the presence of equivalent amounts of barium and sulfate ions ought to furnish the optimum condition for the formation of the clearest "solution" of barium sulfate. This assumption was then tested by two experiments; (1) by keeping the barium chloride and sodium citrate concentrations constant at 0.1 *N* and 0.2 *N*, respectively, and varying the sulfate concentration, and (2) by keeping the potassium sulfate and sodium citrate concentrations constant at 0.1 *N* and 0.2 *N* and varying the barium chloride concentrations. In both cases the barium salt was added last.

The results of these tests are plotted qualitatively in Fig. 2. It can be seen that the optimum condition for the formation of the clearest and most permanent "solutions" was as assumed, although a small excess of barium ions was not detrimental. The presence of the excess of barium was proved by testing the clear supernatant liquid for barium and sulfate, after the precipitate had been formed by heating with hydrochloric acid.

In all of the previous experiments sodium sulfate or potassium sulfate, sodium citrate and barium nitrate or barium chloride solutions have been used to prepare the "solutions." The use of various salts to furnish the barium, sulfate and citrate ions was studied in order to determine whether any specific substance was necessary. It was found that the formation of the barium sulfate "solution" is not dependent on any salt in particular but only on the barium, sulfate and citrate ions, so long as these latter are not in the presence of enough mineral acid to convert the citrate into citric acid. The best results were obtained when no acid was present.

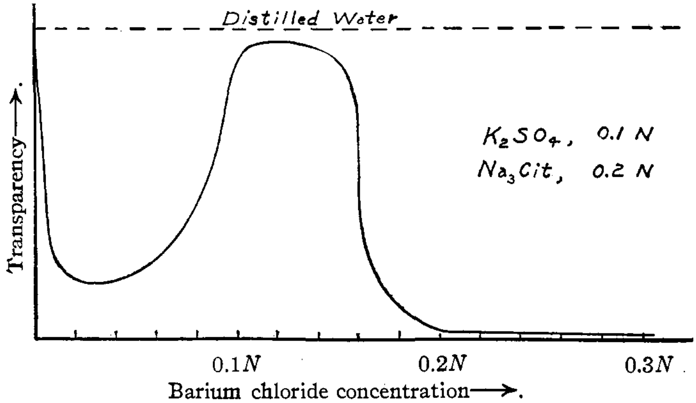

Fig. 2.—Influence of barium-ion concentration on the barium sulfate "solution."

The formation of these "solutions" also depends on the temperature, the increase in turbidity varying almost directly with the rise in temperature. Those prepared between 15° and 0° were so clear that the eye could not distinguish them from true solutions.

Considering the relatively enormous quantities of barium sulfate which can be held in these "solutions" and also the variation in transparency from practically that of distilled water in a 0.1 *N* or lower concentration of barium sulfate to the slightly translucent, quite opalescent "solution" obtained with a concentration of 1.5 *N* or stronger, it was quite apparent that the barium sulfate is probably present in the colloidal state. Some of the clearest "solutions" were, therefore, subjected to dialysis tests with a collodion membrane, both distilled water and a solution containing the same concentration of citrate being used as the dialyzing medium. After several days no barium sulfate could be detected in the dialyzing medium.

The coagulating effect of various substances upon the clear "solutions" was then investigated to determine whether the colloid was positive or negative. Nitric acid, hydrochloric acid, citric acid, sulfuric acid, aluminum sulfate and aluminum nitrate gave immediate coagulation when present even in small amounts. Under similar conditions sodium sulfate, sodium carbonate, ammonium carbonate, ammonium oxalate, disodium phosphate, barium nitrate, barium chloride, sodium hydroxide, positive hydrous ferric oxide colloid, heat, ferric chloride and potassium hydroxide gave quite rapid coagulation, but acted more slowly than the series of substances previously mentioned. Potassium ferrocyanide, ammonium chloride, potassium and sodium citrates, ammonium hydroxide and negative arsenious sulfide colloid had but little effect.

In connection with the precipitation of the barium sulfate from these "solutions," it should be noted that the barium sulfate, whether precipitated by heat, acid, salts, colloids or long standing, remained quite unlike barium sulfate precipitated under usual conditions, even after it has been digested for some time at temperatures approximating the boiling point. It was quite flocculent, remained in milky suspension for some time after being shaken and passed through filter paper readily. Since the precipitated barium sulfate could not be filtered off and washed, the nature of the precipitate could not be studied satisfactorily. Washing by decantation was unsatisfactory.

One of the very clear "solutions" was put into an endosmose apparatus and subjected to the action of a 110-volt d.c. current for some time. The boundary line between the distilled water and the clear and colorless "solution" of barium sulfate was not distinct and although this experiment was repeated several times, no conclusive evidence of migration toward either pole was obtained. There was, however, apparently a slight motion towards the positive terminal.

The supernatant liquid from the coagulation test with the hydrous ferric oxide colloid was removed with a pipet, treated with hydrochloric acid and heated. No precipitate was formed, proving the absence of barium sulfate. Also, the precipitate from this test was treated with hydrochloric acid and heated. The reddish-brown precipitate of ferric hydroxide dissolved leaving a white precipitate of barium sulfate. This showed that the barium sulfate in the "solution" and the hydrous ferric oxide colloid mutually coagulated each other. This, coupled with the negative results with the arsenious sulfide colloid and the apparent migration of the barium sulfate toward the positive pole under the influence of the electric current, indicated that we were dealing with a negatively charged colloidal solution of barium sulfate.

Some of the clearest of the "solutions" of barium sulfate and some of the distilled water were examined with the ultramicroscope by Dr. C. W. Mason. There were only occasional particles visible in either case. This indicated that the particles of barium sulfate were beyond the range of the ultramicroscope used, that is, less than 5–6 millimicrons in diameter

With these suspensions of barium sulfate, however, there was a decided bluish glow in the path of the light beam through the liquid, evidently the Tyndall effect produced by the presence of very minute particles of barium sulfate. The refractive index of barium sulfate was not determined at this time but it is known that, with the ultramicroscope, barium sulfate particles can be seen with Brownian movement in certain colloids.[6e]

This apparent solution, resulting from the addition of the barium salt to a sulfate in the presence of a citrate might affect the results obtained in an effort to determine sulfur quantitatively in the presence of citrates by precipitation as barium sulfate. Experiments showed that in the determination of sulfur as barium sulfate in the presence of citrates, if slightly more than the amount of hydrochloric acid needed to convert the citrates into citric acid is added before the precipitation with the barium chloride, perfectly satisfactory results will be obtained. Reference to the preceding work will show that the addition of acid after treatment with barium chloride would result in the formation of a precipitate that would be very difficult, if not impossible, to filter and wash. No interference would be expected if the sulfate solution was added last, as the colloidal solution does not form under these conditions.

Discussion

Spiller's conclusion[1] that a soluble double salt is formed does not seem to be a satisfactory explanation of the experimental results. It is known that some double or complex salts of barium have been made, such as barium chromo-oxalate, $Ba_3Cr_2(C_2O_4)_6$, which was isolated by Werner[7] and $MoO_2(C_6H_6O_7)_2Ba$, which was described by Henderson, Orr and Whitehead.[8] However, the properties of the "solution" of barium sulfate are not those of a solution of a double or complex salt.

Double and complex salts, when in solution, form clear solutions regardless of concentrations up to saturation. There is no gradual increase in turbidity with increase in concentration as is indicated by the curves in Fig. 1. When a solid phase does separate, it is in crystalline form, not the flocculent form in which the barium sulfate separates from the "solution" under consideration.

The behavior of the "solution" towards heat is also not characteristic of double or complex salts. Within reasonable limits, it is usually the case that such salts are more soluble at higher temperature, whereas the clear "solution" of barium sulfate becomes more and more turbid with a rise in temperature. This decrease in stability at higher temperature is, however, quite frequently characteristic of colloids, as is shown by Zsigmondy.[9]

[7] Werner, *J. Chem. Soc.*, **51**, 388 (1887).

[8] Henderson, Orr and Whitehead, *J. Chem. Soc.*, **75**, 546 (1899).

[9] Zsigmondy, trans. Spear, "Chemistry of Colloids," Wiley and Sons, **1917**, p. 63.

Furthermore, if the barium sulfate were in solution as a double salt, there would be no reason why neutral salts and certain colloids should flocculate it. The mutual precipitation of the hydrous ferric oxide colloid and the barium sulfate and the detection of these two substances in the precipitate is very conclusive evidence that the barium sulfate is in the colloidal state, since it was found that the hydrous ferric oxide colloid was positively charged and that the colloid of barium sulfate was negatively charged. Crystalloids almost invariably diffuse through collodion membranes.[10] The absence of barium sulfate from the dialyzing media adds to the evidence that the barium sulfate is in the colloidal state.[11]

The fact that the clear "solution" forms only when the barium compound is added last is very significant. When a solution of a double or complex salt is to be made, the method of preparation is not important. A double salt would form as readily when the sulfate was added last as when the barium compound was added last. This idea is contrary to the results of the experiment in which sulfate was added last. The course of the reaction in this case is probably as follows: the sodium citrate and barium chloride form barium citrate, but the barium citrate does not precipitate in the presence of the excess citrate. The concentration of the barium ion is considerably diminished by the formation of the barium citrate, but is not reduced to a value that is even near the minimum amount required to satisfy the solubility product of barium sulfate. When the sulfate is added, some of the barium ions are removed from solution by forming barium sulfate, but an equivalent amount is added to the solution by the ionization of some of the barium citrate in restoring the equilibrium: $Ba_3Cit_2 \rightleftharpoons 3Ba^{++} + 2Cit^{---}$. With this small, but appreciable, concentration of barium ions existing continuously in the mixture during the formation of the barium sulfate, the latter, if peptized and negatively charged by the citrate ions, would be instantly coagulated by the bivalent positive barium ions, and would settle out at once. This is in agreement with the experimental results.

On the other hand, when the barium salt is added to the mixture of sodium citrate and sodium sulfate, the barium sulfate is formed in the presence of negative sulfate ions, as well as citrate ions, and as fast as the barium sulfate forms it is peptized by the citrate ions and held in colloidal solution. After the colloid has once been formed, the concentration of the barium ion may be made slightly greater than that of the sulfate without causing any decrease in the clearness of the colloidal solution. However, a larger excess will cause the precipitation of the barium sulfate, on account of the coagulating influence of the bivalent positive barium ion.

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[10] It is stated by Zsigmondy that some crystalloids of very high molecular weight do not diffuse through membranes.

[11] Bancroft, *J. Phys. Chem.*, **29**, 966 (1925).

The possibility of the separation of barium citrate while the barium salt is being added does not alter the situation. Whether the reaction takes place directly between the barium salt and the sulfate, or whether barium citrate is formed as an intermediate product, the reaction takes place between barium and sulfate ions, in the presence of an excess of sulfate ions, $Ba^{++} + x\ SO_4^{--} = BaSO_4 + (x-1)SO_4^{--}$, until, at the end of the reaction, the last of both ions would be removed in forming barium sulfate.

Further substantiation of the conclusion that the "solution" under investigation is a colloidal dispersion of barium sulfate is found in the account of a colloid of barium sulfate prepared by Von Weimarn[6d] by mixing concentrated solutions of barium thiocyanate and manganous sulfate. The colloid was gelatinous, translucent for a time and the particles could not be differentiated even with the ultramicroscope. It was very similar in many respects to the "solution" described in this paper. The most outstanding common characteristic of these two colloids was that neither gave evidence of the presence of individual particles when examined with the ultramicroscope. The "solution" of barium sulfate gave a bluish glow in the path of the light beam through the liquid when examined with the ultramicroscope. This indicated the presence of aggregates of molecules large enough to produce the Tyndall blue, which would eliminate the possibility of barium sulfate being in true solution.

The consideration of the experimental evidence presented leads the authors to conclude that when a barium salt is added to a sulfate in the presence of a citrate, a negatively charged colloidal solution of barium sulfate is formed and not a true solution of a double salt as suggested by Spiller.

Summary

1. The conditions under which apparently true solutions of barium sulfate of various concentrations could be prepared were determined.

2. The nature and characteristics of the apparent solution were considered in detail.

3. The "solution" was found to be a negatively charged colloidal dispersion of barium sulfate, in which the particles were in an extremely fine state of subdivision.

4. Determinations involving the precipitation of barium sulfate in the presence of citrates can be made satisfactorily, provided slightly more than enough acid to convert the citrates to citric acid is added before the precipitation is begun.

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