

sulfate, potassium sulfate acts powerfully to decrease the solubility of potassium permanganate in solutions of sodium sulfate, while sodium sulfate increases its solubility in solutions of potassium sulfate to a much smaller degree.

FAYETTEVILLE, ARKANSAS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

## ADSORPTION OF IODINE BY SILVER IODIDE

BY FRANK E. E. GERMANN AND RALPH N. TRAXLER

Received July 25, 1921

On page 98 of Bancroft's "Applied Colloid Chemistry,"<sup>1</sup> we find the following statement:

"Carey Lea<sup>2</sup> has shown that silver iodide adsorbs iodine strongly. This property of silver iodide was verified by shaking portions of freshly precipitated and still moist AgI with iodine solutions. An alcoholic solution of iodine, diluted until it has a pale sherry-wine color is quickly decolorized by AgI and the same thing happens with a very dilute solution of iodine in KI which in a few minutes becomes as colorless as water. It is probably this adsorption which makes silver iodide photographic emulsions apparently less sensitive than the silver bromide emulsions. If so, it should not be difficult to overcome this trouble."

Experiments were performed to determine whether adsorption did take place. Acetone, water-free methyl alcohol, 95% ethyl alcohol, and a water solution of potassium iodide were used as solvents for the iodine, which was purified several times by grinding with potassium iodide and then subliming. Standardized sodium thiosulfate solution (1 cc. = 0.0023 g. of iodine) was used for titration. Silver iodide was made by precipitating from solutions of potassium iodide and silver nitrate of strength ranging from *M* to 0.1 *M*. The potassium iodide and silver nitrate used were purified by recrystallization. All experiments were performed in a room with no actinic light present.

In the first series of experiments the precipitated silver iodide made from *M* solutions of silver nitrate and potassium iodide was thoroughly washed, dried and passed through a 100-mesh screen, in order to have fairly uniform particles. In each of these experiments 0.2 g. of dry, powdered silver iodide was added to 25 cc. of the solvent containing 0.05 g. of the purified iodine. The container was stoppered and the mixture shaken for 1 minute, 5, 10, 15, 20 and 30 minutes. Care was taken not to increase the temperature appreciably while shaking. The mixture was filtered rapidly by suction, and the filtrate titrated with sodium thiosulfate solution for free

<sup>1</sup> Bancroft, "Applied Colloid Chemistry," McGraw Hill Book Co., 1921.

<sup>2</sup> *Am. J. Sci.*, [3] 33, 492 (1887); See also Problem 54 of Bancroft's "Research Problems in Colloid Chemistry." Nat. Research Council Reprint No. 13, 1921.

iodine. In none of the experiments was an adsorption of iodine noted, within a low limit of experimental error.

Experiments using the same kind and quantities of material were made, and the mixture was boiled for 15 minutes to 1 hour under a reflux condenser at a pressure of 62 cm. of mercury. These upon being filtered and titrated showed no decrease in iodine content.

Several very dilute solutions of iodine (about 0.01 g. in 25 cc. of solvent) were run qualitatively with amounts of silver iodide larger than 0.2 g. No decolorization of the iodine was noted. Also, several determinations were made in the presence of actinic light, but no iodine was removed by such a procedure.

Silver iodide was then made from the same strength of solutions and thoroughly washed with distilled water, but added to the iodine solutions without being dried. This conformed with the former experimenter's "freshly precipitated still moist silver iodide." Still there was no decolorization of the iodine solutions.

Another series of experiments was run using silver iodide made from approximately 0.1 *M* solutions of potassium iodide and silver nitrate. A very slight excess of potassium iodide was used in the precipitation, which caused the formation of a fine, almost colloidal silver iodide. This was filtered with a great deal of difficulty, washed thoroughly with water, very dil. ammonia and water and then with very dil. nitric acid followed by distilled water.<sup>3</sup> The freshly precipitated, moist, thoroughly washed silver iodide was added to a sherry-wine red solution of iodine in 95% alcohol. No decolorization of the solution could be detected.

Next a series of experiments was run using silver iodide precipitated as above except that a very slight excess of silver nitrate was used instead of an excess of potassium iodide. The excess of silver nitrate or of potassium iodide in either case was not over 1%. The silver iodide precipitated by this method settled more readily than that made with a slight excess of potassium iodide and was more easily filtered. The precipitate was washed by decantation with water, ammonia and nitric acid followed by water, then filtered by suction. Various amounts were added to a sherry-wine red solution of iodine in ethyl alcohol with very slight decolorization.

In searching for a reason for the complete decolorization of the solutions of the former experimenter it was noted that no mention was made in his work of any washing of the silver iodide. More silver iodide was made from *M* solutions of potassium iodide and silver nitrate using a 10% excess of silver nitrate, but was filtered upon a Büchner filter without any washing, thus leaving any adsorbed or occluded silver nitrate in the precipitate. When approximately 1.0 g. (calculated dry) of this moist, unwashed silver iodide was added to 25 cc. of solvent containing 0.05

<sup>3</sup> Lottermosser and Rothe, *Z. physik. Chem.*, **62**, 363 (1908).

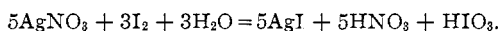
g. of iodine, shaken for 30 seconds and filtered, 0.02 g. of the iodine disappeared. Approximately 3.0 g. of this silver iodide in a similar solution removed all the free iodine, leaving a water-white solution.

Silver iodide was also made by precipitating from dil. solutions of potassium iodide and silver nitrate (approximately 0.1 *M*) using a 10% excess of silver nitrate. The precipitate was filtered upon a Büchner filter without washing and it was found that about 1 g. of the moist silver iodide decolorized a sherry-wine red solution of iodine in ethyl alcohol. The precipitate was washed with 250% of its own weight of water by suction on the Büchner filter and still it was found that 1.5 g. of it would decolorize a sherry-red solution of iodine. After washing with 500% of water in the same way, 2 g. of the silver iodide was required to effect complete decolorization.

The same experiments using unwashed silver iodide precipitated both from conc. and dil. solutions of potassium iodide and silver nitrate and using 10% excess of silver nitrate were tried upon a sherry-red solution of iodine in potassium iodide-water solution. About 3.5 g. of silver iodide precipitated from the concentrated solutions was required to effect complete decolorization of such a solution of iodine. Silver iodide precipitated from more dilute solutions decolorized the iodine solutions more easily, due to the greater amount of silver nitrate adsorbed by the finer precipitate and the greater quantity of solution held by the greater porosity. The same experiments on washing the precipitate upon the filter were tried in this case and a gradual decline of the decolorizing power of the silver iodide noted with increased amount of washing.

From the results of these experiments using unwashed silver iodide it was concluded that the silver iodide of the former experimenter must not have been washed free from the silver nitrate. Such a conclusion led to the belief that a chemical reaction and not adsorption caused the complete decolorization of Carey Lea's solutions.

When the silver iodide was unwashed there was undoubtedly silver nitrate occluded in the flocculent precipitate. Also there was silver nitrate adsorbed by the silver iodide, which could not be removed without considerable washing. The silver nitrate from both of these sources when added to the iodine solutions in alcohol and to the iodine in potassium iodide reacted with them destroying the color of free iodine. The reaction between silver nitrate and iodine is set forth by V. E. Pavlov and S. D. Shein<sup>4</sup> as follows.



This reaction occurs when there is an excess of iodine present.

We must remember that there is nothing quantitative in Carey Lea's pub-

<sup>4</sup> Pavlov and Shein, *J. Russ. Phys. Chem. Soc.*, **39**, 943-7 (1907); *C. A.*, **2**, 772 (1908).

lication on this subject, so that we have no way of checking him absolutely.

Some substances such as wood- and blood-charcoal adsorb great quantities of material from solutions, and by their use we are able to remove practically all coloring matter from impure sugar solutions. This, however, is rather the exception than the rule. For example, Lottermosser and Rothe,<sup>5</sup> studying the adsorption of silver nitrate and potassium iodide by silver iodide used from 0.23 to 0.93 g. of silver iodide in 25 cc. of potassium iodide solutions, obtaining values of the adsorption of the order of 0.009 millimol per gram of adsorbent. The solution in equilibrium still contained 0.075 millimol in the 25 cc. In the case of the adsorption of silver nitrate, the maximum adsorption noted was 0.005 millimol per gram when there still remained 0.350 millimol in the 25 cc. The greatest percentage change in composition takes place in the case of the most dilute solutions, being in Lottermosser and Rothe's case 56% as a maximum. The same general results have been obtained by one of us<sup>6</sup> in the case of the adsorption of radium by barium sulfate.

A sherry-wine colored iodine solution contains approximately 2 g. of iodine per liter or about 0.008 millimol per cc. Had Carey Lea used 1 g. of silver iodide in 25 cc. of solution and obtained complete decolorization he would have had 0.2 millimol per gram adsorbed. This value not only seems very large, but also very improbable, since complete adsorption would certainly require a great mass of silver iodide.

It should also be noted that any adsorbed material is efficiently removed only by washing by decantation, as was done by us in order to remove the silver nitrate from the silver iodide. As has been shown, washing on a Büchner funnel removes adsorbed substances only very slowly.

Since Lea used a colorimetric method and hence could make no error on the resulting iodine content, we must conclude that the resulting solution was as "colorless as water." It thus would seem that some chemical reaction rather than adsorption should be taken as the explanation of the decolorization.

In view of the possible experimental error in the procedures used, it may be stated that there is no adsorption of iodine in solutions of acetone, water-free methyl alcohol, 95% ethyl alcohol, and a water solution of potassium iodide, by silver iodide above a maximum limit of 0.02 millimol per gram of silver iodide. Carey Lea claimed to have obtained a rapid and complete decolorization of sherry-wine colored solutions of iodine. The present experiments show conclusively that not sufficient adsorption takes place to cause a change in color of any such magnitude. If there is an adsorption it must be below the limit above stated.

<sup>5</sup> Lottermosser and Rothe, Ref. 3, p. 359.

<sup>6</sup> Germann, "Adsorption of Radium by Barium Sulfate," *THIS JOURNAL*, **43**, 1615 (1921).

### Summary

1. Carey Lea's experiments indicated that iodine was strongly adsorbed from solution by silver iodide.

2. Dry, thoroughly washed silver iodide precipitated from  $M$  solutions of silver nitrate and potassium iodide was added to alcoholic and potassium iodide water solutions of iodine with no decolorization. Varying lengths of time of agitation and various conditions were tried with no appreciable adsorption.

3. Likewise, moist silver iodide precipitated from  $M$  and from  $0.1 M$  solutions and washed with ammonium hydroxide and nitric acid by decantation was added to similar solutions with negative results.

4. Decolorization was obtained with unwashed silver iodide precipitated both from  $M$  and from  $0.1 M$  solutions, using an excess of silver nitrate. The decolorization was due to a chemical reaction between the iodine in solution and the silver nitrate occluded in the silver iodide and adsorbed upon its surface.

5. Unwashed silver iodide precipitated from dilute solutions of silver nitrate and potassium iodide decolorized the iodine solutions most easily, due to the greater adsorption of silver nitrate by the silver iodide and the larger quantity of solution held because of the increased porosity.

6. A sherry-wine red solution of iodine contains about 0.008 millimol per cc. From the above experimental work it may be concluded that there is no adsorption of iodine from solution by silver iodide above a maximum limit of 0.02 millimol per gram of silver iodide. Hence, if Carey Lea worked with 25 cc. of sherry-wine colored iodine solution containing 0.2 millimol he must have added well over 10 g. of silver iodide to obtain anywhere near complete decolorization.

7. The above results point to the probability that Carey Lea was dealing with a chemical rather than an adsorption phenomenon.

BOULDER, COLORADO

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[CONTRIBUTION NO. 4 FROM THE RESEARCH LABORATORY OF THE NATIONAL BISCUIT COMPANY]

## FURTHER STUDIES OF THE PHYSICAL CHARACTERISTICS OF GELATIN SOLUTIONS

BY CLARKE E. DAVIS AND EARLE T. OAKES

Received August 5, 1921

In a previous article<sup>1</sup> an investigation of the viscosity of solutions of various gelatins at 25° was reported.

The present paper covers an investigation of the following properties of gelatin solutions: (1) density~temperature 0-60°; (2) density~concentration at 40°; (3) transition point of gel-to-sol; (4) viscosity~

<sup>1</sup> Davis, Oakes and Brown, *THIS JOURNAL*, **43**, 1526 (1921).