

ADSORPTION BY PRECIPITATES.

V. N. MORRIS, DuPont Fellow, University of Minnesota.

Where is the analyst who has not had his precipitate of barium sulfate contaminated by iron or barium chloride? If his sulfates have escaped, voluminous hydroxides may be his pet abomination. Lucky indeed is the analytical chemist who is not continually struggling against the tendency of his precipitates to adsorb foreign material. True it is that not all contamination can be traced to the colloid chemist's favorite phenomenon, adsorption, but much of it can. There was a time when the explanation of this contamination on the basis of adsorption received little credence, but it is quite difficult at present to account for all of the cases observed without resorting to adsorption. Mention should be made of the fact that the term "occlusion", which is quite common in the text-book, is generally used as a broader term than adsorption, and may include, in addition to the latter, cases of solid solution, such as that discussed by Miller,¹ and of insoluble complex formation as pointed out by Smith² in the case of barium sulfate.

Among the various factors which have been investigated in connection with adsorption by precipitates is the relation of the valence of an adsorbed ion to the degree of adsorption. The early work of Schulze³ led to the now more or less disputed Schulze's law, i. e., the power of active ions to precipitate colloidal solutions is a function of their valence. The results of some investigators have tended to confirm this law, while those of others have tended to disprove it. The work of Dhar and Chatterji,⁴ for instance, has brought to light cases where monovalent ions such as silver are adsorbed more completely than divalent and the latter in turn more than trivalent.

The specificity of adsorption has been frequently observed but has been given no particularly systematic study. Bancroft⁵ discusses the fact that salts show decided adsorptions for their own ions. Thus silver bromide adsorbs silver nitrate and potassium bromide, but not potassium nitrate. Taking up the subject from a slightly different angle, Ostwald⁶ states that acids are in general adsorbed more than their salts; that organic salts are adsorbed more than inorganic; and that substances with high molecular weight and colloids are especially susceptible to adsorption. In connection with the latter, a recent study by Ghosh and Dhar⁷ has brought out that freshly precipitated barium

¹ U. S. Public Health Repts. 39, 1502 (1924).

² Contamination of Precipitates. *J. Am. Chem. Soc.* 39, 1152 (1917).

³ Arsenous Sulfide in Aqueous Solution. *J. Prakt. Chem.* (2) 25, 43 (1882).

⁴ Studies in Adsorption. II. *Kolloid-Z.* 33, 29 (1923).

⁵ Applied Colloid Chemistry, pp. 111, 113 (1921).

⁶ Theoretical and Applied Colloid Chemistry, p. 128 (1922).

⁷ Studies in Adsorption. VIII. *Kolloid-Z.* 35, 144 (1924).

sulfate will give almost complete adsorption from colloidal solutions of metals, sulfides, halides and other common colloids.

Peptization of precipitates may sometimes be accomplished by means of adsorbed substances. This is particularly easy with freshly precipitated substances, but becomes progressively less so as the precipitates age. Examples of this phenomenon are: the peptization of silver halides by silver nitrate; and of zinc hydroxide temporarily by alkalis. Bancroft⁸ concluded that, while adsorption will cause peptization under suitable conditions, the disintegrating power of the adsorbed substance is relatively small.

In considering specific examples of adsorption by precipitates, a wide and sometimes quite unexpected variety in both adsorbed material and adsorbents can be cited. Thus, Rakusin⁹ found that aluminium hydroxide adsorbs proteins and enzymes; Eleyer¹⁰ mentions that this substance will adsorb bacterial immune agglutinins; while Jacoby and Shimizu¹¹ have demonstrated that freshly precipitated calcium phosphate will adsorb urease and zymogen. Interesting adsorbents mentioned by Stocks¹² and others include precipitated starches, dextrans, and gums. Incidentally, the familiar starch iodide of the analysts has been shown by Kuster¹³ and Berczeller¹⁴ not to be a definite compound, as the distribution of iodine between starch and water indicates adsorption. That such adsorption does not occur in solutions of carbon disulfide or benzene is taken as a confirmation of the law that adsorption varies inversely as the solubility of the adsorbed substance in the solvent.

The classes of precipitates whose adsorptions have been studied most extensively are the sulfates and hydrous oxides. Those which have been studied to a lesser extent are the phosphates, carbonates, sulfides, silver halides, and manganese dioxide. A brief discussion of these latter will be taken up first.

Dhar, Sen and Chatterji¹⁵ as a part of a rather comprehensive study of adsorption by precipitates, found that the phosphates of iron, aluminium and chromium adsorb the calcium ion; and that the alkaline earth carbonates adsorb ferric and magnesium ions.

Adsorption by freshly precipitated manganese dioxide has been studied by Ganguly and Dhar.¹⁶ Among other things an abnormally high adsorption of ferric salts was noted. Their explanation of this fact, which is similar to that of Geloso,¹⁷ is the decomposition of these salts with the formation of hydrous ferric oxide. Some generaliza-

⁸ Colloid Report: Brit. Assn. for Adv. of Sci. 3 (1918).

⁹ The Adsorption of Proteins, Enzymes and Sera by Aluminium Hydroxide. *Z. Immunitäts* 34, 155 (1922).

¹⁰ Adsorption of Bacteria and Agglutinins by Suspensions and Colloids. *Z. Immunitäts* Abt. 1, Orig. 33, 478 (1922).

¹¹ Adsorption of Ferments and Zymogen. *Biochem. Z.* 128, 100 (1922).

¹² Colloid Report: Brit. Assn. for Adv. of Sci. 52, 48, 57, 63, 65 (1917).

¹³ Starch Iodide and Its Molecular Structure. *Ann.* 283, 364 (1891).

¹⁴ Starch Iodide. *Biochem. Z.* 133, 502 (1922).

¹⁵ Studies in Adsorption. II. *Kolloid-Z.* 33, 29 (1923).

¹⁶ Adsorption of Ions by Freshly Precipitated Manganese Dioxide. *J. Phys. Chem.* 26, 836 (1922).

¹⁷ Adsorption of Iron by Manganese Dioxide. *Compt. rend.* 174, 1629 (1922); 178, 1001 (1924).

tions they drew were: that the adsorption of elements in the same group of the periodic table is generally in the order of the atomic weights; and that, while the effects of anions on the adsorption of cations is quite marked, the reverse is not necessarily true.

Adsorption by silver halides is interesting from an historical standpoint at least. It was Carey Lea¹⁸ who showed that silver iodide adsorbs iodine strongly. Germann and Traxler¹⁹ have recently shown that the silver iodide must be freshly precipitated and unwashed since the dry or washed substance will not decolorize an alcoholic solution of iodine. Fajans and Franfenburger,²⁰ working on the adsorption of silver ions by silver bromide, have recently made determinations of the total adsorbing surface and the adsorbed ions, and have calculated that in a silver ion solution of a concentration of 1.8×10^{-2} gram ions per liter, approximately every fourth to tenth bromine atom of the silver bromide surface takes up an extra silver ion.

Adsorption by sulfides has not received a great deal of attention. Dhar and Sen²¹ have observed that arsenic sulfide, usually a typical negative colloid, may be made positive by the adsorption of ions such as barium, aluminium, and hydrogen. Auger and Odinet²² have recently found that while stannic sulfide adsorbs cobalt and nickel, stannous sulfide does not. Ghosh and Dhar²³ have made the interesting observation that certain sols such as arsenous sulfide and antimonous sulfide when coagulated with monovalent electrolytes such as the chlorides of potassium or lithium violate the usual rule and require more electrolyte when dilute than when concentrated. The explanation offered is that these sols can adsorb ions carrying the same charge as the colloid particles and thus have their stability increased.

Dhar, Sen and Chatterji²⁴ have shown that reprecipitation is often necessary due to inability to wash precipitates, such as alkaline earth sulfates, free from adsorbed ions. In this connection they showed that strontium sulfate, precipitated in the presence of chlorides and sulfates of various metals, adsorb ferric ions, aluminium ions and other ions to a smaller extent, but did not adsorb mercuric ions at all. Calcium and barium sulfates adsorb ferric ions particularly.

Probably the greatest amount of work on any precipitate has been done on barium sulfate, so a somewhat detailed discussion of this substance and its adsorptive properties are in order. The explanation of its tendency to carry down barium chloride, for instance, is not very difficult from the standpoint of adsorption. Thus Bassett²⁵ brings out that barium sulfate is usually positively charged due to the preferential adsorption of the barium ions. Since chloride ions are carried down by

¹⁸ Action of Light and Reducing Agents on Silver Salts. *Am. Jour. Sci.* (3) *33*, 492 (1887).

¹⁹ Adsorption of Iodine by Silver Iodide. *J. Am. Chem. Soc.* *44*, 460 (1922).

²⁰ The Thickness of the Adsorbed Layer in the Adsorption of Silver Ions by Silver Bromide. *Zeit. Phys. Chem.* *105*, 255 (1923).

²¹ Studies in Adsorption. IV. *J. Phys. Chem.* *27*, 376 (1923).

²² Adsorption of Cobalt and Nickel by Stannic Sulfide. *Compt. rend.* *178*, 710 (1924).

²³ Studies in Adsorption. X, XI: Studies in Adsorption. IX. *J. Phys. Chem.* *29*, 435, 659 (1925); *Kolloid-Z.* *36*, 129 (1925).

²⁴ Studies in Adsorption. II. *Kolloid-Z.* *33*, 29 (1923).

²⁵ Colloid Report: *Brit. Assn. Adv. Sci.* *5* (1922).

the attraction of particles owing their charges to adsorbed barium ions, it is quite correct to say, as is usually done, that barium chloride is carried down. Some of the early advocates of the adsorption theory as an explanation of the phenomenon were Kuster and Theil²⁶ and Korte.²⁷

In the systematic study, two general methods for determining the relative adsorption of ions have been more or less in vogue. One consists in determining the effect of various ions of one charge on the precipitation of a colloid that owes its stability to the preferential adsorption of ions of the opposite charge. This method was first made use of by Schulze.²⁸ The experimental difficulties make the accuracy rather doubtful. A second method consists in shaking a solution of known concentration with a known weight of solid and pipetting off some of the supernatant liquid to be subsequently analyzed. Correct results cannot be obtained unless the solution taken up by the solid is given consideration.

In view of the deficiencies of the above methods, Weiser and Sherrick²⁹ developed the process of analyzing for the adsorbed ions directly from the precipitated barium sulfate. A constant amount of barium sulfate was precipitated by mixing a solution of a given sulfate with a solution of a barium salt. Thus three ions are kept constant and a fourth is varied. The small amounts adsorbed necessitated special methods of analysis, which caused no great difficulty, however.

They obtained several interesting results by the above described method. The order of decreasing adsorption of the anions studied was: ferrocyanide, nitrate, nitrite, chlorate, permanganate, ferricyanide, chloride, bromide, cyanide, thiocyanate and iodide. This order is in general not in agreement with Schulze's law. The barium ion is adsorbed more strongly than the sulfate ion, so that peptization and anion adsorption are greater in presence of excess sulfate ions. They concluded that the two factors which determine adsorption of ions by the adsorbing agent are: the nature of the ion, and the valence of the ion. The latter predominates, of course, in the case of ions of the same general nature.

Weiser³⁰ in an earlier paper showed that barium sulfate could be stabilized by the preferential adsorption of either barium or sulfate ions. Barium sulfate comes down very much finer when precipitated with barium chloride in excess than sulfuric acid, the explanation being that barium sulfate adsorbs barium, sulfate, and hydrogen ions strongly. When sulfuric acid is precipitated by barium chloride, the strong adsorption of a barium and hydrogen ions allows a finely divided precipitate, but in the inverse case the strongly adsorbed hydrogen ions cut down the adsorption of the sulfate ions and the precipitate is not so fine.

²⁶ The Determination of Sulfuric Acid in the Presence of Iron. *Zeit. anorg. Chem.* 22, 424 (1899).

²⁷ Solid Solutions. *J. Chem. Soc.* 81, 1503 (1905).

²⁸ Arsenous Sulfide in Aqueous Solution. *J. prakt. Chem.* (2) 25, 43 (1882).

²⁹ Adsorption by Precipitates. I. *J. Phys. Chem.* 23, 205 (1919).

³⁰ Adsorption by Precipitated Barium Sulfate. *J. Phys. Chem.* 21, 314 (1917).

Ghosh and Dhar³¹ have made an interesting study of the effect of varying the amount of barium sulfate present. With 0.8923 grams in a total volume of 100 cc. there was practically no adsorption of electrolytes, sugars, dyes, and similar substances but with 3.2092 grams present the electrolytes were noticeably adsorbed.

Before leaving barium sulfate it is only just to mention that this usually troublesome tendency may be put to some service, as Pierce³² has devised a method of using a precipitate of barium sulfate as a carrier for adsorbed material such as titanium hydrate.

Considerable study has been devoted to hydrous ferric oxide. Dhar and Sen³³ have been interested in the charge reversal of this precipitate, and have found that the freshly precipitated substance, ordinarily positive, passes into a negative colloid when shaken with arsenous acid, boric acid, or tartaric acid. Weiser and Middleton,³⁴ by analyses of precipitates, found different amounts of chloride, bromide, iodide, and nitrate ions to be absorbed by hydrous ferric oxide, while Kato,³⁵ judging from coagulation effects, concluded that the same amounts were adsorbed. The former authors explain their variable results by the fact that, since neutralization of a colloid by an electrolyte precedes precipitation, there are two phases in the adsorption process. The total amount of ions carried down then is the sum of those adsorbed by the charged particle during neutralization and by the neutral particle during settling. Equivalent amounts will be adsorbed in neutralizing but varying amounts afterwards.

Hydrous aluminium oxide has been studied to such an extent that it may well be considered the rival of barium sulfate for the greatest popularity among adsorption workers. Mention of this substance has already been made in the case of enzymes and proteins. Davison³⁶ has shown how this hydrous oxide will decolorize various dye solutions, while Lockemann and Pancke³⁷ have studied its tendency to carry down arsenic from solutions.

Charriou³⁸ has used hydrous aluminium oxide in his studies of the replacement by other ions of the chromate ion, which is adsorbed in proportion to its concentration in the solution. His first observation was that the adsorbed chromate ions, which impart a yellow color to the precipitate, could not be removed by washing with hot water or the usual salt solutions, but could be removed by washing with ammonium hydrogen carbonate solution. Evidently carbonate ions are adsorbed more than chromate ions. More extensive studies brought out that halides, nitrates and acetates did not displace adsorbed chromate ions, but that phosphates, sulfides, sulfates, oxalates, and tartrates entirely displaced them. He drew two general conclusions to the effect that adsorbed

³¹ Studies in Adsorption. VIII. *Kolloid-Z.* 35, 144 (1924).

³² U. S. Patent 1,468,867: *C. A.* 18, 155 (1924).

³³ Studies in Adsorption. IV. *J. Phys. Chem.* 27, 376 (1923).

³⁴ Adsorption by Precipitates. II. *J. Phys. Chem.* 24, 30 (1920).

³⁵ Colloidal Barium Sulfate. *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.* 2, 187 (1909).

³⁶ Experiments in Dyeing. *J. Phys. Chem.* 17, 737 (1913).

³⁷ Detection of Small Amounts of Arsenic in Organic Materials. *Z. Kolloidchem.* 8, 273 (1911).

³⁸ Adsorption of Acids by Hydrated Alumina Precipitates. *Compt. rend.* 176, 679, 1890 (1923).

substances are replaced from precipitates by substances of the same kind but of higher valence, and that if two substances have the same valence, the more concentrated will displace the less concentrated.

That adsorption may disturb chemical equilibrium is indicated by Ishizaka's³⁹ observation that potassium dichromate is converted into chromate by the presence of powdered alumina. Weiser and Middleton,⁴⁰ in discussing this case, call attention to the fact that an equilibrium exists—



Alumina adsorbs hydrogen ions much more strongly than it does the other ions present, the result being of course to shift the equilibrium to the right, since adsorbed hydrogen cannot react.

Weiser⁴¹ has also made a study of hydrous chromic oxide. The precipitating power of anions on the positive colloid was found to be much the same as with hydrous ferric oxide, while that of cations on the colloid when negatively charged decreased in the order: barium, lithium, sodium, and potassium ions.

One other hydrous oxide, that of tin, has been given attention by Weiser.⁴² He concluded that "purples", such as the famous "purple of Cassius", result from the adsorption of colloidal gold, silver and platinum by hydrous stannic oxide. He also explained the interesting fact that a mixture of the hydrous oxides of tin and iron are dissolved by dilute ammonia, whereas ferric oxide alone is not. Hydrous stannic oxide is peptized by hydroxyl ions. The colloidal oxide thus produced adsorbs ferric oxide and carries it into colloidal solution.

Precipitations in the presence of mixtures of electrolytes have been studied by Ghosh and Dhar⁴³ and Weiser.⁴⁴ The adsorbents with which the studies were made by the latter investigator were hydrous ferric oxide and arsenic sulfide. He found that, when the precipitating power of the ions in a mixture is similar, the total action of the mixture is additive, since the adsorption of the precipitating ions is similar. On the other hand, when the mixture contains electrolytes of widely differing power, the effect of the mixture may be far from additive. One ion may have an "antagonistic" action on another, or tend to stabilize a colloid of the same charge. Cases have been found where the precipitating value of the mixture is even greater than additive. This condition was observed in the case of arsenous sulfide using mixtures of lithium chloride and either barium or magnesium chloride, and mixtures of hydrochloric acid and magnesium chloride.

Any attempt at summarizing the various contributions to the subject as a whole could not fail to disclose more or less of a tendency toward discrepancy in the results obtained. This state of affairs should not cause any alarm, however, as a similar condition is encountered in the

³⁹ The Relation between the Precipitation of Colloids and Adsorption. *Z. Phys. Chem.* 83, 97 (1913).

⁴⁰ Adsorption by Precipitates. III. *J. Phys. Chem.* 24, 630 (1920).

⁴¹ Hydrous Oxides. III. *J. Phys. Chem.* 26, 491 (1922).

⁴² Hydrous Oxides. IV. *J. Phys. Chem.* 26, 654 (1922).

⁴³ Studies in Adsorption. X, XI. *Studies in Adsorption.* IX. *J. Phys. Chem.* 29, 435, 659 (1925). *Kolloid-Z.* 36, 129 (1925).

⁴⁴ Adsorption by Precipitates. V, VI. *J. Phys. Chem.* 25, 665 (1921); 28, 232 (1924).

early stages of any branch of the science, when a standardization of methods has not yet been established. As the study becomes more comprehensive, as it has been becoming during each of the last four or five years, various standardizations of methods should make results more comparable, and it is quite justifiable to expect that within the near future the knowledge of adsorption by precipitates will be on a somewhat more exact basis than is the case at present.