that, "definitions of flour proteins based on solubility in a solution such as 70% alcohol are purely arbitrary." Their work has no bearing on the specific problem of the definition of globulins but is of importance in the general problem of protein classification.

Undoubtedly the solubilities of different proteins are a reflection of the kind and arrangement of their constituent amino acids. Any definition must necessarily be inadequate and empirical until more is known about the composition of proteins.

Conclusions

1. The amount of nitrogenous material extracted from certain seed meals by saturated sodium chloride solutions is almost as large as that extracted by N solutions. In those seed meals where this conclusion is true, the material which is extracted appears to consist almost wholly of a crystalline or hemi-crystalline protein having the characteristics of a globulin.
2. When a solution of given concentration is used for the extraction of nitrogenous material, a marked temperature coefficient is found.
3. The ordinary textbook definitions of globulins do not adequately consider the solubility properties of globulins.

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[A CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Mechanism of Coprecipitation of Anions by Barium Sulfate[1]

BY FRANK SCHNEIDER[2] AND WILLIAM RIEMAN, III

Five theories[3] have been advanced to account for the contamination of precipitates, *viz.*, formation of mixed crystals, occlusion, surface adsorption after the formation of the precipitate, compound formation and postprecipitation. If coprecipitation is defined as the retention of soluble substances by a precipitate, compound formation and postprecipitation cannot be regarded as true coprecipitation. Surface adsorption is important only in the cases of amorphous and flocculent precipitates. Therefore, coprecipitation by barium sulfate is due either to the formation of mixed crystals or to occlusion. By occlusion is meant the adsorption of foreign ions during the growth of the crystals of the precipitate and subsequent entrapping of these foreign ions by the growing crystals.[3]

All conditions of precipitation such as temperature, concentration, time of addition of reagents, time of digestion, etc., being the same, the amount of coprecipitated ion in a precipitate should depend upon some specific property of this ion. As stated by Paneth[4] and Fajans,[5] the occlusion theory maintains that this determining factor is the solubility of the compound formed by the coprecipitated ion and the ion of opposite charge of the precipitate. On the other hand, the mixed-crystal theory of Grimm[6] and coworkers holds that this property is the similarity in crystal structure of the precipitated and coprecipitated substances. Otto Hahn[7] was among the first to recognize that both explanations might be correct. He also stated that mixed crystals may be formed even when Grimm's[8] conditions are not fulfilled. His rules, however, are not very clear and are apparently contradictory in certain respects.

A study of the coprecipitation of various anions by barium sulfate throws considerable light upon this subject. Weiser and Sherrick[9] determined the quantity of coprecipitated anions under identical conditions of precipitation. They did not use the Paneth–Fajans rule to interpret their results and hence were somewhat at a loss to explain them. Sofin[10] repeated their work under more carefully controlled conditions. Using iodide, chloride, bromide, nitrite, nitrate and chlorate, he found that, in accord with the Paneth–Fajans rule, the lower the solubility of the barium

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 92d Meeting of the American Chemical Society, Pittsburgh, September 7-11, 1936.

(2) Abstracted from a thesis by Frank Schneider, presented to the Graduate Faculty of Rutgers University in partial fulfilment of the requirements for the Ph.D. degree.

(3) For a discussion of these theories see Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932).

(4) Paneth, *Physik. Z.*, **15**, 924 (1914).

(5) Fajans and Beer, *Ber.*, **46**, 3486 (1913).

(6) Grimm and Wagner, *Z. physik. Chem.*, **132**, 131 (1928).

(7) O. Hahn, Erzbacher and Feichtinger, *Ber.*, **59**, 2014 (1926).

(8) Grimm, *Z. Elektrochem.*, **30**, 467 (1924).

(9) Weiser and Sherrick, *J. Phys. Chem.*, **23**, 205 (1919).

(10) Sofin, Master's Thesis, Rutgers University, 1934.

salt of the anion, the greater was the amount coprecipitated. The nitrite, however, was an exception. He attempted to show, without success, that the abnormally high amount of coprecipitated nitrite was due to the formation of mixed crystals of sodium nitrite and barium sulfate.

Differences between Occlusion and Mixed-Crystal Formation.—Contamination by occlusion differs from contamination by mixed-crystal formation in the following respects.

(1) As Hahn[7] has pointed out, the extent of occlusion is dependent upon the ion of the precipitate which is present in excess in the solution at the time of precipitation. If barium sulfate is precipitated by adding a sulfate to an excess of barium ion, the growing crystals are charged positively; hence they adsorb and occlude foreign anions to a greater extent than when the precipitate is formed by pouring a barium salt into an excess of sulfate ion. On the other hand, the excess of lattice ion is unimportant in the case of mixed-crystal formation; in this case the contamination is proportional to the concentration of the ion which is coprecipitated.

(2) The adsorptive forces which attract foreign ions to a growing crystal depend primarily on the solubility of the compound which these ions form with the oppositely charged lattice ions. Therefore, contamination by occlusion follows the Paneth–Fajans rule. If the adsorbed ions fit well into the crystal lattice of the precipitate, a larger portion of them is retained by the growing crystals than would otherwise be the case. Therefore, contamination by mixed-crystal formation is greater than the Paneth–Fajans rule indicates. The simple relationship between adsorption and solubility is subject to some exceptions, however. Therefore, deviations from the Paneth–Fajans rule for coprecipitation should not be interpreted as mixed-crystal formation unless the effect of excess lattice ion, the crystal size and the effect of digestion (paragraphs 1, 3 and 4, respectively) also indicate the formation of mixed crystals.

(3) It is well known that the growth of a crystal is retarded by the presence of an adsorbed layer on its surface. If the adsorbed layer can fit into the crystal lattice, however, the retardation is much less than it would be otherwise. Therefore, extensive occlusion causes a fine grained precipitate, whereas contamination by mixed-crystal formation has little effect on crystal size.

(4) Digestion is more effective in removing occluded contamination than in removing mixed-crystal contamination, because the crystals are smaller in the former case, and because their impurities are less uniformly distributed than in the case of mixed crystals.

(5) X-Ray examination may be helpful. It must be emphasized, however, that a small displacement of the lattice dimensions does not indicate that mixed-crystal formation is the sole or even the major cause of the contamination. A given precipitate may be contaminated by both occlusion and mixed-crystal formation.

Application to Coprecipitation of Anions by Barium Sulfate.—As pointed out previously, the amount of nitrite ion coprecipitated by barium sulfate is greater than would be expected from the Paneth–Fajans rule. On the basis of the theory just outlined, it is postulated that (1) iodide, bromide, chloride, chlorate and nitrate ions are coprecipitated by occlusion and (2) that nitrite ion is coprecipitated by the formation of mixed crystals of barium nitrite with barium sulfate. If these postulates are true, it follows that:

(1) The quantity of iodide, bromide, chloride, chlorate and nitrate coprecipitated when the respective barium salt is added to excess sodium sulfate will be much less than when sodium sulfate is added to an excess of the barium salt. In the case of the nitrite, the excess of the precipitating ion will be much less important. The amounts of nitrite coprecipitated will be proportional to the total concentrations of nitrite ion present.

(2) Digestion should be comparatively effective in removing the ions which are occluded but relatively ineffective with the precipitate containing the nitrite.

(3) Extensive coprecipitation of iodide, chloride, bromide, nitrate and chlorate should result in a very fine grained precipitate.

Experimental Work

In order to test this hypothesis, two sets of experiments were carried out. First, barium sulfate was precipitated (a) in the presence of an excess of the barium salt and (b) in the presence of an excess of sodium sulfate. Second, the barium sulfate was precipitated as in the first set of experiments (both a and b) but allowed to digest for a period of twenty-two days before filtering and determining the amount of coprecipitated anion.

Procedure.—Solutions (0.1000 *M*) of barium iodide, bromide, chloride, nitrite, nitrate and chlorate were prepared. A sodium sulfate solution was also made up to

0.1000 *M*. The actual precipitations were carried out as follows: 90 ml. of the barium solution was added to 120 ml. of water; then 40 ml. of the sodium sulfate solution was run in in thirty seconds with vigorous stirring. All solutions were at 30°. Precipitate and solution were allowed to stand for ten minutes after the beginning of precipitation. Separation of solution and precipitate was effected by centrifuging and decanting. The precipitate was washed with 120 ml. of water, and the coprecipitated anion was then determined in the precipitates. The time of centrifuging and washing was carefully controlled to take exactly fifty-five minutes. The experiment was then repeated exactly as before except that 40 ml. of barium salt solution was added to 9 mmol. of sodium sulfate dissolved in 210 ml. of solution.

The precipitates containing iodide, chloride, bromide and chlorate were fused with a carbonate mixture, and the anion was determined in the extract from the melt. The iodide was determined iodometrically, the bromide, chloride and chlorate gravimetrically as the silver salt. The nitrate and nitrite were determined by the method described by Walden and Cohen.[11] In this method the precipitate is digested with a sodium hydroxide–carbonate solution; Devarda's alloy is added; the ammonia is distilled off and countertitrated. In the case of the precipitates formed from barium chloride, the coprecipitated sodium was also determined by the method of Allen and Johnston.[12] The results of this set of experiments are shown in Table I.

TABLE I

Ion	Micromoles of anion per 4 mmol. $BaSO_4$[a] Excess Ba salt	Excess Na_2SO_4	Ratio	Soly. of barium salt at 30° in moles per 1000 g. water
Iodide	1.3	0.20	6.5	5.64
Bromide	66	14	4.7	3.55
Chloride	107	18	5.9	1.83
Chlorate	390	107	3.6	1.37
Nitrite	408	177	2.3	3.49
Nitrate	783	217	3.6	0.455
Sodium	163	355	1/2.2	

[a] Averages of duplicate determinations. The relative mean deviation was 5% or less except for the iodide, where the relative mean deviation was 20%.

It can be seen that the amount of contaminant increases as the solubility of the barium salt decreases, with the notable exception of the nitrite. The latter is present in an amount far in excess of what would be expected if the solubility of the barium salt were the only determining factor. This indicates that the nitrite is probably coprecipitated by the formation of mixed crystals of barium sulfate and anhydrous barium nitrite and that the other ions are coprecipitated by occlusion. In support of this hypothesis we observed that the precipitate containing 177 micromoles of nitrite ion was much coarser than the precipitates containing 217 micromoles of nitrate ion or 107 micromoles of chlorate ion. Furthermore, the influence of the excess precipitant (barium ion or sulfate ion) was much less in the case of the nitrite ion. Indeed, the observed ratio of 2.3 corresponds surprisingly well to the theoretical value of 9/4 or 2.25 (the ratio of the quantities of nitrite ion used).

Effect of Digestion.—The barium sulfate was precipitated in the same way but was allowed to digest in contact with the mother liquor for a period of twenty-two days at 30° before being centrifuged and analyzed. The results of these experiments compared with the results of the first set are shown in Table II.

TABLE II

Ion		Micromoles of ion per 4 mmol. $BaSO_4$ Before digestion	After digestion	% Loss
Nitrite				
(A)	Excess of Ba salt	408	160	61
(B)	Excess of Na_2SO_4	177	111	37
Nitrate				
(A)	Excess of Ba salt	783	172	78
(B)	Excess of Na_2SO_4	217	0	100
Chloride				
(A)	Excess of Ba salt	107	42	61
(B)	Excess of Na_2SO_4	18	0	100
Sodium				
(A)	Excess of Na_2SO_4	355	207	42
(B)	Excess of $BaCl_2$	163	110	32

Discussion

The precipitates containing the nitrate and chloride ions lost the impurities more rapidly than the precipitates containing nitrite ion.

Thus it is seen that the nitrite ion behaves differently from the other anions in regard to (1) the Paneth–Fajans rule, (2) the effect of excess lattice ion, (3) the influence on crystal size and (4) the effect of digestion. All these differences support the hypothesis that the nitrite is coprecipitated by mixed-crystal formation, whereas the others are occluded. It is of interest to note that the loss of sodium on digestion indicates that it is held by the barium sulfate in the form of mixed crystals, probably as sodium sulfate.

In connection with the experiments on barium nitrate which showed that the nitrate was present as occluded material, it is of interest to note the recent work of Walden and Cohen.[11] These two authors studied the lattice parameters of precipitates containing coprecipitated nitrate. They have related the lattice parameters to the nitrate content, showing that the parameters increased with increased nitrate content. They concluded, therefore, that the nitrate was present in the form of solid solution or mixed crystals. This conclusion is not supported by our investigation.

Their data unquestionably indicate that mixed crystals were formed to a certain extent, not

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(11) Walden and Cohen, THIS JOURNAL, **57**, 2591 (1935).

(12) Allen and Johnston, *ibid.*, **32**, 588 (1910).

necessarily to a large extent. Walden and Cohen, themselves, realized the possibility that other mechanisms may have played a role in the contamination of their precipitates, for they stated, "That such mechanisms (occlusion or adsorption) may account for a part of the contamination is of course not ruled out by the present investigation, but even this may be questioned because of the remarkably homogeneous and strain-free character of the precipitates." The following considerations indicate that occlusion was probably the major cause of the coprecipitation.

(1) The coprecipitation of 4.53% of nitrate ion increases the volume of the unit cell by only 0.4%. Unless the second component of the mixed crystals (barium nitrate or nitric acid) is unusually similar crystallographically to barium sulfate, a much greater change in the volume of the unit cell is to be expected.

(2) The relationship between the lattice dimensions and the composition differed from linearity more than is to be expected in the case of mixed-crystal formation between salts.

(3) When mixed crystals are in equilibrium with the mother liquor, the partition law is valid.

$$\frac{\text{component A in crystals}}{\text{component B in crystals}} = K\,\frac{\text{component A in solution}}{\text{component B in solution}}$$

Unless the crystallization is performed extremely slowly, equilibrium may not be established, and the partition law may not be strictly valid. Nevertheless, there is abundant evidence[13] to prove that the mole percentage of the minor constituent in the mixed crystals is dependent primarily on the concentration of this substance in the aqueous solution. On the other hand, Walden and Cohen remark in discussing their results, "A very striking feature of these results, and one hardly to be anticipated, is that the nitrate content of the precipitates is practically independent of the nitrate content of the precipitating solutions. . . . To be noted, however, is the fact that the nitrate content of the precipitates varies with barium ion concentration." These observations are at odds with the hypothesis that mixed-crystal formation is the major cause of the contamination of their precipitates and entirely in harmony with our belief that occlusion was the major phenomenon.

(4) Walden and Cohen remark that extending the range of concentration for further study will have to lead to the use of more dilute solutions since "in the more concentrated range the precipitates settle as muds which are difficult to wash and filter and which give poor X-ray photograms." Since contamination by mixed-crystal formation has only a slight effect on the particle size of the precipitate, the formation of these muds is another indication that the coprecipitation was due chiefly to occlusion.

We conclude, therefore, that occlusion is a more important factor than the formation of mixed crystals in accounting for the contamination of their precipitates.

Summary

(1) Precipitates that are contaminated by occlusion differ from those that are contaminated by mixed-crystal formation in respect to (a) the effect of excess of the lattice ion during precipitation, (b) application of the Paneth–Fajans rule, (c) the size of the crystals and (d) the effect of digestion.

(2) Iodide, bromide, chloride, nitrate and chlorate anions are occluded by barium sulfate, whereas nitrite ion is coprecipitated by mixed-crystal formation. These conclusions are based on the following observations: (a) The excess of lattice ion influences the coprecipitation of nitrite ion much less than it influences the coprecipitation of the other anions. (b) All these anions except the nitrite follow the Paneth–Fajans rule. (c) The size of the crystals of the precipitate is decreased much less by the coprecipitation of nitrite ion than by the coprecipitation of the other anions. (d) The nitrite ion is removed on digestion more slowly than the other anions.

(3) The conclusions of Walden and Cohen are discussed.

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[13] Doerner and Hoskins, THIS JOURNAL, **47**, 662 (1925); Henderson and Kracek, *ibid.*, **49**, 738 (1927); Grimm and Wagner, ref. 6; Chlopin, Polessitsky and Tolmatscheff, *Z. physik. Chem.*, **145A**, 57 (1929); Chlopin, Polessitsky, Ratner and Tolmatscheff, *Ber.*, **64**, 2653 (1931); Mumbrauer, *Z. physik. Chem.*, **156A**, 113 (1931); Ratner, Polessitsky and Tolmatscheff, *ibid.*, **A165**, 472 (1933).