

of  $1.4 \times 10^{-9}$  may be obtained. Solutions of sodium iodide in this alcohol appear to be entirely stable, varying only a fraction of 1% over a period of 14 hours.

2. The conductance of solutions of sodium iodide in amyl alcohol at  $18^\circ$  was measured from a concentration of  $1.0 \times 10^{-5}$  to approximately  $17 \times 10^{-5} N$ . The mean variation of the results does not exceed 0.1%. In the more dilute solutions, the points conform to the requirements of the mass-action law within the limits of the experimental error. At the higher concentration there is a small although consistent deviation from the mass-action relation.

3. From an extrapolation of the plot to zero concentration there is obtained for  $\Lambda_0$  the value 11.059, and for  $K$  the value  $2.933 \times 10^{-4}$ . The value of  $\Lambda_0$  is not in agreement with that of Keyes and Winninghoff and of Dutoit and Dupertuis. The source of this discrepancy remains uncertain.

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## THE ROLE OF HYDROGEN-ION CONCENTRATION IN THE PRECIPITATION OF COLLOIDS (Preliminary Report)

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A large amount of experimental work has been done on the precipitation of colloids by electrolytes. An extensive review of the literature on this subject would be out of place here; for this information the reader is referred to standard texts on colloid chemistry and to certain papers, especially to Burton,<sup>1</sup> Whitney and Ober,<sup>2</sup> and Wo. Ostwald.<sup>3</sup> In spite of the extensive work in this field, there are at present only a very limited number of generalizations and these are not quantitative. For this paper, it will suffice to point out and discuss briefly only those factors which have a very direct relation to the experimental results presented.

For many years it has been known that the precipitation of a suspensoid is determined primarily by the ion of the added electrolyte which has an electric charge opposite in sign to that of the colloidal particles. But different concentrations of salts containing the same precipitating ion are required for the precipitation of equal amounts of a given colloid; for example, different concentrations of potassium acetate and potassium

<sup>1</sup> Burton, "The Physical Properties of Colloidal Solutions," Longmans, Green and Co., second ed., 1921, Chap. VIII.

<sup>2</sup> Whitney and Ober, *THIS JOURNAL*, **23**, 842 (1901).

<sup>3</sup> Ostwald, *Z. Kolloidchem.*, **26**, 28 and 69 (1920).

chloride are necessary for the precipitation of a given quantity of a negative sol. This variation has commonly been ascribed to a stabilizing or peptizing effect of the ion bearing the charge of like sign to that of the suspensoid particles. Numerous references to this so-called stabilizing effect of the second ion occur in the literature. Further, it is claimed<sup>3</sup> that any satisfactory theory of the precipitation of colloids must take into account the important role of this second ion.

Varying results have been reported of the influence of the concentration of the colloids on the amount of electrolytes necessary for their precipitation.

The first work was done by Freundlich<sup>4</sup> using colloidal arsenious sulfide, with barium chloride, potassium chloride and calcium nitrate as the precipitating reagents. He found that the ratio of the concentrations of potassium chloride required to precipitate arsenious sulfide at different concentrations was the same as that for each of the other salts for the same variation in concentration of the colloid. In other words, the precipitating concentrations of electrolytes for different concentrations of the same colloid bear a constant ratio to each other.

Kruyt and van der Spek<sup>5</sup> using more careful conditions of experimentation to secure comparable results, failed to confirm Freundlich's findings. They found from experiments on colloidal arsenious sulfide with potassium chloride, barium chloride and potassium aluminum sulfate as precipitants that as the concentration of the potassium ion decreased, that of the barium ion remained substantially the same, and of the aluminum ion increased with increasing concentration of the solution. To explain these results they state: "For a correct understanding of the relationship between colloid concentration and precipitation we have to recognize two opposing tendencies. Since a smaller amount needs to be adsorbed for reaching the same adsorption value in the case of a dilute colloid, it follows that a smaller amount of electrolyte is required for a dilute colloid than for a concentrated one. On the other hand, since the probability of collision of the particles is smaller for the colloid of lesser concentration, the dilute colloid requires a greater amount of the electrolyte than the concentrated so that the lesser probability of collision is compensated by an increased probability of coalescence, and the same coagulation can result in the same time."<sup>6</sup>

Burton and Bishop<sup>7</sup> have studied the effect of concentration of colloid on the amount of electrolyte required for precipitation and, from their results with colloidal arsenious sulfide, copper and mastic, have deduced the following laws: "I. For univalent ions the concentration of ion necessary to produce coagulation increases with decreasing concentration, this increase being very rapid with low concentrations of the colloid. II. For bivalent ions the concentration of ion necessary to produce coagulation is almost constant and independent of the concentration of the colloid. III. For trivalent ions the concentration of ion necessary to produce coagulation varies almost directly with the concentration of the colloid."

Very recently, Weiser and Nicholas<sup>8</sup> have given their findings of the precipitating values of electrolytes on varying concentrations of colloidal hydrous chromic oxide, Prussian blue, hydrous ferric oxide and arsenious sulfide. They conclude that "the

<sup>4</sup> Freundlich, *Z. physik. Chem.*, **44**, 129 (1903).

<sup>5</sup> Kruyt and van der Spek, *Z. Kolloidchem.*, **25**, 11 (1919).

<sup>6</sup> This translation is taken from Weiser and Nicholas, Ref. 8, p. 743.

<sup>7</sup> Burton and Bishop, *J. Phys. Chem.*, **24**, 701 (1920).

<sup>8</sup> Weiser and Nicholas, *ibid.*, **25**, 742 (1921).

manner in which the precipitating value of an electrolyte varies with the concentration of colloid is determined to large extent by the relative absorbability of the precipitating ion and the stabilizing ion." These investigators also show that the laws of Burton and Bishop given above are of quite limited applicability and that "Kruyt and van der Spek's theory of the nature of coagulation is inadequate since it fails to take into account the influence of the stabilizing ions of the electrolytes."

For some time one of the writers has believed that both the so-called stabilizing effect of the ion of similar charge to the colloid particle and the variation in the precipitating value of electrolytes for different concentration of colloid, are due in a large measure, if not entirely, to variation in the hydrogen-ion concentration at the point of precipitation. This idea came from the work of Linder and Picton<sup>9</sup> and of Whitney and Ober<sup>2</sup> who demonstrated that when a negative suspensoid such as arsenious sulfide is precipitated by a neutral salt, some of the basic ion is carried down by the precipitate and there is a simultaneous increase in the acidity of the dispersion medium. Although this result was published more than 20 years ago and has been widely quoted, no systematic study has been made of hydrogen-ion concentration as a factor in the precipitation of suspensoids.

During the summer of 1918 preliminary work in this laboratory showed that the hydrogen ion exercises a very definite and important influence in this phenomenon. Further experiments were made in 1920 with Mr. A. J. Patty but these were discontinued because Mr. Patty was soon called to work elsewhere. Meanwhile the very beautiful and important work of Loeb<sup>10</sup> has been published which brings out in a striking manner the effect of hydrogen-ion concentration on the properties of colloidal protein substances. Loeb's results, although obtained with amphoteric colloids of the emulsoid type, have given the writers confidence that the findings reported herein will be of wide application to suspensoids.

### Experimental Part

**Preparation of Colloids.**—The colloids used were suspensions of mastic and gamboge. These were chosen because of their ease of preparation, and their stability and adaptability for use with a hydrogen electrode; also, because they are negatively charged. Each solution was prepared in the usual manner by allowing a conc. alcoholic solution to run very slowly into water from a buret whose tip was held under the surface while the mixture was constantly and rapidly stirred. Neutral alcohol was used and 25 cc. of the alcohol solution was taken per liter of water. Although the solutions were apparently quite homogeneous they were filtered through loose cotton plugs to remove any large particles, and then allowed to stand for 3 weeks to permit settling. The final so-

<sup>9</sup> Linder and Picton, *J. Chem. Soc.*, 67, 63 (1895).

<sup>10</sup> Loeb, numerous papers, *J. Gen. Physiol.*, 1, 2, 3 (1918-1921). "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., 1922.

lutions contained approximately 0.3% of suspended material. The specific conductivity was  $4.8 \times 10^{-5}$  and  $2.5 \times 10^{-5}$  for the mastic and the gamboge, respectively.

**Method of Procedure.**—In all cases the method of effecting the precipitation was the same. A solution of the precipitating agent or agents was put in a large test-tube and sufficient distilled water added to make the volume 20 cc. Then 20 cc. of the colloid was placed in a second test-tube and the contents of the first tube rapidly poured into the second and then from one tube to the other 8 times to insure proper mixing. The resulting mixture was set aside for 24 hours at room temperature. By using different concentrations of the precipitants the minimal concentration for complete precipitation was ascertained. The supernatant clear liquid was next removed and its hydrogen-ion concentration determined electrometrically.

**Experimental Results.**—First a study of the effects of different acids was made, the acids used being hydrochloric, acetic, sulfuric, oxalic and phosphoric. These were selected to give a comparison of strong and weak acids and of anions having different valences. Besides the original sols, dilutions of  $1/2$  and  $3/4$  were employed to bring out any variation due

TABLE I  
THE PRECIPITATION OF MASTIC AND GAMBOGE COLLOIDS WITH ACIDS

Acid	MASTIC					
	Original solution		Solution diluted 50%		Solution diluted 75%	
	Conc. of acid Milli-equiv- alents per liter	Hydrogen- ion conc. $P_H$	Conc. of acid Milli-equiv- alents per liter	Hydrogen- ion conc. $P_H$	Conc. of acid Milli-equiv- alents per liter	Hydrogen- ion conc. $P_H$
Hydrochloric.	3.04	2.65	2.84	2.6	2.88	2.6
Acetic.....	350.0	2.55	300.0	2.6	200.0	2.6
Sulfuric.....	3.12	2.65	2.96	2.6	2.96	2.6
Oxalic.....	6.50	2.5	6.50	2.45	4.75	2.7
Phosphoric...	5.33	2.65	5.33	2.6	5.33	2.55

  

Acid	GAMBOGE					
	Original solution		Solution diluted 50%		Solution diluted 75%	
	Conc. of acid Milli-equiv- alents per liter	Hydrogen- ion conc. $P_H$	Conc. of acid Milli-equiv- alents per liter	Hydrogen- ion conc. $P_H$	Conc. of acid Milli-equiv- alents per liter	Hydrogen- ion conc. $P_H$
Hydrochloric....	4.00	2.5	3.90	2.5	3.90	2.5
Acetic.....	550.0	2.5	750.0	2.5	600.0	2.7
Sulfuric.....	3.6	2.5	3.6	2.55	3.68	2.6
Oxalic.....	9.50	2.5	9.50	2.6	9.00	2.4
Phosphoric.....	7.50	2.5	7.20	2.55	7.40	2.5

to change in concentration of the colloid. The results obtained are given in Table I. The hydrogen-ion concentrations are stated in terms of Sørensen units,  $P_H$ , and the amounts of the acids in milli-equivalents per liter. The amount of acid or of salt employed is in each case the minimum required for complete precipitation of the sol.

Precipitations with salts containing the monovalent positive ions, potassium and ammonium, were also carried out. The salts used were the chlorides, acetates, sulfates, oxalates and monohydrogen orthophosphates. These were tried alone and also with additions of the corresponding acids, that is, with each salt the acid containing the same anion. It was found that for both the mastic and the gamboge, potassium chloride gave the smallest precipitation value and also the greatest hydrogen-ion concentration. The value obtained for this salt for each sol was taken as the starting point for the tests in which the additions of the acids were made. The other salts, both of ammonium and potassium, were each added in the same amount as required for potassium chloride together with enough of the corresponding acid to effect complete precipitation. Experiments were also made on 50% dilutions of the sols with acidified solutions of the acetates, oxalates and phosphates. The data secured are reported in Table II.

TABLE II  
THE PRECIPITATION OF MASTIC AND GAMBUGE COLLOIDS WITH SALT SOLUTIONS AND ACIDIFIED SALT SOLUTIONS

Salt used	MASTIC			Solution diluted 50%		
	Original Solutions		Hydrogen-	Solution diluted 50%		Hydrogen-
	Salt conc. Milli-equiv- alents	Acid conc. Milli-equiv- alents	ion conc. $P_H$	Salt conc. Milli-equiv- alents	Acid conc. Milli-equiv- alents	ion conc. $P_H$
KCl.....	75	....	4.3	...	....	..
KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	400	....	8.0	...	....	..
K <sub>2</sub> SO <sub>4</sub> .....	75	62.5	4.5	37.5	15.0	3.9
	225	....	4.4	...	....	..
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .....	75	0.15	4.0	...	....	..
	275	....	5.9	...	....	..
K <sub>2</sub> HPO <sub>4</sub> .....	75	7.5	4.4	37.5	10	4.25
	100	....	4.8	50.0	....	7.25
NH <sub>4</sub> Cl.....	75	13.6	4.3	37.5	75	4.05
	125	....	4.40	...	....	..
NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	225	....	5.8	...	....	..
	75	3.6	4.4	37.5	162.5	4.08
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	125	....	5.8	...	....	..
	75	0.15	4.5	...	....	..
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .....	Too insoluble for use for complete precipitation					
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	75	6.70	4.6	37.5	0.40	4.15
	500	....	6.6	...	....	..
	75	32.1	4.3	37.5	8.33	4.20
	<b>GAMBUGE</b>					
KCl.....	112.5	...	4.65	...	....	..
KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	462.5	....	7.6	...	....	..
	112.5	43.8	4.5	56.25	7.0	4.54
K <sub>2</sub> SO <sub>4</sub> .....	500	....	5.0	...	....	..
	112.5	0.004	4.35	...	....	..

K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .....	500	....	6.85	...	....	..
	112.5	5.0	4.8	56.25	7.5	4.30
K <sub>2</sub> HPO <sub>4</sub> .....	500	....	7.3	...	....	..
	112.5	18.7	4.40	56.25	32.1	4.5
NH <sub>4</sub> Cl.....	137.5	....	5.45	...	....	..
NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	225	....	5.85	...	....	..
	112.5	37.5	5.1	56.25	100	4.4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	375	....	5.80	...	....	..
	112.5	0.15	4.45	...	....	..
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .....	Too insoluble for use for complete precipitation					
	112	0.20	4.4	56.25	5.5	4.55
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	500	....	6.55	...	....	..
	112.5	45.75	4.8	56.25	8.33	4.00

### Discussion of Results

The data in Table I show that, while different amounts of acids are required, each sol is precipitated at a quite definite hydrogen-ion concentration regardless of the concentration of the colloid. Evidently the so-called stabilizing effect of the anion does not take place. The hydrogen ion is the sole precipitating agent.

The results of the experiments with straight salt solutions show that widely varying amounts of salts yielding the same cation but different anions, are required for precipitation. The hydrogen-ion concentrations of the supernatant liquids resulting from the precipitation of the sols vary within a considerable range, for example, from  $P_H$  4.3 to 8.0 for potassium salts with the mastic sol. The vastly different precipitation values of the salts are typical for the experiments which have been frequently cited as a basis for the oft recurring statement that the ion bearing the same charge as the colloidal particle has a pronounced effect.

When the same amounts of the salts were used for each sol as was required for potassium chloride and acidified with the corresponding acids, precipitation takes place at hydrogen-ion concentrations which do not differ widely. The variations are greater than with the acids as precipitants. It is very possible that with the most carefully controlled methods of experimentation these differences might be no greater than the experimental error. The results show that when the hydrogen-ion concentrations are made more nearly uniform, precipitation occurs at the same salt concentration. Apparently, the anion has but little, if any, influence in the precipitation. The ammonium and potassium ions have the same precipitating value.

Further, the tests with the sols diluted  $1/2$  bring out the fact that they are precipitated by  $1/2$  the concentration of the salts used for the original sol, provided the hydrogen-ion concentration is kept approximately the same. These precipitations were complete in 24 hours.

The experimental results given above lead one to believe that Burton and Bishop's<sup>7</sup> law for the effect of concentration of colloid on the precipi-

tating value of univalent ions is erroneous. Their mistaken deduction is due to the fact that the concentration of the hydrogen ion was not taken into account. Since the precipitations with the diluted sols occurred in 24 hours, Kruyt and van der Spek's<sup>5</sup> contention that a dilute colloid requires a greater concentration of electrolyte than the concentrated because of the less probability of the collisions of the particles, does not appear to be of much consequence.

Preliminary experiments with other colloids indicate a hydrogen-ion effect analogous to that given above for mastic and gamboge.

In conclusion the writers desire to point out that if the findings here are of general application, much of the literature on this subject is markedly deficient because one of the main factors of precipitation has been neglected: also, that some very important questions are raised such as that of chemical combination or physical adsorption during precipitation, the relation of hydrogen-ion concentration to the amount of charge on the colloidal particle, the relative precipitating values of ions of different valence and a number of others. Further work is now in progress in this laboratory.

#### Summary

1. A study has been made of the effect of hydrogen-ion concentration on the precipitation of mastic and gamboge sols by acids and salt solutions.
2. Acids cause precipitation at the same hydrogen-ion concentration regardless of the concentration of the colloid. The negative ion of the acid is without effect.
3. Various potassium and ammonium salts precipitate the sols at the same concentration provided the hydrogen-ion concentration is kept approximately constant. The precipitating values of the salts vary directly as the concentration of the colloid at the same hydrogen-ion concentration. The stabilizing or peptizing effect of the ion bearing a charge similar to that of the colloidal particle has been shown to be very limited if it exists at all.

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