[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 308.]

THE FALLACY OF DETERMINING ELECTRICAL CHARGE OF COLLOIDS BY CAPILLARITY.

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Received August 13, 1917.

The capillarity method for the determination of the sign of the electrical charge of colloids is fallacious. This method, proposed by Sahlbohm[1] and Fichter,[2] is recommended by Wo. Ostwald[3] under the name of "Capillary Analysis" as a convenient method of distinguishing between positively charged and negatively charged colloids. Due to its simplicity it is widely used by those who are primarily interested in colloids.

According to the authors of the method, negatively charged colloids ascend strips of filter paper which are dipped into their dispersions while positively charged colloids do not ascend, but coagulate on the paper a slight distance above the level of the dispersion into which the filter paper is dipping, and the explanation offered is that the filter paper, or cellulose, is negatively charged against water and hence an oppositely charged colloid will have its charge neutralized and precipitate on the paper while a like charged colloid will be unaffected and consequently climb up the paper by capillarity.

Our experience has verified the method in the cases of the negatively charged colloids—gold, platinum, arsenious sulfide, etc., as ordinarily prepared, which are *dilute*, and in the case of the positively charged colloids—hydrous ferric oxide when prepared in the *concentrated* form by the method of peptization of ferric hydroxide by ferric chloride.

We were led to investigate the method, however, by the conduct of a *dilute* hydrous ferric oxide sol which *ascended* filter paper strips. This sol had been prepared by the method of hydrolyzing ferric chloride by addition of a small amount of this salt to a large volume of boiling water.

Report of a few of our experiments, which are sufficient to condemn the "capillary analysis" method, follows.

Method.

Ten cc. of the colloidal dispersion to be tested were placed in a small (15 cc.) evaporating dish and a strip of filter paper (Schleicher and Schüll No. 597) about 1 cm. wide and 15 cm. long was suspended with the lower end dipping below the surface of the liquid, but not touching the dish. A glass case was placed over this outfit to prevent excessive evaporation, and to protect from drafts and dust. Observation of the height to which

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[1] *Kolloidchem. Beihefte*, 2, 79–141 (1910).

[2] *Kolloid Z.*, 8, 1–2 (1911).

[3] "Handbook of Colloid Chemistry," p. 15.

the dispersion ascended was made at the end of a suitable interval, generally 48 hours.

Inorganic Dispersions Used.

(I) **Hydrous Ferric Oxide** Sol by **Peptization Method** (a positive colloid).—This hydrosol was prepared by peptization of freshly precipitated ferric hydroxide with ferric chloride. 135 g. of ferric chloride were dissolved in 100 cc. of distilled water and small quantities (about 1 cc. at a time) of 3 *N* ammonium hydroxide solution were added, followed by shaking to allow the ferric hydroxide to "dissolve," that is, to be peptized by the excess of ferric chloride present. When by the slowness of peptization it was observed that nearly all of the iron was in the hydrosol condition, the dispersion was placed in collodion sacks, dialyzed for 6 hours against running tap water and then against distilled water for 156 hours, changing the water twice daily. By this time the dialysate gave but a faint test for chloride.

Analysis of this hydrosol showed a content of 0.0143 g. Fe_2O_3 and 0.0018 g. Cl per cc.

(II) **Hydrous Ferric Oxide Sol by Hydrolysis Method** (a positive colloid).—This hydrosol was prepared by hydrolysis of ferric chloride. Five cc. of a 10% ferric chloride solution were boiled with 500 cc. of distilled water for 10 minutes and then dialyzed against distilled water for 5 days.

(III) **Hydrous Chromic Oxide** Sol (a positive colloid).—This hydrosol was prepared from chromic chloride in a manner similar to (I), described above. It was dialyzed against running water for 34 hours and then against distilled water for 48 hours.

Upon analysis it showed 0.0012 g. Cr_2O_3 per cc. and but a faint trace of chloride present.

(IV) **Arsenious Sulfide** Sol (a negative colloid).—A saturated solution of arsenious acid, prepared by boiling an excess of arsenious oxide with distilled water and filtering, was saturated with hydrogen sulfide by passing the gas through it for 12 hours and shaking frequently. A very concentrated, though clear, hydrosol was obtained. It was not dialyzed for fear of coagulation.

Analysis showed it to contain 0.013 g. As_2S_3 per cc.

(V) **Antimony Sulfide Sol, Undialyzed** (a negative colloid).—2.5 g. of potassium antimonyl tartrate (tartar emetic) were dissolved in 500 cc. of distilled water and the solution was saturated with hydrogen sulfide.

(VI) **Antimony Sulfide Sol, Dialyzed.**—400 cc. of (V) were dialyzed for 3 days against distilled water, changing the water twice daily.

This hydrosol contained 0.0017 g. Sb_2S_3 per cc.

(VII) **"Molybdenum Blue"** Sol (a negative colloid).—This hydrosol was prepared according to Biltz.[1] It was dialyzed for several days against distilled water.

Experimental.

From the observation which suggested this investigation, *i. e.*, that a *dilute* ferric oxide hydrosol ascends filter paper strips, we suspected that dilution of the sol is the cause of the ascent since all other iron oxide hydrosols which had been used formerly and which did not ascend filter paper strips, were quite *concentrated.* The concentrated sols were prepared by the "Peptization" method while the dilute sol was a result of the "Hydrolysis" method of preparation.

The effect of dilution upon capillarity was accordingly studied with the results given below.

HYDROSOL (I).

Conc. of sol	1.0[2]	0.1[3]	0.05[3]	0.02	0.002	0.001
Ascent in cm. after 48 hrs	1	1	1	5	5	5

Hydrosol (II), even when undiluted, readily ascended to the tops of the filter paper strips.

It is evident, therefore, that the positively charged colloid, hydrous ferric oxide, will ascend a strip of filter paper by capillarity if it is sufficiently dilute.

Since Miss Sahlbohm[4] noted that an incompletely dialyzed positive hydrosol would ascend a strip of filter paper, we tried the effect of addition of electrolyte to the ferric oxide sol. The concentrations of electrolyte cited below refer to the final concentration of the electrolyte in the mixture.

EFFECT OF FERRIC CHLORIDE ON HYDROSOL (I).

Conc. of sol	0.5	0.5	0.5	0.5	0.05	0.05	0.05	0.05	0.05
Conc. of $FeCl_3$	0	0.001 *M*	0.01 *M*	0.1 *M*	0	0.0001 *M*	0.001 *M*	0.01 *M*	0.1 *M*
Ascent in cm. after 48 hrs	1	1	1	5	1	2.5	3.5	7	8.5

Note that the capillary ascent was forced by adding ferric chloride to 0.1 *M* concentration to the fairly concentrated sol (0.5) and when the sol was ten times dilute (but still concentrated enough so that it would not ascend), it ascended when as little as 0.0001 *M* ferric chloride was present.

EFFECT OF HYDROCHLORIC ACID ON HYDROSOL (I).

Conc. of sol	0.05	0.05	0.05	0.05
Conc. of HCl	0	0.0001 *M*	0.001 *M*	0.01 *M*
Ascent in cm. after 48 hrs	2	5	4	5

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[1] "Laboratory Methods of Inorganic Chemistry," **1909**, p. 39.

[2] This means that the sol was used undiluted.

[3] These numbers mean that to each 0.1 cc. of sol (I), 0.9 cc. of distilled water was added, and to 0.05 cc. of (I), 0.95 cc. of water was added, and so on.

[4] *Kolloidchem. Beihefte*, **2**, 79 (1910).

Analysis of the wetted part of the strip of paper above the level to which the sol had ascended, showed the presence of hydrochloric acid.

Neutral electrolytes did not cause the ferric oxide sols to ascend, with the possible exception of ammonium chloride, which, in concentrations of 0.01 molar, seemed to cause a slight ascent of the sol of 0.05 concentration. This is attributed to the fact that this salt is slightly acid in reaction. Hence we may state that electrolyte of acid reaction, or the presence of hydrogen ion will cause a positive colloid, such as ferric oxide hydrosol, to ascend filter paper strips.

Effect of Dilution upon Hydrosol (III). Chromic Oxide.

Conc. of sol	1	0.8	0.6
Ascent in cm. after 48 hrs	2	5	6

Since the color of this sol was quite faint, we had difficulty in detecting the height of ascent. By moistening the papers with dilute alkali and immersing in bromine vapors, oxidation to chromate resulted in a yellow color which was plainly visible with the concentrations given above, but could not be used with concentrations lower than the 0.6 given above.

Note that this positive colloid also ascends when sufficiently dilute.

The next step in the proof of the fallacy of the method of "capillary analysis" was to prepare some negative colloids so concentrated that they would not run up the filter paper. We succeeded in our attempt as shown by the following record:

Effect of Dilution upon Arsenious Sulfide Hydrosol (IV).

Conc. of sol	1	0.1	0.05
Ascent in cm. after 96 hrs	2	4	12

The above recorded heights were reached in 24 hours and did not alter during the additional 72 hours. Distinct coagulum lines were formed on the strips at the heights noted, just as in the case of the ferric oxide hydrosol. Note in the directions of preparation, given earlier in this report, that we took special care to make this sol as concentrated as possible. When arsenious sulfide sols are made by the ordinary method of mixing equal volumes of saturated arsenious acid solution and hydrogen sulfide water, they readily climb the paper strips since they are so dilute.

Effect of Dilution upon Antimony Sulfide Hydrosol (VI).

Conc. of sol	1	0.5	0.1
Ascent in cm. after 48 hrs	0.5	2	8

After much longer standing the above sols did not climb any further.

In the presence of 0.02 *M* sodium hydroxide, the concentrated one ascended 5 cm. Hence hydroxyl ion will cause a negative colloid to ascend by capillarity just as hydrogen ion does in the case of the positive colloids.

Effect of Dilution upon Antimony Sulfide Hydrosol, Undialyzed (V).

Conc. of sol	1	0.5
Ascent in cm. after 48 hrs	0.5	2

Note that this negative colloid did not ascend the papers as far as the positive colloid (I) did.

EFFECT OF DILUTION UPON "MOLYBDENUM BLUE" HYDROSOL (VII).

Conc. of sol....................	Original sol.	Concd. 60 times
Ascent in cm. after 48 hrs......	15	4.5

It is evident from these experiments that the ascent of the filter paper strips is a function of the concentration of the colloid even when it is negatively charged.

Another interesting observation which was made, and which constitutes another argument against the validity of the method of capillarity, was that if the papers up which the sol had not climbed, and upon the lower end of which there was a coagulation rim of the sol, were shaken so as to wet above this line of coagulation, or if the paper were permitted to cling to the side of the glass vessel containing the sol, then the sol would ascend for several centimeters regardless of the nature of its charge.

Capillary Conduct of Some "Colloidal" Dyestuffs.

Since the preparation of very concentrated negative hydrosols, in the absence of an emulsoid or protective colloid, seemed to be rather difficult and due to the fact that we desired to try more than the three negative sols reported above, our attention was turned to those dyestuffs which are described as colloids.

We selected two so-called positive colloidal dyes[1]—Bismarck brown and methylene blue—and two so-called negative colloidal dyes—eosin and fuchsin, and made saturated aqueous dispersions of them. They all ascended filter paper strips alike, even when ten times diluted with water. Since there was a possibility of electrolyte impurities affecting the conduct of these dyes, they were then dialyzed to remove the electrolytes, but with the result that the dyes themselves diffused through the collodion dialyzing membranes. Hence the colloidal nature of these dyes is very doubtful and a revision of the generally accepted statements concerning their colloidal nature is suggested.

Effect of the Nature of Filter Paper on Capillarity.

Since Miss Sahlbohm found that a positively charged colloid would climb an acid-washed filter paper, it was considered interesting to compare the capillarity ascent of a colloid upon different kinds of filter paper. Several grades of Whatman and of Schleicher and Schüll papers were tried, using ferric oxide hydrosol (I) of different dilutions, with the result that a different height of ascent was obtained with a given dilution of (I) for each kind of paper. This is another objection to the method. Two specimens of the same grade of paper, one being much older than the other, gave discordant results also.

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[1] Burton, "Physical Properties of Colloidal Solutions," 1916, p. 126.

The last objection is not needed in the condemnation of the method, however, since it is very plain that there is no relation between the sign of the electrical charge of a colloid and its capillarity ascent of a strip of filter paper which may be immersed in it.

The height of ascent is dependent upon the dilution of the sol, the presence of electrolyte, the external conditions such as surrounding atmosphere, and the nature of the filter paper used.

We believe that the method was innocently proposed due to the result of the peculiar circumstance that the positive colloids which the originators of the methods used were concentrated while their negative colloids were dilute. In fact it is very difficult to obtain the negative colloids in a concentrated state in the absence of a protective colloid. It is impossible to get the colloidal noble metals concentrated, we succeeded only with the sulfides.

NEW YORK CITY.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION NO. 29.]

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.

I. THE WATER CORRECTION.

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Received September 25, 1917.

CONTENTS.—1. Introduction to the Series. 2. The Magnitude and Nature of the Water Correction. 3. The Stability of Conductivity Water in Contact with the Atmosphere. 4. The Carbonic Acid Concentration and the Acidity of Conductivity Water. 5. The Relation between Specific Conductance and Degree of Ionization. 6. Calculation of the Carbonic Acid Metathesis Correction. 7. Salts of Strong Acids and Bases. 8. Influence of Saline Impurities upon the Metathesis Correction. 9. Salts of Weak Acids and Bases. 10. Salts of Higher Valence Types. 11. Acids and Alkalies.

1. Introduction to the Series.—Any theoretical interpretation, in terms of the Ionic Theory, of the properties and behavior of solutions containing electrolytes involves as one of its essential factors a knowledge of the degrees of ionization of the electrolytes present in the solution. The most reliable method of determining the degree of ionization, α, of a uni-univalent electrolyte at the concentration C is by means of the relationship $\alpha = \Lambda_c/\Lambda_0$ where Λ_c is the *true equivalent conductance* of the electrolyte at the concentration C (corrected, if necessary, for viscosity influences) and Λ_0 is its *true equivalent conductance* at zero concentration.

By *true equivalent conductance* is meant the equivalent conductance of the electrolyte at the concentration in question, when the solution contains no ions other than those resulting from the direct ionization of the elec-