[CONTRIBUTION FROM THE BUTTERFIELD CHEMICAL LABORATORY, UNION COLLEGE]

Studies on Silicic Acid Gels. XIV. Dialysis of Silica Hydrosol and Hydrogel

BY CHARLES B. HURD AND PAUL L. MERZ[1]

Introduction

In his classic work on diffusion, Graham[2] distinguished between crystalloids, which diffused rapidly in solution, and colloids, which diffused slowly, if at all. This difference was more marked if the diffusion took place through a membrane. This phenomenon has been explained on the basis of particle size.

The condensation theory for the formation of silicic acid gel assumes that monosilicic acid is first formed, for example, by the reaction of sodium silicate with an acid.[3,4]

If a monosilicic acid is thus present in the hydrosol when it is first formed, which conclusion Mylius and Groschuff[3] reached on the basis of their albumin test, it should be possible to withdraw the monoacid by diffusion through a membrane. As condensation occurs, forming larger and larger molecules of polysilicic acids, this ability to diffuse through a membrane should decrease and finally cease altogether, even before the particles become large enough to form the gel.

It might be noted that certain workers[5,6,7] have shown from freezing point measurements that when first formed the silicic acid has a molecular weight between 60 and 100. This increased steadily, the accuracy of the method failing before the molecular weight reached 10,000 and some time before the gel set.[8] This method, of course, gave the average molecular weight but did not indicate the distribution of particle size.

There are only scattered references in the literature to particle size in hydrosols of silica. Zsigmondy[9] reported that silicic acid passed through a membrane impervious to colloidal silver but that little passed through fish bladder. Bechhold[10] thought that colloidal silica had particles not very much larger than crystalloids. He studied diffusion through different membranes and really showed a method for finding particle size. Tourky[11] studied the effect of *p*H of his solutions on the particle size.

It is evident that the time element has been neglected and that the time element is very important. We have, accordingly, attempted to determine the amount of silica capable of diffusing from the hydrosol, through standard membranes, as a function of the age of the sol. The results of this study are presented here.

Experimental

Materials and Apparatus

Collodion sacks were selected as the most convenient membranes. They were made by pouring collodion solution, U. S. P., General Chemical Company, Code Number 1611, into clean, dry, 6-inch test-tubes. The tubes were inverted and allowed to drain. A record was made of the drying time, since longer drying gave sacks with smaller pore size. After being dried, the tubes were filled with distilled water and allowed to stand ten minutes. The sacks were then easily removed. They were kept under distilled water.

Drying time controls pore size, the latter being determined by the air pressure method.[12,13] This method at least gives comparative results, even though they may not be absolute.

The sacks were tested to ascertain if exposure to the solutes present with the silica in the hydrosols had any effect on the pore size. Dilute acids or salts apparently had little if any effect. Strongly acid solutions made the sacks a little more permeable to silica, strongly basic solutions affected and finally destroyed the membranes.

The silica content of all solutions was determined by the ordinary gravimetric method. The sodium silicate solution, prepared from "E" brand silicate supplied by the Philadelphia Quartz Company, was analyzed by titrating its sodium hydroxide equivalent with standard hydrochloric acid, using methyl orange. The solution was 1.35 *N*.

Two methods of dialysis were used. In the first, a 10-cc. sample of the sol was placed in a fresh sack, and the sack was placed in an 8-inch test-tube containing 40 cc. of distilled water or solution of sodium acetate and acetic acid. The open end of the sack was held between the rubber stopper and one side of the test-tube. After a measured time interval, this 40 cc. of solution was withdrawn and replaced by 40 cc. of distilled water. The solution withdrawn was analyzed. We have called this the "ordinary method."

In the second or "continuous method," a 10-cc. sample in a sack was held in an 8-inch test-tube, while distilled water dropped very slowly into the 40 cc. surrounding the sack. This outer solution drained away continuously from the bottom of the tube through a constant level exit tube.

Dialysis of the Sodium Silicate Solution

It was essential to study the dialysis of the sodium silicate solution, to which no acid had been added.

Using the "ordinary method" we found only 0.0034 g. of silicon dioxide remaining in the contents of the sack after eight successive dialyses. The solution of the 1.35 *N* sodium silicate in the sack at the start contained 1.2570 g. of silicon dioxide.

By using the continuous method for two weeks, we found only 0.0025 g. of silicon dioxide remaining in the sack out of 1.2570 g. present originally.

Also a number of 10-cc. samples of the 1.35 *N* sodium silicate were placed in identical membranes in different 8-inch test-tubes, each containing 40 cc. of water. Diffusion was allowed to proceed for different lengths of time in each tube. The amount of silica which had diffused

---

[1] Present address: Beechnut Packing Company, Canajoharie, New York.

[2] Graham, *Trans. Roy. Soc.* (London), **151**, 183 (1861).

[3] Mylius and Groschuff, *Ber.*, **39**, 116 (1906).

[4] Hurd, *Chem. Rev.*, **22**, 403 (1938).

[5] Gruner and Elöd, *Z. anorg. Chem.*, **208**, 317 (1932).

[6] Willstätter, Kraut and Lobinger, *Ber.*, **58B**, 2462 (1925).

[7] Treadwell, *Trans. Faraday Soc.*, **31**, 297 (1935).

[8] Brintzinger and Brintzinger, *Z. anorg. Chem.*, **196**, 44 (1931).

[9] Zsigmondy, *Kolloid-Z.*, **8**, 55 (1911).

[10] Bechhold, *Z. physik. Chem.*, **60**, 257 (1907).

[11] Tourky, *Z. anorg. Chem.*, **240**, 198 (1939); **240**, 209 (1939).

[12] Alexander, "Colloid Chemistry," Vol. I, Chemical Catalog Co., 1926, p. 830.

[13] Bartell, "Laboratory Manual of Colloid and Surface Chemistry," Edwards Bros., 1936, p. 76.

through the membrane was then plotted in each case against the time allowed for diffusion. Figure 1 shows such a graph. It gives a rough measure of the speed of diffusion.

The results of these determinations appear to show that essentially all of the silica in the sodium silicate solution will diffuse through the collodion membranes, given time and fresh water to receive it.

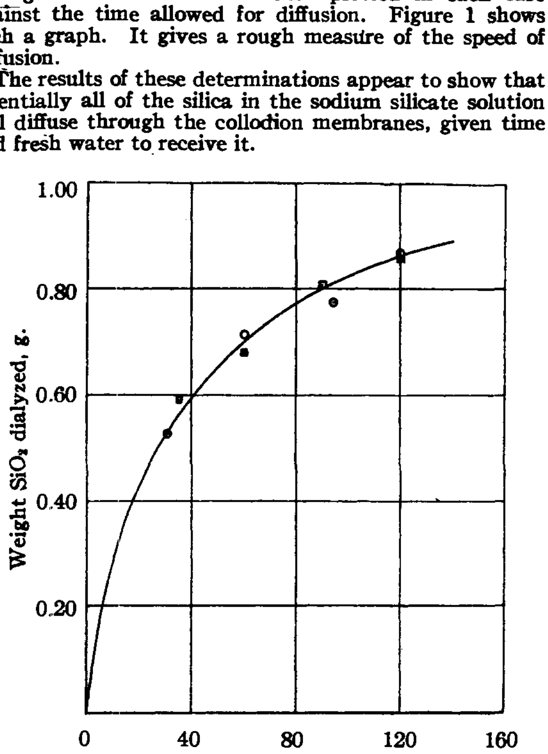

Fig. 1.—Weight of silica dialyzed out of sodium silicate solution as a function of time.

Dialysis of the Silica Hydrosols

Dialysis of the hydrosols of silica, made by pouring the sodium silicate solution into the acetic acid solution in the correct proportions with proper mixing, at 25°, was carried out as follows: The mixture was allowed to stand for fifteen minutes at 25°, then a 10-cc. sample was quickly placed in a fresh membrane and allowed to dialyze for ten minutes into 40 cc. of a solution of sodium acetate and acetic acid, equal in concentration and having the same pH as the solution in the sack. The silica inside the sack thus was all that should diffuse through the sack, no depletion of sodium acetate nor acetic acid occurring within the sack, such as would have been the case if pure water had been used outside the sack. After ten minutes, the outside solution was removed and the silica content determined gravimetrically.

When the original mixture of sodium silicate and acetic acid had stood for thirty minutes, another 10-cc. sample was removed and dialyzed for ten minutes, using a fresh sack and another 40 cc. of sodium acetate and acetic acid solution. The process was repeated every fifteen minutes.

Fresh membranes were used, since it has been shown[14] that a layer of silicic acid forms on the surfaces of the membranes during dialysis of silica hydrosols.

We have used different gel mixtures in our investigation, also membranes of different drying time and pore size. All results were similar, differing only in degree. It is obvious that a finite time, ten minutes, was used for the dialysis and that some change has occurred in the particle size of the silica in the sack during that time. The only reasonable way to handle this was to add half of the time consumed in dialysis to the time elapsed before the sample was taken from the mixture. Thus, we have taken fifteen minutes as the time which elapsed before the sample was taken, added a half minute for transferring and half of ten minutes, making twenty and one-half minutes. The amount of silica dialyzed was plotted for this point against twenty and one-half minutes.

Some data are given in Table I, and two curves plotted in Fig. 2. The value of grams of silicon dioxide diffusing through at zero time on the graph was obtained from the diffusion of sodium silicate itself through the membrane. No method of doing this experimentally for the silica hydrosol could be used since, during the ten minutes used for the diffusion, a considerable change would have occurred in a mixture of sodium silicate and acetic acid.

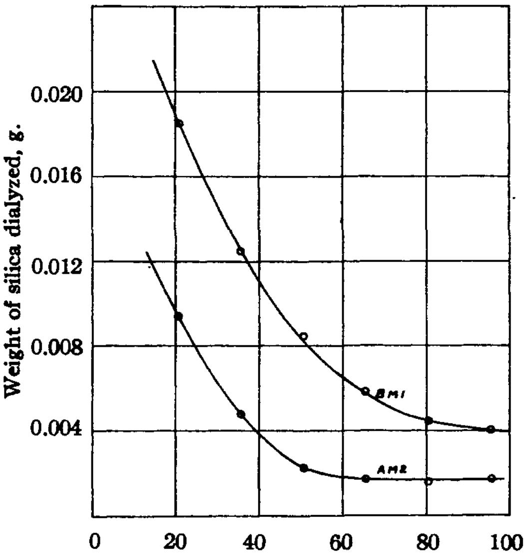

Fig. 2.—Weight of silica dialyzed in a fixed interval of 10 minutes as a function of the age of the hydrosol.

These values are also shown by the curve in Fig. 2. The method used is not absolutely satisfactory since, during the ten minutes used for the dialysis of the sample, a considerable amount of change in the sample may occur, Gel Mixture A setting in 115 minutes and Gel Mixture B in 270 minutes. The answer to this objection is, of course, to use gel mixtures with a very long setting time. We hope to do this later.

Since it was apparent from the results of Table I and Fig. 2 that appreciable quantities of silica were diffusing through the collodion membranes even after the gel mixtures had become opalescent and noticeably more viscous, it was suspected that some silica would be able to diffuse through the membrane from a gel already set. This idea was tested as follows: A gel was made containing SiO_2 0.64, Na^+ 0.78, and Ac^- 0.77, with $pH = 7.0$; setting time 14.25 minutes. A sample of 6.53 g. in 3.5 cc. of distilled water was placed in a fifteen minute collodion sack. In thirty minutes, 0.0010 g. of silicon dioxide diffused out into 40 cc. of 0.7 *N* sodium acetate solution, pH 7.05 at 25°. More silicon dioxide diffused out as longer time was allowed. This result will be unexpected to many workers in the field.

Discussion

It is clear from these results that nearly all of the silicon dioxide in a 1.35 *N* sodium silicate solution is able to diffuse through these collodion membranes. The solution into which the silicon dioxide had diffused gave a very faint Tyndall cone. The intensity of this cone remained constant with the lapse of time.

When, however, a Tyndall test was made of the solution into which the silicon dioxide had dif-

---

[14] Zsigmondy and Heyer, *Z. anorg. Chem.*, **68**, 169 (1910).

TABLE I

WEIGHT OF SILICA DIFFUSING THROUGH COLLODION MEMBRANES AS A FUNCTION OF THE TIME ELAPSED SINCE FORMATION OF A SILICA HYDROSOL

Time, min.	Gel mixture	Membrane	Wt. SiO_2, g.
21.5	A	M_1	0.0186
36.5	A	M_1	.0053
51.5	A	M_1	.0028
66.5	A	M_1	.0013
81.5	A	M_1	.0017
20.5	B	M_1	.0185
35.5	B	M_1	.0125
50.5	B	M_1	.0082
65.5	B	M_1	.0059
80.5	B	M_1	.0045
95.5	B	M_1	.0040
20.5	A	M_2	.0094
35.5	A	M_2	.0048
50.5	A	M_2	.0023
65.5	A	M_2	.0018
80.5	A	M_2	.0016
95.5	A	M_2	.0018
21.5	B	M_3	.0158
36.5	B	M_3	.0083
51.5	B	M_3	.0058
66.5	B	M_3	.0057
81.5	B	M_3	.0049

Gel Mixture A: Conc. Na 0.424; SiO_2 0.696; $HC_2H_3O_2$ 0.680; pH 4.7.

Gel Mixture B: Conc. Na 0.389; SiO_2 0.636; $HC_2H_3O_2$ 0.708; pH 4.4.

All concentrations are in gram moles per liter.

Membrane M_1 5 minute drying—average pore size 10,250 Å.

Membrane M_2 85 minute drying—average pore size 1,050 Å.

Membrane M_3 135 minute drying—average pore size 650 Å.

fused from a freshly made silicic acid gel mixture, a very faint Tyndall cone was observed. The membrane and its contents had been removed from this solution. As the solution aged, the Tyndall cone become brighter, indicating increasing particle size. This result is in line with the theory.

Thus, while the silica in the sodium silicate solution remains in the ionic form or in the form of very small colloidal particles, that in the mixture of silicate and acid is at first in the form of ions or small colloidal particles, where it is able to pass through the membrane, but these particles increase in size as they age, shown by the increased intensity of the Tyndall cone.

From conductivity and transport data, Harman[15] has given strong evidence that silica is present mainly in simple ions, in ordinary solutions of sodium silicate.

This evidence would reinforce the point of view already presented,[4] that when a silica hydrosol is first formed by reaction of solutions of sodium silicate and an acid, the silica is present in the form of a simple silicic acid or its ions. It is impossible, unfortunately, to carry out a dialysis instantly. Here we must depend on the molecular weight measurements already mentioned.[5,6,7]

The results of the dialysis, Table I, show that while at first a large fraction of the silica is capable of passing through the collodion membrane, this fraction decreases as the sol ages. This checks again with the results of the molecular weight determinations, showing clearly that the particle size is increasing.

According to the theory of condensation, or polymerization, the simple particles should have disappeared long before the gel sets. We find from the data of Table I, however, that the amount of silica capable of diffusing from the hydrosol through the membrane appears to approach a constant value. The presence of this material was even shown in the gel some time after it had set.

This unexpected result appears to be explained by the following theory: The process of setting of a silicic acid gel, whatever it may be, does not run entirely to completion but consists of a series of equilibria very much displaced toward the more complex side. Dialysis removes the simpler particles with a shift in the equilibrium toward the simpler materials.

The attack of sodium hydroxide upon silicic acid gel substantiates this point of view, as shown by a study of the process.[16]

It is often loosely stated in the literature that sodium hydroxide peptizes colloidal hydrated silica. It is probably more nearly correct to say that sodium hydroxide reacts with the simple silicic acid present, displacing the equilibrium and causing eventually the solution of all of the silicic acid gel.

If sodium hydroxide simply acted upon the large molecules of polysilicic acid which are present, according to theory, in the gel, it should form large ions, of the same size, and these would neither be capable of passing into solution nor of dialyzing through the membrane.

It would be interesting to dialyze some silicic acid gel, broken up and suspended in water, for a long time, in an attempt to see whether it would all eventually pass into solution in the water and dialyze through the membrane.

Summary

A study has been made of the dialysis, through collodion membranes, of sodium silicate solutions, of silica hydrosol and silica hydrogel.

Essentially all of the silica in 1.35 N sodium silicate solution was found capable of dialyzing through the membrane.

Although a freshly formed silica hydrosol contained much of its silica in a form capable of dialyzing through the membrane, this fraction decreased with lapse of time. A small fraction remained able to diffuse through the membrane, even in the gels after setting.

---

[15] Harman, *J. Phys. Chem.*, **29**, 1155 (1925); **30**, 359 (1926).

[16] Unpublished thesis, S. H. Laning, Union College, 1940.

It is suggested that not quite all of the simple silicic acid condenses to form the large polysilicic acids, but remains in equilibrium with the products of condensation. It is able to diffuse through the membrane, upsetting the equilibrium and forming more simple acid molecules. This probably explains the attack of sodium hydroxide solution upon the gel.

SCHENECTADY, NEW YORK RECEIVED[17] APRIL 9, 1945

---

[17] Original manuscript received February 15, 1943.

The Polymorphism of Sulfapyridine

BY RAYMOND N. CASTLE[1a,b] AND NORMAN F. WITT

In the course of the determination of the optical crystallographic properties of some of the sulfanilamide drugs and their derivatives, five polymorphic forms of sulfapyridine (2-sulfanilamidopyridine) were discovered.[2]

The methods of preparation of these forms, their melting points and analyses (Table I), their optical crystallographic properties (Table II), and their photomicrographs (Figs. 1–5) are presented.

Experimental

Preparation of the Forms of Sulfapyridine

Sulfapyridine, Phase I.—This form of sulfapyridine was obtained by crystallization from hot water or methanol, and is the form occurring in commercial preparations of sulfapyridine. This form appears to be the stable modification at room temperature because all other forms (except Phase IV[3]) have been observed to change into Phase I on standing at room temperature in the dry state, well protected from light and moisture.

Fig. 1.—Sulfapyridine, Phase I (× 56).

Sulfapyridine, Phase II.—In order to prepare this form of sulfapyridine, a slightly less than saturated solution of sulfapyridine in hot *n*-propyl alcohol was allowed to stand on the steam-bath at about 80°, until crystals began to form. The solution was allowed to cool slowly undisturbed to about 40°, then rapidly filtered, and the crystals were washed with ether and air dried at room temperature. Usually this method gave a preparation consisting of pure Phase II. However, it was necessary to exercise great care with this procedure or the product was a mixture of Phases II and IV, the latter predominating. When difficulty was experienced in obtaining Phase II in pure form, a process of selective seeding was applied. A crop of crystals containing a mixture of Phases II and IV was used to seed the hot *n*-propyl alcohol solution. The conditions described above were followed and the crop of crystals filtered, dried and examined microscopically. By repeating this process of selective seeding with crops of crystals successively richer in Phase II, a pure preparation was obtained.

Fig. 2.—Sulfapyridine, Phase II (× 56).

When crystals of Phase II from *n*-propyl alcohol were allowed to stand in contact with the mother liquor, a mixture of Phase I and Phase IV was obtained. Phase II slowly changed into Phase I at room temperature, even when carefully dried and stored in well-stoppered bottles protected from light.

Sulfapyridine, Phase III.—This form of sulfapyridine was prepared by allowing a hot saturated solution of sulfapyridine in *n*-butyl, isobutyl, or *n*-amyl alcohol to cool undistrubed to about 35°. The solution was filtered rapidly, and the crystals were washed with ether, and air dried at room temperature.

Crystals of Phase III changed completely into crystals of Phase I on standing in contact with the mother liquor for two days at room temperature. Crystals of Phase III changed into crystals of Phase I at a fairly rapid rate even when perfectly dry. The crystals of Phase III were found to be somewhat soluble in the immersion liquids used in studying the optical properties. After crystals of Phase

---

[1a] From a portion of the Ph.D. thesis, Department of Chemistry, University of Colorado.

[1b] Present address, Battelle Memorial Institute, Columbus 1, Ohio.

[2] After this work on sulfapyridine was completed, an abstract of the work of F. Reimers appeared: *C. A.*, **38**, 2250 (1944).

[3] Phase IV changes into Phase I after melting (174–175°).