

6-1944

The Relation between Viscosity and Silica Concentration of Silicic Acid Gels

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THE RELATION
BETWEEN
VISCOSITY AND SILICA CONCENTRATION
OF
SILICIC ACID GELS

A thesis, presented to the Department of
Chemistry of Union College, in partial ful-
fillment of the requirements for the Degree
of Bachelor of Science in Chemistry, by

Approved by

Jules D. Viglielmo
Charles B. Hurd.

February 16, 1944

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September 12, 1947

THE RELATION BETWEEN VISCOSITY
AND SILICA CONCENTRATION OF
SILICIC ACID GELS

INTRODUCTION

The formation of silicic acid gels from sols of colloidal silica has been found to be affected by such factors as the concentration of silica and acid, pH, degree of agitation, temperature, type of silicate used, and the amount of added soluble materials. In the past the effect of these variables has been studied as a function of the gelation time or so called time of set using the tilted rod method as described by Hurd(1). In this work we have again been concerned with the silica concentration but have elected to use viscosity measurements as a means of studying the process of gelation rather than the former method used by Hurd and Sheffer(2). As pointed out by Hurd and Santora(3), who used the viscometer in studying the effect of added electrolytes the process of gelation may in this way be observed. One can follow it from the time of mix and subsequent chemical union of sodium silicate and acetic acid yielding colloidal silicic acid, through the growth or agglomeration of colloidal sized particles, and finally the gelatinization of the hydrated colloidal particles themselves.

Our main objective was to find whether sols

could be prepared of such dilution as to yield a constant viscosity after a lapse of time. All factors other than the concentration of silica were maintained as constant as our apparatus and laboratory technique would permit.

PROCEDURE

Preparation of Solutions:

About 2 gallons of silicate solution were prepared by diluting commercial water glass with freshly boiled distilled water, the latter precaution being taken since CO_2 has a coagulating effect on the silicate. E brand silicate manufactured by the Philadelphia Quartz Company was used since it has proven most satisfactory in the past, 320 ml. of water being used for every 100 ml. of silicate to yield a solution almost equivalent to 1.25 N sodium hydroxide, this concentration being a convenient starting point in silica gel studies. The actual normality, as its equivalent in sodium hydroxide, was found to be 1.24 by titration with a standard sulfuric acid solution using methyl orange as indicator. Care should be taken here to prevent the mixture from setting during titration by first diluting the silicate with about an equal volume of water and carrying out the determination as rapidly as possible.

An equal quantity of acetic acid was made up by diluting 99.5% glacial acetic with boiled distilled water to reduce it to a concentration of about 2 N. By titration with a sodium hydroxide solution which had been standardized against oxalic acid, the normality was found to be 2.04.

Phenolphthalein was used as indicator.

Preparation of Gel Mixtures:

In every case a total of 150 ml. of gel mixture were made up; 5 ml. to be used for viscosity measurements, 80 ml. in determining the time of set by tilted rod, and 65 ml. for obtaining the pH. Each time equal quantities of silicate and acetic acid solutions were used, the balance being made up with boiled distilled water which had been prepared and stored in a stoppered bottle for this work.

By means of pipettes the required amounts of silicate and acetic acid for each run were carefully measured and placed in separate, dry 200 ml. Erlenmeyer flasks. The necessary water was added at this time to that flask containing the acid, both Erlenmeyer's then being covered with watch glasses and placed in the water bath already holding the viscometer at a temperature of 25.0°C. When the two solutions had attained bath temperature, they were removed and thoroughly mixed by first pouring the silicate into the acid, and then pouring the mixture back and forth between the flasks again. The amounts necessary for the various determinations were then apportioned out, the beaker containing the gel for obtaining time of set was covered with a watch glass and again returned to the water bath.

The above procedure is not to be considered too detailed since the success with which one may duplicate

his results depends in a large measure upon these preliminary approaches.

The Ostwald Viscometer:

The fact that we were interested here in the relative viscosities only permitted our use of the Ostwald viscometer. Not only is the instrument easy to work with but its results are reproducible to a fair degree of accuracy. Hurd and Santora(3) have described its operation fully and we have in this work followed the same procedure; that is, calibration against pure water and use of a stop watch in recording time of flow. Since some of our more dilute mixtures remained in the viscometer for days at a time, however, measures had to be taken to prevent evaporation of the water since this would seriously affect the concentration of the sol. This was accomplished by first removing the syringe bulb attachment, which was used in forcing the mixture up the capillary, after each run. A rubber policeman was then drawn over the smaller tube and a short piece of rubber hose was pulled over the larger. The hose was tightly closed then with a Fisher clamp. For each run the "time after mix" was recorded at the instant the sol passed the first scratch. In short runs this point might seem trivial but where it's a matter of ten or more minutes before the sol has passed the second mark, it's important that one be consistent as to where he shall record his "time after mix."

Determination of Time of Set with Tilted Rod:

This method consists merely of inserting a glass rod into the gel at an angle of about 15° to the vertical and considering the gel set when it can support the rod in this tilted position. Care must be taken not to puncture the gel too often since every rupture will retard its setting. Nor should one test the gel along the sides of the beaker for it is here that the gel first sets and any readings so taken would be no indication as to what's happening in the main body of the gel. The glass rod used was of the same dimensions as those made by other investigators; 3 mm. in diameter, 10 cm. in length, with one end drawn to a stubby point.

Determination of pH:

Since our work was in the acid region entirely, the quinhydrone potentiometer using the calomel electrode was applied throughout. A platinum wire electrode was used in the gel and cleaned off after each determination with concentrated sodium hydroxide solution. This method has in the past, Hurd and Griffeth(4), been found to give reliable results with silicic acid gels and our work has also carried this out.

THEORY AND DISCUSSION OF DATA

Our curves, included in the back of this thesis, confirmed the theory in every respect. That is, with the more dilute sols a greater lapse of time was necessary before setting took place; the viscosity changing but

gradually until the final stages of condensation were reached. The viscosity then increased rapidly with the sol soon becoming so viscous that its passage through the capillary was no longer possible. It is interesting to note, that with the more dilute mixtures, gels 10 and 11, a stage was reached in which the viscosity hovered about a mean value for quite some time before clogging of the capillary took place. A curve was not plotted for sol 11 since no great increase in viscosity ever took place and at best, the data could be represented only by a broken line graph. Instead of the usual upswing, there followed a period in which the sol would flow partly through the viscometer bulb and then stop. The gel never did actually set in the viscometer nor did it ever support the tilted rod, yet this stage was reached permitting no further measurements. We feel that with even more dilute mixtures a constant viscosity might be reached with the particles remaining small enough so as not to clog the capillary.

The short arrows at the top of each graph denote the time of set for each gel using the tilted rod. In the first we have the time recorded in minutes as plotted and in the second the log has been taken.

Since our study here included only that of the single variable, concentration of silica, it was necessary that we maintain the pH constant as well as the other more easily controlled factors. This was done by changing the concentration of the acid as we did that of the silica, always using equal quantities of both solutions. As our

data bears out we were successful in this respect, our spread being only .40 in pH throughout our work.

It would perhaps be fitting to mention briefly here the steps involved in the actual mechanism of condensation for silicic acid gels. From the evidence available at present a reasonable picture may be had if we assume:

- (1) That a monosilicic acid or more correctly, silicon hydroxide is formed in the first step of the process.
 - (2) That this acid, or hydroxide, is amphoteric, giving either hydrogen or hydroxyl ions.
 - (3) That condensation occurs when the positive and negative ions containing the silicon come into contact.
 - (4) That water remains combined or adsorbed, in the resulting structure.
- The fact that these gels have been referred to throughout this thesis as silicic acid gels is then, not because we believe that any simple silicic acid is present in the final gel, but because it appears certain that the starting material is monosilicic acid.

Mention should be made here of the apparent discrepancy in the two sets of calibration data. The shorter time of flow recorded at the end of our work is due to the dissolving action of the silicate upon the glass of the viscometer tube and consequent enlargement of the capillary bore. This probably did not occur until we made our longest runs since prior to this the silicate was in the tube no longer than necessary to obtain the necessary data. Our work by this time was done and we therefore feel

that this deviation is not too serious.

SUGGESTIONS FOR FURTHER WORK

Although our work has increased our knowledge of silicic acid gels it only introduced us to the more fruitful fields, namely that of low concentrations. It is here that Einstein's linear equation for high polymers may be applied. He showed that the viscosity N of the suspension, relative to that of the solvent N_0 , is a function of the volume fraction C_v and is independent of the particle size. Specifically,

$$N/N_0 = N_r = 1 + 2.5 C_v$$

or

$$N_r - 1 = N_{sp} = 2.5 C_v$$

where N_{sp} may be called the specific viscosity increment. This linear relation holds strictly only over a narrow range of concentration, and the curve for relative viscosity (As well as the specific viscosity increment) vs. concentration soon becomes convex to the concentration axis. This is carried out further for macromolecular solutions in general by Kraemer(5) with modifications suggested for higher concentrations in which the relative viscosity is no longer a linear function of the concentration. Such treatment was impossible in our case since the viscosity at any one particular concentration was continually changing.

Having obtained measurements under the conditions described above, one need go but a step further to determine the molecular weight of silicic acid gels using

Standinger's equation.

$$*Nsp / Cgm = K mM$$

*Nsp is again the specific viscosity increment, Cgm is the concentration in molarity of polymeric unit (in our case this would be the H₂ Si O₃ group) and Km is a constant of proportionality. Since this is an empirical rule, the difficulty lies in the measurement of the molecular weights to be used in determining the constant. Both the osmotic pressure and freezing point methods are limited to the very low molecular weights by the very nature of the equations used; M appearing in the denominator on the left hand side thus reducing the accuracy the greater the molecular weight. For example, the highest values recorded by

$$p = \frac{g}{Mv} RT$$

$$t = k \frac{w}{WM}$$

Treadwell(6) for polysilicic acid by the freezing point lowering are in the neighborhood of 6000. The pressure of sodium acetate in the sols as prepared by us also complicates these determinations.

In contrast, ultracentrifugal methods have many advantages but unfortunately there have so far been published only a few ultracentrifugal researches on the molecular weights of macromolecules of high intrinsic viscosity - certainly none on silicic acid gels. It was for this very reason that we were unable to make any calculations ourselves. Although a truly constant viscosity was not

attained in even our most dilute mixture, we might have easily compared molecular weights of the various gels at the same "time after mix."

Standing's rule has received a great deal of discussion and checking and it is believed to have been adequately confirmed qualitatively for linear macromolecules. Further work along the above lines should prove of definite value then since it provides in many cases the most convenient method for estimating relative molecular weights.

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VISCOMETER CALIBRATION

5 ml. pure water at 25.00° C
determined 9-21-43

Time of Flow
in Min. and Sec.

1:30.2

1:30.6

1:30.6

1:30.8

1:30.8

1:30.6

1:30.8

1:30.8

1:31.0

AVG. 1:30.8

5 ml. pure water at 25.00° C
determined 1-25-44

1:29.6

1:29.2

1:29.2

1:29.0

1:29.4

AVG. 1:29.3

CURVE 1

Mixture as follows:

70 ml	Sodium Silicate
70 ml	Acetic Acid
10 ml	Water
4.80	pH
39 min.	Time of Set
1.591	Log Time of Set

Time after Mix

Time of Flow

6 Min.	2:19.4
11	2:30.8
15	2:48.0
20	3:15.4
26	4:30.8

CURVE 2

Mixture as follows:

60 ml	Sodium Silicate
60 ml	Acetic Acid
30 ml	Water
4.80	pH
53 min.	Time of Set
1.724	Log Time of Set

Time after Mix

Time of Flow

6 Min.	2:17.6
10	2:25.6
15	2:38.4
20	2:57.0
25	3:23.8
35	5:42.4

CURVE 3

Mixture as follows:

50 ml	Sodium Silicate
50 ml	Acetic Acid
50 ml	Water
4.63	pH
83 Min.	Time of Set
1.919	Log Time of Set

Time after Mix

Time of Flow

4 Min.	1:56.4
10	2:00.2
15	2:09.2
25	2:14.3
40	2:39.6
45	2:52.4
52	3:13.6
56	3:42.2
60	4:14.4
66	5:26.4
73	8:55.0

CURVE 4

Mixtures as follows:

40 ml	Sodium Silicate
40 ml	Acetic Acid
70 ml	Water
4.90	pH
146 Min.	Time of Set
2.164	Log Time of Set

Time after Mix

Time of Flow

5 Min.	1:49.0
15	1:53.6
30	2:00.6
45	2:11.4
60	2:26.2
75	2:51.2
90	3:33.0
95	4:04.2
101	4:34.2
107	5:42.4
114	7:53.2

CURVE 5

Mixture as follows:

30 ml	Sodium Silicate
30 ml	Acetic Acid
90 ml	Water
4.87	pH
273 Min.	Time of Set
2.436	Log Time of Set

Time of Mix

Time of Flow

6 Min.	1:43.4
16	1:45.0
50	1:52.0
81	2:01.2
96	2:06.3
117	2:15.2
125	2:24.2
135	2:32.4
146	2:42.6
159	2:53.3
172	3:13.3
183	3:43.2
195	4:20.4
200	4:40.4
206	5:09.4
212	5:47.0
219	6:43.2
227	8:25.8

CURVE 6

Mixtures as follows:

25 ml	Sodium Silicate
25 ml	Acetic Acid
100 ml	Water
4.92	pH
417 Min.	Time of Set
2.620	Log Time of Set

Time after Mix

Time of Flow

5 Min.	1:41.0
10	1:41.6
30	1:43.4
93	1:51.0
150	2:01.8
195	2:16.4
225	2:30.4
255	2:50.0
290	3:24.4
340	5:04.6
351	5:46.2
360	6:33.4
363	7:32.8
376	9:41.0
388	24:15.0

CURVE 7

Mixture as follows:

20 ml	Sodium Silicate
20 ml	Acetic Acid
110 ml	Water
4.71	pH
734 Min.	Time of Set
2.866	Log Time of Set

Time after Mix

Time of Flow

5 Min.	1:37.0
65	1:41.0
125	1:45.0
155	1:47.6
200	1:52.2
245	1:58.6
275	2:03.3
290	2:06.3
305	2:12.4
320	2:14.0
335	2:18.2
350	2:22.8
382	2:34.8
395	2:40.0
410	2:47.2
425	2:55.0
440	3:04.8
455	3:16.8
470	3:28.0
485	3:42.6
500	4:00.4
505	4:07.6
515	4:25.0
523	4:36.0
530	4:49.0
545	5:21.6
555	5:51.4
565	6:31.2

CURVE 8

Mixture as follows:

15 ml	Sodium Silicate
15 ml	Acetic Acid
120 ml	Water
4.89	pH
1200 Min.	Time of Set
3.079	Log Time of Set

Time after Mix

Time of Flow

5 Min.	1:36.4
65	1:37.4
140	1:39.2
182	1:40.6
261	1:43.6
295	1:44.2
336	1:46.8
360	1:48.0
390	1:50.2
410	1:51.2
430	1:52.6
450	1:54.2
470	1:54.8
490	1:57.0
508	1:58.6
610	2:09.2
640	2:12.2
670	2:16.2
700	2:22.4
730	2:33.6
760	2:40.6
790	2:48.4
820	2:57.0
850	3:08.6
880	3:18.0
910	3:34.0
1010	4:22.0
1061	5:23.6
1112	8:38.8
1122	9:27.6
1134	12:19.8

CURVE 9

Mixture as follows:

10 ml	Sodium Silicate
10 ml	Acetic Acid
130 ml	Water
4.79	pH
6 Days(8640 Min.)	Time of Set
3.937	Log Time of Set

Time after Mix	Time of Flow
5 Min.	1:34.0
30	1:34.4
60	1:34.6
1071	1:49.6
1136	1:51.0
1152	1:51.2
1220	1:53.0
1245	1:54.0
1332	1:56.4
1513	2:03.0
1672	2:12.2
1713	2:13.2
1770	2:18.2
1790	2:19.4
1816	2:21.6
1830	2:22.4
1860	2:24.4
1890	2:27.2
2449	3:38.8
2504	3:54.2
2531	4:10.2
2550	4:31.6
2563	5:03.4
2572	5:54.4
2578	7:34.0
2586	10:50.8
2598	19:44.2

CURVE 10

Mixture as follows:

8 ml	Sodium Silicate
8 ml	Acetic Acid
134 ml	Water
4.59	pH
	Did not set

Time after Mix

Time of Flow

3 Min.	1:32.8
30	1:33.2
60	1:33.4
90	1:33.6
120	1:33.4
1140	1:42.6
1200	1:44.2
1260	1:44.6
1380	1:46.8
1599	1:50.4
2577	2:24.6
2830	2:40.0
2875	2:43.0
2915	2:45.8
3000	2:52.4
3955	5:22.0

CURVE 11

Mixture as follows:

5 ml	Sodium Silicate
5 ml	Acetic Acid
140 ml	Water
4.52	pH
	Did not set

Date	Set Time	Time of Flow
12-29-43	4:15 P.M.	mixed
29	4:20	1:35.6
29	4:30	1:35.8
30	10:30 A.M.	1:33.2
31	9:25 A.M.	1:35.2
31	2:23 P.M.	1:35.2
1- 1-44	11:30 A.M.	1:37.8
3	4:53 P.M.	1:45.0
4	10:30 A.M.	1:49.6
4	2:20 P.M.	1:50.4
5	2:25	2:02.8
7	9:30 A.M.	2:08.8
	10:15	2:10.6
	2:45 P.M.	2:10.8
	3:30 P.M.	2:13.4
10	9:45 A.M.	2:19.4
11	10:25 A.M.	2:23.0
	2:00 P.M.	2:28.2
	4:00	2:36.8
	5:00	2:36.4
12	1:45 P.M.	2:27.4
	3:00	2:21.6
	3:40	2:21.6
13	10:25 A.M.	2:16.8
14	1:45 P.M.	2:09.6
	2:30	2:25.0
	3:15	2:29.2

F L O W

TIME AFTER MIX IN MIN. FROM CURVES

Time in
Min.

	1	2	3	4	5	6	7	8
1:35								5
1:36							5	65
1:39							45	
1:41						5		
1:42					6			
1:45					16	43	120	295
1:49				5				
1:54				15				
1:56			4					
2:00			12	30	77	141	255	520
2:13	6	7						
2:30	11	13	35	63	132	225	372	736
3:00	18	21	47	79	160	267	433	854
4:00	24.6	30	59	95	190	315	500	984
5:00	27	34	64.5	103.6	204	339	536	1045
6:00	28	35.5	68	109	214	354	558	1074
7:00		36.2	70.6	112	221	364	570	1091
8:00			72	114	226	370		1104
9:00			73.2	115.4	228.7	374		1116
10:00			74	117	230.3	376		

Flow
Time
in Min.

LOG OF TIME AFTER MIX

	1	2	3	4	5	6	7	8
1:35								.699
1:36							.699	1.813
1:39							1.591	
1:41						.699		
1:42					.778			
1:45					1.204	1.633	2.079	2.470
1:49				.699				
1:54				1.176				
1:56			.602					
2:00			1.079	1.477	1.886	2.149	2.407	2.716
2:18		.778	.845					
2:30	1.041	1.114	1.544	1.799	2.121	2.352	2.571	2.864
3:00	1.255	1.322	1.672	1.898	2.204	2.427	2.636	2.930
4:00	1.381	1.477	1.771	1.978	2.279	2.498	2.699	2.991
5:00	1.431	1.531	1.807	2.015	2.310	2.530	2.729	3.019
6:00	1.447	1.545	1.833	2.037	2.330	2.549	2.747	3.031
7:00		1.557	1.845	2.049	2.344	2.561	2.756	3.038
8:00			1.857	2.057	2.354	2.568		3.043
9:00			1.863	2.062	2.359	2.573		3.048
10:00			1.869	2.068	2.362	2.575		

FLOW Time in Min.	CURVE 9		CURVE 10	
	Time after Mix in Min.	Log Time After Mix	Time after Mix in Min.	Log Time After Mix
1:32.8			3	.477
1:33.0	5	.699		
1:33.2			30	1.477
1:33.4			60	1.778
1:33.6			90	1.954
1:33.4			120	2.079
1:34.0	120	2.079		
1:37.0	360	2.556		
1:41.0	720	2.857		
1:42.6			1140	3.057
1:45.0	960	2.982		
1:50.4			1599	3.204
1:54.0	1260	3.100		
2:06.0	1590	3.201		
2:24.6			2577	3.411
2:36.0	2000	3.301		
2:45.8			2915	3.465
3:00.0	2250	3.352		
4:09.0	2531	3.403		
5:00.0	2562	3.409		
5:22			3955	3.597
7:00	2577	3.411		
9:00	2582	3.412		
10:51	2586	3.413		

1 ↓ 2 ↓

TIME OF FLOW IN MIN. AND SEC.

10
9
8
7
6
5
4
3
2
1

5 1 15

LOG OF T



