

with 123.3 g. (0.5 mole) of myristoyl chloride dissolved in 150 cc. of dry ether. The mixture was then refluxed with stirring for ten hours. A yield of 67.8 g. (64%) of product was obtained which melted at 53.5–54.5° after three crystallizations from a 3:1 acetone–benzene solution. After two more crystallizations the product had a constant melting point of 54–55°.

Anal. Calcd. for $C_{36}H_{108}O_4$: C, 79.55; H, 12.88; iodine no., 30.0; sap. no., 132. Found: C, 79.41; H, 12.57; iodine no., 30.9; sap. no., 138.

A sample of the diester was saponified and the myristoin crystallized from alcohol to a constant melting point of 71–72°. The myristic acid obtained melted at 53–54°. The 2-tridecylbenzimidazole was prepared, m. p. and mixed m. p. 105–105.5°.

Preparation of the Dipalmitate of 16-Dotriacontene-16,17-diol.—This was prepared similarly. The crude product weighed 83 g., and after three crystallizations from dry 3:1 acetone–benzene 61 g. (70% yield) of a product melting at 50–60° was obtained. It was crystallized four times from dry 3:1 acetone–benzene and twice from 1:1 ether–alcohol to a constant melting point of 61–62°.

Anal. Calcd. for $C_{64}H_{124}O_4$: C, 80.26; H, 13.05; iodine no., 26.6; sap. no., 117. Found: C, 80.31; H, 12.70; iodine no., 26.7; sap. no., 117.

Saponification of this product gave palmitoin, m. p. 74–75°, and palmitic acid, m. p. 62–63°. The 2-pentadecylbenzimidazole was prepared, m. p. and mixed m. p. 95–96°.

Preparation of the Distearate of 18-Hexatriacontene-18,19-diol.—This was prepared similarly. The crude product was obtained in 67% yield, 36.1 g., m. p. 61–67°. This was crystallized to a constant melting point of 67–68°.

Anal. Calcd. for $C_{72}H_{140}O_4$: C, 80.83; H, 13.19; iodine no., 23.7; sap. no., 105. Found: C, 80.31; H, 12.86; iodine no., 23.4; sap. no., 109.

Saponification of the diester gave stearoin, m. p. 83–84° (Hansley⁶ reported 82–83°), and stearic acid, m. p. 69–70°. The 2-heptadecylbenzimidazole had m. p. and mixed m. p. of 69–70°.

Summary

1. Lauroyl, myristoyl, palmitoyl and stearyl chlorides react with metallic sodium in anhydrous ether to give the respective diesters of the enediols.

2. A mechanism for the reaction has been proposed.

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RECEIVED JANUARY 6, 1939

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN]

Silica Gels from Various Acids. Effect of Concentration and Mixtures on Setting Time¹

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Many extensive investigations demonstrate that the time required for a mixture of sodium silicate and acid to set depends on the concentration of silica, the pH value, and the temperature.^{2,3} The purposes of the present work were: (a) to show a range of common acid concentrations over which gels setting in an hour or less might be obtained with a commercial sodium silicate yielding 3.7% silica in the final system, (b) to seek a demonstrable lyotropic effect of negative ion of the acid, and (c) to investigate the behavior of mixtures of two acids.

Preparation of the Gels

The sodium silicate employed for all tests was the Number 9 grade from du Pont, sold as having 8.9% sodium oxide and 29% silicon dioxide or a ratio of 1:3.25. The original material was diluted with two volumes of distilled water, giving a specific gravity of 1.162, and titration with

standard acid showed it to be 1.55 *N* alkali using phenolphthalein, and 1.70 *N* alkali, using methyl orange as indicator. Standard 4.0 *N* solutions of hydrochloric, sulfuric, phosphoric, and acetic acids were prepared using phenolphthalein, so that phosphoric acid was treated as a dibasic acid. Especially in the rapidly setting gels the order of mixing is significant, so that for all tests here reported 40 ml. of acid was poured into 25 ml. of the silicate solution in a 100-ml. beaker at room temperature (25°), and the solutions mixed by pouring back and forth several times. Rapid mixing of the well-agitated solutions prevented local precipitation, and the mixtures remained fairly clear until the time for setting approached. The gel was considered set when a 7-inm. glass rod 9 cm. long, inserted in the mixture to the bottom of the beaker at about 20° from the vertical just failed to fall.² The setting seems to be preceded by the formation of a relatively tough surface film which must be broken. Too many tests in one place do interfere with the final set so that new areas of the gel must be chosen. Observation of these precautions resulted in good check determinations for most of the systems reported.

The 4 *N* acids were diluted to 1.0 and 2.0 *N* by means of calibrated burets, and the proper volumes of these acids taken so that dilution to 40 ml. gave the desired normality. For the strongly acid systems, appropriate volumes of the standardized c. p. concentrated acids were diluted to 40

(1) Read at the Milwaukee meeting of the American Chemical Society, September, 1938.

(2) C. B. Hurd, *J. Chem. Ed.*, **14**, 84 (1937).

(3) H. B. Weiser, "Inorganic Colloid Chemistry," Vol. II, "The Hydrous Oxides and Hydroxides," John Wiley and Sons, Inc., New York, 1935, p. 194.

ml. The results for the moderate concentrations are shown in Table I and Fig. 1, and those for the same acids in concentrated acid systems in Table II and Fig. 2. No figure is shown for concentrated acetic acid since the only gel prepared, one with glacial acetic acid, required forty-five minutes to set. Other values not shown include three with phosphoric acid in which 1.6, 1.9, and 2.0 *N* systems required 3.7, 13.5, and 36.1 minutes, respectively. These results are comparable to those reported by Holmes in 1918,⁴ and by Hurd.⁵

The results for the mixed acids are shown in Table III and Fig. 3. For these systems the acids were diluted to 0.56 and 0.60 *N*, and the required volumes mixed to make 40 ml. of the compositions shown. Using the determined alkalinity of the sodium silicate, it is evident that when the 40 ml. of acid is 0.97 *N*, the gel system will be neutral to phenolphthalein, and when the 40 ml. of acid is 1.06 *N* the gel system will be neutral to methyl orange. Another consequence of this relation is that when the acid is 0.6 *N*, the final system is still about 0.23 *N* with respect to alkali, and these gels set fairly rapidly. While the finding that neutral or alkaline gels set more rapidly agrees with some previously reported results, it is wholly probable that the position of the curves for these acids is a reflection of differences in *pH*, as Hurd has so conclusively demonstrated.

investigate the interval between 1 and 6 *N* hydrochloric acid additions. As indicated in Table I, the curve rises very steeply, and then descends almost as steeply. When the normalities are 1.05, 1.10, 1.15, and 5.88 *N* hydrochloric acid, the

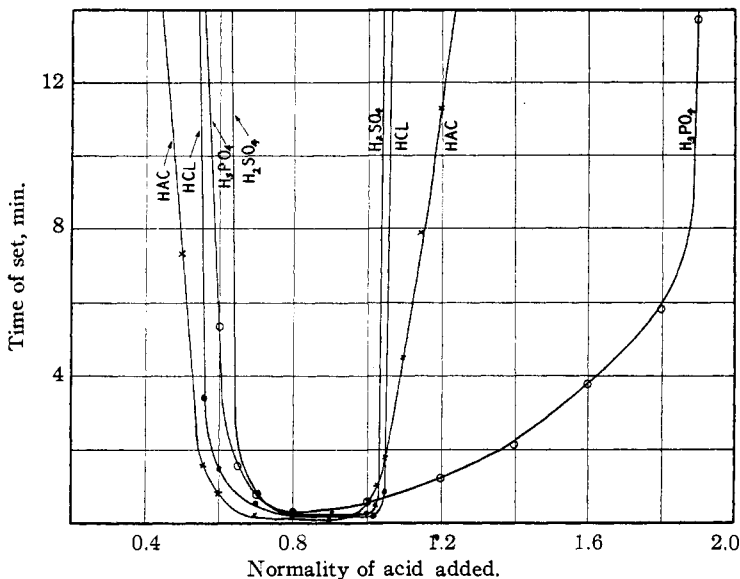


Fig. 1.—Time of set of silica gels against normality of acid added.

corresponding times are 47, 5460, 4200, and 36 minutes, respectively. It appears that all these acids may produce gels over the whole range if

TABLE I
TIME OF SET IN MINUTES WITH VARIOUS ACIDS

Normality of 40 ml. of acid	HCl	H ₂ SO ₄	H ₃ PO ₄	CH ₃ COOH
0.4	>14 hrs.
.5	75	<17 hrs.	102	7.4
.56	3.6	64.0	...	1.5
.6	1.4	13.6	5.5	0.7
.7	0.4	0.7	0.7	.2
.8	.2	.2	.3	..
.9	..	.11
1.0	.2	.1	.5	.4
1.02	.1	.3
1.05	.8	<17 hrs.	...	1.7
1.1	>17 hrs.	<17 hrs.	...	4.4
1.15	7.9
1.2	1.2	11.3

TABLE II
TIME OF SET IN MINUTES FOR CONCENTRATED ACID SYSTEMS

HCl		H ₂ SO ₄		H ₃ PO ₄	
Normality	Time	Normality	Time	Normality	Time
5.0	71.8	4.32	77.0	15.0	33.7
6.5	23.2	5.4	29.2	16.5	22.5
7.0	17.8	6.5	11.0	18.0	12.2
8.0	10.1	7.0	8.6	19.5	7.0
9.0	6.2	8.65	1.9	22.5	2.3
10.0	3.4	11.4	0.5	28.5	0.7
11.96	1.4	14.6	.1	29.9	0.5

TABLE III
TIME OF SET IN MINUTES FOR MIXED ACID SYSTEMS

% Normality due to H ₂ SO ₄	H ₂ SO ₄ -HCl 0.56 N	H ₂ SO ₄ -CH ₃ COOH 0.56 N	H ₂ SO ₄ -HCl 0.60 N
100	64.0	64.0	13.6
90	42.6	26.4	10.0
80	32.2	21.2	7.2
70	23.4	12.4	5.8
60	16.7	8.5	4.2
50	13.1	6.5	3.4
40	10.0	4.3	3.0
30	6.9	..	2.2
20	5.7	2.4	1.7
10	4.0
0	3.6	1.5	1.4

Since this paper was read, P. A. Forni has used the same silicate to check certain points and to

(4) H. N. Holmes, *J. Phys. Chem.*, **22**, 510 (1918).
 (5) C. B. Hurd, K. J. Frederick and C. R. Haynes, *ibid.*, **42**, 85 (1938).

one waits long enough, but an acid silica sol liquid for ninety hours is remarkable.

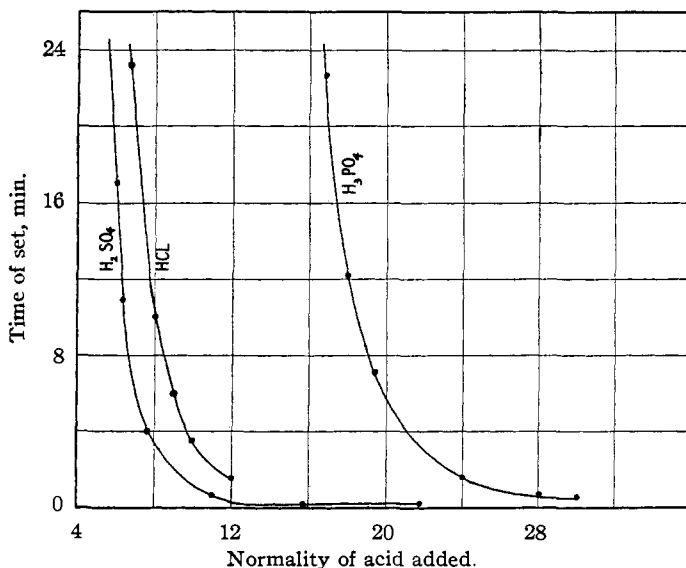


Fig. 2.—Time of set of silica gels against normality of acid added.

The Interpretation of the Results

In spite of many ingenious theories as to the composition and structure of silica sols and gels,^{2,5,7} there appears no clear evidence that in "sodium silicate" solutions we have anything more complicated than colloidal silica peptized by hydroxyl ions.³ If this be the situation, the setting to a gel will in the first place depend on a lowering of the zeta potential on the silica, and then the gel structure will be influenced by the hydrophilic properties of the agglomerated particles. It is clear that, within limits, by a suitable dilution of the sodium silicate and by varying the acid concentrations, silica gels may be obtained at any desired setting time. The steepness of the strong acid curves is remarkable, while with the weaker acids a buffer action is probably in part responsible for their lesser peptization. Many careful investigations by Hurd and his students^{2,5,8} have demonstrated that in the moderately acid systems there is a linear

(6) H. Freundlich, *J. Phys. Chem.*, **41**, 901 (1937).

(7) J. O. Vail, "Soluble Silicates in Industry," Chemical Catalog Company, New York, 1928, p. 55.

(8) C. B. Hurd, C. L. Raymond and P. S. Miller, *J. Phys. Chem.*, **38**, 663 (1934).

relation between pH and the log of the time of set. Practically all of their systems are on the acid side, and the lower the pH the longer the time of set.

The demonstration of any lyotropic series effect is difficult. In the alkaline systems, the more complete the neutralization of the hydroxyl ions on the silica by the hydrogen ions, the more rapid the set of the gel. Sorption of the negative ion of the acid, however, will tend to oppose this and to retard the setting. On such an assumption, the degree of sorption on negative silica would be acetate < chloride < phosphate < sulfate, with the phosphate present as the tertiary and secondary ion in the alkaline solutions. In similar fashion, the dispersion of the silica by hydrogen ions in the acid systems would be opposed by the sorption of the negative ions which would now accelerate the setting. Thus the order of sorption on positive silica would be phosphate > acetate > chloride > sulfate. A reversal of this order is normal in passing from alkaline to acid systems, but the phosphate is most erratic. By a control

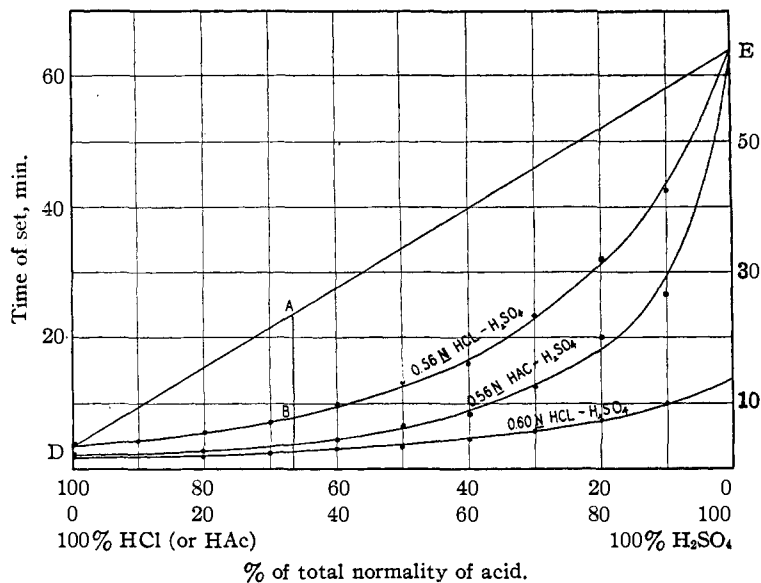


Fig. 3.—Time of set of silica gels with mixed acids, total normality of acids being kept constant.

of pH , Hurd, Raymond and Miller showed that added salts decrease the time of set, chloride being most effective and sulfate least effective, which agrees with our data that the acid chloride systems set more rapidly than the sulfate ones.

A recent review of the phenomena of lyotropy by Voet⁹ has shown that for a number of properties, these ions are rated chloride, acetate, phosphate, sulfate, where the chloride ion is least hydrated. It appears probable that if the difficulties of measurement of *p*H especially in the alkaline systems are surmounted, a plot of time of set against the *p*H for such systems as are covered in Fig. 1 will demonstrate more clearly the lyotropic effect which is here indicated.

In the mixed acid systems the ratio AB:AC (Fig. 3) represents the fractional reduction in time of set referred to the linear relation. The maximum departure from the linear relation is 67% in 0.56 *N* systems at 20% sulfuric acid and 80% hydrochloric acid. It is 49% in 0.56 *N* systems at 25% sulfuric acid and 75% acetic acid. Since these systems are all so alkaline that only the simple anions can arise from the acids, the curves appear to be another manifestation of the lyotropic effects.

The usual explanation for the formation of the second series of gels with the concentrated acids is that they result from the dehydrating action of the acids. Although this may be true, Hurd and Carver¹⁰ found that glycerol had no effect on the setting time of moderately acid systems, while acetone nearly doubled the time required, and alcohol raised it 60%. Such substances are usually dehydrating agents, but they appear to retard setting instead of accelerating gel formation. Possibly a strong adsorption on silica may enable them to displace water and inhibit formation of the usual hydrous bonds in the gel. It appears worth while to consider the simple possibility of an irregular series in these systems. With increasing acid concentrations we have first stable alkaline sols of negatively charged silica, then a range of gels, then stable acid sols of positively charged silica, and finally a second series of gels. If one may consider gel formation as a type of precipitation, the analogy to the usual picture¹¹ is complete.

One of the favorite theories for the composition of silica gels regards them as products of a chemical

reaction producing various silicic acids. The fairly constant heat of formation constitutes a notable support to this view. While the heat evolved during the formation of these gels (16,370 to 21,580 cal.) may be a heat of reaction, there are at least six other possible sources of heat to be considered. These include: the neutralization of the hydroxyl ions on the silica particles and in the solution, the sorption of hydrogen ions on the particles, the sorption of the acid anions on the silica, the energy liberated as a result of the decrease of free surface as agglomeration of the silica proceeds, the hydration change of the silica as its charge is varied, and the heat of dilution of the acid added. The experiments here reported agree with the concept that colloidal silica represents nothing more complicated than a generally hydrophobic material, with some hydrophilic properties, in which the *p*H of the systems affects the most important variable—the sign and magnitude of the electrokinetic potential.

Summary

Silica gels produced by mixing sodium silicate with varying concentrations of hydrochloric, sulfuric, phosphoric and acetic acids set in a minimum time when the final system is at *p*H 8 or somewhat more alkaline than this. Departure from this zone of rapid setting produces a sharp rise in the time of set, except where a buffer action enters in the acid systems. All of these acids produce a series of rapidly setting gels in strongly acid systems. It has been shown that a very small excess of hydrochloric acid causes the setting time to rise steeply to a sharp maximum, and it appears that for the other acids similar closed curves exist. For mixtures of sulfuric acid with hydrochloric acid or acetic acid in which the total acid normality is kept constant, the time of set is not a linear function of the composition of the mixture. On increasing the concentration of acid added to sodium silicate, one finds four types of systems: stable alkaline negative silica sols, rapidly setting gels, stable acid positive silica sols, and finally a second series of gels in concentrated acid systems.

(9) A. Voet, *Chem. Rev.*, **20**, 169 (1937).

(10) Hurd and D. H. Carver, *J. Phys. Chem.*, **37**, 321 (1933).

(11) H. R. Kruyt, "Colloids," John Wiley and Sons, Inc., New York, 1930, p. 89.