Thixotropy of Alginate Gels

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The various metal alginate gels are known to be formed by the reactions between metallic and alginate ions in solution. The resulting gels exhibit thixotropy which does not seem to be reported precisely in the literature of the subject. The present paper describes the details of such a thixotropy of alginate gels.

Experimental

Purification of sodium alginate was carried out by repeated precipitations by acid and dissolutions by alkali. The purified sodium alginate, whose polymerization degree was about 80[1] was dried at 80°C. Two cc. of 2% sodium alginate solution was pipetted in the test tube of an inner diameter

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[1] Polymerization degree of sodium alginate was determined viscometrically in the presence of sodium chloride according to K. Inokuchi. *Mem. Fac. Science, Kyûshû Univ. Series C*, **1**, 115 (1950).

being about 1.6 cm. to which 2 cc. of the electrolyte solution was added and the whole content was mixed intimately. Thixotropy was observed simply by measuring the setting time which was detected by inverting the tube. All measurements were conducted at 20℃.

Experimental Results

Thixotropic gels were obtained by adding appropriate amounts of cupric chloride, barium chloride, calcium chloride, lead nitrate, cadmium sulfate, zinc sulfate and nickel sulfate to sodium alginate solutions The setting times of resulting transparent gels are shown in Table I.

TABLE I

SETTING TIME OF THIXOTROPIC GELS FORMED BY ADDING VARIOUS ELECTROLYTES TO 2% SODIUM ALGINATE SOLUTION

(a) $CuCl_2$ addition

$CuCl_2$ added (10^{-5} mole)	Setting time			
	Immediately after add.	1 day after	5 days afters	10 days afters
2.08	∞	∞	∞	∞
2.34	27 min.	31 min.	1.7 hr.	48 hr.
2.60	30 sec.	2 min.	12.7 min.	6 min.
2.86	5 sec.	0 sec.	0 sec.	0 sec.
3.12	0 sec.	〃	〃	〃
3.38	〃	〃	〃	〃
3.64	〃	〃	Coag.	〃
4.16	5 sec.	Coag.	〃	〃
4.68	Coag.	〃	〃	〃

(b) $BaCl_2$ addition

$BaCl_2$ added (10^{-5} mole)	Setting time			
	Immediately after add.	1 day after	3 days after	8 days after
1.76	∞	∞	∞	∞
2.05	4.1 hr.	——	11 hr.	48 hr.
2.34	5 min.	1.6 hr.	2.8 hr.	〃
2.64	4 min.	〃	41 min.	〃
2.93	2 min.	5.3 hr.	48 hr.	Coag.
3.22	44 min.	Coog.	Coag.	〃
3.52	Coag.	〃	〃	〃
3.81	〃	〃	〃	〃

(c) $Pb(NO_3)_2$ addition

$Pb(NO_3)_2$ added (10^{-5} mole)	Setting time	
	Immediately after add.	1 day after addition
1.20	20 hr.	96 hr.
1.60	〃	〃
2.00	〃	24 hr.
2.40	8 min.	96 hr.
2.80	3 min.	〃
3.20	4 min.	〃
3.60	6.5 min.	Coag.
4.00	9 min.	〃
4.40	16 hr.	〃
4.80	Coag.	〃

(d) $CaCl_2$ addition

$CaCl_2$ added (10^{-5} mole)	Setting time	
	Immediately after addition	1 day after addition
1.61	∞	∞
2.42	〃	〃
3.22	17 hr.	24 hr.
4.03	26 min.	〃
4.84	2 min.	Coag.
5.64	Coag.	〃
6.45	〃	〃

(e) $CdSO_4$ and (f) $ZnSO_4$ addition

Electrolyte added	Setting time immediately after addition	
(10^{-5} mole)	$CdSO_4$	$ZnSO_4$
3.50	∞	∞
4.00	〃	〃
4.50	23 hr.	〃
5.00	22 hr.	20 hr.
5.50	2 min.	〃
6.00	21 hr.	Coag.
6.50	Coag.	〃

(g) $NiSO_4$ addition

$NiSO_4$ added (10^{-5} mole)	Setting time immediately after addition
3.60	∞
5.70	ca. 6 days
6.42	〃
7.13	〃
7.84	〃
8.56	〃
9.98	〃
10.7	Coag.

From these results, it is seen that the addition of neither too little amount nor too large excess of the electrolyte rendered the gel thixotropic, and we see as a whole that the thixotropic setting time decreases at first and then shows the tendency to increase with increasing amounts of electrolytes. Furthermore, it is seen that the setting time changes with the ageing of the gels. In the cases of adding other electorlytes such as hydrochloric acid, silver nitrate, manganese sulfate, aluminum sulfate and ferric chloride, the thixotropic gel was not obtained and the coagulation of the corresponding metal alginates occurred at once from the sol state. Next, the effects of the several experimental conditions on thixotropy were studied. The effect of changing volume was first studied for the systems containing the constant amount (40 mg.) of sodium alginate, as shown in Table II.

In Table II, we can see that thixotropy occurs at the intermediate alginate concentration, namely it occurs as the intermediate state between sol and coagel. This is in accord with the accepted view that the thixotropy and coagulation parallel each other[2]. The thixotropic setting time is

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[2] H. Freundlich und K. Söllner, *Kolloid-Z.*, **45**, 348 (1928).

TABLE II

THIXOTROPY VERS. CONCENTRATION OF GEL

Volume of the system (cc.)	Amount of $CuCl_2$ added (unit 10^{-5} mole)									
	2.72	2.94	3.10	3.30	3.64	4.04	4.36	4.72	4.96	5.18
4	T*	T	T	T	T	T	T	T	T	T
8	Sol	T	T	T	T	T	T	Coag	Coag	Coag
12	Sol	Sol	Sol	Sol	Sol	T	T	Coag	T	Coag
16	Sol	Sol	Sol	Sol	Sol	Sol	Sol	Sol	Sol	Sol

* "T" shows that the system is thixotropic.

therefore expected to depend on the polymerization degree of the alginate just as it is the case with coagulation. Table III shows these results.

TABLE III

THIXOTROPIC SETTING TIME OF COPPER ALGINATE GELS VERS. POLYMERIZATION DEGREES OF ALGINATES

$CuCl_2$ added to 2 cc. of 2% sodium alginate (10^{-5} mole)	Polymerization degree[1] of alginate			
	15	80	300	670
0.24	∞	∞	∞	∞
0.60	〃	〃	10 min.	Hard gel*
0.96	〃	〃	13 min.	〃
1.29	〃	〃	10 sec.	〃
2.34	〃	27 min.	Coag.	Coag.
2.60	〃	30 sec.	〃	〃
2.86	〃	5 sec.	〃	〃

From Table III, it can be seen that thixotropy and coagulation were easily observed for the samples of relatively high polymerization degree upon the addition of small amounts of the electrolyte. Next, the effect of pH on the thixotropy was studied. When hydrochloric acid or sodium hydroxide alone was added to sodium alginate solution, no thixotropic gel was obtained. On the contrary, the setting time was markedly influenced by pH in the presence of cupric and barium chlorides, as seen in Table IV.

TABLE IV

THIXOTROPIC SETTING TIME VERS. pH IN THE PRESENCE OF CUPRIC AND BARIUM CHLORIDES IN THE SOLUTION OF SODIUM ALGINATE

pH	$2.60 \cdot 10^{-5}$ mole $CuCl_2$	$2.93 \cdot 10^{-5}$ mole $BaCl_2$
0.5	Coagulation	Coagulation
2.5	〃	〃
3.3	〃	〃
4.1	〃	〃
4.6	10 sec.	—
6.0	—	2.5 min.
6.3	40 sec.	—
6.7	4 min.	—
7.0	3 min.	—
7.5	∞	3 min.
7.9	〃	3.5 min.
9.5	〃	〃*
11.0	〃	2.5 min.
11.7	〃	3 min.
12.3	〃	4 min.
12.6	$Cu(OH)_2$ ppt.	—

As a whole, thixotropy was observed in neither regions of strong acidity nor alkalinity. In the region of intermediate pH, the thixotropic setting time was observed which changed with pH. In the case of barium chloride addition, the setting time increased and rapidly attained a constant value. As stated before, thixotropy was caused by the addition of a suitable amount of cupric chloride to the sodium alginate solution. We compared this amount with the combining capacity of cupric ion towards sodium alginate, which was measured as follows. Two cc. of 2% sodium alginate solution was added to 10 cc. of cupric chloride solution of varying concentrations. After the equilibrium was attained, the concentrations (C) of cupric and chlorine ions in supernatant liquid were determined and they were plotted against the total concentration of Cu^{++} (C_0) as shown in Fig. 1. In this figure, it is seen that the cupric ion combines with sodium alginate and the combining capacity of cupric ion towards sodium alginate calculated from the abcissa of the point A in Fig. 1 is $9.3 \cdot 10^{-5}$ mole per/40 mg. sodium alginate. Comparing this value with the composition of thixotropic gel formation shown in Table I (a), it is found that the thixotropy of copper alginate occurs when 25~45% of the alginate ions are combined with cupric ions, and coagulation of alginate ion occurs when more than half of the total alginate ions are combined

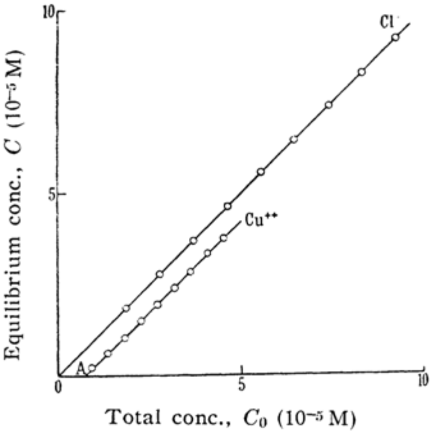

Fig. 1. Total and equilibrium concentration of cupric and chlorine ions before and after cupric chloride was added to the solution of sodium alginate.

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* The term "hard gel" represents such a gel as cannot be transformed into sol by hand-shaking.

* At pH values exceeding 9.5, white turbidity was seen on the addition of $BaCl_2$.

with cupric ions. Finally, it was found that the thixotropic gel could be obtained also from the once coagulated copper alginate by adding a suitable amount of sodium alginate. Thus, copper alginate was first precipitated by adding $7.8 \cdot 10^{-5}$ mole of cupric chloride to 4 cc. of 1% sodium alginate solution. Then more sodium alginate was added to make the total volume 16 cc., and the thixotropy was measured. The results are shown in Table V.

TABLE V

THIXOTROPY OF THE SYSTEM OBTAINED BY ADDING SODIUM ALGINATE TO COPPER ALGINATE PRECIPITATE

Sodium alginate added (mg.)	Thixotropy	
	Immediately after add.	24 hr. after add.
0	Coag.	Coag.
20	〃	〃
40	Thixotropic	Thixotropic
60	〃	〃
80	〃	〃
100	〃	〃
120	〃	Sol
140	Sol	〃
160	〃	〃

From this table, it can be confirmed that the coagulation of copper alginate ceased to persist when combined copper was decreased to less than 56% of the available alginate ion. This agreed qualitatively with the condition of the gelation mentioned above.

Summary

Thixotropy was observed on the gels formed by the addition of the suitable amounts of cupric chloride, barium chloride, lead nitrate, calcium chloride, cadmium sulfate, zinc sulfate and nickel sulfate to the solutions of sodium alginate. The setting time of the thixotropic gels was observed to change with the amount of the electrolyte added, the ageing time of the gels, the degree of polymerization of sodium alginate used and pH of the system. The thixotropic behavior was observed to change also with the volume of the system. Furthermore, it was found that thixotropy was observed when about 25–54% of the total alginate ions combine with cupric ions, whereas the combination of more than half of the total alginate ion results in non-thixotropic gelation. The thixotropic gel could be formed also by the addition of sodium alginate to the once precipitated copper alginate.

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