Studies on Thixotropy. I. On the Thixotropic Gelation Process*

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A number of studies concerning thixotropy, have been carried out by various kinds of methods. Taking as an example the bentonite-water system, which may be regarded as a typical thixotropic system, the studies have been made by the analysis of flow curve[1-9], the measurement of time required for gelation[10-14], and by both the rate constant of thixotropic gelation and the maximum gel strength (maximum yield value) developed as a consequence of completion of gel formation[15-18].

The third method may be said to be the one by which the process of gel formation can be actually followed and expressed in proper terms. The author et al.[16] have also made studies on bentonite (Gumma Bentonite) and some other clays, employing a method of the same kind and found that the thixotropic gel formation of clays generally proceeds in two first order processes which take place successively. Later, as phenomena similar to the above, in the case of the surface film of high polymer, Tachibana et al.[19] found that the thixotropic recovery of the surface elasticity or the surface pressure proceeds also in two steps.

In the present experiments, the author has also made studies on other thixotropic systems than bentonite, e. g. vanadium pentoxide sol, graphite suspension, etc., and found that in any system, in which the form of dispersed particles is plate- or rod-like, the thixotropic gelation generally proceeds in two steps. The conditions, under which the thixotropic gel formation proceeds thus in two steps, are examined and discussed.

Experimental

Materials. — *Bentonite.* — Gumma Bentonite; a product from Gumma Prefecture, which was a finely ground powder, was used. A 10% aqueous suspension of the bentonite was let stand for 5 days and after the removal of the larger sized particles by sedimentation, the suspension (concn. about 5%) was collected and concentrated on a water bath at about 60°C.

Yamagata Bentonite: a 3% aqueous suspension of an original soil from Yamagata Prefecture which was eventually let stand for 5 years after preparation was used. The upper part of the suspension was first filtered by cotton wool and the filtrate (concn. about 1%) was concentrated.

Volclay (Wyoming Bentonite): after sedimentation of a 7% aqueous suspension of the powdery product for 5 days, its upper part (concn. about 3%) was taken and concentrated.

Tixoton: a product of the firm "Deutsche Bentonit" was used as an aqueous suspension.

The order of the capacity of swelling of the above four bentonites is as follows.

Yamagata Bentonite>Volclay>Tixoton>Gumma Bentonite.

The X-ray spectrographic analysis showed that Yamagata Bentonite contained no appreciable impurity, while Volclay contained small amounts of impurity which may be α-quartz and α-crystobalite, and Tixoton a small amounts of α-quartz and Gumma Bentonite a relatively large amount of α-crystobalite compared with the other three.

Kaolin.—Three kinds of products from Tochigi Prefecture (Kampaku mine), Korea and Hongkong, respectively, were used as aqueous suspensions.

Sericite. — The original powdery product from Niigata Prefecture was sieved through 250 mesh and used as an aqueous suspension.

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1) O. Kimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*). **56**, 1346 (1935).
2) B. Tamamushi ibid., **61**, 280 (1940).
3) H. Akamatu, ibid., **63**, 1275 (1942).
4) T. Alfrey, Jr. and C. W. Rodewald, *J. Colloid Sci.*, **4**, 283 (1949).
5) P. Rehbinder, *Discussions Faraday Soc.*, **18**, 151 (1954).
6) H. van Olphen, "Proceedings of the Fourth National Conference on Clays and Clay Minerals", publication 456, National Academy of Sciences, National Research Council, Washington (1956), p. 204.
7) S. Peter and I. Stolle, *Z. physik. Chem.* (*Frankfurt*), **11**, 251 (1957).
8) Sven-Eric Dahlgren, *J. Colloid Sci.*, **13**, 151, (1958).
9) H. Enneking, *Rheologica Acta*. **1**, 234 (1958).
10) E. A. Hauser, *Kolloid-Z.*, **48**, 57 (1929).
11) H. Freundlich, O. Schmidt and G. Lindau, *Kolloid-Beih.*, **36**, 43 (1932).
12) U. Hofmann, *Kolloid-Z.*, **125**, 86 (1952).
13) S. Ono and T. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 463 (1953).
14) H. v. Platen and H. G. F. Winkler, *Kolloid-Z.*, **158**, 3 (1958).
15) H. Braune and I. Richter, ibid., **113**, 20 (1949).
16) T. Watanabe and S. Matsumoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1215 (1955).
17) A. Packter, *Kolloid-Z.*, **150**, 60 (1957).
18) T. Watanabe and Y. Takasaki, *Naturwissenschaften*, **45**, 334 (1958).
19) T. Tachibana and N. Okuda, presented at the 9th (1956) and the 10th (1957) Annual Meetings of the Chemical Society of Japan.

Vanadium pentoxide. An aqueous sol was prepared according to Biltz's method, and the heat treatment of the sol was carried out at 96°C for 10 hr. as suggested by Sato[20]. Afterwards the sol was let stand for one month.

Graphite. — Flaky powder was used as an aqueous suspension.

In the case of experiments with the suspension in the electrolyte solution, the electrolyte solution was added to the above aqueous suspension until its requisite concentration was attained.

Organophilic Bentonite.—Gumma Bentonite was converted into an organophilic bentonite by cation-exchange reaction using oleyl-picolinium chloride or lauryl-picolinium chloride as cation active agent. A dried powdery product was obtained and used as a benzene suspension.

Apparatus and Procedure. — The measurement of yield value of the above mentioned suspensions was carried out using Du Noüy torsion balance. The length and diameter of the torsion wire are 40 and 0.025 cm., respectively. A small glass sphere (diameter about 0.7 cm.) is hung from the hook of the apparatus with a thin palladium wire (diameter 0.1 mm.). The force which causes the glass sphere to move upward, is given by twisting the torsion wire and is read on the dial scale.

In kinetic studies, measurements should be carried out at constant temperature. In the present experiments, however, all the measurements were made at room temperature, since the characteristics of the observed phenomena and also the maximum yield value are only slightly influenced by the change of temperature in the neighborhood of room temperature.

Experiments have been made as follows. The suspension is taken into a test tube (inner diameter 2.1 cm.) and thoroughly shaken or stirred. Then the glass sphere is immersed into the suspension about 3 cm. below the meniscus. Then, force is added until the glass sphere begins to show a minute upward movement (about 1/60 mm.). The preceding procedure should be performed within 30 sec. after stopping the stirring. The moment at which the above procedure was done, is regarded as the starting point of the experiment. Then, at 5 min. intervals, the force is superimposingly added in the same manner as stated above. In this experiment, the yield value (unit, dyn./cm^2) is expressed with the value obtained by dividing the force with the equatorial cross-section of the glass sphere. The yield value is taken versus the value obtained in the same manner as the above only with the dispersion medium. To observe the upward movement of the glass sphere, a small mirror was attached to the top of the hook and its movement was observed under twenty times enlargement using a lamp and scale. In the course of the application of the additional force, no upward movement of the glass sphere is observed until the total amount of the force has exceeded a certain amount. The force with which the upward movement of the glass sphere of about 1/60 mm. (i.e. that of 0.3 mm. on the scale) is brought about, is used to evaluate the yield value. It was observed that if the excess of force which caused the upward movement was removed immediately after the movement had been induced, the glass sphere returned to the position before the movement. Therefore, it may be said that the experiment has been carried out under the condition where the deformation applied to the suspension is within elastic limit.

With some of the samples used, experiments were also made using the torsion wire of 15 cm. besides one of 40 cm. In these cases, sensibility to detect a minute deformation was poor so that the amount of the added force became inevitably about two times greater than the case of 40 cm. Therefore, after the cessation of the additional increase of the force at the point where the upward movement of 0.3 mm. on the scale had been observed, a further gradual upward movement of 0.3～0.5 mm. was followed during the ensuing interval of about one minute. This movement may be a visco-elastic flow accompanied with the deformation over elastic limit induced by the force above stated.

Results

Experiments have been made with the various kinds of suspensions stated above. In Fig. 1 the yield value is plotted versus the setting time. The curve shows that the increase of yield value with time proceeds in two processes which take place successively. The first process starts to develop immediately after the cessation of stirring or shaking. The second one reveals itself successively after some development of the first.

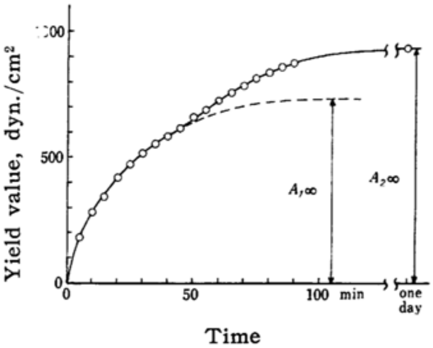

Fig. 1. The process of thixotropic gel formation (result obtained with 3.4% Yamagata Bentonite aqueous suspension).

The increase of the yield value varies according to the first order kinetics for each separate process. These may be expressed as follows:

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[20] K. Sato, "Symposium on Colloid Science (Kōshitsugaku Ronsō", Kawade Shobō, Tokyo (1943), p. 93.

$$k_1=\ln\frac{A_{1\infty}}{A_{1\infty}-A_t}\cdot\frac{1}{t}$$

$$k_2=\ln\frac{A_{2\infty}}{A_{2\infty}-A_t}\cdot\frac{1}{t}$$

where A_t is the yield value at time t and $A_{1\infty}$ is the maximum yield value of the first process which is obtained from the curve as shown in Fig. 1. $A_{2\infty}$ is the maximum yield value of the second process. k_1 and k_2 are the rate constants for the first and the second processes, respectively. Similar plots such as that shown in Fig. 1 were generally obtained with the system where the dispersed particles have plate- or rod-like forms. In Table I the systems in which the increase of the yield value proceeds in two steps are collected. In the system to which an electrolyte was added, the two step process was detected, when no marked coagulation of the dispersed particles was observed. On the other hand, in the case where marked coagulation was observed, for example, Gumma Bentonite in 0.01 M $FeCl_3$, the process of the thixotropic gel formation was completed in a single step. The same phenomenon was also observed with the thixotropic sol of ferric oxide in 0.1 M NaCl.

TABLE I. THE SYSTEMS IN WHICH THE THIXOTROPIC GEL FORMATION PROCEEDS IN TWO STEPS

Dispersed particles	Medium*
Gumma Bentonite	Water, 0.1 M NaCl, 0.4 M NaCl, 0.1 M LiCl
Yamagata Bentonite	Water
Volclay	Water, 0.1 M NaCl, 0.01 M $FeCl_3$, 0.005 M $Th(NO_3)_4$
Tixoton	Water, 0.1 M NaCl, 0.01 M $FeCl_3$, 0.005 M $Th(NO_3)_4$
Organophilic Bentonite	Benzene
Kaolin	Water
Sericite	Water
Vanadium pentoxide	Water
Graphite	Water, 0.1 M NaCl, 0.05 M $FeCl_3$

* The resulting preparations may contain small amounts of some ions other than those listed, which are due to the nature of the dispersed particles.

For some systems, experiments were carried out at several concentrations of dispersed particles. These results are shown in Table II. And the relation between $A_{1\infty}$ or $A_{2\infty}$ and the concentration (C) was derived as shown in Table III.

Another experiment was made by using torsion wires of 15 and 40 cm., respectively. For example, results obtained with 3.1%

TABLE II. EXPERIMENTAL RESULTS WITH YAMAGATA BENTONITE-, VOLCLAY-, AND VANADIUM PENTOXIDE-WATER SYSTEMS

(Temp., room temp. i. e. in the neighborhood of 15°C)

System	Concn. of disperesed particles g./100 g.	$k_1\times10^2$ min^{-1}	$A_{1\infty}$ dyn./cm²	$k_2\times10^2$ min^{-1}	$A_{2\infty}$ dyn./cm²
Yamagata Bentonite-water	3.7	2	870	3	1000
	3.4	4	730	4	930
	3.1	3	690	4	910
	2.9	2	600	3	800
	2.7	3	520	4	750
Volclay-water	9.3	2	650	6	760
	8.8	3	540	6	700
	8.4	2	430	6	620
Vanadium pentoxide-water	2.3	6	1100	5	1600
	2.1	4	930	7	1200
	1.9	4	740	7	920
	1.8*	8	690	—	—

* Complete in a single step.

TABLE III. RELATIONS BETWEEN THE MAXIMUM YIELD VALUE OF THE FIRST STEP ($A_{1\infty}$) OR THE SECOND ($A_{2\infty}$) AND CONCENTRATION (C)

System	Relations
Yamagata Bentonite-water	$A_{1\infty}\propto C^2$ & $A_{2\infty}\propto C$
Volclay-water	$A_{1\infty}\propto C^4$ & $A_{2\infty}\propto C^2$
Vanadium pentoxide-water	$A_{1\infty}\propto C^2$ & $A_{2\infty}\propto C^3$

TABLE IV. DATA OBTAINED WITH THE SAME SUSPENSION (3.1% YAMAGATA BENTONITE) USING A DIFFERENT LENGTH OF TORSION WIRE

Wire length, cm.	$k_1 \times 10^2$, min^{-1}	$A_{1\infty}$, dyn./cm^2	$k_2 \times 10^2$, min^{-1}	$A_{2\infty}$, dyn./cm^2
40	3	690	4	910
15	6	1500	3	2100

Yamagata Bentonite aqueous suspension are shown in Table IV. The difference of the value of k_2 between the two cases is small but that of k_1 is cosiderable. The latter may be due to the following conditions. In the case of 15 cm. wire, the visco-elastic flow has been observed in each measurement as stated above, and consequently the thixotropic gel formation proceeds under small shearing motions which facilitate the formation of the gel structure, i.e. the phenomenon of rheopexy has been observed. In the case of 40 cm. wire such an experimental condition was not established so that the phenomenon of rheopexy was not observed.

Discussion

In the first place, let us consider the bentonite suspension. As a structure of thixotropic gel, it is adopted in such a network structure that plate-like particles link with each other in a short distance at the junction point. Furthermore as a model of structure, the 'house of cards' structure which was proposed by Hofmann[12] and whose existence in a xerogel was proved by Weiss et al.[21], is recommended.

In the present experiments, it was observed that the dependence on the concentration of $A_{1\infty}$ was different from that of $A_{2\infty}$. This fact can not be explained with the assumption that the yield value of the gel is determined by all the particles in the structure. Therefore, it must be assumed that the particular group of particles contributes to the yield value of the gel. Such a particular particle group which plays the part of a mechanical unit to the yield value, is named 'structural unit' (abbr. S. U.). Further, the particle group which acts as S. U. is classified into two types, i. e. one is the particle group forming linear ribbon and another is that of cross-linkage.

In the structure, the particles are linked at such small distances at any junction point that the steric hindrance caused by the interaction of linking particles must be taken into consideration. In these circumstances, the steric conditions such as freedom of rotation or flexibility around the junction point, may be the same as each other, in any particle group, so far as the co-operation between particles is concerned.

Considering the steric conditions, the association of plate-like particles may be classified into three types as follows.

P–1 association: Two adjacent particles are linked with each other at one point.

P–2 association: Two adjacent particles are linked at two or more points belonging to one straight line.

P–3 association: Two adjacent particles are linked at three or more points so that they are associated with surface-to-surface linkage.

By the third type of association a voluminous structure can not be expected to be formed, so that the discussions are undertaken leaving the third type out of consideration.

Next, it may be assumed that the magnitude of the cohesive force at junction points of S. U., remains constant in a given system unless the range of concentration studied is great. Therefore, as a first approximation, it may be assumed that the contribution to the yield value of each of the same kind of particle group, i. e. the strength of (b) the corresponding S. U. is constant, and the yield value (A) of any system will be determined by the number (N_s) of the S. U. in unit volume as follows:

$$A = bN_s \tag{1}$$

In this case, the evaluation of the value of N_s is necessary. At first, probability of permanent junction between adjacent particles (abbr. probability of junction) will be considered. The probability of junction where a given particle in a gel is linked to an adjacent one with P–1 association, will be determined by the number of free dispersed particles in unit volume (N_p) which may exist when the gel is transformed to sol by stirring etc. In other words, the probability of junction will vary as the concentration of the dispersed particles (C). Generally, the probability of junction between a particle and

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[21] A. Weiss, R. Fahn and U. Hofmann, *Naturwissenschaften*, **39**, 351 (1952); *Ber. deut. keram. Ges.*, **30**, 21 (1953).

its adjacent l particles with P-1 association will vary as C^l, where $l \ll N_p$ and l is a positive integer.

The probability of junction will be evaluated in the case of P-2 association. In this case, the above probability will be determined by the following two probabilities. The one is that of orientation of the particle in sol state to the position where the particle can be linked with P-2 association to a given particle. The other is that of formation of junction between particles. The two probabilities will be proportional to N_p, i.e. C. Therefore, the discussed probability of junction should vary as $C \times C = C^2$. Generally, the probability of junction between a particle and its adjacent m particles in the same manner as stated above will vary as C^{2m}, where m is a positive integer.

Let us consider the linear ribbons which act as S.U. The linear ribbons are formed from the aligned particles and in order to act as S.U. they must also be linked to two or more other linear ribbons. In general the linear ribbons are not formed from exactly equal numbers of particles. However, in the present case, the cohesive force between particles is considered to remain constant, so that the yield value may be determined by the number of junction points between particles in unit volume of the gel. The assumptions are made on the way whereby the linear ribbons are formed, i.e. how many particles are separately linked with what type of association to any one particle. And the relations between the yield value and the concentration in the case where the assumed linear ribbons act as S.U., are derived on the basis of the knowledge on the probability of junction above stated. The results are shown in Table V.

The consideration will be given to the cross-linkage. Cross-linkage is a particle group which plays the part of junction between the linear ribbons in structure. When it contributes to the yield value as S.U., it may be expected that one of the particles forming cross-linkage, could not move in accordance with the deformation of the gel under the applied force, but would behave as if it were restricted at a fixed position. Therefore, the characteristics of the cross-linkage are determined by two factors. One of them is the number of effective linear ribbons linked to the above fixed particle and the other is the type of association between particles forming the cross-linkage. In addition, it may be assumed that the degrees of steric hindrance of the junction points between the particles forming a cross-linkage must be the same as each other and further they must be the same as, or higher than, that of forming the linear ribbons participating in the cross-linkage. According to the above considerations, the relations between the yield value and the concentration of the gel are derived from the knowledge of the probability of junction and shown in Table VI. In this table the necessary type of association of the particles forming linear ribbons is also listed.

Considering the process of development of gel structure which is applicable for the two cases of Yamagata Bentonite and Volclay, it must be assumed that S.U. in

TABLE V. THE RELATION BETWEEN THE YIELD VALUE (A) AND THE CONCENTRATION (C) OF THE GEL IN WHICH THE LINEAR RIBBON ACTS AS STRUCTURAL UNIT

Nomenclature of structural unit	Mode of formation of linear ribbon	Relations between A and C
L-1	P-1 association $l=1$	$A \propto C$
L-2	$l=2$	$A \propto C^2$
L-3	$l=3$	$A \propto C^3$
L-4	P-2 association $m=1$	$A \propto C^2$
L-5	$m=2$	$A \propto C^4$

TABLE VI. THE RELATION BETWEEN THE YIELD VALUE (A) AND THE CONCENTRATION (C) OF THE GEL IN WHICH THE CROSS-LINKAGE ACTS AS STRUCTURAL UNIT

Nomenclature of structural unit	Mode of formation of cross-linkage	Relations between A and C	Necessary type of association of linear ribbon
M-1	P-1 association $l=2$	$A \propto C^2$	P-1
M-2	$l=3$	$A \propto C^3$	P-1
M-3	$l=4$	$A \propto C^4$	P-1
M-4	P-2 association $m=1$	$A \propto C^2$	P-1
M-5	$m=2$	$A \propto C^4$	P-1, P-2

the first step of gel formation is cross-linkage and that of the second is linear ribbon. Therefore, in the case of Yamagata Bentonite having $A_{1\infty} \propto C^2$ and $A_{2\infty} \propto C$, the S. U. for the first step is M–1 or M–4 in Table VI and that of the second is L–1 in Table V, since the linear ribbons of this sample must be formed from the particles linked together by P–1 association. Also in the case of Volclay, the linear ribbons are formed by P–2 association, and the S. U. of the first step is M–5 and that of the second is L–4, since this sample shows the relation, $A_{1\infty} \propto C^4$ and $A_{2\infty} \propto C^2$.

According to the above considerations, it may be explained that the thixotropic gel formation of bentonite will proceed as follows. During the first step, some of the dispersed particles align to form linear ribbons, and the latter further cross-link with neighboring ones to develop into a loose gel structure. In the second step, many particles or linear ribbons having no part in the formation of the first loose gel structure, begin to participate in structure to complete a rigid gel structure. On the other hand, in the first step, the increase of yield value is proportional to the increase in number of cross-linkage and the latter will be accelerated under small shearing motions so that the phenomenon of rheopexy will markedly appear. In the second step, both the increase in number of cross-linkage and that of linear ribbons participating in the formation of the cross-linkage, will simultaneously occur and these will lead to the increase of continuity of the linear ribbons in the gel structure so that the linear ribbons will come to act as S. U. Therefore, though the cross-linkage acting as S. U. in the first step, does not decrease in number nor disappear, its contribution to the yield value as S. U. gradually diminishes in the second step. Moreover, the rheopectic phenomenon can not be observed distinctly in the second step, since the rate of increase of yield value of this step is not determined by the rate of increase of the cross-linkage as in the case of the first step.

In the case of vanadium pentoxide sol, the experimental facts may be explained as follows. It is not necessary to make such a distinction between P–1 and P–2 association as in the case of bentonite, since the vanadium pentoxide particle has a thin rod-like form. It may be assumed that the particle group which acts as S. U. both in the first and in the second step, is the particle group forming cross-linkage. During the first step, a loose gel structure may be developed, in which the dispersed particles are linearly associated and a relatively small number of cross-linkage or entanglement can be seen between the linear chains of particles, and in the second step, it reaches another structure, i. e. a rigid gel structure which may be due to the appreciable increase of cross-linkage between chains. The difference in structure between the loose and rigid one is due to the variance in number of linear chains participating in the formation of the cross-linkage which acts as S. U. The number of linear chains linked to the fixed particle of the cross-linkage is two in the former structure and is three in the latter one, since this sample shows the relation, $A_{1\infty} \propto C^2$ and $A_{2\infty} \propto C^3$. In the course where the rigid gel structure is developed from the loose one, cross-linkage which contributes to the yield value proportional to C^2 is transformed to the cross-linkage proportional to C^3, according to the increase in number of linear chains linked to form the cross-linkage.

Summary

(1) In this system, in which the form of dispersed particles is plate- or rod-like, the thixotropic gelation generally proceeds in two steps.

(2) During the first step of thixotropic gel formation, a loose gel structure may be developed and a rigid gel structure in the second step.

(3) In the case of bentonite, the structural unit which contributes to the yield value of the gel in the first step is cross-linkage and that of the second is linear ribbon.

(4) In the case of vanadium pentoxide, the structural unit is cross-linkage both in the first and in the second step.

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