Studies on Thixotropy. II.[*,1] *On the Thixotropic Gel Structure of Bentonite*

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(Received August 10, 1959)

There are two kinds of structure which are currently taken as a model for thixotropic gel of bentonite. One of them is the structure in which dispersed plate-like particles are linked together at a short distance to build up a network. The other[2,3] is the structure in which particles are regularly oriented to each other at a considerable distance. According to the latter structure, however, it was difficult to explain the process of thixotropic gel formation which proceeds in two steps as described in the previous paper[1]. By making light-scattering, birefringence and viscoelastic studies on mono-disperse sol of Wyoming Bentonite, M'Ewen et al.[4] have suggested that particles are oriented edge-to-edge in the form of flat ribbons. Olphen[5] has also concluded from the results obtained by the study of the surface conductance of bentonite suspension that particles are linked with each other at a short distance. These results show that the former structure, e. g. "house of cards" structure[6] in which the particles are linked at

TABLE I. RELATIONS BETWEEN RHEOLOGICAL PROPERTIES AND CONCENTRATION

Investigator	Apparatus or Method	Relation presented	Relation derived by the present author
Braune et al.[7]	Kämpf viscometer	$A_\infty \propto C^2$	
Peter et al.[8]	Couette viscometer	$\tau_B \propto C^2$	at low concn. $\tau_B \propto C^2$ at high concn. $\tau_B \propto C^4$
Olphen[9]	Stormer viscometer	$\tau_B \propto (C-C_m)^2$	at low concn. $\tau_B \propto C^2$ at high concn. $\tau_B \propto C^4$
	Shear propagation	$\mu \propto (C-C_m)^3$	$\mu \propto C^6$
Packter[10]	Stormer viscometer	$S_\infty \propto C^6$	
Watanabe[1]	Torsion balance	$\begin{cases} A_{1\infty} \propto C^2, \\ A_{2\infty} \propto C \end{cases}$ or $\begin{cases} A_{1\infty} \propto C^4, \\ A_{2\infty} \propto C^2 \end{cases}$	

A_∞ : max. yield value ; τ_B : Bingham yield stress ; μ : modulus of elasticity ; S_∞ : max. gel strength : $A_{1\infty}$ and $A_{2\infty}$: max. yield value for the first and the second step of gel formation, respectively ; C : concentration ; C_m : a constant.

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[*] Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

1) Part I: T. Watanabe, This Bulletin, 33, 347 (1960).

2) E. A. Hauser and D. S. LeBeau, *J. Phys. Chem.*, 45, 54 (1941); E. A. Hauser, "Silicic Science", D. van Nostrand Co., Inc., Princeton, New Jersey (1955), p.36.

3) E. Forslind, "Proceedings of the Second International Congress on Rheology", Butterworths Scientific Publications, London (1954), p. 50.

4) M. B. M'Ewen and M. I. Pratt, *Trans. Faraday Soc.*, 53, 535 (1957); M. B. M'Ewen and D. L. Mould, ibid., 53, 548 (1957).

5) H. van Olphen, *J. Phys. Chem.*, 61, 1276 (1957); H. van Olphen and M. H. Waxman, "Fifth National Conference on Clays and Clay Minerals", Publ. 566, National Academy of Sciences, National Research Council, Washington (1958), p. 61.

6) U. Hofmann, *Kolloid-Z.*, 125, 86 (1952).

7) H. Braune and I. Richter, ibid., 113, 20 (1949).

8) S. Peter and I. Stolle, *Z. physik. Chem.* [*N. F.*], 11, 251 (1957).

9) H. van Olphen, "Proceedings of the Fourth National Conference on Clays and Clay Minerals", Publ. 456, National Academy of Sciences, National Research Council, Washington (1956), p. 204.

10) A. Packter, *Kolloid-Z.*, 150, 60 (1957).

a short distance, is favored. Therefore, in this report, discussions will be carried out on this structure on the basis of the rheological data.

Discussion and Proposal of Gel Structure

In Table I are collected the relations between the rheological properties and the concentration of thixotropic gel of bentonite presented by different investigators, and those derived by the present author using the data obtained by other authors. Furthermore, from the experimental data provided by Peter et al.[8] the relations between shearing stress (τ) and concentration (C) at a fixed rate of shear (q) are derived and given in Table II. The relation between τ and C is also dependent on C. Referring to the study of Enneking[11], in which he discussed experimental conditions similar to Peter's, in the range where the values of τ in Table II are proportional to C^6, the flow may be induced not in the whole but in a localized part of the gel. Therefore, it may be said that in the flowing part, the actual value of q is higher than those listed. Consequently, this high q is to be suddenly induced to the set gel. It may further be reasonable to assume that the experimental conditions, under which some of the measurements for Table I were carried out, must be essentially similar to those above stated. Therefore, μ and S_∞ can be proportional to C^6.

TABLE II. RELATIONS BETWEEN π (SHEARING STRESS) AND C (CONCENTRATION) AT FIXED q (RATE OF SHEAR) VALUES, DERIVED FROM THE DATA OF PETER ET AL.[8]

Geisenheim Bentonite in Water

$C(\%)$ / $q(\mathrm{sec}^{-1})$	1	2	3	3.47	3.92
4.16	$\tau\propto C^2$	$\tau\propto C^4$		$\tau\propto C^6$	
25.7	$\tau\propto C^2$			$\tau\propto C^6$	
102.9	$\tau\propto C^2$			$\tau\propto C^4$	
662	$\tau\propto C$	$\tau\propto C^2$			

Algeria Bentonite in water

$C(\%)$ / $q(\mathrm{sec}^{-1})$	1.79	2.71	3.61	4.49	5.10	5.92
4.16	$\tau\propto C^2$			$\tau\propto C^6$		
6.44	$\tau\propto C^2$			$\tau\propto C^6$		
66.5	$\tau\propto C^2$			$\tau\propto C^4$		
411	$\tau\propto C$	$\tau\propto C^2$				

Tables I and II show that the relations between rheological properties (in the following, represented by "strength") and concentration are dependent on the condition of measurement, so that it may be expected that the particles constituting the gel do not orientate so regularly as ions in crystal lattice but link with each other at random to build up the gel structure. This leads to the conclusion that, in the gel, several kinds of agglomerated particle groups can coexist. It may also be expected that under a certain experimental condition, the gel strength is determined by a particular particle group in the gel. Namely, if the observed gel strength is proportional to C^p where p is a positive integer, there exists a particular particle group which performs the role of structural unit. And in this case, provided that the contribution to the gel strength is equal in each particle group of the same kind, it may be concluded that the number of the particle group per unit volume of the gel varies as C^p. In other words, the probability of the existence of this particle group is proportional to C^p. In the following discussion, a particle group such as stated above will be named structural unit-C^p (abbr. S. U.-C^p). If many kinds of particle groups which act as S. U.-C^p, exist in the system, the gel strength may be determined by one of them, or by a set of particle groups which make equal contribution to the gel strength in cooperation with each other.

Since the form of bentonite particle is platelike, the association between particles may be classified into three types based on the steric condition of the junction point as described in the previous paper[1]. In the first type, two particles are linked with each other at one point (P-1 association); while, in the second, particles are linked at two or more points belonging to one straight line (P-2 association) and, in the third, particles are linked at three or more points belonging to one plane (P-3 association). Also the number of junction points in unit volume in which two adjacent particles are linked with P-1, P-2 or P-3 association is proportional to C, C^2 or C^3, respectively.

In the first place, it is assumed that, in the gel structure, all particles are linked to each other with P-1 association. In this case, consideration is made based on the experimental results with Yamagata Bentonite reported in the previous paper[1]. This sample shows the maximum yield value proportional to C^2, or C according to the first or the second gelation process, respectively. Therefore, it is concluded that S. U.-C^2 contributes to the gel strength in the first step and S. U.-C in the second. Furthermore, from the results discussed in the

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[11] H. Enneking, *Rheologica Acta*, 1, 234 (1958).

previous paper1), it has been ascertained that the particle group which acts as a structural unit in the first step does not disappear, but its contribution to the yield value diminishes in the second step under the experimental method employed. Considering the process of gel formation, the structure developed in the second step is doubtless more rigid than that of the first. S. U.-C^2 in the first step, is the cross-linkage in which two linear ribbons are linked to the hypothetical fixed particle which behaves as if it were restricted at a fixed position when the cross-linkage acts as structural unit. Therefore, in the second step, the existence of cross-linkage may be expected, of which more than two linear ribbons are linked to the fixed particle. Namely, there exists the S. U.-C^p where $p>2$ in the second step. Consequently, the structure which satisfies all the relations listed in Tables I and II, may be as follows. The structure is formed by cross-linking of the linear ribbons which are formed of the aligned particles linked by P-1 association. For the cross-linkage, there must coexist at least five kinds of cross-linkage in which two to six linear ribbons, respectively, are linked to the fixed particle.

Based on the above consideration on the structure, in the case of Yamagata Bentonite, the structural unit is S. U.-C, namely, the linear ribbons; since the maximum yield value developed in the second step ($A_{2\infty}$) varies as C. The result obtained with Volclay1) where $A_{2\infty}\propto C^2$ and also with Braune's results, $A_{\infty}\propto C^2$, may be explained as follows. The structural unit is S. U.-C^2, that is, the cross-linkage formed by two linear ribbons linking to the fixed particle.

Next, it is assumed that all particles in structure are linked by P-2 association. In this case, the consideration must be made based on the results obtained with Volclay in the previous paper1). By treatment similar to that described above in completely set gel, there must exist S. U.-C^6 besides S. U.-C^2 and S. U.-C^4. S. U.-C^2 is the linear ribbons which are formed by the aligned particles linked by P-2 association. S. U.-C^4 or S. U.-C^6 is the cross-linkage in which two or three linear ribbons, respectively, link to the fixed particle. Using this model of structure, it is possible to explain all the experimental results listed in Tables I and II except that of Yamagata Bentonite. However, as to the S. U.-C^6 it is not enough to consider such a simple model as that mentioned above, it must satisfy the following requirements.

(1) Among the strengths of bentonite gel measured by various methods, the one proportional to C^6 has the largest value of p. Therefore, the particle group which acts as S.U.-C^6 must be the one which plays the part of constituting a rigid gel structure.

(2) Packter10) has suggested that the rate of gel formation varies as C^6 in the case where the maximum gel strength S_∞ is proportional to C^6 as shown in Table I. To satisfy this fact, S. U.-C^6 must be the cross-linkage formed in the process where six adjacent particles which participate in the formation of separate linear ribbons, orientate to the fixed particle.

Considering the above requirements, the cross-linkage which acts as S. U.-C^6 will be as follows. The fixed particle is linked to three linear ribbons composed of a certain number of particles, of which each one nearest to the fixed particle must be further linked to another different linear ribbon. The particle group formed in such a way as stated above is an overlapping assembly of the four particle groups, each of which is expected to act as S. U.-C^6.

Considering such a particle group, it is safely assumed that such a cross-linkage plays an important role in the rigid gel structure which satisfies requirement 1, and the rate of formation of the cross-linkage varies as C^6 and requirement 2 is also fulfiled.

In the above consideration, only the case of P-2 association is treated. However, provided that similar structural conditions exist in the case of P-1 association, it may be expected that a rigid gel structure is built up from the three kinds of particle groups which will be able to act as S. U.-C, S. U.-C^2 and S. U.-C^3, respectively.

Now, it is assumed that four states of particle agglomerate will appear in the course of thixotropic gel-sol-gel transformation. Possible

TABLE III. STRUCTURAL UNITS WHICH EXIST IN FOUR RHEOLOGICAL STATES OF THIXOTROPIC GEL-SOL-GEL TRANSFORMATION

Type of structure	Type of association	Rheological state			
		Rigid gel	Loose gel	Sol I	Sol II
I	P-1	S. U.-C	S. U.-C	S. U.-C	Dispersed particles
		S. U.-C^2	S. U.-C^2		
		S. U.-C^3			
II	P-2	S. U.-C^2	S. U.-C^2	S. U.-C^2	Dispersed particles
		S. U.-C^4	S. U.-C^4		
		S. U.-C^6			

S. U.-C^p which may contribute to the strength at each state is collected in Table III. In the state where two or more structural units exist, the strength is determined by one of them, depending on the experimental condition. S. U.-C in type I structure and S. U.-C^2 in type II are listed on both gel and sol states. These are the linear ribbons which participate in the structure in the gel state and are free in the sol state.

As described in the previous paper[1], during the first step of the thixotropic gel formation, the increase of the yield value of the gel in the loose gel state with setting time was measured and during the second step that of the gel in the rigid gel state was measured. In the case of the second step, experiments have been made to measure the yield value corresponding to the stress necessary to induce a fixed elastic deformation to the gel in which linear ribbons act as the structural unit. This deformation may be classified as a complete, recoverable, non-ideal one[12]. Therefore, the gel at this step shows retarded elasticity. Accordingly, if the deformation within the elastic limit has been induced gradually to the gel in rigid gel state of type II, its strength varies as C^2 since the linear ribbons act as the structural unit. On the contrary, when the deformation has been induced to the gel under the condition where the stress is suddenly applied to the system accompanying a fairly high rate of shear, the linear ribbons may not respond to this deformation, and as a result they come to play no rôle as the structural unit. The cross-linkage then comes to act as the structural unit so that the strength of the gel varies as C^6.

When experiments are carried out to obtain a flow curve, the rate of shear induced to the system is gradually increased and the stress corresponding to a given rate of shear is estimated. In this case, the observations are made on the variation of the state, starting from the rigid gel state and ending at the sol state II, listed in Table III. In the course of this experiment, a breakdown of the cross-linkage will occur at the initial stage and will be followed by the disintegration of the linear ribbons into individual particles at a later stage. Therefore, the results derived from the curve reported by Peter et al. or Olphen as shown in Tables I and II are explained as follows.

In these experiments, it may be expected that these systems take a structure of type II shown in Table III. From the results given in Table II, the relations between the stress and the concentration at a fixed rate of shear are dependent on the concentration of the system. Similar dependence on the above is also observed with the relation between the Bingham yield stress and the concentration as shown in Table I. It was observed in the previous experiment[1] that both the ratio of $A_{2\infty}$ to $A_{1\infty}$ and the difference between the values of $A_{2\infty}$ and $A_{1\infty}$ are larger in the case of the lower concentration. Therefore, it may be expected that in the gel which is in the rigid gel state, the ratio of the number of S. U.-C^2 to that of S. U.-C^4 or S. U.-C^6 of low concentration is larger than that of high concentration. Hence, at low concentrations, even the gel standing for a long period has a structure of either a loose gel state or a state not strictly distinguishable from sol state I. According to the above consideration, the relations listed in Table II may be elucidated with the concept given in Table III. The Bingham yield stress (τ_B) is obtained from the intersection of the extraporated straight line with the stress axis so that the relation between τ_B and concentration is determined by the kind of structural unit in the range in which a linear relationship between the rates of shear and stress is obtained.

There has been no information regarding the condition under which the particles take either the structure of type I or II. However, it may be assumed that if the dispersed bentonite particles are in the form of unit layer, they will constitute a structure of type I, and if the dispersed particles are composed of stacking of several unit layers, a structure of type II will be formed.

P-1 association may be represented typically by the edge-to-edge linkage and P-2 association by the edge-to-surface linkage.

Packter[10] has reported that the maximum gel strength is proportional to C^3 in non-heterocoagulated system where polyanion is added to the bentonite suspension. The results can be clearly explained by the assumption that the particles in the structure are linked by P-3 association. However, the gel structure which is formed by the particles linked by P-3 association is a very compact one compared with those listed in Table III and it is inadequate to accept this structure as that of thixotropic gel.

Summary

(1) Discussions are carried out on the structure of the thixotropic gel of bentonite on the basis of the relation between the gel strength and the concentration, and the steric conditions of the junction point between two particles participating in structure.

(2) The gel strength is determined by the

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[12] J. M. Burgers and G. W. Scott Blair, "Report on the Principles of Rheological Nomenclature", North-Holland Publishing Co., Amsterdam (1949), p. 49.

particular group of particles in the structure which acts as the structural unit.

(3) The particle group which plays the part of the structural unit is not limited to one kind but more than one may coexist in a system. The gel strength is determined by one kind of the particle groups according to the experimental method used.

(4) The structure of the thixotropic gel of bentonite is classified into two types according to the mode of association between particles. One of them is the structure in which linear ribbons, which act as structural units, are formed by the aligned particles linking each other at one point. The other is the structure in which linear ribbons are formed by the particles linking at two or more points on one straight line.

The author would like to express his gratitude to Professor Sôzaburo Ono for his kind guidance and discussion throughout this work.

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