BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 88—91 (1966)

The Flocculation of Kaolin and Precipitated Calcium Carbonate by Polymers

By Kahei SAKAGUCHI and Kunihiko NAGASE

Industrial Research Laboratories, Kao Soap Co., Ltd., Wakayama-shi

(Received May 7, 1965)

The subsidence rate of a suspension of kaolin or precipitated calcium carbonate flocculated by polyacrylamide increases with an increase in the intrinsic viscosity of the polymer, and it shows a marked acceleration above an intrinsic viscosity of 5—6. However, in the case of the flocculation of the precipitated calcium carbonate flocculated by sodium polyacrylate, the subsidence rate depends linearly upon the intrinsic viscosity of the polymer. The results have been discussed in terms of Verwey and Overbeek's theory. The real unperturbed dimension of polyacrylamide has been calculated from the equations proposed by Kurata, Stockmayer and Fixman. As a consequence, it has been suggested that the dimension of a polymer has a close relationship with its flocculation behavior.

It has been suggested by Michaels(1,2) and by other authors(3-5) that the flocculation of the suspension brought about by water-soluble high polymers is caused by the cross-linking of the solid particles with the adsorbed polymer molecules. In the case of the flocculation of a clay suspension by polyacrylamide, it has been reported by Toyoshima(5) that the subsidence rate depends linearly upon the molecular weight of the polymer. However, his observations were confined to the region where the intrinsic viscosity of the polymer solution was less than 6.

In the present work we have investigated the dependence of the molecular weight of polyacrylamide and sodium polyacrylate on the subsidence rate of kaolin or of precipitated calcium carbonate in suspensions. The results will be discussed in terms of Verwey and Overbeek's theory(6); the conclusion that the flocculation is closely related to the dimension of a polymer will be obtained.

Experimental

Materials.—Both the polyacrylamides and the sodium polyacrylates used in this experiment were prepared by the aqueous polymerization of the corresponding monomers, using ammonium persulfate as an initiator. The viscosities of the resultant polymer solution were measured at 30°C with an Ubbelohde viscometer.

Kaolin was supplied by the Sanko Seiyaku Kogyo Co., Ltd.; its composition and particle-size distribution are shown in Table I and Fig. 1 respectively. The PH of a 5% suspension of this kaolin in water is 4.0.

The precipitated calcium carbonate was supplied by the Shiseido Seiyaku Co., Ltd.; its particle-size distribution is shown in Fig. 2. The PH of a 5% suspension of this carbonate is 9.5.

TABLE I

Componemt	Weight percentage
SiO_2	77.1
Al_2O_3	15.9
Fe_2O_3	0.1
CaO and MgO	trace
Ignition loss (800°C)	3.5

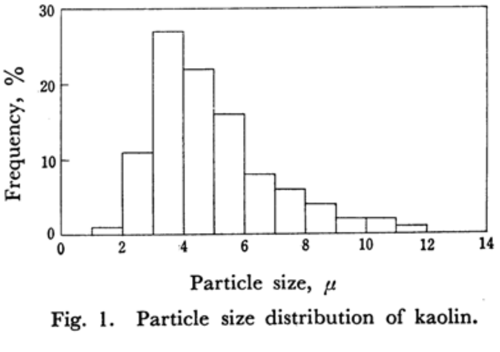

Fig. 1. Particle size distribution of kaolin.

---

1) A. S. Michaels, *Ind. Eng. Chem.*, **46**, 1485 (1954).

2) A. S. Michaels and O. Morelos, ibid., **47**, 1801 (1955).

3) V. K. LaMer et al., *J. Colloid Sci.*, **11**, 704, 710, 720 (1956); **12**, 230, 566 (1957); **13**, 589 (1958).

4) R. A. Ruhrwein and D. W. Ward, *Soil Sci.*, **73**, 485 (1952).

5) Y. Toyoshima, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82**, 1295, 1297, 1301 (1961).

6) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elesevier, Amsterdam, New York (1948).

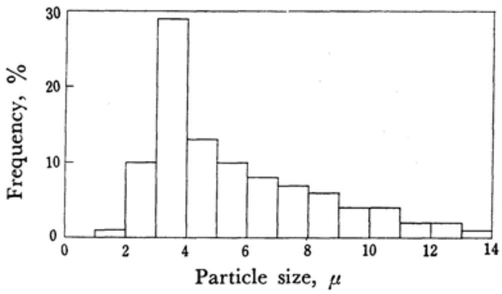

Fig. 2. Particle size distribution of precipitated calcium carbonate.

Methods.—The subsidence data were obtained at room temperature using 25-ml., graduated cylinders 1.2 cm. in inner diameter and 19.4 cm. long. After 1.25 g. of kaolin or calcium carbonate had been weighed into the cylinder, 20 ml. of water was added. The cylinder was then shaken vigorously in order to obtain a suspension. An aqueous solution of a polymer was added to make a total of 25 ml. The amount of the polymer was 0.01% of the solid. The content was mixed by inverting the cylinder 20 times a minute; then it was allowed to settle. The subsidence rates were determined by plotting the height of the solid-liquid boundary as a function of the time.

Results

Figure 3 shows the subsidence rate of a kaolin suspension flocculated by polyacrylamide as a function of the intrinsic viscosity of the polymer. Figure 4 shows the results of the flocculation of the precipitated calcium carbonate suspension by polyacrylamide. In each case, the subsidence rate increases with an increase in the intrinsic viscosity and shows a marked acceleration above an intrinsic viscosity of 5—6. Upon the sedimentation of precipitated calcium carbonate flocculated by sodium polyacrylate, as is shown in Fig. 5, the subsidence rate depends linearly upon the intrinsic viscosity of the polymer.

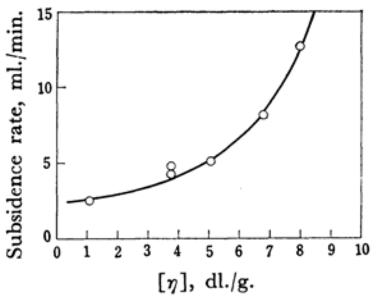

Fig. 3. The relation between the subsidence rate and the intrinsic viscosity of polyacrylamide in the flocculation of kaolin suspension.

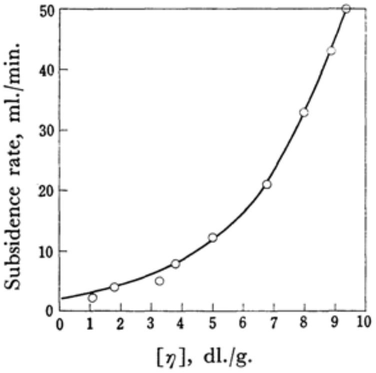

Fig. 4. The relation between the subsidence rate and the intrinsic viscosity of polyacrylamide at the flocculation of calcium carbonate suspension.

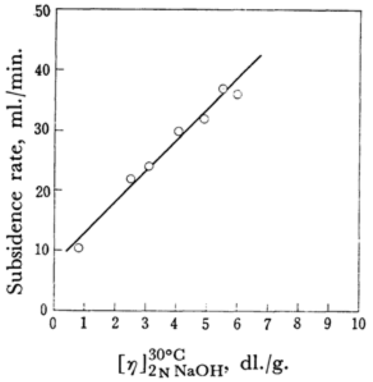

Fig. 5. The relation between the subsidence rate and the intrinsic viscosity (in 2 N NaOH aqueous solution) of sodium polyacrylate in the flocculation of precipitated calcium carbonate.

In the flocculation of a kaolin or precipitated calcium carbonate suspension by polyacrylamide, it appears that a polymer with an intrinsic viscosity of 5 or more has a special property to facilitate the crosslinking of the suspended particles with each other. On the other hand, sodium polyacrylate, in contrast to polyacrylamide, shows a moderate flocculating power, even at a low intrinsic viscosity, and it shows a typical linear relationship between the subsidence rate and the intrinsic viscosity. Some of these results have been discussed in another paper.7)

Discussion

These results seem to suggest that the dimensions of a polymer in an aqueous medium are closely related to the flocculating power. In a dilute aqueous solution of sodium polyacrylate, the configuration of the polymer chain may be greatly expanded by the electrostatic repulsion between carboxyl groups. The intrinsic viscosities of sodium polyacrylates were determined in 2 N sodium hydroxide. Consequently, the actual

---

7) K. Sakaguchi and K. Nagase, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), to be published.

dimensions of the polymer chain in an aqueous solution may be much larger than that of polyacrylamide, even if the intrinsic viscosity is same. Polyacrylamide is essentially nonionic, and it is not believed that the configuration of the polymer chain is as expanded as in the case of a polyelectrolyte.

On the stability of lyophobic sols, Verwey and Overbeek[6] and Derjaguin and Landau[8-10] have proposed a theory that a flocculation occurs when the London - van der Waals' force exceeds the repulsion force. For coarser particles of polystyrene in dilute salt solutions, Schenkel and Kitchener[11] showed that flocculation takes place at the "secondary minimum" in the potential energy curves, at which the interparticle distance is 500—1000 Å. Hachisu and Furusawa[12] reported that, at low concentrations of sodium chloride, a loose flocculation of "tungustic acid sol" occurs at an interparticular distance of 800—1000 Å; this flocculation at the "secondary minimum" is explained as a balance between the London - van der Waals' force and the repulsion force. The bond combining the particles is easily broken by a mild shock, for the "secondary minimum" is in any case rather shallow. This state of flocculation is a "pseudo flocculation," in which flocculation-deflocculation is reversible.

In order to flocculate the suspension irreversibly, it is necessary to reduce the repulsion force (or the ζ-potential) between the particles by adding larger amounts of electrolytes. Then the interparticular distance becomes narrower than 100 Å, and the aggregate can not be destroyed easily by a mild shock.

The size of the kaolin or of the precipitated calcium carbonate used in the present study was rather coarse; its average diameter was 2—6μ. When these particles were suspended in water in the absence of a polyacrylamide flocculating agent, a loose flocculation of suspensions occurred spontaneously, and the suspensions were deflocculated easily by a mere mechanical shock. The interparticular distance under these conditions could be assumed to be around 1000 Å.

In order to obtain a stable aggregate, one in which the particles are combined stronlgy with each other, the dimensions of a polymer which is to be adsorbed onto the solid surface to facilitate the crosslinking of the particles should be at least larger than 1000 Å. As is demonstrated in Figs. 3 and 4, the polyacrylamides with intrinsic viscosities higher than 5—6 are very effective flocculants. Moreover, as the polyacrylamides used in this study were essentially nonionic, it can be assumed that the adsorption of this polymer causes little change in the repulsion force between particles. In this connection, it would be very interesting to calculate the dimensions of polyacrylamide molecules in water and to examine the relationship between these dimensions and its flocculating behavior.

Recent theoretical investigations by Stockmayer and Fixman[13-15] into the expansion factor of a coiled-chain molecule and its role in the viscosity give these simple intrinsic viscosity equations:

$$[\eta]=[\eta]_\theta \alpha_\eta{}^3 \tag{1}$$

$$[\eta]=KM^{1/2} \tag{2}$$

$$K=\Phi_0 A^3 \tag{3}$$

$$\alpha_\eta{}^3=1+1.55\,Z \tag{4}$$

where $[\eta]$ and $[\eta]_\theta$ represent the intrinsic viscosities in ordinary and theta solvents respectively. M is the molecular weight of the polymer; Φ_0 is an universal constant, 2.87×10^{23} (c. g. s.); α_η is the viscosity expansion factor, and A and Z are shown in Eqs. 5 and 6 respectively:

$$A^2=\langle R_0{}^2\rangle M^{-1} \tag{5}$$

$$Z=\left(\frac{3}{2\pi}\right)^{3/2} BA^{-3}M \tag{6}$$

where $\langle R_0{}^2\rangle$ is the mean-square dimension of the polymer chain and where B is a parameter measuring the polymer-solvent interactions. By combining these equations, we obtain:

$$[\eta]=KM^{1/2}+0.51\Phi_0 BM \tag{7}$$

Rewriting Eq. 7 gives:

$$[\eta]M^{-1/2}=K+0.51\Phi_0 BM^{1/2} \tag{8}$$

On plotting $[\eta]M^{-1/2}$ against $M^{1/2}$, the intercept is equal to K and the slope of the straight line is $0.51\Phi_0 B$. By substituting K in Eq. 3, $\langle R_0{}^2\rangle$ can be determined from Eq. 5. By then substituting B into Eq. 6, Z is determined. Then α_η can be calculated from Eq. 4. The relationship between the mean-square dimension of the polymer chain, $\langle R_0{}^2\rangle$, and the unperturbed mean-square radius of gyration, $\langle S_0{}^2\rangle$, is :

$$\langle S_0{}^2\rangle=(1/6)\langle R_0{}^2\rangle \tag{9}$$

The real unperturbed mean-square radius of gyration, $\langle S^2\rangle$, is :

$$\frac{\langle S^2\rangle}{\langle S_0{}^2\rangle}=\alpha_s \tag{10}$$

where $\alpha_s{}^3=\alpha_\eta{}^{2.43}$ (11)

The relationship between the intrinsic viscosity

---

8) B. Derjaguin, *Trans. Faraday Soc.*, **36**, 203, 730 (1940).

9) B. Derjaguin and L. D. Landau, *Acta Physicochim. U. R. S. S.*, **14**, 633 (1941).

10) B. Derjaguin and L. D. Landau, *J. Exptl. Theoret. Phys.* U. S. S. R., **11**, 802 (1941).

11) J. H. Schenkel and J. A. Kitchener, *Trans. Faraday Soc.*, **56**, 161 (1960).

12) S. Hachisu and K. Furusawa, *Science of Light*, **12**, 1157 (1963).

13) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym.-Forsch.*, **3**, 196 (1963).

14) M. Kurata and W. H. Stockmayer, *Rept. Prog. Polymer Phys. Japan*, **5**, 23 (1951).

15) W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, **C1**, 137 (1963).

and the molecular weight for polyacrylamide has been reported by Dainton et al.[16] to be:

$$[\eta]=6.8\times10^{-4}M^{0.66} \tag{12}$$

where $[\eta]$ is the intrinsic viscosity in an aqueous solution at 30°C, dl./g., and where M is the number-average molecular weight. By plotting $[\eta]M^{-1/2}$ against $M^{1/2}$, values which were calculated from Eq. 12, the curve shown in Fig. 6 was obtained.

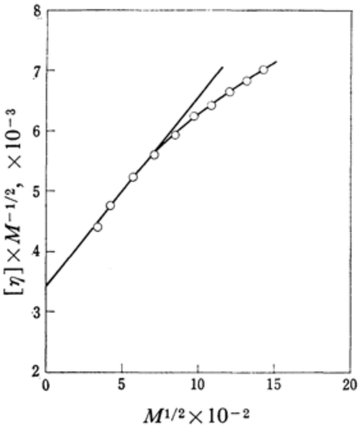

Fig. 6. Plots of $[\eta]M^{-1/2}$ versus $M^{1/2}$.

K and B were determined from the intercept and from the slope of a straight line in the lower molecular weight region respectively:

$$K=3.40\times10^{-3} \tag{13}$$

$$B=2.10\times10^{-27} \tag{14}$$

From Eq. 12, when $[\eta]$ is 6, M is 942000. Substituting K and M values into Eqs. 3 and 5 gives:

$$\langle R_0{}^2\rangle=1.047\times10^{-10} \tag{15}$$

$$\langle R_0{}^2\rangle^{1/2}=1.024\times10^{-5} \tag{15'}$$

Consequently, the dimension of the polymer chain in a theta solvent is 1024 Å. Using a B value of 2.10×10^{-27}, the Z, α_η and α_s values were calculated successively:

$$Z=0.573 \tag{16}$$

$$\alpha_\eta=1.236 \tag{17}$$

$$\alpha_s=1.187 \tag{18}$$

Subsequently, $\langle S^2\rangle$, $\langle S^2\rangle^{1/2}$ and $\langle R^2\rangle^{1/2}$ were obtained:

$$\langle S^2\rangle=2.07\times10^{-9} \tag{19}$$

$$\langle S^2\rangle^{1/2}=4.55\times10^{-6} \tag{20}$$

$$\langle R^2\rangle^{1/2}=6^{1/2}\langle S^2\rangle^{1/2}=1.114\times10^{-5} \tag{21}$$

Thus, the "real dimension" (the root mean-square end-to-end distance of the chain, $\langle R^2\rangle^{1/2}$) of the polyacrylamide molecules with the intrinsic viscosity of 6 was calculated to be 1114 Å.

Figure 7 shows the relationship between $\langle R^2\rangle^{1/2}$ and the intrinsic viscosity of polyacrylamide. When $[\eta]$ is 5.3, $\langle R^2\rangle^{1/2}$ equals 1000 Å.

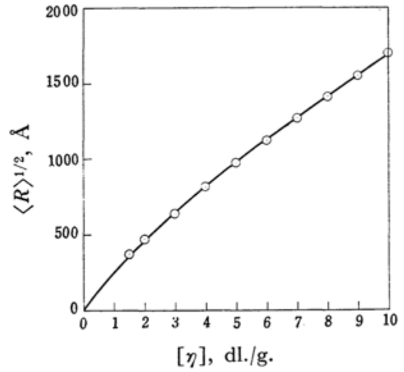

Fig. 7. Plots of $\langle R^2\rangle^{1/2}$ versus $[\eta]$.

This is in good accord with the value of 1000 Å which had been predicted.

Conclusion

At the "secondary minimum" in the potential curve of the Verwey and Overbeek theory, the particles can approach each other up to an interparticular distance of 1000 Å. However, in this state, the flocculation is not complete. When a polymer with a dimension of 1000 Å or more is added to this suspension, the particles are bound together to give a stable aggregate. Thus, by the addition of polyacrylamide with a dimension larger than 1000 Å, which corresponds to the intrinsic viscosity of 5—6, the suspension is effectively flocculated. Sodium polyacrylate, on the other hand, because of its chain expansion in solution due to the repulsion between carboxyl groups, shows a moderate flocculating power even at a lower intrinsic viscosity. Thus, it gives a linear intrinsic viscosity - subsidence rate relation.

The authors wish to express their thanks to Dr. Eiichi Wada of the Institute of Physical and Chemical Research, Tokyo, for his valuable suggestions.

---

[16] E. Collinson, F. S. Dainton and G. S. McNaughton, *Trans. Faraday Soc.*, **53**, 489 (1957).