SHORT COMMUNICATIONS

A New Rapid Method of Determining Molecular Weight of Water Soluble Linear Polymers by the Measurement of Rate of Settling of Clay Suspensions

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During the past decade it has been reported that certain water-soluble linear polymers can give rise to the aggregation of clay particles in a state of aqueous suspension[1,2]. In this communication this fact was investigated in a more quantitative manner by observing the relation between the rate of (hindered[3]) settling v of clay suspensions under addition of a linear polymer and the molecular weight of the polymer.

Itaya clay (product of Yamagata Prefecture) levigated and after removing pebbles and large aggregates, was dried and used as suspensoid. Polymers used in this study were purified as described in a previous article[4].

The suspension was introduced in a sedimentation tube of 67.3 cm. long, which was agitated by rotating the tube for 15 min. at a speed of 5 revolutions per minute. After stopping agitation, settling rate of the suspension was measured at 30.0±0.1°C. Intrinsic viscosity of the polymer freshly dissolved in aqueous 1 M sodium nitrate solution was also measured at 30.00±0.01°C in a capillary viscometer of the Ubbelohde type, and the molecular weight of the polymer was determined from it.

In Figs. 1 and 2 $v \sim [\eta]^{30^\circ C}_{1\,\mathrm{M}\,\mathrm{NaNO_3}}$ relation was shown for thy system in which 0.02% (to the amount of clay) of polymer was added to the 5% clay suspension. A linear relationship between v and $[\eta]^{30^\circ C}_{1\,\mathrm{M}\,\mathrm{NaNO_3}}$ was confirmed. A similar linearity was also found for a different content of polymers (below 0.02%) and a different concentrations of clay suspensions (above 5%) so long as the other experimental conditions were kept constant. We may discuss in details the mechanism of aggregation

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

[2] M. Noda, *Kōgyō Yōsui*, **30**, 33 (1961).

[3] C. Orr, Jr. and J. M. DallaValle, "Fine Particle Measurement", The Macmillan Co., New York (1959), p. 48.

[4] Y. Toyoshima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1295 (1961).

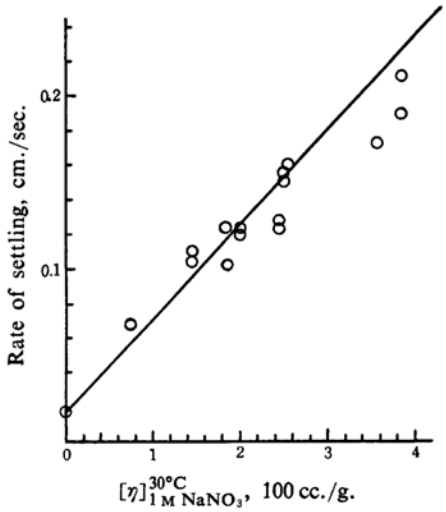

Fig. 1. The relationship between $[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\,\mathrm{NaNO_3}}$ and v for polyacrylamides.

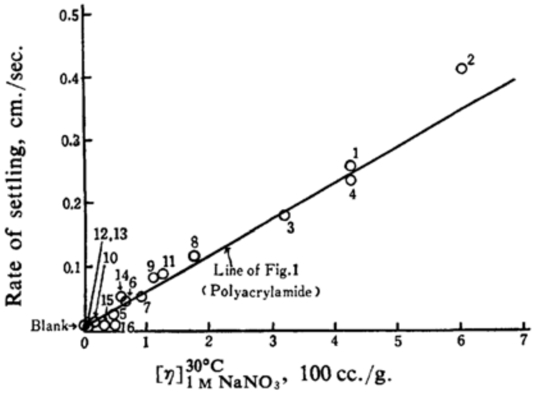

Fig. 2. The relationship between $[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\,\mathrm{NaNO_3}}$ and v for various water soluble linear polymers.

1 2 3 4	Partially hydrolyzed polyacrylamide
5 6 7	Polyvinyl alcohol
8 9	Sodium carboxymethylcellulose
10 11	Polyvinylpyrrolidone
12 13	Dialdehyde starch
14	Agar
15	Gelatin
16	Polyethylene oxide

of clay particles referring to this linearity in a separate reports*. Here we should like rather to draw attention to the fact that using this relation between v and $[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\,\mathrm{NaNO_3}}$ together with the known relation between $[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\,\mathrm{NaNO_3}}$ and molecular weight M of the polymer, we can correlate v with M, and that using such a relationship we can determine the molecular weight from the measurement of sedimentation velocity, which is easier to practise than a similar and well known method of molecular weight determination by the measurement of intrinsic viscosity.

In the case of polyacrylamide, $v \sim [\eta]$ relation is expressed as

$$v = K[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\,\mathrm{NaNO_3}} + a \tag{1}$$

while that of $[\eta]$ and M is

$$[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\,\mathrm{NaNO_3}} = 3.73 \times 10^{-4} M^{0.66} \tag{2}$$

therefore we obtain from 1 and 2,

$$\log(v-a) = 0.66 \log M + \log(3.73K \times 10^{-4}) \tag{3}$$

where K is a constant, and a the rate of settling without the addition of polymer. Measurement of $[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\,\mathrm{NaNO_3}}$, v and a shows that such a linear relationship really holds as shown in Fig. 3. Hence it enables a rapid determination of the molecular weight of unknown polyacrylamide from the simple determination of rate of settling under the definite condition of sedimentation test using the clay suspension of the same origin. As for the other various water-soluble linear polymers, for instance, partially hydrolyzed polyacrylamide, polyvinyl alcohol, sodium carboxymethylcellulose, polyvinylpyrrolidone, dialdehyde starch, agar, gelatin, and polyethylene oxide, the same linear relationship as in Fig. 1 was also obtained as shown in Fig. 2. Hence their molecular weights can be rapidly determined from the rate of settling of

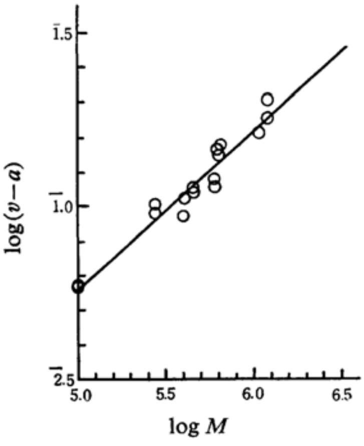

Fig. 3. The relationship between log M and log$(v-a)$ for polyacrylamides.

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5) New Product Bulletin, No. 34, American Cyanamid Co., New York (1955), p. 2.

* The details will be published in a near future.

clay suspensions as in the case of polyacrylamide if the relationships between $[\eta]^{30^\circ\mathrm{C}}_{1\,\mathrm{M}\ \mathrm{NaNO_3}}$ and molecular weights for these polymers are determined previously by the method, for instance, of light scattering or osmotic pressure. As a routine procedure for product control, this new method is perhaps one of the rapid and simple methods for determining molecular weights of water-soluble linear polymers.

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