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The Rheological Behavior of Suspensions of Ion-exchange Resin Particles

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The flow properties of the suspensions of ion-exchange resin particles, the highly-crosslinked polyelectrolyte gel particles, were examined, especially in relation to their charged state. The steady viscosities and the dynamic viscoelasticities of these suspensions were measured, and the results were interpreted in terms of the dispersion state of the suspended particles. The flow system of the highly-charged particles, such as Na-form resin particles, exhibits a high viscoelasticity and is in a well-dispersed state. On the contrary, the flow system of the lower-charged particles, such as Ba-form particles, is not viscoelastic, but viscous and dilatant. This behavior may be attributed to the variation in the electrical double layers around the suspended particles.

Ion-exchange resin particles are excellent model substances of the colloidal system for investigating its behavior in relation to the structure, because they have a well-defined polyelectrolyte structure and vary in the surface state according to the kind of counter-ions in their fixed dissociation groups. We have previously investigated the aggregation behavior of these particles¹⁾ and measured their electro-kinematic potential.²⁾ As one extention of these investigations, we will now report on the rheological behavior of a suspension of these particles. This investigation will reveal how the rheological behavior of the suspension is affected by the charged state of the suspended particles.

Experimental

The ion-exchange resin particles used were composed of Amberlite resin (Rohm & Haas), IR-120. This is a strongly-dissociated cation-exchange resin which had been prepared from polystyrene sulfonic acid crosslinked with divinylbenzene. The resin particles from commercial sources were ground in a wet state in a ball mill and sieved in water. The part which

TABLE I. THE CHARACTERIZATION OF SAMPLES OF SUSPENDING PARTICLES, AMBERLITE IR-120

Ionic form	Real density g./cm^3	Water content %	Apparent density g./cm^3
H	1.55	48.4	1.22
Na	1.64	46.2	1.26
Ca	1.60	42.8	1.27
Ba	1.88	36.3	1.56

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1) M. Senō and T. Yamabe, This Bulletin, **34**, 1002 (1961).
2) M. Senō and T. Yamabe, *Nature*, **202**, 1110 (1964).

had settled after 1—10 hr. was collected and washed thoroughly after conditioning; from this part the sample in various ionic forms was prepared. The ionic forms were the H–, Na–, Ca, and Ba–form. They are 2—20μ in size; their water contents and real densities were as shown in Table I.

The viscosity of the dilute suspensions was measured with an Ostwald-type capillary viscometer. The viscosity and the dynamic visco elasticity were measured with a rotational viscometer (McMichael type) and with a rheometer which was described in a preceding paper.[3]

Results and Discussion

The viscosities of the ion-exchange resin particle suspension in the range of relatively small concentrations are shown in Fig. 1 as a function of the volume fraction of particles. The rate of the increase in the viscosity with the increasing concentration is larger in the order; H->Na->Ca->Ba-form. The relationship between the relative viscosity and the volume fraction is ruled regularly by the following equation, proposed by Asbeck et al.[4]:

$$\ln \eta_{\mathrm{rel}} = \frac{K\varphi}{\varphi_c - \varphi}$$

The linear relation of $1/\log \eta_{\mathrm{rel}}$ and $1/\varphi$ is shown in Fig. 2, from which the parameters, K and φ_c, are obtained. The former is a shape factor, while the latter is a crowding factor which represents the extent of the packing of suspended particles or that of the immobilization of the dispersing media.[5] The results are shown in Table II.

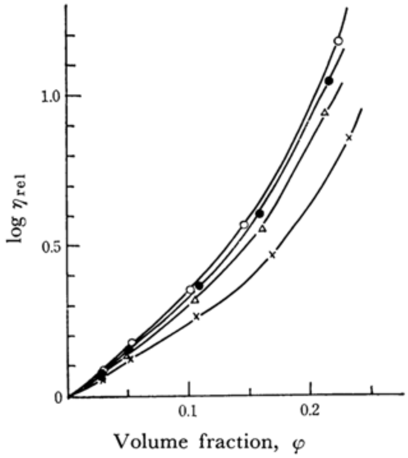

Fig. 1. Viscometric behavior of suspensions of ion-exchange resin particles.

- ○ H-form particles
- ● Na-form particles
- △ Ca-form particles
- × Ba-form particles

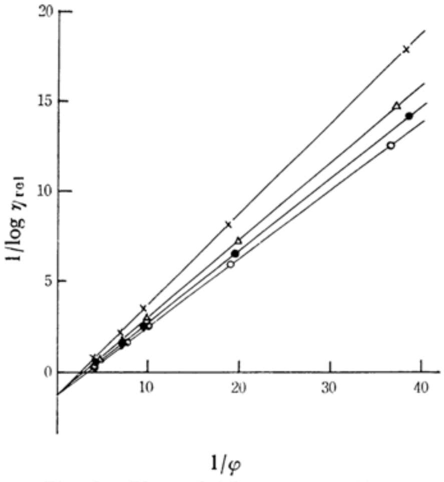

Fig. 2. Plots of $1/\log \eta_{\mathrm{rel}}$ vs. $1/\varphi$. Symbols are the same as in Fig. 1.

From this table, the following important finding is derived. The shape factor, K, is identical for all suspensions, independently of their ionic forms, and approximately equals 2.5, which is the value for the spherical particles. On the contrary, the crowding factor, φ_c, is greatly dependent on the ionic forms of the suspending particles. This value is 0.502 for the Ba-form, which is the value for the cubic packing, the loosest closed-packing. The values for the other ionic forms are smaller than that for the Ba-form. This indicates either that these suspensions are in the looser packing state, or that the suspending medium is immobilized by the particles to a greater extent.

TABLE II. THE ANALYSIS OF THE RELATION OF VISCOSITY AND CONCENTRATION BY THE EQUATION $\ln \eta_{\mathrm{rel}} = K\varphi/(\varphi_c - \varphi)$

Ionic form	K	φ_c
H	2.56	0.377
Na	2.56	0.391
Ca	2.56	0.427
Ba	2.56	0.502

This finding may be interpreted reasonably. For the sulfonate group, hydrogen and sodium ions are highly dissociated counterions, calcium ions are hardly dissociated, and barium ions are undissociated. The order of the degree of dissociation is in accordance with that of the interfacial electro-kinematic potential of the particles. That is, the ion-exchange resin particles of highly-dissociated counterions are accompanied by a highly-extended interfacial electrical double-layer. The same particles with a well-established electrical double-layer do not approach nearer to each other, since the electrical repulsion force is exerted between the double-layers with charges of the same sign. Therefore, such a suspending particle takes a loose packing state, accompanied

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[3] T. Nakagawa and M. Senō, This Bulletin, **29**, 471 (1956).

[4] W. K. Asbeck and G. A. Scherer, *Ind. Eng. Chem.*, **47**, 1472 (1955).

[5] J. Robinson, *J. Phys. & Colloid Chem.*, **53**, 1042 (1949); M. Mooney, *J. Colloid Sci.*, **6**, 162 (1951).

by the immobilization of the suspending medium.

The rheological properties of the suspension exhibit a more characteristic feature in the higher concentration region according to the variation in the charged state of the particles. One of the results is provided by the measurements using the rheometer of the forced-oscillation type. The coefficients of the dynamic viscoelasticity are given in Table III. The suspensions in which the particles have highly-dissociated counterions show large values of the dynamic viscosity and rigidity, and the suspension of the undissociated barium-ion form particles is nearly viscous. This establishes that the viscoelasticity of this suspension results from the repulsion forces between the double-layers established around the suspending particles. The same has been proposed by Bolt.6)

TABLE III. THE DYNAMIC VISCOSITY AND RIGIDITY OF THE CONCENTRATED SUSPENSIONS

(30°C and 30—35 sec./cycle)

Ionic form	Volume fraction of particles	Dynamic viscosity poise	Dynamic rigidity dyn./cm^2
H	0.291	25.06	8.23
Na	0.295	9.91	3.70
Ca	0.304	3.06	0.44
Ba	0.328	0.76	0.09

Another characteristic of the concentrated suspensions is revealed by the observation on the dilatancy behavior. It was clearly observed that the dilatancy of the suspensions the suspending particles of which have more undissociated counterions is more remarkable. Although no exact method for the estimation of the dilatancy has yet been established, an estimate is provided by the measurements using a rotational viscometer. The results are shown in Fig. 3.

TABLE IV. THE PROPERTIES OF THE SUSPENSIONS OF ION-EXCHANGE RESIN PARTICLES

Ionic form	Concentration range of characteristic flow	Characterization	Volume fraction at settling
H	0.26∼0.295	Viscoelastic	0.295
Na	0.27∼0.30	Viscoelastic	0.302
Ca	0.27∼0.31	Viscoelastic	0.315
Ba	0.28∼0.33	Dilatant-viscous	0.394

No anomalous behavior is detected in the suspensions of H–, Na–, and Ca–form particles in the region of the measuring conditions, but, for the suspension of the Ba-form particles, an abrupt increase in the viscosity is observed, accompanied by the occurence of a turbulent flow, over the radial viscosity of 7.2 sec^{-1}. This value corresponds to values of 1.80 sec^{-1} for the rate of shear and of 3.0 for the Reynolds number. The latter is very small compared to the critical Reynolds number (about 1200—2000); therefore, it may be said that this suspension exhibits the anomalous turbulent flow which occurs at a very small Reynolds number. However, no exact interpretation of the relation of the dilatancy and the anomalous turbulent flow has yet been established, altough their intimate relation is recognized.7) This suggests that the interfacial electrical double-layer reduces the friction between the particles as a result of the repulsive interaction of the double-layers, and that the Ba-form particle suspension, of which the double-layers are infant, is dilatant, while the H- and Na-form particle suspensions, the double-layers of which are well-established, are not dilatant. These characteristics are summarized in Table IV.

The suspensions of H- and Na-form particles are viscoelastic, the suspension of Ba-form particles is dilatant-viscous, and the suspension of Ca-form particles is intermediate in nature, in the characteristic concentration range covered in Table IV. In the lower concentration range, all the suspensions are purely viscous, while in the higher concentration range they are powdery solids.

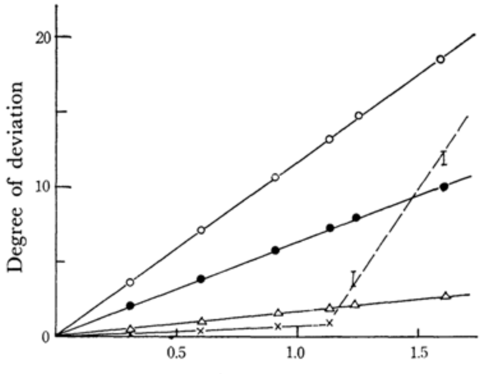

Fig. 3. Measurements using a rotational viscometer. Symbols are the same as in Fig. 1.

Table IV also shows the concentration of the sedimentation state of these suspensions. It is clear that the dispersed system with the lower-charged particles is in the more compact state at the settling; this accords with the generally accepted concept.

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6) G. H. Bolt, *Geotechnique*, 6, (6) (1956).

7) G. V. Vinogradov, A. Ya. Malkin and A. I. Leonov, *Koll.-Z.*, **191**, 25 (1963).