Aggregation of Ion-exchange Resin Particles

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(Received December 20, 1960)

An ion-exchange resin is a crosslinked polyelectrolyte gel, which dissociates to produce cations or anions. Polystyrenesulfonic acid-divinylbenzene and polyvinylbenzyltrimethylammonium hydroxide-divinylbenzene are a typical cation-exchange resin and a typical anion-exchange resin used now, respectively. These resins exhibit a remarkable swelling behavior when the degree of crosslinking, e. g., the content of divinylbenzene is small[1]. Resins with a high degree of crosslinking scarcely swell at all and, using these resins, researches not on the swelling behavior of resins but on the aggregation behavior are able to be carried out.

The cation- and the anion-exchange resins have negative and positive charges, respectively, in the dissociated states and, therefore, it is expected that the interparticlar interaction exerts itself between two kinds of these resin particles. In practice, it is often observed that such an aggregation takes place in a mixed bed water purification apparatus. In this paper, some observation on the aggregation behavior will be presented. Independently of this investigation, Grubhofer described recently a similar observation[2]. It is believed that this behavior is of interest colloid-chemically and the ion-exchange resins are interesting samples to investigate colloid-chemical phenomena in this respect. Recently, Schenkel and Kitchener used similar particles to test the Derjaguin-Verwey-Overbeek theory[3].

Experimental

Ion-exchage resins used primarily in this experiment are commercially-available ones, Dowex 50W and Dowex 1, which are strongly acidic and strongly basic polystyrene-based resins with sulfonic acid group or quarternary ammonium group, respectively. In addition, the following resins were used; Amberlite IR-120 (strongly acidic), Amberlite IRA-400 (strongly basic), Amberlite IRC-50 (weakly acidic) and Amberlite IR-4B (weakly basic). The former two are polystyrene-type resins and the later two are polyalkene-type ones with carboxyl acid group and secondary or tertiary amino group, respectively. The H^+-form cation exchanger or the OH^--form anion-exchanger is prepared by treating them with hydrochloric acid or sodium hydroxide solution, respectively, after conditioning them several times and washing them thoroughly with deionized water.

The aggregation behavior was observed directly with the naked eye or by microphotography and, as a measure of the degree of aggregation, the sedimentation volumes were measured. About 1 g. of air-dried resins was taken into 20 ml. of suspending media in the sedimentation tube, which is 15 cm. in height and 1.5 cm. in inner diameter. The suspending media were deionized water except when stated otherwise. After being stirred vigorously, the sedimentation tube was settled in the quiescent state overnight at room temperature, 20~25°C, and the sedimentation volume was read. By correcting for the moisture content of resins, the specific sedimentation volume was gained. The moisture content was measured gravimetrically by drying them on phosphorus pentoxide in vacuo.

Results and Discussion

Formation of Aggregation.—Dowex 50W resins of hydrogen-form or Dowex 1 resins of hydroxyl-form, individually, form dense sediments in water, the specific sedimentation volume being 2.6 ml./g., respectively. When both kinds of resins are mixed, remarkable aggregation takes place; very bulky sediment is formed and the specific sedimentation volume is 21 ml./g. (volume fraction of particles in the sediment is 0.04). By observing the microscopic photograph of these systems shown in Fig. 1, it is clear that, although each kind of resins, individually, disperses uniformly, in the mixture of them both resins combine with each other to form agglomerates with large voids.

It is well-known that, the stronger is the attracting interaction between the particles, the larger is the sedimentation volume of the particles. Recently, Vold[4] calculated the sedimentation volume of the colloidal particles whose attracting range extends over a distance r times larger than the particle radius from their surface. According to her calculation, the ion-exchange particles under study now have a range of attraction nearly equal to the particle radius ($r \approx 1$).

These agglomerates are formed in the systems of weakly dissociated resins, e. g., between

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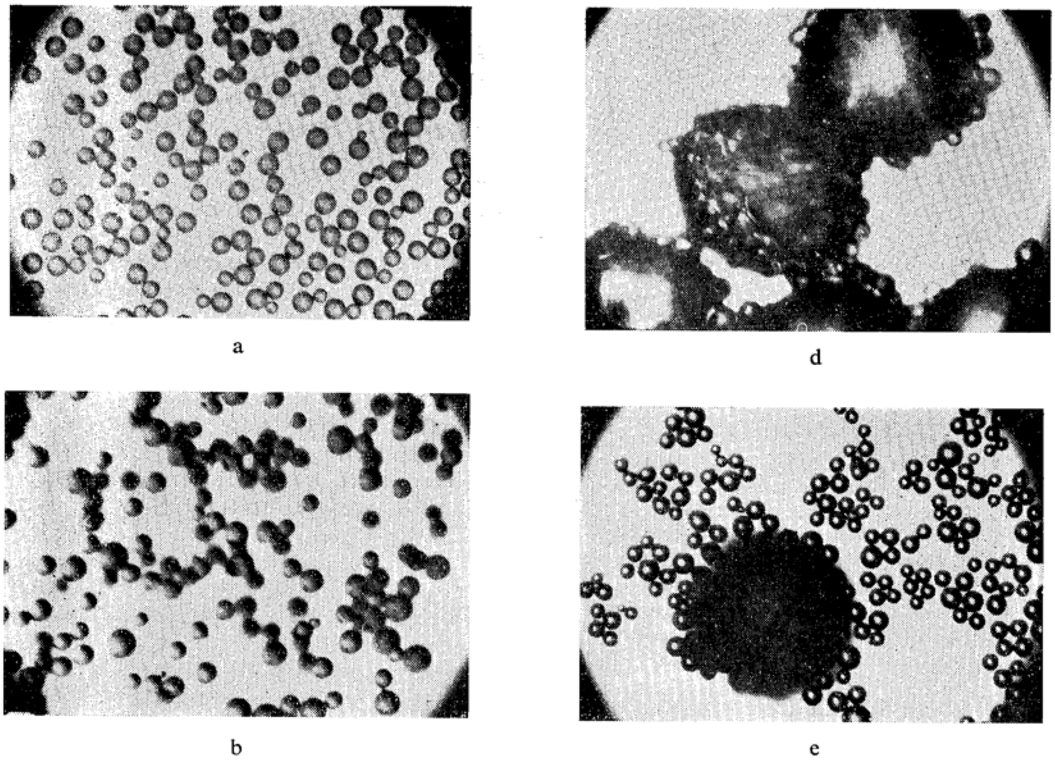
[1] M. Senō and T. Yamabe, presented at the 9th Annual Meeting of the Society of Polymer Science, Osaka, May, 1960.

[2] N. Grubhofer, *Angew. Chem.*, **71**, 215 (1959).

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

[4] M. J. Vold, *J. Colloid Sci.*, **14**, 168 (1959).



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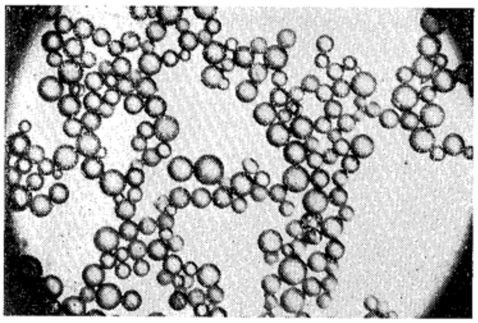

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Fig. 1. Microphotographs of various ion-exchange systems (×60).

- a. Dowex 50W-X8, 200 mesh. (Particles disperse uniformly.)
- b. Dowex 50W-X8, 200 mesh-Dowex 1-X8, 200 mesh, 10 : 1 by wt. ratio. (Small agglomerates are formed.)
- c. Dowex 50W-X8, 200 mesh-Dowex 1-X8, 200 mesh, 1 : 1 by wt. ratio. (Large agglomerates are formed over a whole system.)
- d. Dowex 50W-X8, 20 mesh-Dowex 1-X8, 200 mesh, 10 : 1 by wt. ratio. (Larger particles combine each other through the medium of smaller particles.)
- e. Dowex 50W-X8, 20 mesh-Dowex 1-X8, 200 mesh, 1 : 1 by wt. ratio. (Larger particles are covered with smaller particles and stabilized.)

Amberlite IR-120 and Amberlite IRA-400, Amberlite IR-120 and Amberlite IR-4B, Amberlite IRC-50 and Amberlite IRA-400, and Amberlite IRC-50 and Amberlite IR-4B. But the last system, e. g., the weakly acidic and the weakly basic resins, do aggregate only to less extent. The degree of aggregation of these systems is given in Table I.

TABLE I. DEGREE OF AGGREGATION OF VARIOUS PARTICLE SYSTEMS

System*	Degree of aggregation**
IR-120-IRA-400	2.8
IR-120-IR-4B	1.9
IRC-50-IRA-400	2.5
IRC-50-IR-4B	1.3

* All the particles are Amberlite ion-exchange resins, 20 mesh of particle size and 1 : 1 mixture by weight.

** Degree of aggregation are defined as the ratio of sedimentation volume (aggregate) in pure water to the volume (non-aggregate) in 1 N sodium chloride.

Effect of Addition of Salts.—The aggregates are destroyed by addition of salts. The specific sedimentation volumes diminish on addition of salts such as sodium chloride as shown in Fig. 2. As for the breaking-down of aggregates by

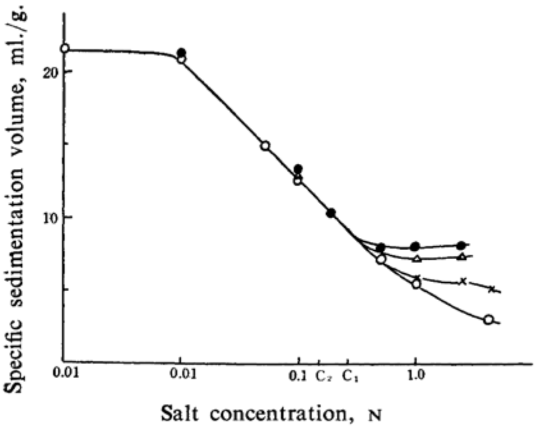

Fig. 2. Effects of addition of salts on sedimentation volume. System; Dowex 50W (200 mesh)-Dowex 1 (200 mesh), 1 : 1 by weight. -○- NaCl, -×- $MgCl_2$, -△- Na_2SO_4, -●- $MgSO_4$. C_1 and C_2 are saturation concentrations of Dowex 50W and Dowex 1, calculated from the total exchange capacities of resins.

addition of salts the following results are to be pointed out;

(1) The effect of destruction of agglomerates is primarily governed by equivalent concentration of salt solution, independently of variation of the kind of salts.

(2) In high concentration range of salts, in which the aggregates are completely broken down, the specific sedimentation volume changes with the variation of salts. But this difference is primarily due to the difference in the density of the salt solution, and it is finally observed that the anion-exchange resin, the lighter one, is separated from the cation-exchange resin, the heavier one, and floats up.

(3) When the saturation concentration which is calculated from the total exchange capacity of resins is reached, the hydrogen ions or the hydroxyl ions may be largely replaced for, say, the sodium ions or the chloride ions and at this concentration the aggregate is completely broken down. In the far lower concentration range than this saturation concentration, the aggregate is destroyed considerably and there is a linear relationship between the specific sedimentation volume and the logarithm of the concentration of the added salt solution.

(4) The aggregates are broken down by the addition of acids or alkaline solutions. The strongly acidic resin-the weakly basic resin (Amberlite IR-120-Amberlite IR-4B) destroyed with hydrochloric acid, and the weakly acidic resin-the strongly basic resin (Amberlite IRC-50-Amberliet IRA-400) destroyed with sodium hydroxide become to form aggregation again, on washing them with deionized water. It may be due to hydrolysis of weakly dissociated resins.

Aggregation in Non-aqueous Media.—As it appears that the interparticlar force is electrostatic in nature, it seems to be interesting to investigate the aggregation behavior in non-aqueous media, the dielectric constant of which is small. It is well-known that the minute amount of water influences greatly the electrostatic coagulation and the air-dried ion-exchange resins contain the considerable amount of water, for these are very lyophilic gels, and hence the air-dried resins must be dried on phosphorus pentoxide in vacuo to remove moisture from them completely. The sedimentation volume of these dried resins in dried benzene was measured and was shown in Fig. 3. As seen in this figure, in which the specific sedimentation volume is plotted against the moisture content of resins, the resins do not form an aggregate in the complete absence of water.

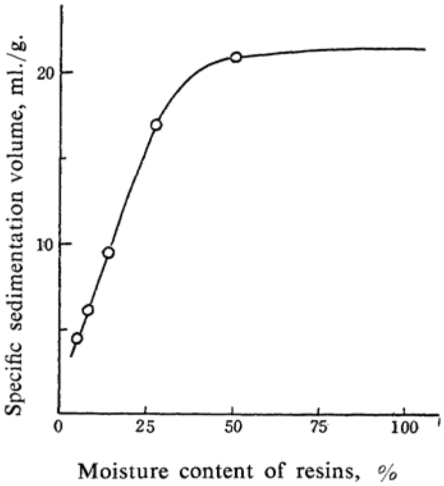

Fig. 3 Effect of moisture on sedimentation volumes of resins in benzene. Dowex 50W (200 mesh)-Dowex 1 (200 mesh)

Mechanism of Aggregation.—It is supported by the above-mentioned results that the interparticlar force which causes aggregation is electrostatic in nature. The agglomeration takes place between the hydrogen-form cation-exchange resins and the hydroxyl-form anion-exchange resins. A kind of neutralization reaction occurs between the particles of hydrogen-form resin and the hydroxyl-form resin and results in producing the negatively charged and the positively charged resin particles and Coulombic interaction is exerted between these charged particles. Such a coagulation behavior was observed also between a polymeric acid and a polymeric base by Deuel et al.[5]

The presence of small additional ions such as sodium or chloride ions screens the charges on the particles and the interparticlar Coulombic attraction decreases. In benzene free from water the degree of dissociation of counterions is so small that the neutralization does not proceed between hydrogen- and hydroxyl-form particles. Hence the aggregates are not formed in such a system.

Steric Factor on Aggregation.—It is well-known that the steric factors such as the size and shape of particles affect greatly the aggregation behavior of colloidal particles. The ion-exchange particles used in this investigation are very large in size and spherical in shape. Therefore, it seems that the effect of size ratio of both particles participated with aggregation is more interesting than that of the size and shape itself. In Fig. 4, the aggregation behavior of the ion-exchange resin particles, Dowex 50W and Dowex 1, with different sizes is shown. As seen in this figure, the particles with the same sizes show a maximum aggregation on mixing at the equal amounts of both resins and the particles with the different sizes show a maximum aggregation on mixing at a larger amount of the larger particle and a smaller amount of the smaller particle. The weight fraction of the cation-exchange resin, Dowex 50W, that gives the maximum aggregation is shown against the ratio of radii between both of the resin particles in Fig. 5. It is clearly noticed that the difference in size between both particles influences markedly the aggregation behavior.

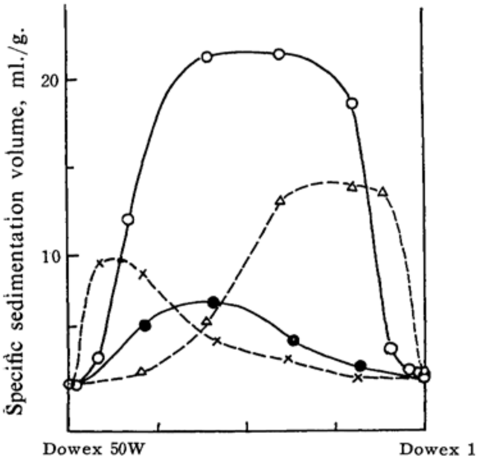

Fig. 4 Sedimentation volumes of mixtures of resins of various particle sizes.

Mesh size;	Dowex 50 W	Dowex 1
—○—	200(0.043 mm.)	200(0.055 mm.)
--×--	20(0.375 mm.)	200
--△--	200	40(0.190 mm.)
—●—	20	40

Average radii of resin particles are given in parentheses.

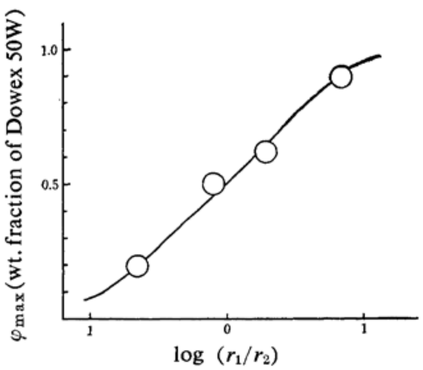

Fig. 5. Relation of the mixing ratio of maximum aggregation and the particle size ratio.

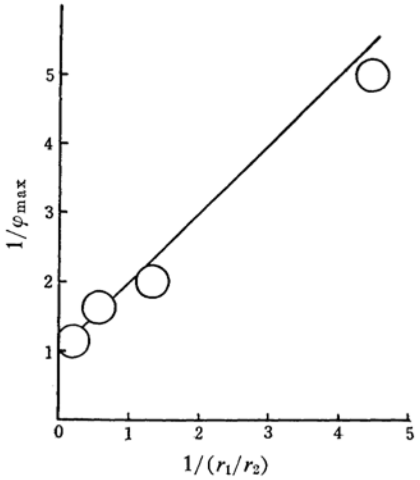

Fig. 6. Plots of $1/\varphi_{max}$ against r_2/r_1. Full line is the theoretical.

Now, it is assumed that the maximum aggregation takes place in the case where the total surface areas of the two kinds of particles are equal. The following formula is derived from this assumption.

$$\varphi_{max}=\frac{r_1}{r_1+r_2}$$

where φ_{max} is the weight fraction of Dowex 50W giving maximum aggregation, and r_1 and r_2 are radii of Dowex 50W and Dowex 1 particles, respectively. In Fig. 6, the reciprocal of φ_{max} is plotted against the reciprocal of r_1/r_2. If the above-mentioned assumption is valid, this plot should be a straight line

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[5] H. Deuel, J. Solms and A. Denzler, *Helv. Chim. Acta*, 36, 1671 (1953).

intersecting the ordinate at unity. As shown in Fig. 6, it is confirmed that this is the case in the present systems.

Summary

Some observations are presented on the aggregation behavior of the ion-exchange resin particles. On mixing the hydrogen-form cation-exchange resin particles with the hydroxyl-form anion-exchange resin particles, remarkable aggregation takes place. It seems that this aggregation is due to the electrostatic attraction force exerted between resin particles. This is supported by the results that the aggregation is destroyed by addition of salts and that the agglomerates are not formed in nonpolar medium in the complete absence of water. Moreover, it was demonstrated that the variation of the size ratio of particles influences markedly the aggregation behavior. A simple explanation is given for such a coagulation phenomena.

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Added in proof:

It was shown by further observations done after contribution of this paper that salt-form ion-exchange resin particles, for example, sodium-form cation-exchange resin and chloride-form anion-exchange resin aggregate in pure water where no additional salt is completely absent and also red color due to the formation of ferric thiocyanate complex does not appear when ferric-form cation-exchange resin and thiocyanate-form anion-exchange resin are mixed in pure water. From these observations it is clear that no chemical reaction takes place practically between these particles and some modifications should be applied to the coagulation mechanism proposed in the present paper. A portion of counterions distributes outside of the resin particle, so that the fixed charges of the resin are not completely neutralized by the counterions in the volume occupied by the particle. Therefore, the cation-exchange resin particles carry negative charges and the anion-exchange resin particles carry positive charges in their suspension. Electrostatic interaction is exerted between these particles. Distribution of counterions would be largely affected by the salt concentration, the dielectric constant of medium and the degree of dissociation of fixed ionized groups. The details will be reported later.