Sedimentation Volume of Alginic Acid Powder in Electrolyte Solution

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Although there have been many studies on alginic acid and its salts, few studies have been carried out on the properties of alginic acid powder as a dispersed phase. In the present paper, it was attempted to study the colloid chemical properties such as sedimentation volume, degree of swelling, electrokinetic potential and cation exchange capacity of alginic acid powder in electrolyte solution.

Experimental

Alginic acid powder was prepared as follows. Alginic acid was precipitated from sodium alginate solution (polymerization degree being about 198) by adding hydrochloric acid, washed, and it was then dissolved in sodium carbonate solution. This procedure was repeated three times, after which alginic acid was precipitated, washed with water, methanol and ether, and then dried at 50°C for five hours. Dry alginic acid was ground in an agate mortar and the portion of 200~280 mesh was taken and kept in a glass bottle. The size and shape of particles were such that their longer axis was between about 0.02 and 0.1 mm. and the ratio of longer to shorter axis was less than about 1.4. The ash content of the sample was about 0.2 %. Electrolytes used were also purified by the usual method.

Sedimentation Volume.—10 cc. of an electrolyte solution was pipetted in a flat bottom glass tube of 1cm. inner diameter and 19 cm. height. 0.3 g of alginic acid powder was then added and the tube was shaken vigorously. The sedimentation volume reached a constant value after 3∼7 days which was recorded as an equilibrium value.

Swelling Degree.—Sedimentation volume is considered to increase with increasing degree of coagulation(1),(2),(3),(4) as well as the swelling of the powder. Assuming that the sedimentation volume is proportional to the swollen volume when the coagulation degree does not change, the following relation is obtained.

$$S=(V_w \cdot X/X_w-v_w)/v_w \quad (1)$$

Here, S is the swelling degree of alginic acid, V_w the sedimentation volume in water, X_w and X the swollen volume in water and in an electrolyte solution respectively, all referred to one gram of dry alginic acid. The quantity v_w is an apparent volume per gram of dry powder under the same degree of coagulation as in water. X and v_w are calculated by the following relations.

$$X=\{U-(W-p \cdot w_0)/d\}/p \quad (2)$$

$$v_w=V_w/X_w \cdot \rho \quad (3)$$

Here, U and W are the volume and weight of electrolyte solution with swollen alginic acid containing p gram of dry acid, respectively, w_0 the weight of swollen alginic acid per gram of dry substance, and d and ρ, densities of electrolyte solution and dry alginic acid, respectively. Of these quantities, w_0 was obtained by the measurement, in dry and swollen state, of the weights of alginic acid film prepared on a microscopic slide.

Coagulation Degree.—In general, the sedimentation volume increases with the increasing degree of coagulation. Assuming that swelling and coagulation contribute to the sedimentation volume additively, coagulation degree C is expressed as follows.

$$C=(V_E-V_w \cdot X/X_w)/v_w \quad (4)$$

Here, V_E is the sedimentation volume in an electrolyte solution. The value of C in water was taken as the standard. From (1) and (4),

$$\Delta v \equiv S+C=(V_E-v_w)/v_w \quad (5)$$

results, which means that the specific sedimentation volume Δv is the sum of the degrees of swelling and coagulation.

Electrokinetic Potential.—Cataphoretic velocity and ζ-potential of alginic acid were measured for particles suspended in various electrolyte solutions. Namely, a dilute suspension of alginic acid is introduced in U-tube and the sedimentation velocity u_1 is measured under a definite gradient of electrostatic field E. The field is reversed and the velocity u_2 is measured again. Then the following relation holds.

$$G+k\zeta E=au_1 \quad (6a)$$

$$G-k\zeta E=au_2 \quad (6b)$$

Here, G represents the force due to gravity and k and a, two constants. Then,

$$\zeta=a(u_1-u_2)/2k \cdot E \quad (7)$$

gives ζ-potential when we use proper value for a/k(5).

Cation Exchange Amount.—Alginates formed by mixing alginic acid powder and the electrolyte solutions of varying concentration were washed and burnt in a crucible. Cation exchange amounts for the electrolytes of various concentrations were estimated from the amount of metal oxide formed. Values of pH of electrolyte solutions were 1.5∼1.8 for cupric, aluminum and ferric chlorides.

Experimental Results

Preliminary experiments were carried out to study the effects of temperature, particle size and the redispersion upon the sedimentation volume as shown in Tables 1 and 2.

Table 1
Effects of temperature, particle size on sedimentation volume*

Temp. (°C.)	Particle Size (Mesh)	Sed. Vol. in 3N KCl Solution (cc./g.)
0	280<	7.9
10	〃	7.0
37	〃	5.9
10	〃	7.0
10	200∼280	5.4
10	110∼150	4.3
10	70∼100	4.4

Table 2
Effect of redispersing the sediment on sedimentation volume*

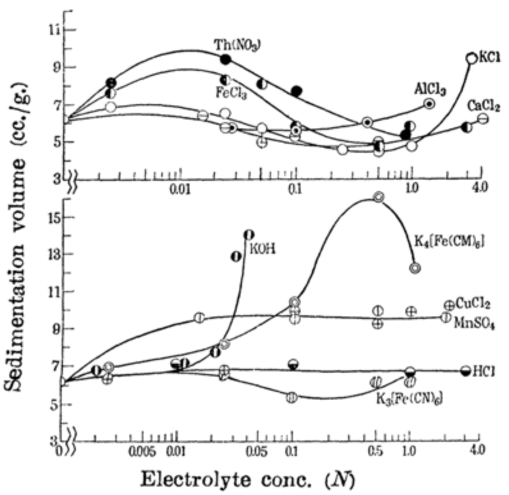
Temp. (°C.)	Particle Size (Mesh)	Sed. Vol. (cc./g.) in 3N KCl after Repeated Disp.			
		0	1st	2nd	3rd
10	280<	7.9	6.2	5.9	5.8

The maximum error introduced in the sedimentation volume measurement was ±13% for

(1) P. Ehrenberg, "Bodenkolloide", p. 83, 84, Dresden (1918).
(2) A. v. Buzágh, *Kolloidchem. Beih.*, **32**, 114 (1931).
(3) G. F. Kandilarou, *Kolloid-Z.*, **90**, 320 (1940).
(4) W. Gallay and I. E. Puddington, *Can. J. Research*, **21** B, 171 (1943); **22** B, 16 (1944).

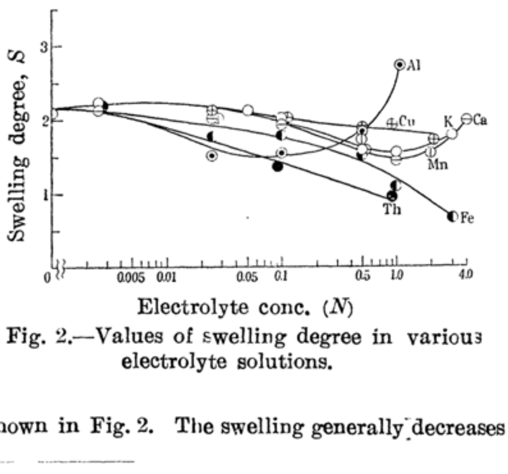
(5) H. A. Abramson, "Electrokinetic Phenomena", p. 111, Chem. Catalog, New York (1934).
* Alginic acid powder stored for about five months after purification was used.

thorium nitrate solution and about ± 7% for most other cases. Values of sedimentation volume in various electrolyte solutions are shown in Fig. 1.* Values of pH of these solutions were 2.0∼2.2 for potassium and calcium chlorides, 1.5∼1.8 for cupric, aluminum and ferric chlorides and 1.7∼1.9 for thorium nitrate. The effects of its change on the sedimentation volume proved to be negligible. We can see as a whole in this figure that the sedimentation volume exhibits a maximum at relatively low concentration of electrolyte and minimum in the region of larger concentration. The maximum is especially marked in the case of thorium and ferric salts. We should, however, note the anomalous case for potassium hydroxide and potassium ferrocyanide where the anomalies are due perhaps to a strong basicity and negative polyvalency. We then calculated the swelling degree S according to the equation (1) which was shown in Fig. 2. The swelling generally decreases with increasing concentration of electrolyte. It increases, however, at fairly large concentrations for some electrolytes. Further, the coagulation degree C was shown in Fig. 3a. In the cases of ferric chloride and thorium nitrate, the values of C showed a marked maximum at about 0.01 N of electrolyte concentration, while the rest of the salt gave rather a flat maxima at the same region of concentration. At higher concentration region, the values of C after passing a minimum tended to increase for all cases examined.



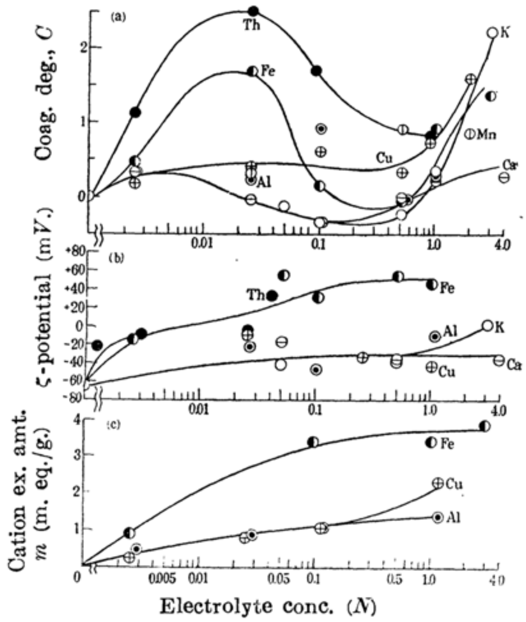
Electrolyte conc. (N)

Fig. 1.—Sedimentation volume of alginic acid powder in various electrolyte solutions.



Electrolyte conc. (N)

Fig. 2.—Values of swelling degree in various electrolyte solutions.



Electrolyte conc. (N)

Fig. 3.—Coagulation degree, electrokinetic potential and cation exchange amount of alginic acid powder in various electrolyte solutions.

The electrokinetic potential was calculated using the equation (7), and shown in Fig. 3b. For the calculation, a/k was equated to $4\pi\eta/D$, (η, being the viscosity coefficient and D the dielectric constant of water) according to the classical Helmholtz theory, since we were not interested here in the exact evaluation of a/k. It can be confirmed that the inversion of sign of ζ-potential takes place with increasing concentrations of electrolyte in the cases of ferric chloride and thorium nitrate and the isoelectric points of alginic acid particle correspond to the maxima of coagulation degree. Besides, the values of swelling degree S and coagulation degree C in various solutions of electrolytes with common cation or anion were measured and shown in Table 3. It seems that the differences of the effects of various electrolytes on coagulation degree are explained by the difference in amount of cation exchange adsorption which was shown in Fig. 3c.

From this table, the following series of decreas-

* Here a fresh sample of alginic acid was used.

ing order were obtained for anions (or cations) composing salt of common cation (or anion), with regard to the degrees of swelling and coagulation.

Table 3
Swelling and coagulation degrees in solutions of electrolytes with common cation or anion

Electrolyte	Conc. (N)	Sed.Vol. (cc./g.)	Swollen Wt., w	Swell. Deg., S	Coag. Deg., C
NH_4Cl	3.00	6.7	2.46	+1.08	+1.45
NaCl	3.00	6.8	2.56	+1.11	+1.47
KCl	3.00	9.4	2.93	+1.73	+2.22
$MgCl_2$	3.00	5.7	2.38	—	—
$CaCl_2$	3.00	5.6	2.51	—	—
$BaCl_2$	3.00	5.9	2.66	—	—
KCl	1.00	4.6	2.23	+1.52	−0.11
KBr	1.00	5.0	2.27	+1.52	+0.11
KNO_3	1.00	5.3	2.43	+1.78	0.0
KI	1.00	6.2	2.51	+1.69	+0.58
KCNS	1.00	7.2	2.33	+1.61	+1.16

Swelling $K > Na > NH_4$, $Ba > Ca > Mg$,
$NO_3 > I > CNS > Br = Cl$

Coagulation $K > Na > NH_4$,
$CNS > I > Br > NO_3 > Cl$

Discussion

Effects of temperature, particle size and redispersing the sediment once settled on the sedimentation volume of alginic acid in 3 N potassium chloride solution shown in Table 1 and 2 seem to indicate the effects of coagulation which has a profound influence upon this phenomenon. According to Buzágh[6], the adhesion force which brings about the coagulation of particles decreases at first and then increases with the rise of temperature in aqueous solution. The coagulation degree may also increase in the case of small particles. The decrease of sedimentation volume caused by redispersing the sediment may be explained by the destruction of the structure once formed by coagulation. Decrease of sedimentation volume in water which is observed on a sample kept dry for several months, may be due to the decrease of swelling. It can be seen in Figs. 2 and 3 a that the contribution of swelling to the sedimentation volume is as a whole larger than that of coagulation in most electrolyte solutions. But in solutions of ferric chloride and thorium nitrate, coagulation is pronounced and swelling effect is weak. In fact, coagulation of particles was observed by the naked eye and the microscope in these solutions. Maxima of coagulation degree were observed at relatively small concentration of ferric chloride and thorium nitrate as shown in Fig. 3 a. These maxima corresponded to the isoelectric points which were detected by the electrokinetic potential measurement. Thus a coagulation degree can be estimated from electrokinetic data. This is similar to the cases of quartz[7] and calcium carbonate[8] powder reported by Buzágh. Increase of the electrokinetic potential is due to the adsorption of polyvalent cations on alginic acid which is evident from the comparison of potential with cation exchange amount m.

(6) A. v. Buzágh, loc. cit. (2).

Summary

The sedimentation volume and swelling degree of alginic acid in electrolyte solutions were measured and the coagulation degree was calculated from these values. It was observed that the coagulation degree showed large values, giving maxima at relatively low concalculated from these values. It was observed nitrate. These maxima corresponded to the isoelectric points shown on the electrokinetic potential curve. A close correlation was seen among coagulation degree, electrokinetic potential and cation exchange amount.

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(7) A. v. Buzágh, *Kolloid-Z.*, **51**, 230 (1930); **52**, 46 (1930); **76**, 2 (1936).
(8) A. v. Buzágh, *Kolloid-Z.*, **83**, 279 (1938).