BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3008—3012 (1975) [Vol. 48, No. 11

Coagulation-dispersion and Precipitation-flotation Behavior of Bentonite and Cadmium-ion Flotation

Toyono INAKAZU,* Koichi KOBAYASHI,** and Tsunetaka SASAKI***

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

(Received December 9, 1974)

The states of dispersion and the precipitation-flotation behavior of bentonite particles in an aqueous solution of hexadecyltrimethylammonium chloride (HTAC) were studied, and the effect of the HTAC on the coagulation and dispersion was discussed in connection with its adsorption on bentonite. The coagulation precipitation of bentonite began to occur at the ratio of the adsorbed amount to an exchange capacity, A/T, of about 0.05. It changed to coagulation flotation in the vicinity of $A/T=1.2$. The change was very sharp. The results suggest that the change from precipitation to flotation is produced by the adsorption of HTAC a little in excess of the first-layer formation, where a slight hydrophilization begins. It seems likely that, in the above state, the bubbles are easily accessible to bentonite particles because the agglomerates assume an open structure. The redispersion occurred near the point of sufficient hydrophilization of bentonite particles because of the adsorption of the second layer of cationic surfactant molecules.

There have been a number of studies of the coagulation and redispersion of suspension by the addition of inorganic electrolytes, macromolecular substances, and surfactants.[1–4] Thus, the sensitizing and stabilizing action of gelation on hydrophobic sol; the addition to the colloidal suspension of an electrolyte with a polyvalent ion with the charge opposite to that of the colloidal, particle, known as the irregular series, is a popular instance.[5] The effect of the addition of ionic[4,6] and nonionic surfactants[7] on the flocculation-deflocculation behavior of sulfathiazole and other suspensions, in particular the bentonite suspension, has also been reported. In such cases, the suspension often foams and the suspended particles coagulate and float. However, such phenomena have not received much attention,[2,8] though they are properly suitable to the removal of many different ions from solutions.

In the present paper, the coagulation and redispersion, accompanied by the precipitation and flotation upon the addition of a cationic surfactant, will be described for the bentonite suspension. The adsorption of the surfactant on bentonite was also studied, and the mechanisms of the coagulation, flotation, and redispersion of bentonite will be discussed in connection with its adsorption on bentonite. Further, the ion flotation of Cd^{2+} ions will be studied in parallel with the bentonite flotation.

Experimental

Materials. The bentonite used was of a commercial grade (origin; Gunma, Japan, montmorillonite type) and was supplied by the Wako Pure Chemical Co., Ltd; the fraction passing through a 350-mesh sieve was collected. A stock suspension of bentonite was prepared first by dispersing the bentonite in distilled water; then it was allowed to stand for 24 hr after shaking. Then, the supernatant solution was taken in the visking dialysis tube and dialyzed while the suspension was being stirred by passing nitrogen gas through it. The dialysis was continued for 5 days, frequently exchanging the outer water with fresh ion-exchange water. The dialysis of the bentonite suspension was continued until a constant specific conductivity of about 10^{-5} Ω/cm was reached. The stock suspension of about 10000—20000 ppm bentonite thus obtained was well shaken before use. A preliminary experiment showed that the bentonite suspension thus prepared scarecely sedimentated at all within a week, but no solution aged longer than a week was used. Pure-grade hexadecyltrimethylammonium chloride (HTAC), supplied by the Kao Soap Co., Ltd., was dried under reduced pressure and kept in a desiccator containing silica gel. The sodium octadecylsulfate (SOS) used for titrating HTAC was obtained from the Kao Soap Co., Ltd., and was used without further treatment.

A stock solution of Cd^{2+} ions of a 1.78×10^{-4} mol/l concentration was prepared by dissolving in nitric acid pure metals (purity>99.99%) kindly supplied from the Laboratory of General Chemistry of our department.

Water was refluxed overnight with a mixture of sulfuric acid and potassium permanganate and then triply distilled using a borosilicate glass apparatus.

All the experiments were carried out at room temperatures from 25 to 27 °C.

Measurement of the Coagulation and Redispersion of Bentonite. Varying amounts of the bentonite suspension and of the HTAC solution were placed in a test tube with a ground-glass stopper, 1.5 cm in inner diameter and 13 cm in length, and the total volume of the solution was made up to 10 ml with water. The pH values of suspension thus prepared ranged from 5.7 to 6.4. The test tube was turned upside down 3 times, then shaken by hand for 10 s again turned upside down 3 times, and finally allowed to stand for 30 min. The appearances of the dispersion, coagulation precipitation, coagulation flotation, and redispersion of the suspension were judged by the naked eye, and the regions of the compositions of systems showing these phenomena were plotted as a diagram.

Measurement of the Adsorption of HTAC on Bentonite. In the ground test tube, a fixed amount of the dialyzed bentonite suspension and varying amounts of the HTAC solution were placed. The volume of the solution was made up to 10 ml with water. After shaking the test tube for 10 s or by turning the test tube upside down 20 times with a 2-min period, bentonite particles were removed from the solution by (a) centrifugation, (b) ultrafiltration, or (c) electrodialysis

---

* Present address: Century Research Center, 2-3, Nihonbashi-Honcho, Chuo-ku, Tokyo 103.

** Address all correspondence to present address: Laboratory of Chemistry, Musashi Institute of Technology, 1-28-1, Tamatsutsumi, Setagaya, Tokyo 158.

*** Present address: Department of Chemistry, Faculty of Science, Tokai University, Hiratsuka, Kanagawa 259-12.

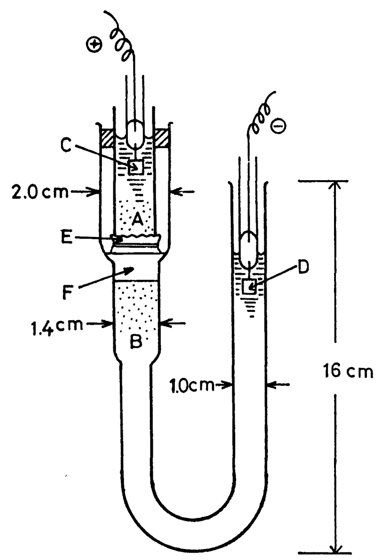

Fig. 1. Apparatus used for electrodialysis. A: glass tube with visking membrane E, B: glass U-tube, C, D: platinum electrodes, F: clear solution for analysis.

as the case required. The concentration of HTAC remaining in the solution was titrated with a SOS solution of a known concentration, with the addition of dilute hydrochloric acid and of bromophenol blue as an indicator.[9]

The amount of HTAC adsorbed on the bentonite was calculated from the difference between the HTAC concentration before and after adsorption. (a) Centrifugation. A suspension containing bentonite particles was centrifuged for 10 min at about 2500 rpm. The aqueous supernatant thus obtained was used for the determination of the HTAC concentration. (b) Ultrafiltration. The aqueous suspension was filtered using a visking membrane supported by a glass filter with a porosity of No. 4 under reduced pressure. The filtrate was then used for the determination of the HTAC concentration. (b) Electrodialysis. Electrodialysis was carried out for a stable suspension containing concentrated HTAC; neither method, (a) or (b), could be applied. The apparatus used for the electrodialysis is shown in Fig. 1.[10] In this figure, a glass tube, A, with a semipermeable visking membrane, E, closing its bottom and a glass U-tube, B, were filled with the solution of a stable bentonite suspension to be dialysed. The tube, A, was adjusted so that the membrane just touched the surface of the solution in the tube, B. The solution in A was renewed after being allowed to stand for 30 min. The electrodialysis was then carried out for 2 to 3 hrs applying a 200-V DC between two platinum electrodes inserted in the solution, as is shown in Fig. 1. The electrodes were 27 cm apart from each other along the axis of the tubes. After the electrodialysis, a transparent layer of the solution was obtained in the tube, B, just below the membrane, which was then carefully taken out for the determination of the HTAC concentration.

Measurement of the Total Base Exchange Capacity of Bentonite.[11] A suspension containing about 4 g of bentonite in 100 ml of a 0.1 M aqueous $BaCl_2$ solution was prepared, and the mixture was stirred for 4 hrs. The precipitates of Ba-bentonite, thus obtained were removed by centrifuging (2500 rpm for 20 min), and the precipitates separated were dispersed in triply distilled water. The free $BaCl_2$ remaining was then removed by dialysis, and the precipitates of Ba-bentonite were again dispersed in a 2: 1 (vol) water-ethanol mixture. The suspension thus obtained was conductometrically titrated with a 0.2 M $MgSO_4$ solution, and the total base exchange capacity of the bentonite was determined from the amount of Mg^{2+} ions added until a sudden increase in the conductance appeared.

Measurement of the Flotation of Cd^{2+} Ions by HTAC. The apparatus and procedure used in the present experiment were the same as have been described in a previous paper.[12] Nitrogen gas humidified with water vapor and controlled to a constant rate of gas flowing was bubbled through a glass filter (No. 4) into a flotation cell containing 10 ml of the sample solution. The concentrations of Cd^{2+} ions before and after flotation were determined by using an atomic absorption spectrometer (Techtron Pty., Ltd., Model-AA-100).

The flotation rate (F) of Cd^{2+} ions is conventionally given by:

$$F = (1 - C_f/C_i) \times 100\%$$

where C_i and C_f denote the concentrations of the Cd^{2+} ions before and after flotation respectively.

Results and Discussion

Coagulation-dispersion Behavior of Bentonite upon the Addition of HTAC. The change in the dispersion state of the bentonite suspension upon the addition of the cationic surfactant HTAC is shown in Fig. 2. As may be seen in the figure, each region—dispersion, coagulation precipitation, coagulation flotation, and redispersion— is distinct.

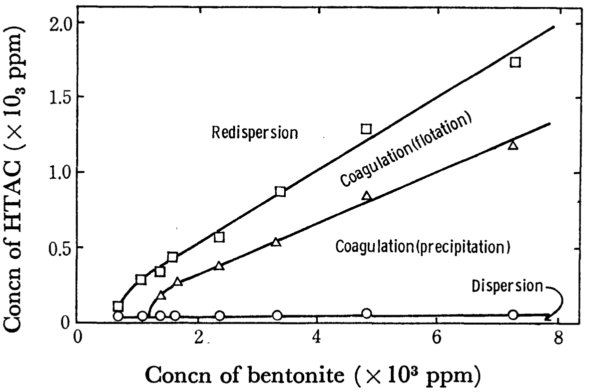

Fig. 2. Effect of HTAC on bentonite suspension.

Dispersion Region. Immediately after the preparation of the solution, the aggregates form slightly, but after shaking they disappear and the suspension is stable even after 30 min. The amount of HTAC is thus insufficient to produce coagulation in this region.

Coagulation Precipitation Region. On an increase in the amount of HTAC, with the amount of bentonite kept constant, fluffy aggregates begin to precipitate. The sedimentation volume increases with a further increase in the amount of HTAC, and a turbid supernatant gradually changes to a clear one.

Coagulation Flotation Region. On a further increase in the amount of HTAC, a sharp point is arrived at which aggregates change suddenly the state of preciptation to that of flotation, while the bentonite particles are still in an aggregated state. In this region, the suspension is readily coagulated by shaking and the coagulates quickly rise to the aqueous surface, leaving a transparent solution below.

Redispersion Region. On continuing the addition of HTAC, the state is arrived at in which the aqueous phase begins to become turbid; this turbidity increases with an increase in the amount of HTAC, while the amount of bentonite floated decreases until the coagulates completely disappear. The foam formation is observed for a sufficiently concentrated solution of HTAC.

The above observation of the change in the dispersion state with an increase on the amount of HTAC leads to the consideration that the coagulation-redispersion and precipitation-flotation phenomena are closely related to the nature of the outermost surface of the bentonite particles modified by the increasing adsorption of HTAC with the concentration. The increase in the amount of adsorption is considered to change the surface properties gradually from those favorable for coagulation precipitation through coagulation flotation to redispersion. To confirm such a reasoning, the following measurements were carried out.

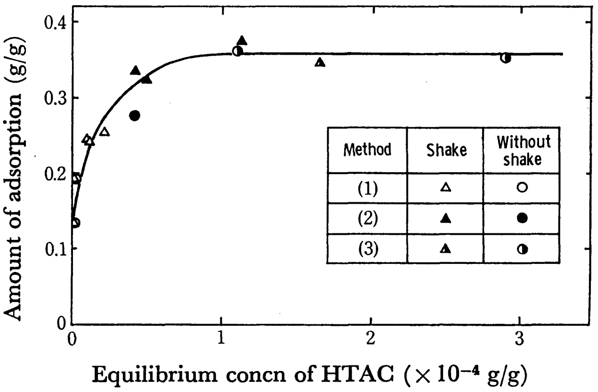

Fig. 3. Adsorption isotherm of HTAC on bentonite. (1) centrifuge, (2) dialysis, (3) ultrafiltration

Amount of the Adsorption of HTAC. The amount of HTAC adsorption of bentonite is plotted against the equilibrium concentration in Fig. 3. The values obtained by the various methods mentioned above may be seen to agree with each other. A sharp initial increase in the amount of adsorption and the saturated adsorption at a low HTAC concentration show the almost complete adsorption of added HTAC on the bentonite up to saturation. Such behavior is indicative of the exchange adsorption being rapid and quantitative. The saturated adsorption is obtained in the region of equilibrium HTAC concentrations larger than 1×10^{-4} g/g water. The fact that the amount adsorption is independent of the shaking also shows that the adsorption of HTAC on air bubbles is negligible.

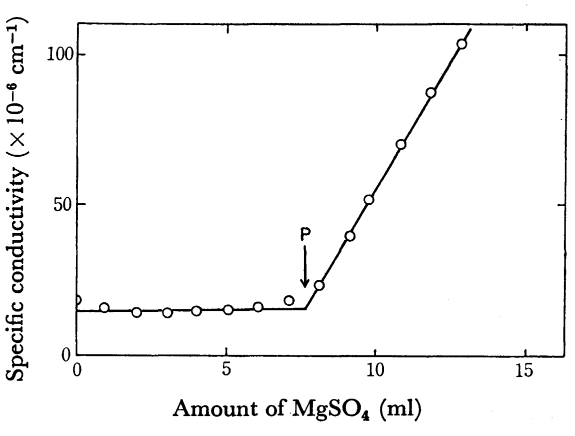

Fig. 4. Conductometric titration of Ba-bentonite. P: total exchange capacity of bentonite.

Total Base Exchange Capacity of Bentonite. In order to measure the exchange capacity of bentonite, the conductance of the Ba-bentonite suspension is plotted against the volume of $MgSO_4$ added in Fig. 4. The exchange capacity, as calculated from the break point corrected for the moisture content of the bentonite, is 42.5 m. e./100 g dry bentonite. The value obtained is somewhat smaller than the value from 60 to 100 m. e./100 g previously reported for bentonite.[13)]

Effect of the HTAC Adsorption on Coagulation and Redispersion. In order to study the relation between the adsorption of HTAC and the coagulation-redispersion behavior of bentonite shown in Fig. 2, the amount of adsorption of HTAC on the bentonite was calculated for the system corresponding to the points on the line of Fig. 2. The amount of adsorption, Γ, can be calculated as the intersection of the isotherm, Γ *vs.* C, shown in Fig. 3 and the straight line where M and m denote the

$$M = m\Gamma - CV$$

total amount of HTAC and the amount of bentonite taken up respectively, and V, the volume of the solution, all of which are known constants corresponding to a given point in Fig. 2. The amount of adsorption thus calculated is shown in Table 1, together with the ratio of the adsorbed amount (A) to the exchange capacity (T).

TABLE 1. EFFECTS OF HTAC ADSORPTION ON COAGULATION—DISPERSION AND PRECIPITATION—FLOTATION

Concn of bentonite (ppm)	Coagulation precipitation		Coagulation flotation		Redispersion	
	$A^{a)}$	$A/T^{b)}$	$A^{a)}$	$A/T^{b)}$	$A^{a)}$	$A/T^{b)}$
3000	0.016	0.12	0.154	0.13	0.236	1.75
4000	0.009	0.07	0.162	1.19	0.243	1.79
6000	0.007	0.05	0.165	1.21	0.245	1.80

a) Minimum amount of adsorption. b) Ratio of minimum amount of adsorption (A) to exchange capacity (T).

It may be seen that coagulation begins at a very low A/T ratio of about 0.05 and that the coagulation precipitation changes to the coagulation flotation at about $A/T=1.2$, *i.e.*, at an amount of adsorption slightly above the exchange capacity, and that the redispersion begins at an A/T ratio larger than about 1.8. On the basis of these experimental results, the state of the adsorption of the cationic surfactant on the bentonite to produce coagulation and redispersion is illustrated in Fig. 5.

In this figure, (a) and (b) show the HTAC adsorption on the single bentonite particle and the state of aggregation of such particles respectively in each concentration range of Fig. 2. At a very concentration of HTAC, the bentonite is dispersed despite the adsorption of the

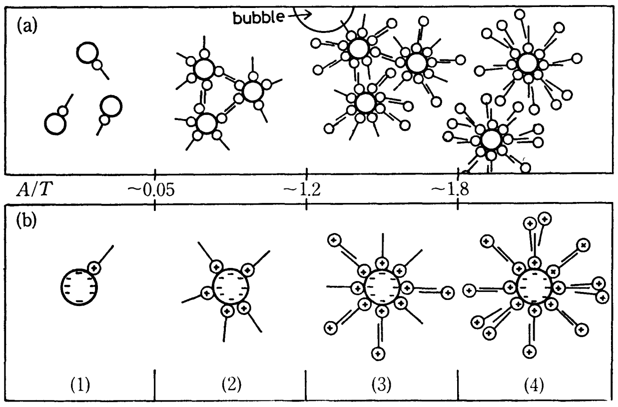

Fig. 5. Adsorption of HTAC and state of dispersion of bentonite (a) and adsorption of HTAC on a bentonite particle (b). (1) dispersion, (2) coagulation precipitation, (3) coagulation flotation, (4) redispersion.

cationic surfactant. With an increase in the concentration of the cationic surfactant, the surface of the particles is rendered hydrophobic by the increasing amount of the adsorption of HTAC, with its hydrophobic tail directed outward, and the coagulation of particles is promoted by the hydrophobic binding of these adsorbed molecules. Since there are no sufficient molecules available for adhering to bubbles, coagulated particles precipitate. As the amount of adsorption increases and comes slightly to exceed the exchange capacity, namely, $A/T > 1.2$, double-layer adsorption takes place, as is shown in Fig. 5, and the coagulates assume an open structure favorable for bubble attachment, resulting in coagulation flotation. At A/T ratios larger than 1.8, the double-layer adsorption is nearly completed and the bentonite particles are rendered hydrophilic, resulting in a redispersion of the particles. In this state, the bentonite particles have sufficient positive charges as a result of the adsorption of the cationic surfactant.[14] This reversl. of the charge was also confirmed by electrodialysis measurements.

Flotation of Cd^{2+} Ions by HTAC and Bentonite. There are various possible types of methods of ion flotation.[15] The combined use of bentonite and a cationic surfactant is especially effective for the removal of both anion and cations in the solution.[16] From this fact, together with the phenomena of coagulation flotation and precipitation mentioned above, the bentonite-cationic surfactant system is considered to be suitable for the flotation of ions in an aqueous solution. Here, cadmium ions are selected as the ions to be floated. The flotation was carried out for a solution containing 1.78×10^{-5} mol/l Cd^{2+}, 1000 ppm bentonite, and varying concentrations of HTAC under a gas-flow rate and a time of 10 ml/min and 7 min respectively and at pH 11.2. The results are shown in Fig. 6.

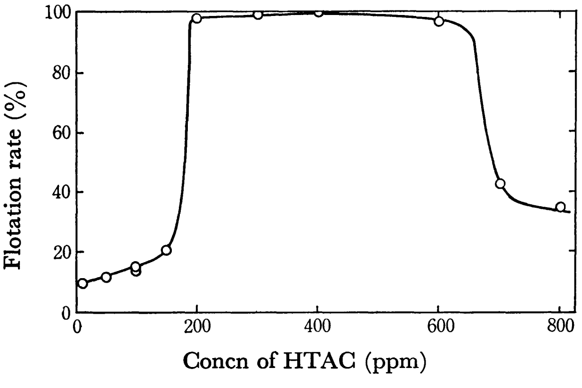

Fig. 6. Rate of Cd^{2+} ion flotation *vs.* concn of HTAC. Cd^{2+}: 1.78×10^{-5} mol/l, bentonite: 1000 ppm, pH: 11.2, gas-flow time: 7 min, gas-flow rate: 10 ml/min, pH adjusted by NaOH.

As may be seen, the flotation rate, F, increases rapidly at an HTAC concentration of about 150 ppm, shows a flat maximum of about 98% in the region of HTAC concentrations from 200 ppm to 600 ppm, and decreases at concentrations of HTAC larger than about 600 ppm. In the region of HTAC concentrations from 200 ppm to 600 ppm, the solutions after flotation look quite transparent, while in the other region of HTAC concentrations they look opaque. These facts indicate that the region of coagulation flotation shown in Fig. 2 corresponds to the optimum region of ion flotation, although the former does not coincide with the latter, perhaps because of difference in the pH at which the flotation measurements were carried out. A rapid decrease in the flotation rate above 600 ppm HTAC may be explained by a redispersion of the bentonite in addition to the replacement of the Cd^{2+} ions on the bentonite by HTAC. It was further confirmed that a stable foam layer was produced for the bentonite concentrations larger than about 400 ppm.

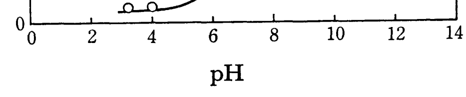

Fig. 7. Rate of Cd^{2+} ion flotation *vs.* pH.
Cd^{2+}: 1.78×10^{-5} mol/l, bentonite: 600 ppm, HTAC: 200 ppm, gas-flow time: 7 min, gas-flow rate: 10 ml/min, pH adjusted by NaOH.

Figure 7 shows the flotation rate *vs.* pH curve under the optimum conditions specified in the figure. As may be seen, the flotation rate begins to increase from almost zero at around pH; the maximum flotation rate of 99% was observed at about pH 11. From these experiments, it may be concluded that the optimum conditions for the bubble flotation of Cd^{2+} ions exist in the region of coagulation flotation and that the region is relatively wide with respect to the amount of HTAC, while it is rather narrow for hydrogen-ion-concentration change, as expressed by the pH. Since the bentonite and the HTAC are confirmed to be removed together with the Cd^{2+}, the above conditions are also the optimum ones for these additives.

References

1) A. S. Michael, *Ind. Eng. Chem.*, **46**, 1485 (1954); M. Noda, *Kogyo Yosui*, No. 25, 60 (1960); *ibid.*, No. 26, 26 (1960); *ibid.*, No. 27, 34 (1960); Y. Toyoshima, *ibid.*, No. 30, 34 (1961); *ibid.*, No. 31, 50 (1961); K. Meguro, *Kogyo Kagaku Zasshi*, **58**, 905 (1955); *Nippon Kagaku Zasshi*, **77**, 72 (1956); **77**, 77 (1956); K. Meguro and T. Kondo, *Nippon Kagaku Zasshi*, **76**, 642 (1955); This Bulletin, **32**, 267 (1959); H. Arai, F. Shigehiro and I. Maruta, *Kogyo Kagaku Zasshi*, **68**, 1090 (1965).

2) V. H. Lange, *Kolloid-Z*, **211**, 106 (1966).

3) R. E. Grim, W. H. Allaway, and F. L. Cuthbert, *J. Amer. Ceram. Soc.*, **30**, 137 (1947); *ibid.*, **30**, 142 (1947).

4) J. P. Law, Jr., and G. W. Kunze, *Soil Sci. Soc. Amer. Proc.*, **30**, 321 (1966); *ibid.*, **30**, 327 (1966).

5) H. R. Kruyt, "Colloid Science," Vol. II, Elsevier Pub. Co. Inc., New York (1949), p. 207.

6) Y. Nakamura, A. Otsuka, and M. Nakagaki, *Yakugaku Zasshi*, **94**, 833 (1974).

7) M. Nakagaki, and N. Kawamura, *ibid.*, **90**, 699 (1970); A. Otsuka, H. Sunada, and Y. Yonezawa, *J. Pharm. Sci.*, **62**, 751 (1973).

8) T. Sasaki, In "Bunri to Seisei," Jikken Kagaku Koza, Ser. 2, Vol. 2, Sec. 15, pp. 565—603; T. Sasaki, *Nippon Kogyo Kaishi*, **85**, 610 (1969).

9) G. S. Hartley and D. F. Runnicler, *Proc. Roy. Soc., Ser. A*, **168**, 420 (1938).

10) S. Okazaki and T. Sasaki, *Kolloid-Z*, **178**, 97 (1961).

11) M. M. Martley and J. L. Mellor, *Soil Sci. Soc. Amer. Proc.*, **18**, 363 (1954).

12) K. Kobayashi, This Bulletin, **48**, 1180 (1975).

13) T. Sudo, "Clay Mineral," Iwanami Zensho, (1969), p. 197.

14) L. Ter. Minassian-Saraga, *J. Chim. Phys.*, **63**, 1278 (1966).

15) R. Lemlich, "Adsorptive Bubble Separation Techniques," Academic Press, New York and London (1972).

16) E. Fukada, K. Kobayashi, and T. Sasaki, This Bulletin, to be published.