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The Influence of Surface-Active Agents on Kaolinite

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The influence of surfactants (CTAB and SDS) on suspensions of monoionic kaolinite (Na^+ and H^+ form) was investigated by adsorption, sedimentation, turbidity, electroosmosis, and rheological measurements, at pH = 3.3 and 10.0. Only small differences are found between the Na^+ and H^+ forms of the kaolinite. The data can be accounted for satisfactorily by a mathematical model based on the DLVO theory for face-face, edge-edge, and edge-face interactions, if some assumptions on the local ψ_6 potentials near edge and face type surfaces are introduced.

INTRODUCTION

Kaolinite particles have two different surfaces (edges and faces) (1), which differ even in sign of the surface charge at some pH values. Because of this, different types of interaction between kaolinite particles in aqueous suspension are possible (edge-edge, edge-face, and face-face) (1, 2), and kaolinite suspensions in water show a rather complex rheological behavior (3, 4) dependent primarily on pH. In addition, other ions (e.g., those of ionogenic surfactants) change the charges on the kaolinite particles (cf. data on analogous systems (5)).

The aim of the present investigation was to correlate the changes effected by cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) on the rheological properties of kaolinite suspensions, with data on adsorption, electrokinetics, and sedimentation; moreover a mathematical model was looked for which can take account of these effects. It was thought especially interesting to check whether the influence of surfactants on the rheological properties of kaolinite suspensions can be accounted for by electrostatic stabilization without invoking the hydro-

philic or hydrophobic character of the surface.

EXPERIMENTAL

Materials

Kaolinite. Monarch kaolinite from Georgia, mined by Cyprus Industrial Minerals Company and obtained through the N. V. Koninklijke Sphinx in Maastricht (Netherlands) was used in this study. The X-ray diffraction diagram, obtained by using a Philips diffractometer PW 1120 with Ni-filtered $\text{Cu } K_\alpha$ -radiation showed that the Monarch kaolinite used, was a well-crystallized kaolinite with no detectable amounts of quartz, illite, or montmorillonite.

The crystallinity index, according to Hinckley (6), is 1.14. From electron micrographs of the kaolinite mineral, shadowed at 30° to the plane of the grid, an axial ratio of 9.6 (twice the radius-height ratio) has been calculated. Street and Buchanan (7) mention for the axial ratio of their kaolinite a value of 11–12 and Norton and Johnson (8) give a value of 7.7–8.2.

From a sedimentation analysis with tetrasodium pyrophosphate as peptisator (9, 10) the average equivalent spherical diameter

TABLE I
Chemical Analysis

	Kaolinite			
	Theoretical	Monarch	H ⁺ -Kao- linite	Na ⁺ -Kao- linite
SiO ₂	46.54	45.60	45.50	45.60
Al ₂ O ₃	39.50	38.60	38.60	38.60
Fe ₂ O ₃	—	0.34	0.34	0.34
TiO ₂	—	1.37	1.37	1.36
CaO	—	—	—	—
MgO	—	—	—	—
K ₂ O	—	0.06	0.06	0.06
Na ₂ O	—	—	—	—
Ignition loss	13.96	13.88	13.91	13.90

was calculated to be 2.8 μm (11). Together with the axial ratio of 9.6 the average diameter and thickness of the kaolinite particles were calculated as 4.54 and 0.473 μm , respectively.

Specific surface was determined by N₂ adsorption in an Areometer ("Ströhlein") based on the BET method. The value obtained was 6.67 m²/g kaolinite. Specific gravity obtained by the use of a pycnometer, was 2.58 g/cm³. The chemical composition of the Monarch kaolinite was determined by X-ray fluorescence analysis using a Philips spectrofotometer PW 1270/10. The results together with the theoretical composition of the ideal kaolinite structure given in Table I.

The organocarbon content of the Monarch kaolinite, determined with a modified potassium dichromate method (wet combustion) (12, 13, 14, 15) was found to be 450 $\mu\text{g g}^{-1}$. This value can be regarded as typical compared to the value of about 500 $\mu\text{g g}^{-1}$ usually found for kaolinites (16).

The cation exchange capacity (cec) was determined with two methods, firstly the ammonium acetate method (17) revealing a value of 1.2 meq/100 g kaolinite and the methylene blue method, revealing a value of 1.8 meq/100 g kaolinite. The pH was measured of a suspension containing 10 g of kaolinite and 100 g of doubly distilled water with pH meter Electrofact type 53A com-

bined with a Philips CA 42 D (single-rod assembly) measuring cell. The pH resulting from this experiment was 4.15.

In clay colloid chemistry it is often necessary to study the behavior of clay suspensions with different cation compositions. An extensive treatment of the different methods of preparation is given in (11).

The method used here, a modification of the method described by Worrall and Ryan (18), employs exchange of ions between a cation exchange resin in sodium and hydrogen form (Dowex 50W-X8) and the kaolinite in suspension in a batch procedure.

The monoionic sodium kaolinite and hydrogen kaolinite, thus prepared, were tested after drying with regard to various properties to ensure that no changes had occurred in the kaolinite mineral. No changes in the X-ray diffraction pattern could be observed in relation to the raw kaolinite. Also the crystallinity index was almost equal for both, viz., sodium kaolinite 1.12 and hydrogen kaolinite 1.09.

The chemical analysis of the monoionic kaolinites incurs no important changes (see Table I), furthermore no increase is found in the organocarbon content of the monoionic kaolinites. The pH of the suspension of 10 g of kaolinite to 100 g of doubly distilled water was 3.25 for the hydrogen kaolinite and 5.85 for the sodium kaolinite.

The determination of the specific surface by N₂ adsorption in an area meter yielded a value of 6.67 m²/g and 6.76 m²/g for sodium kaolinite and hydrogen kaolinite, respectively.

The conclusion, that well-defined monoionic kaolinite can be prepared with a batch procedure, is justified.

Surface-active agents. SDS: *ex* Merck-Schuchardt (purity greater than 90%). The critical micelle concentration (CMC) at 23 \pm 1°C, measured by the conductivity method (19, 20), was 7.8×10^{-3} M, agreeing with literature data (21). CTAB: *ex* Fluka A.G. (purity 98.5%). The CMC at 23 \pm 1°C was 0.95×10^{-3} M, in agreement

with literature data (22). Water: Doubly distilled water was used with a specific conductance of 1 to $3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ and a pH of 5.6.

Methods

The electrokinetic properties of the monoionic kaolinite suspensions which are described here were measured in suspensions of 10 g of kaolinite in 100 g of suspension.

The kaolinite suspension was prepared in a $10^{-3} M$ NaBr solution, which had been saturated toward the kaolinite concerned during one week by daily shaking for half an hour. The NaBr used was of pro analysi grade (*ex* Union Chimique Belg.)

To obtain the pH required for the experiments, HCl and NaOH solutions prepared from titrisol (*ex* Merck) were used. An absorption time of 2 hours was adopted to obtain equilibrium conditions. The amounts of SDS and CTAB adsorbed were calculated from the difference between initial (C_0) and equilibrium (C_{eq}) concentration. The concentration of SDS was measured with a modified two-phase titration according to Epton (23, 24). The amount of CTAB in solution was determined by a titration in glacial acetic acid (25, 26).

Because our kaolinite suspensions sediment under some experimental conditions, we measured the ζ potential with electro-osmosis. The electrokinetic potentials were measured using an apparatus (27), similar to the one described by Lange and Crane (28) and Verwey (29). The ζ potentials were calculated from the data obtained with the formula of Von Smoluchowski (30) using the "rationalized" version introduced by Hunter (31).

No corrections have been made for the so-called relaxation effects (32). With the geometrical data the κa in the case of face-face interaction is 227 and in the case of edge-edge interaction is 23.7. The net charge

behind the electrokinetic slipping plane was calculated using the theory of the electrical double layer according to Gouy (33, 34) and Chapman (35).

This net charge has been calculated using the equation for flat plates, derived for the case of single monovalent binary electrolytes in solution.

The same suspensions were used for sedimentation experiments. Aliquots of 20 ml of suspension were pipetted in measuring cylinders having a diameter of 1.6 cm. The cylinders were closed with a rubber stopper and placed in a room with a temperature of $23^\circ\text{C} \pm 1^\circ\text{C}$. The levels of the interface of the supernatant and sedimented kaolinite were measured at certain times during a period of 2 weeks, after which the sedimentation volume appeared to have reached a constant value.

In the same experiments the turbidity of the supernatant was determined by a method similar to that of Slater and Kitchener (36) and Dollimore (37-39).

Rheological properties were investigated for suspensions with 100 g of kaolinite in 200 g of suspension. The suspensions were mixed thoroughly with a Combimix RM 46 (Janke and Kunkel K. G.) at 300 rpm for 1 hour. An adsorption time of 2 hours was adopted for the surfactants, during which the suspensions were stirred in the same way as mentioned above. After the rheological measurements, the suspension left was centrifuged to determine the equilibrium concentration of the surfactants in the supernatant liquid.

Measurement of the shear stress of a kaolinite suspension as a function of the rate of shear was carried out using a Haake Rotovisko RV3 with a rotating inner cylinder and a stationary outer cylinder. Measuring body MVI ($R_1 = 20.04 \text{ mm}$; $R_0 = 21 \text{ mm}$) was used. The range of shear values from 0 to 2340 sec^{-1} was covered in 10 min.

No distinct hysteresis between scanning with increasing and decreasing shear rate was observed.

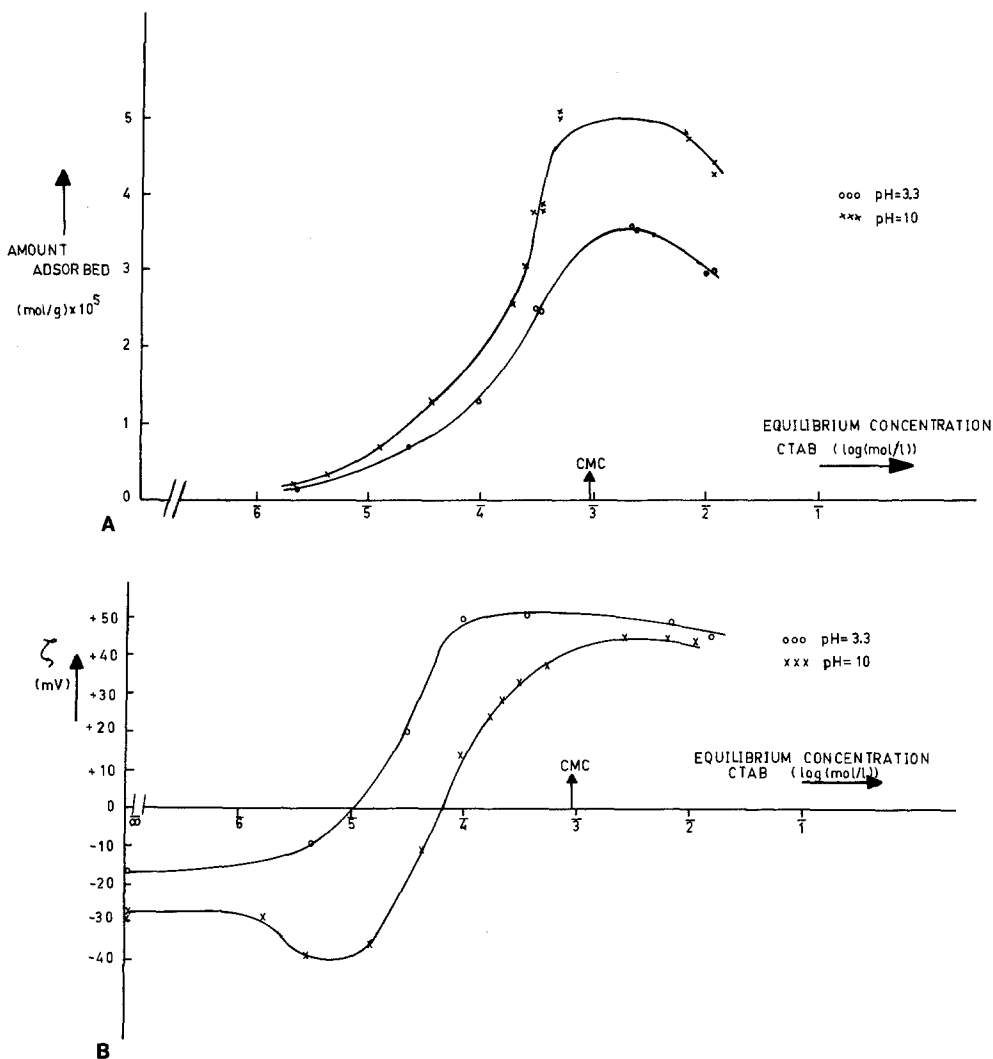


FIG. 1. The amount adsorbed (A), the ζ potential (B), the charge behind the electrokinetic slipping plane (C), the sedimentation volume (D), and the turbidity of the supernatant (E) as a function of the concentration CTAB for Na-kaolinite at two different pH-values.

Results and Discussion

Figures 1 and 2 show the results obtained for Na-kaolinite with regard to the amount of surfactant adsorbed, the ζ potential, the net charge behind the electrokinetic slipping plane, the sedimentation volume, and the light transmission of the supernatant liquid. Similar data were obtained for H-kaolinite.

The adsorption isotherm consists of three parts: part 1, characterized by a low increase in adsorption with surfactant concentration; part 2, characterized by a strong increase in the slope of the isotherm; and part 3, again characterized by a lower increase; in some cases even a decrease is suggested in adsorption in the neighborhood of the CMC of the surfactant involved.

The interpretation of the first two parts

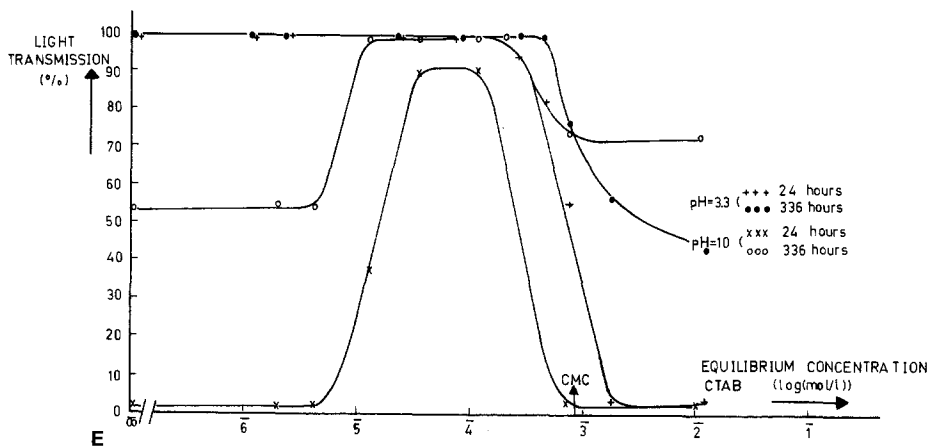
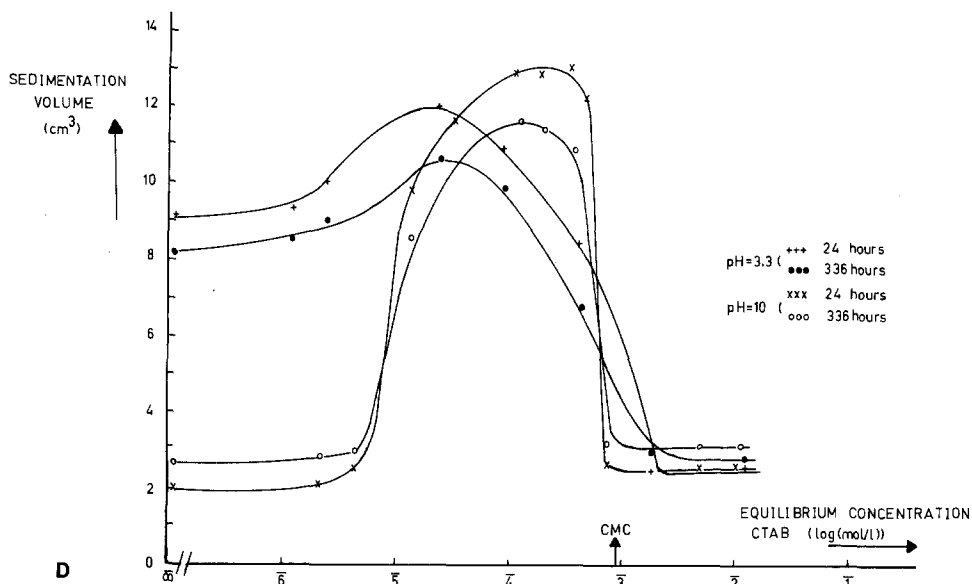
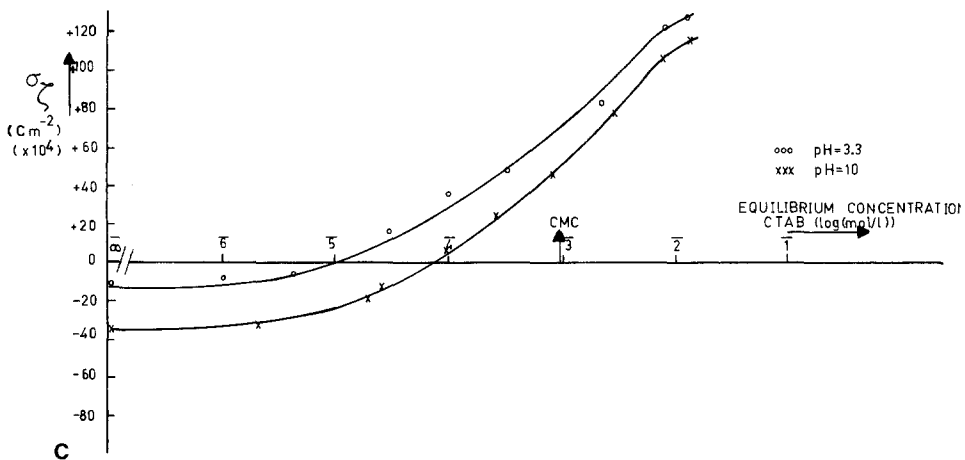


FIG. 1—Continued.

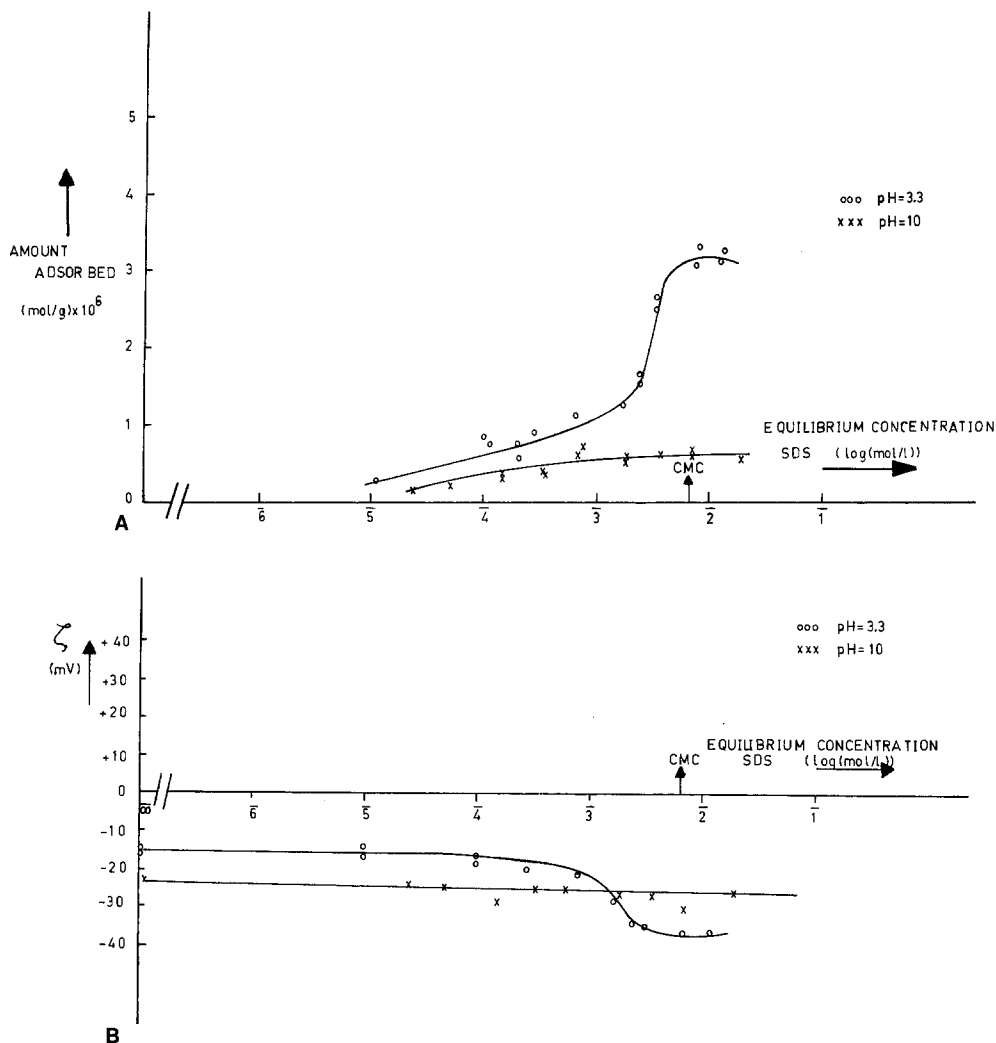


FIG. 2. The amount adsorbed (A), the ζ potential (B), the charge behind the electrokinetic slipping plane (C), the sedimentation volume (D), and the turbidity of the supernatant (E) as a function of the concentration SDS for Na-kaolinite at two different pH-values.

can be identical to the one given by Fuerstenau and co-workers (40–42) in terms of the hemimicelle hypothesis.

Part 3 lies beyond the concentration range investigated by Fuerstenau *et al.* A decrease in adsorption in part 3 is also reported by Zimmels (20, 43). This observation has also been made by Vold and Phansalkar (44) and Fava and Eyring (45). Other experiences of this effect and explanations are summarized by Moilliet *et al.* (46).

From the changes in the ζ potential as a function of the CTAB concentration it is evident that with increasing equilibrium concentration, after a start of almost negligible dependence, the ζ potential increases and reaches its maximum at the range of the conventional CMC.

The relation of the ζ potential and the SDS concentration at pH = 3.3 follows a pattern inverse to that for CTAB. In the case of pH = 10 the ζ potential is almost

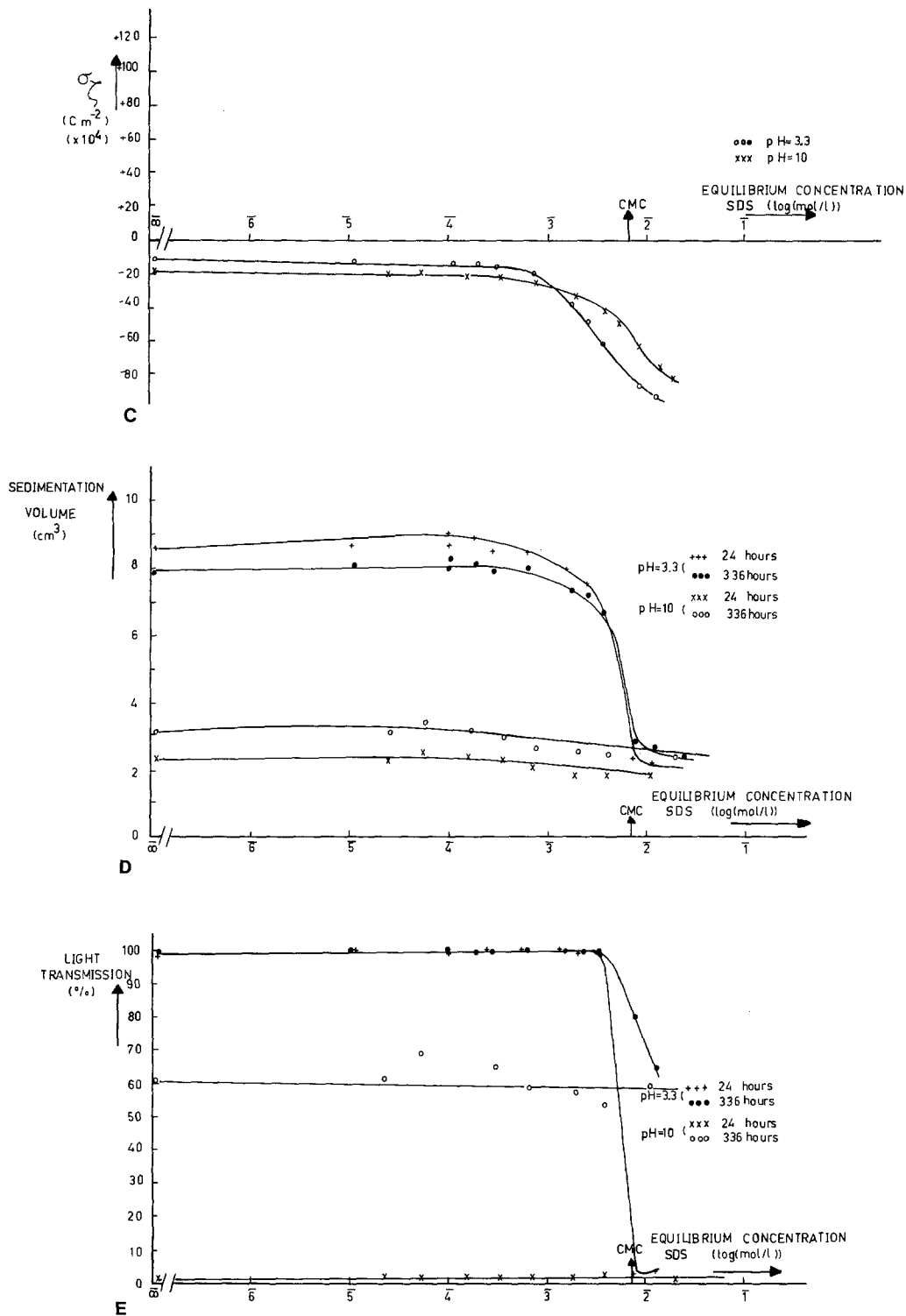


FIG. 2—Continued.

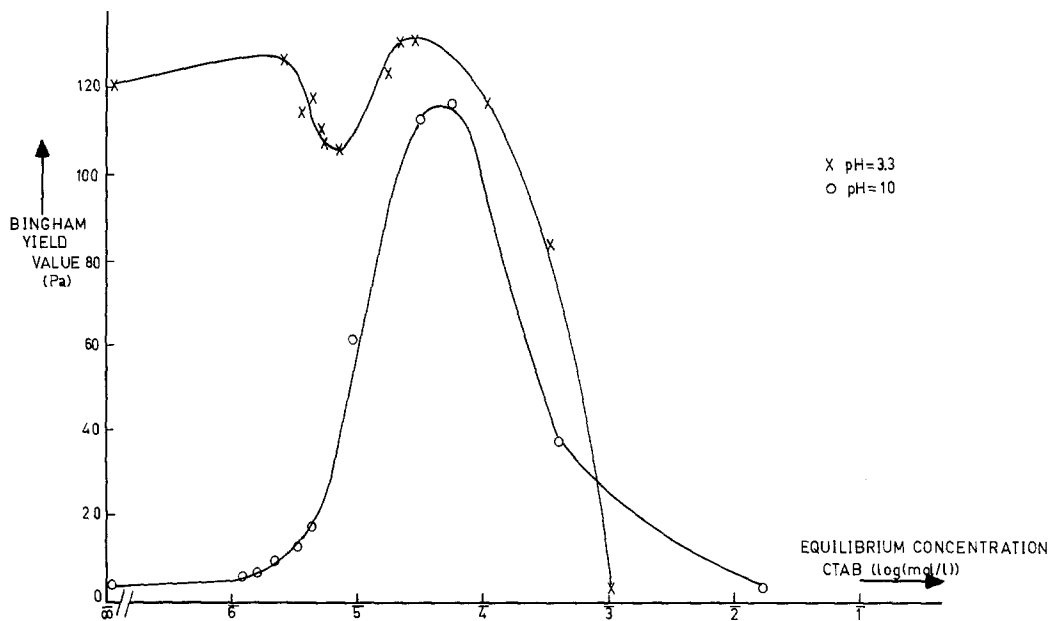


FIG. 3. The Bingham yield value of Na-kaolinite as a function of the equilibrium concentration CTAB.

independent of the SDS concentration. The sedimentation volume (graph D) increases at low pH with increasing cationic detergent CTAB to a maximum. However, with further increasing concentration the sedimentation volume decreases. From the turbidity of the supernatant (graph E) under the same conditions, one can conclude that the suspension then becomes partly deflocculated.

At high pH-values the increasing amount of cationic detergent CTAB changes the structure from a deflocculated one (at concentrations below $10^{-5} M$) into a flocculated one with a very high sedimentation volume (at concentrations between $10^{-5} M$ and somewhat below CMC). At even higher concentrations the suspension becomes deflocculated again.

Influence of the anionic detergent SDS is restricted to the low pH range, because at high pH values both faces and edges are negatively charged. At low pH values the kaolinite suspension which was flocculated becomes deflocculated at high concentrations of SDS.

The results of rheological measurements for Na-kaolinite are shown in the Figs. 3 and 4. Again, the results obtained with H-kaolinite were similar to those obtained with Na-kaolinite. In the figures, the Bingham yield value is shown; graphs showing the (shear dependent) viscosity at one particular shear rate (2340 sec^{-1}) vs the surfactant concentration show a similar course. The differential viscosity is not influenced noticeably by surfactant additions.

In order to correlate these results with the adsorption and ζ potential data, calculations on the interactions between kaolinite particles were carried out, on the basis of the following assumptions:

1. The interaction between the "face" surfaces of two kaolinite particles (face-face interaction) was described by Verwey and Overbeek's formula for electrostatic interaction between two flat plates (47) and de Boer's formula for the van der Waals attraction between flat plates (48).

2. The interaction between the "edge" surfaces of two kaolinite particles (edge-edge interaction) and that between the

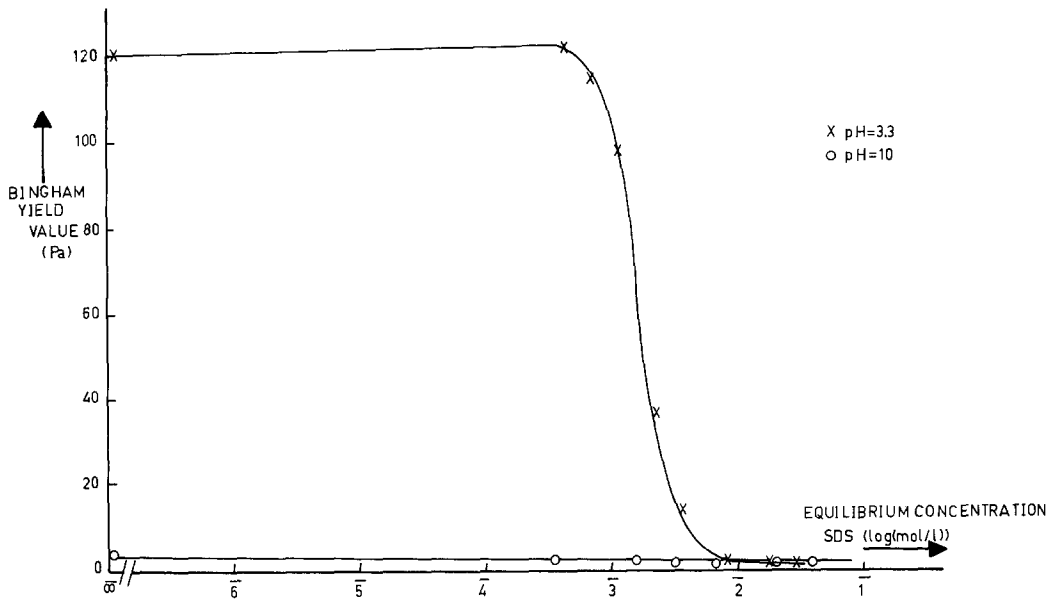


FIG. 4. The Bingham yield value of Na-kaolinite as a function of the equilibrium concentration SDS.

“edge” surface of one particle and the “face” surface of another (edge–face interaction) were described by Hogg, Healy, and Fuerstenau’s formula for electrostatic interaction (49) and Hamaker’s formula for van der Waals attraction (50) for two spherical particles with unequal radii. As “radius” for an edge surface was taken $0.237 \mu\text{m}$, as “radius” for a face surface was taken $2.27 \mu\text{m}$.

3. The influence of adsorbed surfactant layers on the van der Waals attraction was taken into account through a formula analogous to that used by Vincent (51). In order to simplify the calculations, a jump function for the thickness of these layers was assumed: at surfactant concentrations lower than that corresponding to charge reversal of the ζ potential, no adsorbed layer is taken into account; at larger surfactant concentrations, a monolayer is thought to be present.

4. The Stern potential ψ_δ was taken to be equal to the ζ potential, in agreement with Lyklema’s data on AgI (52). However, the kaolinite particles are not uniformly charged since the “edges” behave differently from

the “faces.” This was taken into account by assuming that for one type of surface (edge or face) the local ζ potential is 0, if $\partial^2 \zeta_1 / \partial (\ln c)^2 = 0$ (c = surfactant concentration). Here ζ_1 is the overall electrokinetic potential of the kaolinite particles, calculated as if they had only one type of surface. Because there are in reality two different types of surface, $\zeta_1 \neq 0$ when $\partial^2 \zeta_1 / \partial (\ln c)^2 = 0$. The value for ζ_1 under these conditions is then ascribed to the other type of surface; it should be corrected since that type of surface accounts only for part of the total surface (82.6% for faces, 17.4% for edges for the samples investigated). It should be noted that the criterion for taking the local ζ potential of one type of surface = 0, viz., $\partial^2 \zeta_1 / \partial (\ln c)^2 = 0$, implies that near the other type of surface where $\zeta \neq 0$, $\partial^2 \zeta / \partial (\ln c)^2 = 0$.

Further assumptions were that the local “face” potential is not affected by the pH (4) and is constant in the case of adsorption of SDS at low pH; the “edge” potential on the contrary is a function of pH but independent of [CTAB] at low pH.

5. For kaolinite, a value of the Hamaker

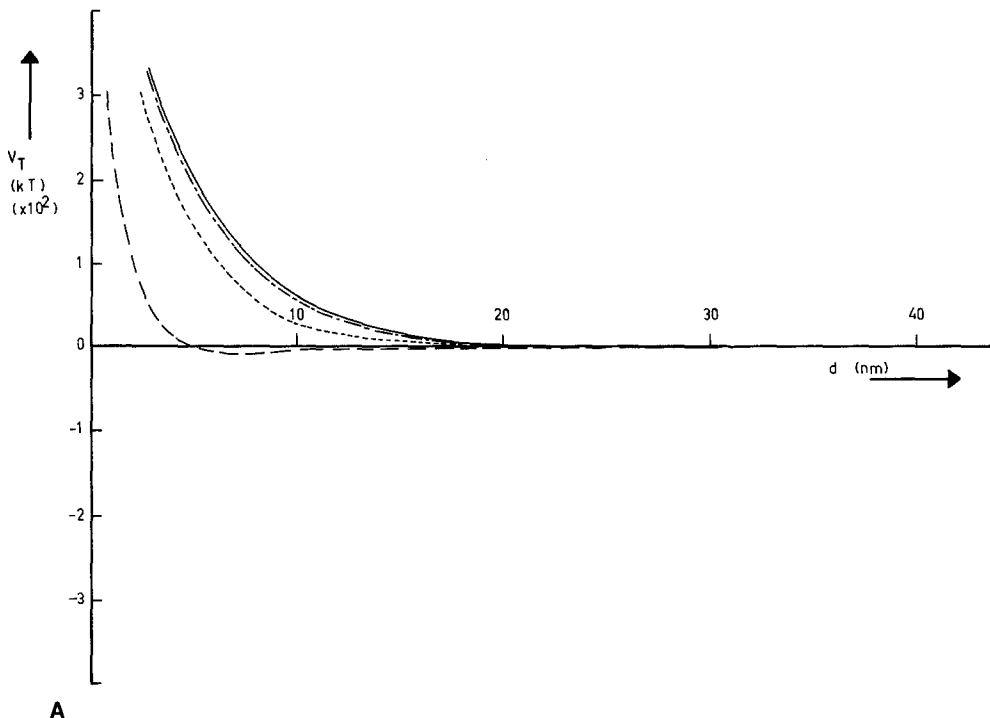


FIG. 5. The total energy of interaction V_T for edge-edge (A), edge-face (B), and face-face (C) interaction as a function of the half-distance of separation d at $\text{pH} = 3.3$. (—, no CTAB; ·····, $2.5 \times 10^{-5} M$ CTAB; ---, $10^{-4} M$ CTAB; - · - · - , $10^{-3} M$ CTAB; and — — —, $1.7 \times 10^{-2} M$ CTAB).

constant of $2.6 \times 10^{-20} \text{ J}$ was calculated from the formulae of Visser (53) (cf. the data of Fowkes (54) showing that Hamaker constants for most oxidic materials in water are comprised between 3 and $8 \times 10^{-20} \text{ J}$). If an adsorbed surfactant layer is taken into account, then for its inner part (thickness $0.3 \mu\text{m}$) a Hamaker constant somewhat lower than that of the oxidic material is chosen, viz., $2 \times 10^{-20} \text{ J}$. For its outer part (estimated thickness $2.3 \mu\text{m}$ (for CTAB, $2.1 \mu\text{m}$ for SDS), a Hamaker constant equal to that of the medium, twice distilled water is chosen).

Figure 5 shows typical results for $\text{pH} = 3.3$ in CTAB containing solutions. The results can be summarized (for a more detailed treatment of the calculations see Ref. (11)) and compared with experimental data as follows:

1. *Influences of CTAB at $\text{pH} = 3.3$* (see

Fig. 5). The calculations predict the following behavior: At low CTAB concentrations, only EF coagulation occurs ($\zeta_E > 0$, $\zeta_F < 0$). Near $2.5 \times 10^{-5} M$, both EF and FF coagulation occur ($\zeta_E > 0$, $\zeta_F \approx 0$). At larger CTAB concentrations, no type of coagulation is possible. ($\zeta_E > 0$, $\zeta_F > 0$).

These results contradict the statement by Goodwin (55) that in kaolinite suspensions face-face coagulation never occurs, which is itself rather strange because of the existence in nature of stocks of kaolinite particles (56).

EF coagulation at very low [CTAB] explains the large sedimentation volume, low turbidity, and high Bingham yield values in this region. With increasing [CTAB], the Bingham yield value decreases; this can be explained by the assumption that some CTA^+ ions are adsorbed on the faces lowering their (negative) surface charges, which

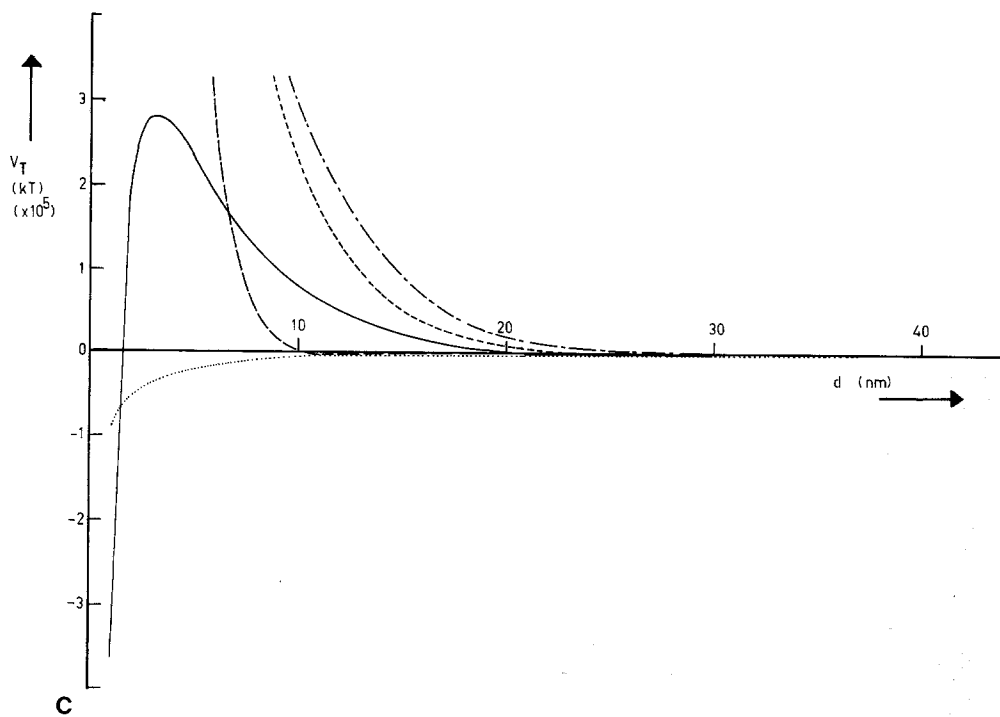
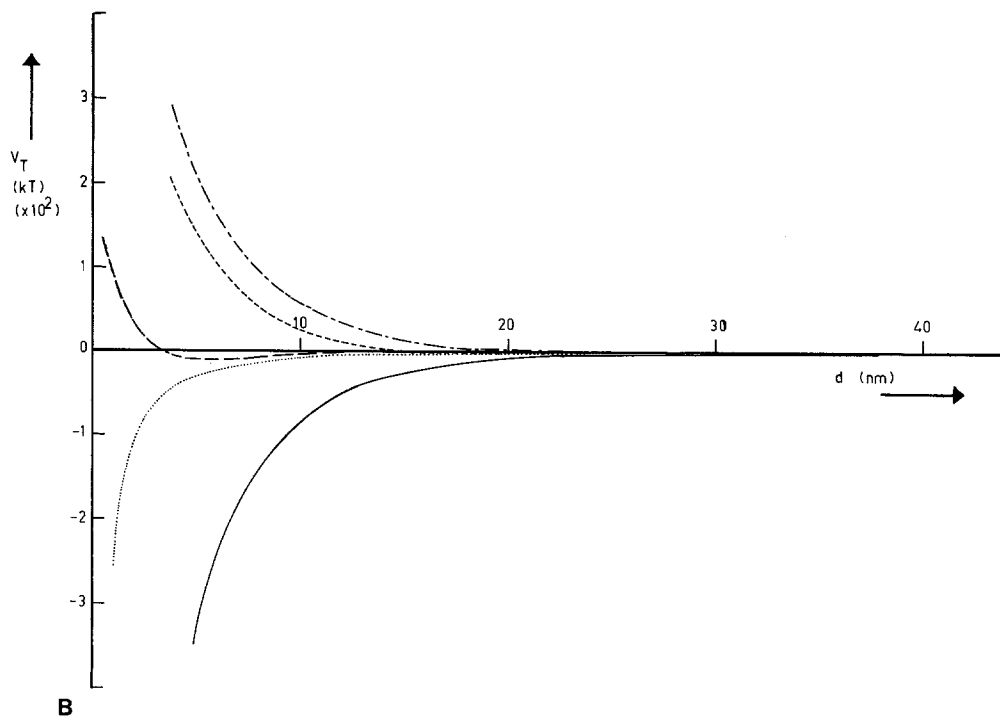


FIG. 5—Continued.

makes EF coagulation less effective. However, turbidity and sedimentation volume remain constant; both are probably less sensitive parameters. Near $[CTAB] = 2.5 \times 10^{-3} M$, however, FF coagulation becomes possible (see Fig. 5C) which makes the Bingham yield value increase again and also increases the sedimentation volume. In this respect our results disagree with Dollimore and Horridge's statement (39) that FF coagulation leads to a lower sedimentation volume.

At $[CTAB] > 2.5 \times 10^{-5} M$, the prevention of all types of coagulation by the positive charge on all surfaces is well born out by the decrease in sedimentation volume and Bingham yield value, and by an increasing turbidity.

2. *Influence of CTAB at pH = 10.* In the absence of CTAB, all surfaces are negative; no coagulation is possible. Both E and F are near their IEP at $[CTAB] \approx 5 \times 10^{-5} M$; coagulation of all types is possible, and the sedimentation volume and Bingham yield value are large, the turbidity is low. At still larger $[CTAB]$, all faces are positively charged which prevents coagulation.

3. *Influence of SDS at pH = 3.3.* At $[SDS]$ up to the IEP of the E surfaces ($1.5 \times 10^{-3} M$) EF coagulation is possible causing an almost constant sedimentation volume and Bingham yield value. Near the IEP of the E surfaces, both EF and EE coagulation are possible; this leads to a slight maximum in the Bingham yield value especially for H-kaolinite (Dollimore and Horridge also report a slight maximum in the sedimentation volume (39)).

4. *Influence of STS at pH = 10.* No coagulation is possible, which agrees well with the experimental data.

Thus, the influence of surfactants on the rheological behavior of kaolinite suspensions can be explained on the basis of the conventional theories on stabilization by surface charges, without invoking the influence of hydrophobic or hydrophobic character of the surfaces.

SUMMARY

Adsorption, sedimentation, turbidity, electroosmosis, and rheological data on monoionic kaolinite suspensions (H^+ and Na^+ forms) as influenced by surfactants can be accounted for by electrostatic stabilization.

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REFERENCES

1. van Olphen, H., "An Introduction to Clay Colloid Chemistry." Wiley, New York, 1963.
2. Swartzen-Allen, E., and Matijevic, E., *Chem. Rev.* **74**, 385 (1974).
3. Michaels, A., and Bolger, J., *Ind. Eng. Chem. Fundam.* **1**, 24 (1962).
4. Melton, I., and Rand, B., *J. Colloid Interface Sci.* **60**, 321, 331 (1977).
5. Schott, H., *J. Colloid Interface Sci.* **26**, 133 (1968).
6. Hinckley, D. N., *Clays Clay Miner.* **11**, 229 (1963).
7. Street, N., and Buchanan, A. S., *Aust. J. Chem.* **9**, 450 (1956).
8. Norton, F. H., and Johnson, A. L., *J. Amer. Ceram. Soc.* **27**, 77 (1944).
9. Koehn, M., *Landwirtsch. Jahrb.* **67**, 485 (1928); *Tondind. Ztg.* **53**, 729 (1929).
10. DIN 51033, Bestimmung der Korngrößen durch Siebung und Sedimentation.
11. Welzen, J. T. A. M., thesis, University of Technology, Eindhoven, 1979.
12. Allison, L. E., *Soil Sci. Soc. Amer. Proc.* **24**, 36 (1960).
13. Allison, L. E., *Agronomy* **9**, 1367 (1965).
14. Allison, L. E., Bollen, W. B., and Moodie, C. D., *Agronomy* **9**, 1346 (1965).
15. Ferris, A. P., and Jepson, W. B., *Analyst* **97**, 940 (1972).
16. Ferris, A. P., and Jepson, W. B., *J. Colloid Interface Sci.* **51**, 245 (1975).
17. Schollenberger, C. J., and Dreibelbis, F. R., *Soil Sci.* **30**, 161 (1930).
18. Worrall, W. E., and Ryan, W., *Trans. VIIIth Int. Ceram. Congr.* **421** (1960).
19. Barry, B. W., and Wilson, R., *Colloid Polym. Sci.* **256**, 251 (1978).

20. Zimmels, Y., and Lin, I. J., *Colloid Polym. Sci.* **252**, 594 (1974).
21. Prins, A., thesis, University of Technology, Eindhoven, 1962.
22. Vassiliades, A. E., in "Cationic Surfactants" (E. Jungermann, Ed.), chap. 12. Dekker, New York, 1970.
23. Epton, S. R., *Trans. Faraday Soc.* **44**, 226 (1948).
24. Epton, S. R., *Nature* **160**, 795 (1947).
25. Markunas, P. C., and Riddick, J. A., *Anal. Chem.* **23**, 337 (1951).
26. Pifer, C. W., and Wollish, E. G., *Anal. Chem.* **24**, 300 (1952).
27. Siskens, C. A. M., thesis, University of Technology, Eindhoven, 1975.
28. Lange, E., and Crane, P. W., *Z. Phys. Chem.* **A141**, 225 (1929).
29. Verwey, E. J. W., *Rec. Trav. Chim.* **60**, 625 (1941).
30. von Smoluchowski, M., *Bull. Int. Acad. Pol. Sci. Lett. Cl. Sci. Math. Natur.* **1903**, 182.
31. Hunter, R. J., *J. Colloid Sci.* **16**, 190 (1961).
32. Weiss, A., and Russow, J., *Proc. Int. Clay Conf., Stockholm* **1**, 203 (1963).
33. Gouy, G., *J. Phys.* **9**, 475 (1910).
34. Gouy, G., *Ann. Phys. Paris* **7**, 129 (1917).
35. Chapman, D. L., *Phil. Mag.* **25**, 475 (1913).
36. Slater, R. W., and Kitchener, J. A., *Discuss. Faraday Soc.* **42**, 267 (1966).
37. Dollimore, D., and Horridge, T. A., *Trans. Brit. Ceram. Soc.* **70**, 191 (1971).
38. Dollimore, D., and Horridge, T. A., *Water Res.* **6**, 703 (1972).
39. Dollimore, D., and Horridge, T. A., *J. Colloid Interface Sci.* **42**, 581 (1973).
40. Fuerstenau, D. W., *J. Phys. Chem.* **60**, 981 (1956).
41. Fuerstenau, D. W., Healy, T. W., and Somasundaran, P., *Trans. Met. Soc. AIME* **229**, 321 (1964).
42. Gaudin, A. M., and Fuerstenau, D. W., *Trans. Met. Soc. AIME* **202**, 958 (1955).
43. Zimmels, Y., Lin, I. J., and Friend, J. P., *Colloid Polym. Sci.* **253**, 404 (1975).
44. Vold, R. D., and Phansalkar, A. K., *Rec. Trav. Chim.* **74**, 41 (1955).
45. Fava, A., and Eyring, H., *J. Phys. Chem.* **60**, 890 (1956).
46. Moilliet, J. L., Collie, B., and Black, W., "Surface Activity," 2nd ed. Spon, London, 1961.
47. Verwey, E. J. W., and Overbeek, J. Th. G., "Theory of the Stability of Lyophobic Colloids," p. 97. Elsevier, New York, 1948.
48. de Boer, J. H., *Trans. Faraday Soc.* **32**, 10 (1936).
49. Hogg, R., Healy, T. W., and Fuerstenau, D. W., *Trans. Faraday Soc.* **62**, 1638 (1966).
50. Hamaker, H. C., *Physica* **4**, 1058 (1937).
51. Vincent, B., *J. Colloid Interface Sci.* **42**, 270 (1973).
52. Lyklema, J., *J. Colloid Interface Sci.* **58**, 242 (1977).
53. Visser, J., *Advan. Colloid Interface Sci.* **3**, 331 (1972).
54. Fowkes, F. M., *Ind. Eng. Chem.* **56**, 40 (1964).
55. Goodwin, J. W., *Trans. Brit. Ceram. Soc.* **70**, 65 (1971).
56. Grim, R. E., "Clay Mineralogy." McGraw-Hill, New York, 1968.