RHEOLOGICAL PROPERTIES OF ORGANOPHILIC SYNTHETIC HECTORITES AND SAPONITES

Takashi Iwasaki, Yoshio Onodera, and Kazuo Torii

Government Industrial Research Institute, Tohoku, Nigatake 4-2-1, Sendai, 983 Japan

Abstract—To determine the dependency of rheological properties on mineralogical characteristics, eleven organophilic hectorite and nine organophilic saponite samples were prepared from hydrothermally synthesized smectites and a quaternary ammonium salt containing mainly octadecyl groups as alkyl chains and were examined by X-ray powder diffraction (XRD), particle size, chemical, and rheological procedures. The rheological properties of the organophilic products dispersed in toluene were found to depend chiefly on (1) particle size, (2) the expansion behavior of the stacked clay platelets, in which the amount and location of negative charge of the silicate layer affected the expandability, and (3) the amount of methanol added as a polar activator. By the addition of 2–4% methanol, apparent viscosities of the hectorite clays were drastically increased at low shear rate, although even a 10% addition did not significantly affect the saponite clays. Under the most suitable gellation conditions, the saponite clays showed lower apparent viscosity than the hectorite clays. Inasmuch as the former had its negative charge near the surface of the silicate layer and formed strong bonds to the organic ion, the expansion of the platelets was apparently difficult. An optimum layer charge for increasing the viscosity was found; specifically 0.45–0.50 and 0.50–0.55 equivalents per half unit cell for saponite and hectorite clays, respectively. Because the saponite clays contained a denser population of organic ions than the hectorite clays, the ion density in the interlayer of both clays was considered to be the same, i.e., about 0.4 organic ions per unit *ab* area.

要旨－鉱物学的性質に対する粘性特性の依存性を調べるため、水熱合成スメクタイトと主としてオクタデシル基をアルキル鎖としてもつ4級アンモニウム塩から、親油性ヘクトライト11試料と親油性サポナイト9試料を作製し、それらのX線粉末回折(XRD)、粒径、化学組成及び粘性特性を検討した。親油性粘土トルエン分散溶液の粘性特性は主として(1)粒径、(2)積層した粘土の膨張の程度（珪酸塩層の陰電荷の量と位置が膨張性に影響を与えている）および(3)極性活性剤として加えたメタノール量に依存する。2－4％メタノールを加えた場合、ヘクトライト分散液の見かけ粘度は低ずり速度で大幅に増加するが、サポナイト分散液に対しては10％加えてもほとんど効果がない。最もゲル化が著しい条件下では、サポナイト分散液の見かけ粘度はヘクトライトの場合より低い。サポナイトの陰電荷は珪酸塩層表面に近く、陽イオンと強く結合しているため、層の膨張は困難である。粘度が最も高いときの層電荷はサポナイトで 0.45～0.50、 ヘクトライトで 0.50～0.55 eq／half unit cellである。 サポナイトはヘクトライトに比べ、 より密に層間有機イオンを有するため、このときの両者の層間イオン密度はほぼ同じであり、単位ab面あたり0.4の有機イオン数となる。

Key Words—Hectorite, Organophilic, Particle aggregation, Rheology, Saponite, Smectite, Viscosity, X-ray powder diffraction.

INTRODUCTION

Organophilic clays are used widely as rheological control agents not only in paints, greases, inks, etc. (Jones, 1983), but, recently, in cosmetics, medicines, and washing agents as well. Such organophilic clays are commonly manufactured from natural bentonites and quaternary ammonium salts, which typically contain one or more octadecyl groups. By selecting the kind of organic matter as the guest ion or the solvent, various rheological characteristics can be imparted to the clay dispersions, and research along this line has been active (Jordan *et al.*, 1950; Cody and Reichert, 1986). The relation between the mineralogical properties of the raw smectite and the resultant rheological characteristics of the dispersion, however, is not well known.

In an attempt to unravel the effect of the mineralogy, especially that of the layer charge, of the smectite on the resultant rheological properties, an investigation was carried out in which the viscosity was measured of the organophilic clay dispersions made from two series of synthetic smectites and a quaternary ammonium salt.

EXPERIMENTAL

Two series of trioctahedral smectites having different cation substitution sites, hectorite and saponite, were synthesized hydrothermally from reagents. The hectorites had negative charge sites in the octahedral sheet, whereas the saponites had negative charge sites in the tetrahedral sheet of the smectite structure. The synthetic procedure (Torii *et al.*, 1986) was as follows: (1)

248

Table 1.   Synthetic conditions of smectites.

Sample	Si	Al	Mg	Li	Na	F	Temp. (°C)	Time (hr)
	Starting compositions (atomic ratio)							
H1	4.00		2.70	0.30	0.35		150	2
H2	4.00		2.70	0.30	0.35		180	2
H3	4.00		2.70	0.30	0.35		200	2
H4	4.00		2.70	0.30	0.35		225	2
H5	4.00		2.70	0.30	0.35	1.50	225	2
H6	4.00		2.70	0.35	0.35		225	2
H7	4.00		2.70	0.40	0.35		225	2
H8	4.00		2.90	0.50	0.35		225	2
H9	4.00		2.70	0.30	0.35		250	2
H10	4.00		2.70	0.30	0.35		280	2
H11	4.00		2.70	0.30	0.35		300	2
S1	3.80	0.20	3.00		0.20		300	3
S2	3.70	0.30	3.00		0.30		300	3
S3	3.70	0.30	3.00		0.35		300	3
S4	3.70	0.30	3.00		0.35	0.50	300	3
S5	3.70	0.30	3.00		0.35	1.00	300	3
S6	3.70	0.30	3.00		0.35	1.50	300	3
S7	3.60	0.40	3.00		0.40		300	3
S8	3.50	0.50	3.00		0.50		300	3
S9	3.40	0.60	3.00		0.60		300	3

A Mg-Si-(Al) solution was prepared having the desired Mg-Si-(Al) ratio by dissolving magnesium chloride and/or aluminum chloride in an acidic silicate solution that had been prepared from sodium silicate solution and nitric acid. (2) Mg-Si-(Al) precipitates were formed by mixing the above solution with alkali solution. (3) The Mg-Si-(Al) precipitates were washed and filtered to remove secondary products, such as sodium nitrate. (4) A slurry was prepared from a Mg-Si-(Al) precipitate, NaOH, and, if necessary, LiOH or HF. (5) The slurry was treated hydrothermally in an autoclave at 150°–300°C under autogenous water vapor pressure for 2–3 hr. (6) The products were dried and powdered. Synthesis conditions are listed in Table 1. Samples H1–H11 have chemical compositions corresponding to hectorite, and samples S1–S9 have chemical compositions corresponding to saponite.

Organophilic clays were prepared from the synthetic smectites and a dialkyl-dimethyl ammonium chloride containing 75% octadecyl, 24% hexadecyl, and 1% octadecanyl groups as alkyl groups (trade name: Arquad 2HT-75, Lion Akzo Co., Ltd.). A preliminary examination showed that the clays complexing this quaternary ammonium ion dispersed easily in toluene and yielded higher viscosity values compared with other quaternary ammoniums containing shorter chain-length alkyl groups. Both smectites and quaternary ammonium were dissolved in hot water (80°C) separately to give a concentration of 2%, and then mixed, stirred, and boiled for 30–60 min. After filtration and washing with warm water, the organophilic clays were dried and powdered. According to Jordan et al. (1950) and Jones (1983), optimum gels are obtained if the amount of amine is equivalent to the cation-exchange capaci-

ties (CEC) of the clays. In the present study, the CECs of the clays estimated from the adsorption of methylene blue (MB) were adopted, because MB adsorption is particularly useful in determining CEC if the clays contain only Na$^+$ (Pham Thi Hang and Brindley, 1970). The amounts of MB equivalent to the amounts of quaternary ammonium used are listed in Table 2.

The chemical composition of samples was determined by X-ray spectrochemical analysis using a Rigaku system 3080E2 X-ray fluorescence spectrometer for Si, Al, Mg, K, and Na, and atomic adsorption spectrophotometry for Li. The amounts of F and organic material present in the clays were measured using a F-selective electrode (Konno and Akizuki, 1982) and thermal gravimetric analysis using a Rigaku Thermoflex thermal balance, respectively. X-ray powder diffraction (XRD) analyses were carried out with a Rigaku diffractometer (RAD-IIB) using monochromatized CuKα radiation. Basal spacings of the oriented specimens of organophilic products were measured under conditions of vacuum (about 10^{-1} Torr) and toluene-saturated vapor. Average particle sizes in the 0.1 and 1.0% dispersions were measured with a Coulter submicrometer particle analyzer, model N4. As the particle sizes tended to increase with increasing concentration, the crystal sizes of the samples were obtained by extrapolation to the values for 0% dispersions. Transmittance was measured by passing 500-nm light through a 1% dispersion using a Shimazu spectrophotometer, model UV-240. The particle size and transmittance measurements were carried out immediately after hand shaking the specimens. The shape of the synthetic smectites was observed by a Hitachi H-300 electron microscope.

Table 2. Methylene blue (MB) adsorption on synthetic smectites, average particle size of sol particles, and transmittance of dispersions.

	Synthetic smectite			Organophilic product
Sample	MB adsorbed (meq/100 g)	Particle size[1] (Å)	Transmittance[2] (%) 1% water dispersion	Transmittance[2] (%) 1% toluene dispersion
H1	70	3530	4.0	88.4
H2	84	1520	59.9	92.8
H3	96	1170	82.7	99.4
H4	108	990	90.4	98.8
H5	116	1560	92.5	98.3
H6	124	1200	81.8	94.3
H7	104	830	88.4	94.6
H8	102	820	85.1	90.5
H9	106	1170	71.3	99.5
H10	106	1660	52.3	97.9
H11	112	1620	61.1	92.2
S1	44	3260	1.2	41.1
S2	88	1730	26.7	86.0
S3	98	980	80.6	96.2
S4	110	1100	78.8	96.1
S5	104	1010	72.7	82.2
S6	100	2440[3]	28.9[3]	59.1[3]
S7	110	1140	66.6	96.3
S8	110	1160	70.9	96.3
S9	104	2080	15.1	93.3

[1] Extrapolated for 0% dispersion from the value measured on 0.1 and 1.0% water dispersions.
[2] Measured with 500-nm light transmitted through the 1% dispersion (solvent = 100%).
[3] Gelation occurred immediately after shaking.

Table 3. 001 and 060 spacings of synthetic smectites and organophilic products.

	d(001) (Å)				
	Synthetic smectite		Organophilic product		
Sample	Air-dried	Ethylene glycolated	Vacuum	Toluene-saturated vapor	d(060)[1]
H1	17.4	20.0	—	—	1.524
H2	17.3	18.5	—	—	1.522
H3	14.3	17.4	—	18.4	1.523
H4	13.2	17.1	26.8	35.0	1.522
H5	13.6	15.8	30.5	37.1	1.515
H6	12.7	16.5	28.5	36.4	1.523
H7	12.8	16.7	25.6	35.8	1.523
H8	13.0	17.0	26.4	29.2	1.523
H9	13.5	17.2	26.8	36.8	1.523
H10	13.5	17.1	27.6	35.4	1.523
H11	13.6	17.1	28.9	37.6	1.523
S1	12.1	17.4	16.6	17.2	1.526
S2	14.5	17.1	21.7	27.5	1.527
S3	14.6	17.1	25.1	32.1	1.528
S4	14.5	17.0	26.9	34.8	1.526
S5	14.9	17.1	26.8	34.6	1.523
S6	15.0	17.1	26.6	34.8	1.522
S7	14.4	17.1	25.7	34.5	1.529
S8	14.3	16.9	30.0	34.2	1.531
S9	14.8	15.0	36.8	38.1	1.532

[1] Synthetic smectite.

Rheological properties were measured on the clay dispersions with a Fann VG viscometer, model 35-SA, at a shear rate of 10.2–1020/s and at 25°C. The toluene dispersions (2, 2.5, 3, 4, and 5 wt. %) were prepared and then methanol (2, 4, 6, 8, and 10 wt. %) was added to the 5% dispersions in expectation of acting as the polar activator, i.e., that methanol would enter the interlayer, adsorb on the silicate surface, and begin the expansion process (Dekany *et al.,* 1975, 1986). The addition of methanol to this system was most effective for increasing the viscosity of the primary alcohols, because methanol molecules could be introduced easily to the interlayer of the smectite (Jordan *et al.,* 1950; Slabaugh and Hanson, 1969).

RESULTS AND DISCUSSION

Mineralogical characterization of the synthetic smectites

The 001 and 060 spacings of the synthetic smectites and organophilic products are listed in Table 3. XRD patterns of the oriented specimens of the synthetic smectites show that these products were essentially pure smectites (Figure 1). Except for samples synthesized at lower temperature (H1, H2) and with low Na content (S1), which showed no clear basal reflections, all samples had non-integral basal reflections, probably due

to heterogeneity of the interlayer distances. According to the peak widths of the 001 reflections, the crystallinity of the hectorite samples appeared to be lower than that of the saponite samples.

The structural formulae of the synthetic smectites and the organophilic products shown in Table 4 were calculated from chemical analyses based on $O_{10}(OH,F)_2$, assuming that the interlayers of the organophilic products contained no Li and Mg, i.e., that all of the Li and Mg detected in the organophilic hectorites and the Mg in the organophilic saponites occupied octahedral sites of silicate layers.

In the hectorite samples, the cation compositions of the silicate layer varied with hydrothermal conditions, even if the samples had the same starting compositions. The tetrahedral sheet contained a few Al ions, which were probably present as impurities in the sodium silicate raw material. The sum of the octahedral cations in the hectorite samples was substantially constant, 2.82 to 2.86, indicating a nearly trioctahedral nature. Samples H1–H4 and H9–H11 had the same starting compositions, however, the synthesis conditions were different. The amount of octahedral Li increased with increasing synthesis temperature (Figure 2). At the same synthesis temperature of 225°C, however, increasing the amount of Li in the starting material did not increase the amount of octahedral Li. The layer charge of the synthetic hectorites was thus due chiefly to octahedral vacancies, which is different from natural hectorite. The amount of substitution of Li for Mg in the octahedral sheets increased with increasing synthesis
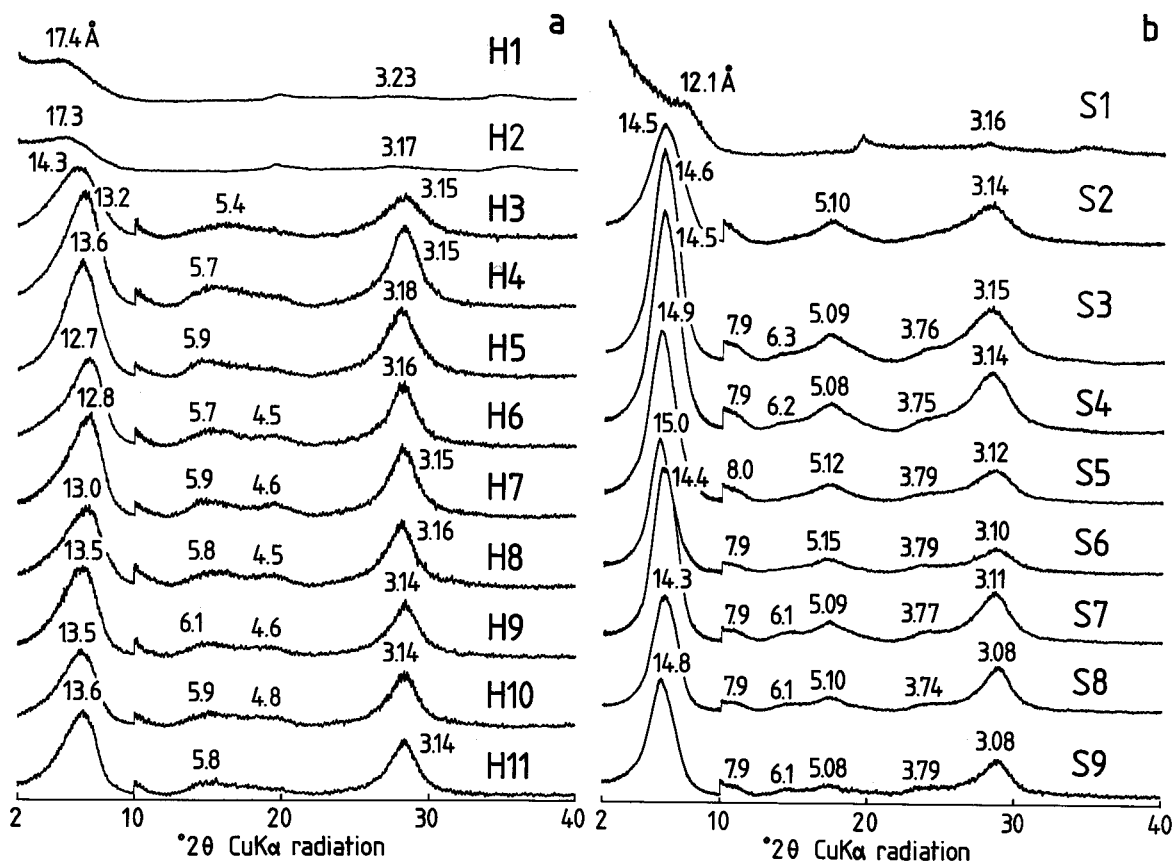
Figure 1. X-ray powder diffraction basal reflections of synthetic smectite samples. a = synthetic hectorite, b = synthetic saponite.

temperature. Samples S1–S9 had structural formulae corresponding to saponite, as indicated by the octahedral population of about 3.0. Reflecting the number of octahedral cations, fluorine-free hectorite samples gave nearly constant b-dimensions of 1.523 Å; however, those of fluorine-free saponite samples ranged from 1.526 to 1.532 Å. Both fluorosmectites showed reduced b-dimensions compared with their fluorine-free counterparts.

The layer charge of the synthetic smectites calculated from the chemical analyses are in line with the variation of the basal spacings of ethylene glycolated material (Figure 3). The 001 spacings changed along the line for the Na-smectite reported by Lagaly (1981), except for samples H1 and H2. These two hectorite samples showed abnormally large spacings, which were observed also in air-dried specimen (Figure 1a), probably due to existence of a component with larger spacing than usual hectorite.

The amount of organic ions taken up in a smectite interlayer increases with the layer charge (Lagaly and Weiss, 1969, 1975). Basal spacings of the organophilic products measured in vacuum and layer charge (Figure 4) showed an almost linear relation with the amount

of interlayer organic ions. The broken line in the illustration shows the ideal variation of d(001) with layer charge, if the organic ions are closely packed in the interlayer. The volume occupied by one quaternary ammonium ion was estimated as 992 Å³, according to the data reported by Barrer et al. (1967). Basal spacings of the saponite samples plotted closer to the line than those of the hectorite samples, i.e., the number of organic ions per layer charge in the hectorite interlayers was relatively small compared with those in the saponite interlayers. Thus, organic ions in the saponite interlayers may have been densely arranged in the interlayer.

Mungan and Jessen (1963) reported that rheological properties are affected by particle shape and size. The particle sizes of the synthetic smectites varied with synthesis conditions (Table 2). The hectorite samples synthesized at 225°C (H4–H8) and the saponite samples having Al = 0.4–0.5 (S7, S8) showed minimum particle size. These samples were morphologically similar, i.e., they occurred as foliated aggregates having maximum diameters of about 1 μm (Figure 5). The transmittance of the 1% water dispersions was inversely proportional to the particle size, and the values of

Table 4. Structural formulae[1] of the synthetic smectites and organophilic products.

| Sample | Silicate layer | | | | | | | | | Interlayer | | |
| | Tetrahedral sheet | | | Octahedral sheet | | | | Layer charge | F | Synthetic smectite | | |
	Si	Al	Charge	Mg	Li	Sum	Charge			Na	Li	Mg
H1	3.99	0.01	−0.01	2.81	0.03	2.84	−0.35	0.36		0.33	0.17	0.00
H2	3.99	0.01	−0.01	2.78	0.04	2.82	−0.40	0.41		0.42	0.14	0.00
H3	3.99	0.01	−0.01	2.72	0.14	2.86	−0.42	0.43		0.29	0.10	0.02
H4	3.98	0.02	−0.02	2.68	0.16	2.84	−0.48	0.50		0.34	0.11	0.01
H5	3.99	0.01	−0.01	2.66	0.20	2.82	−0.56	0.57	1.54	0.27	0.08	0.07
H6	3.98	0.02	−0.02	2.64	0.18	2.82	−0.54	0.56		0.33	0.10	0.00
H7	3.98	0.02	−0.02	2.68	0.17	2.86	−0.45	0.47		0.33	0.15	0.00
H8	3.99	0.01	−0.01	2.67	0.18	2.86	−0.46	0.47		0.27	0.17	0.04
H9	3.98	0.02	−0.02	2.67	0.18	2.85	−0.48	0.50		0.31	0.09	0.01
H10	3.98	0.02	−0.02	2.66	0.20	2.86	−0.48	0.50		0.34	0.05	0.01
H11	3.99	0.01	−0.01	2.64	0.22	2.86	−0.50	0.51		0.31	0.05	0.00
S1	3.77	0.23	−0.23	3.02		3.02	+0.04	0.19		0.16		0.00
S2	3.66	0.34	−0.34	3.00		3.00	0.00	0.34		0.23		0.00
S3	3.66	0.34	−0.34	2.96		2.96	−0.08	0.42		0.27		0.05
S4	3.66	0.34	−0.34	2.93		2.93	−0.14	0.48	0.38	0.28		0.05
S5	3.67	0.33	−0.33	2.95		2.95	−0.10	0.43	0.88	0.25		0.05
S6	3.67	0.33	−0.33	2.95		2.95	−0.10	0.43	1.46	0.28		0.13
S7	3.56	0.44	−0.44	3.00		3.00	0.00	0.44		0.27		0.00
S8	3.47	0.53	−0.53	2.99		2.99	−0.02	0.55		0.33		0.00
S9	3.37	0.63	−0.63	3.01		3.01	+0.02	0.61		0.40		0.00

[1] Calculated from chemical analyses based on $O_{10}(OH, F)_2$.

the organophilic products in toluene were greater for all the samples, but varied in the same manner as the synthetic smectites. Fluorine addition usually increased the particle size. In Figure 6, the average particle sizes of the fluorine-free samples are compared on the basis of layer charge. Hectorite and saponite samples have almost the same particle size range; samples having layer charges of 0.4 to 0.5 have minimum values. The particle size of the hectorite samples changes sharply with layer charge.
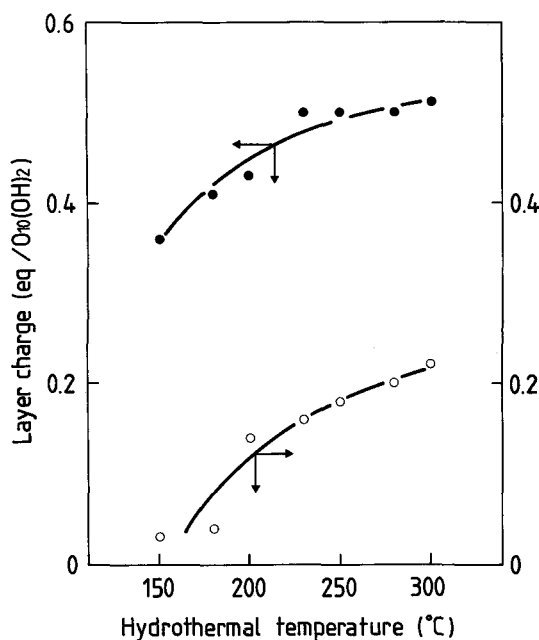

Figure 2. Dependency of layer charge and the number of Li atoms in an octahedral sheet of the synthetic hectorite samples on the hydrothermal temperature of synthesis.
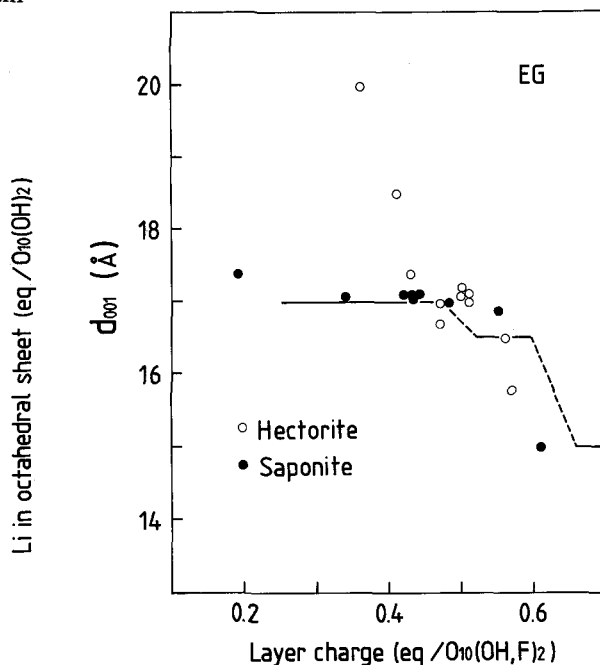

Figure 3. Basal spacing of the ethylene glycolated smectite samples vs. layer charge. Solid and broken lines show the variation of the basal spacings of Na-smectite samples, after Lagaly (1981).

Table 4. Continued.

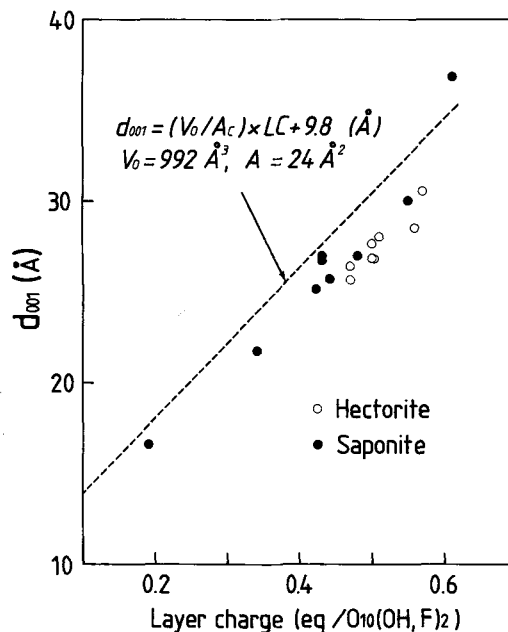| Synthetic smectite		Organophilic product			
K	Charge	Org. ion	Na	K	Charge
0.02	+0.52	0.58	0.02	0.01	+0.61
0.02	+0.58	0.46	0.02	0.01	+0.49
0.02	+0.45	0.49	0.01	0.00	+0.50
0.01	+0.48	0.46	0.01	0.00	+0.47
0.01	+0.50	0.52	0.02	0.01	+0.55
0.01	+0.44	0.52	0.02	0.01	+0.55
0.01	+0.49	0.45	0.01	0.00	+0.46
0.02	+0.54	0.41	0.01	0.00	+0.42
0.01	+0.43	0.44	0.01	0.00	+0.45
0.01	+0.42	0.46	0.02	0.00	+0.48
0.01	+0.37	0.50	0.01	0.00	+0.51
0.01	+0.17	0.19	0.01	0.01	+0.21
0.01	+0.24	0.35	0.01	0.01	+0.37
0.01	+0.38	0.45	0.05	0.01	+0.51
0.01	+0.39	0.49	0.01	0.01	+0.51
0.01	+0.36	0.48	0.04	0.01	+0.53
0.01	+0.55	0.51	0.05	0.01	+0.57
0.01	+0.28	0.46	0.01	0.01	+0.48
0.01	+0.53	0.49	0.03	0.01	+0.53
0.01	+0.41	0.45	0.06	0.01	+0.52

Figure 4. Observed basal spacings measured in vacuum (10^{-1} Torr) vs. layer charge of organophilic products. Broken line shows ideal variation of basal spacings in relation to layer charge calculated according to the data reported by Barrer et al. (1967).

$$d_{001} = (V_0/A_c) \times LC + 9.8 \quad (\text{Å})$$
$$V_0 = 992 \text{ Å}^3, \quad A = 24 \text{ Å}^2$$

Rheological properties of the organophilic clays

Apparent viscosity η_a (mPas) of the organophilic clay dispersion decreased with increasing shear rate D (s^{-1}) in toluene and toluene-methanol solvent systems. Inasmuch as log η_a vs. log D can be approximated by a linear equation in the shear rate range 10.2–1020/s (Figure 7), the equation for pseudoplastic flow can be applied to this system. The relation between apparent viscosity and shear rate is as follows:

$$\eta_a = \mu D^{n-1} (1 > n > 0),$$

where μ is the non-newtonian coefficient of viscosity and n is the non-newtonian index of viscosity. The μ and n values obtained for samples H4 and S7, for example, are given in Figure 8. With increasing concentration of the clay and methanol in the dispersion, n increased and approached newtonian flow (n = 1) at low concentration. Further addition of clay sample or methanol, however, caused the value to move toward a higher μ and lower n region, although the concentration at which the change occurred varied from sample to sample and could not be specified. This tendency was generally evident for all samples, and the values plotted in a fixed place surrounded by the lines in the illustration, although the hectorite and saponite samples occupied somewhat different positions. For the methanol-free system, both series of samples had almost the same μ values up to 10^3 within the solid lines, although the saponite samples gave slightly smaller n values.

The addition of methanol gave rise to different effects for the hectorite and saponite samples. After methanol was added, the μ value increased and the value n decreased, i.e., the apparent viscosity at the low shear rate increased. A methanol concentration range of 2–4% gave a maximum μ value for the hectorite samples. The μ values for the saponite samples increased gradually as the amount of methanol increased within the experimental range; however, they appeared to change slightly, the maximum value of which was one-tenth as large as that of the hectorite samples.

The μ values reflect the stability of the gel structures. Intercrystalline swelling and separation into individual clay platelets increased the size and/or number of gel particles and led to an increase in apparent viscosity. A small addition of methanol caused the hectorite interlayers to swell; however, the effect of methanol in the saponite system was not significant.

Effect of the site and amount of negative charge in the silicate layer on viscosity

For the present solvent system, a concentration of 2–4% methanol in the hectorite dispersions was almost an optimum for increasing the μ values. At this concentration, a relation between the layer charge and the viscosity was noted for both series of samples. Figure 9 is a plot of layer charge vs. μ for toluene-, toluene-4% methanol-, and toluene-10% methanol-organophilic products and water-synthetic smectite systems, the n values of which are listed in Table 5. The relation
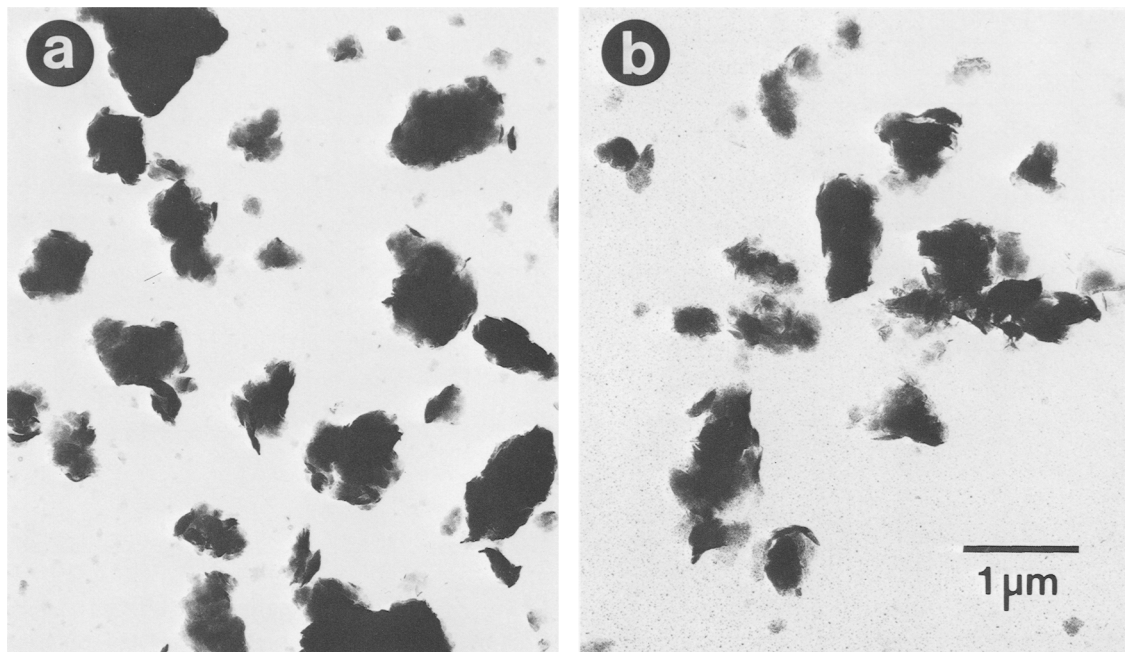
Figure 5. Electron micrographs of synthetic smectite samples. a = sample H4, b = sample S7.

is obscure for the water-smectite and methanol-free-toluene-organophilic products systems, but it is clear for the methanol-added systems. The smectite-water dispersion has been considered to consist of tactoids made up of face to face aggregations of several clay platelets (Fripiat *et al.,* 1982) or a "house-of-cards" structure in which the individual platelets are associated mainly by edge to face bonding (van Olphen, 1977). Insofar as the results of present work are concerned, nothing can be said about the texture of the gel, except that it appears to have an unstable texture, which can be easily destroyed by weak shear stress and recovered thixotropically by releasing the stress. In either state, as the tactoid increases in size by extension of the interlayer and bonds together or as the clay particle
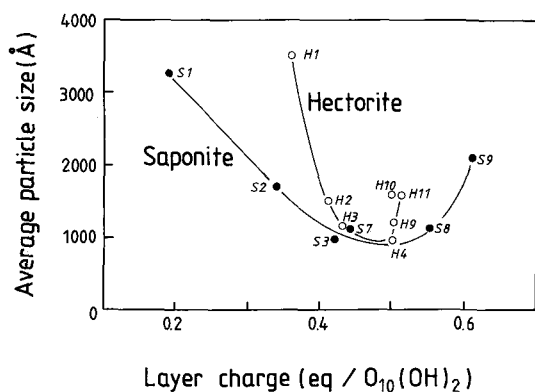
Figure 6. Variation of average particle sizes of synthetic smectite samples as a function of layer charge.
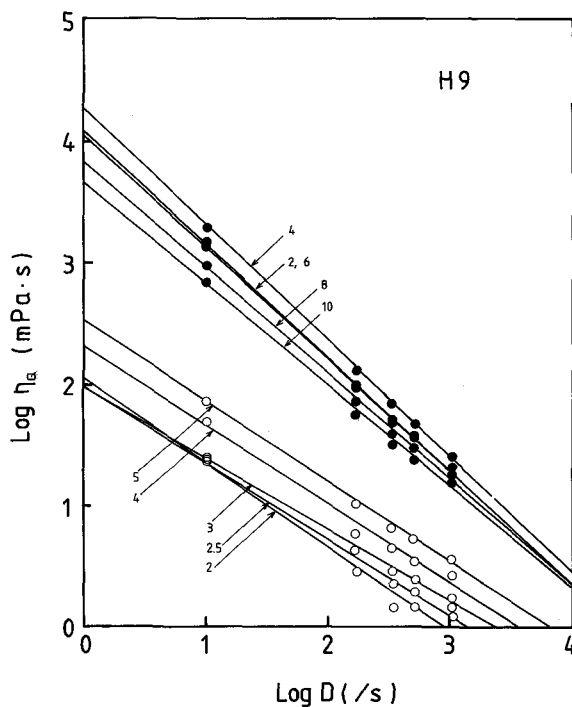

Figure 7. Typical apparent viscosity (η_a) vs. share rate (D) plots. Open circles show values of methanol-free system; numbers give the clay concentrations (wt. %). Solid circles show values of methanol-added system (clay concentration = 5 wt. %); numbers give the methanol concentrations (wt. %).
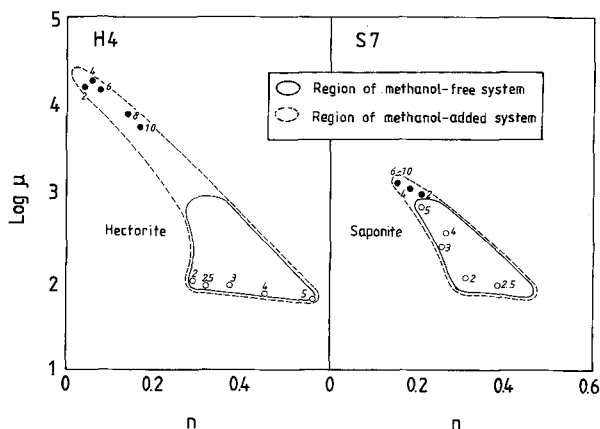
Figure 8. Change of non-newtonian index (n) and non-newtonian coefficient (μ) of organophilic products H4 and S7 dispersed in toluene with increasing clay concentration and amount of methanol. Open circles show values of methanol-free system; numbers give the clay concentrations (wt. %). Solid circles show values of methanol-added system. Methanol concentration is shown by the number affixed to the symbol.

separates to form card-house structures of individual platelets, consequent gel structures may give rise to an increase in viscosity. Several studies have shown that polar molecules, such as methanol, ethanol, and water, can enter the interlayer, come in contact with the silicate surface, and push the hydrocarbon chain away from the surface (Burba and McAtee, 1981; Dekany *et al.*, 1986) or that they increase the mobility of ammonium ions over the surface (Gast and Mortland, 1971; Cody *et al.*, 1986) Thus, the methanol may have contributed to the gel structure by accelerating the ex-

pansion of platelet interlayers and by linking the dispersed clay platelets edge-to-edge or edge-to-face in a hydrogen-bonded matrix. The relation between layer charge and μ was therefore a measure of the ease of the expansion of the interlayers.

The relation between μ and layer charge was clearly recognized in the dispersion of the 4% methanol system. In this system, because the variation of the μ with regard to layer charge agrees with that of average particle sizes (Figure 6), the viscosity was undoubtedly affected by the particle size. But, the maximum μ value of hectorite dispersions, which is ten times as large as the maximum μ value for saponite dispersions, can be ascribed to the silicate layer structure, because the particle size and shape of the hectorite and saponite samples are very similar. Hectorite and saponite samples differed from each other in layer charge giving the maximum μ values; the hectorites had maximum μ values at layer charges of 0.50–0.55 equivalents per half unit cell, which is slightly greater than the maximum layer charge of the saponites (0.45–0.50 equivalents).

The gelling ability of a clay is reported to be sensitive to the amount of organic ions in the clay, and optimum gels are obtained in a specific region of the organic ion/clay ratio (Jordan *et al.*, 1950; Jones, 1983). These authors pointed out that the optimum gellation of a clay occurs if the clay is completely ion exchanged with the organic ammonium salt, i.e., optimum gellation occurs if the organic ion content is equal to the CEC of the clay. Thus, for organic ion contents < CEC, clay interlayers do not fully expand, because polar molecules cannot be introduced beneath the flat-lying alkyl chains on the silicate surfaces, and it is therefore difficult to push the chain from the surface. The reason
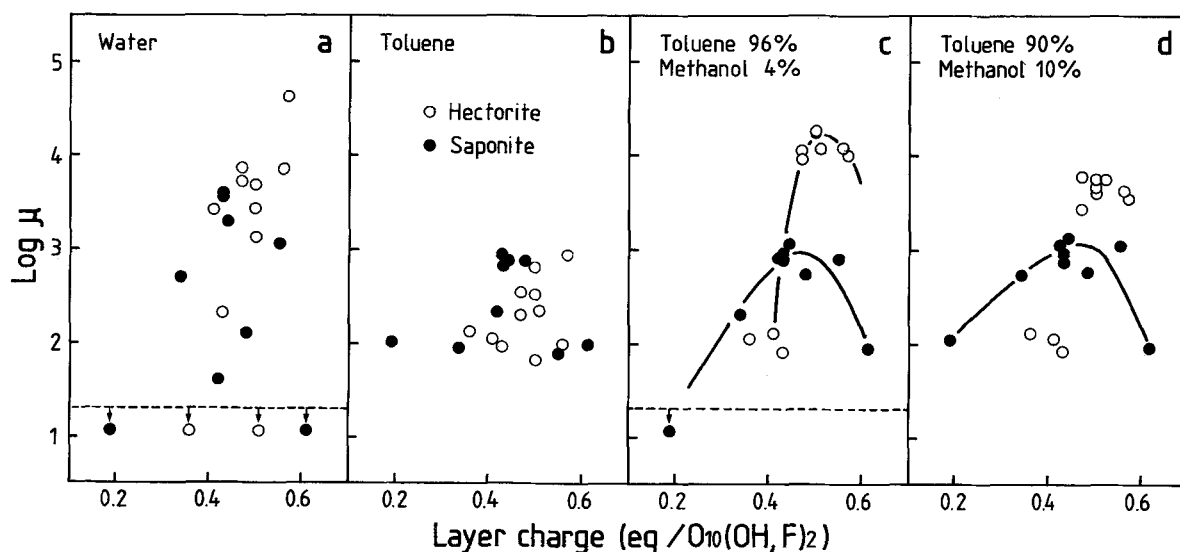

Figure 9. Relation between layer charge of the organophilic clays and the non-newtonian coefficient (μ) of the dispersions. Broken line shows lower limit of the measurement. a = 3.5% raw smectite dispersed in water, b–d = 5% organophilic clay dispersed in toluene adding 0, 4, and 10% methanol, respectively.

Table 5. Non-newtonian coefficients (μ), and non-newtonian indices (n) of synthetic smectite and organophilic product dispersions.[1]

Solvent	Water[2]		Toluene 100%		Toluene 96% Methanol 4%		Toluene 96% Methanol 10%	
Sample conc (%)	3.5		5		5		5	
Sample	μ	n	μ	n	μ	n	μ	n
H1	nd	nd	129	0.22	112	0.26	129	0.22
H2	2630	0.35	112	0.26	125	0.28	112	0.26
H3	206	0.55	89	0.39	80	0.43	81	0.46
H4	4770	0.26	64	0.56	18,800	0.06	5470	0.17
H5	40,800	0.04	863	0.34	10,100	0.05	3570	0.21
H6	7270	0.17	96	0.37	12,200	0.06	4180	0.17
H7	5300	0.22	195	0.39	11,100	0.07	2720	0.20
H8	7310	0.14	338	0.32	9250	0.07	6180	0.13
H9	1330	0.42	333	0.34	18,300	0.05	4590	0.17
H10	2720	0.34	624	0.27	17,000	0.03	4170	0.17
H11	nd	nd	218	0.35	11,700	0.08	5450	0.15
S1	nd	nd	104	0.29	6	0.73	112	0.26
S2	517	0.45	89	0.39	206	0.35	529	0.24
S3	41	0.78	198	0.35	836	0.23	1070	0.19
S4	125	0.57	716	0.22	529	0.24	563	0.22
S5	3950	0.28	652	0.26	705	0.23	717	0.21
S6	3620	0.28	860	0.23	914	0.20	916	0.19
S7	1900	0.38	746	0.21	1240	0.18	1340	0.15
S8	1160	0.63	79	0.44	847	0.21	1120	0.17
S9	7	0.48	96	0.37	89	0.39	89	0.39

[1] Calculated on basis of $\eta_a = \mu D^{n-1}$ for pseudoplastic flow.
[2] Measured on synthetic smectites. nd = not determined.

for the inhibition of gellation at higher organic ion contents is not known, nor is it known whether the excess organic ions are in the interlayer or not. Thus, an optimum density of organic ions in the interlayer must exist for the gellation. The difference of layer charge giving the maximum μ value between hectorite and saponite samples thus can be interpreted as follows: because saponite had a greater density of organic ions in the interlayer than hectorite, the organic ion density for a maximum viscosity was probably the
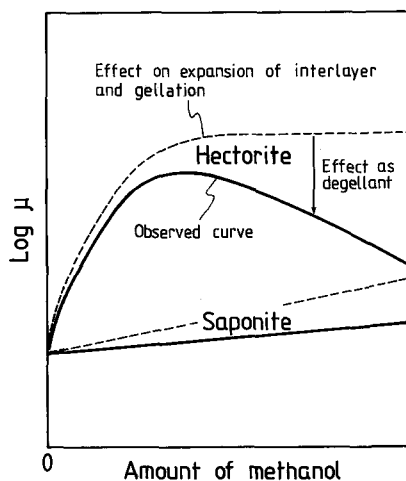

Figure 10. Schematic representation of effect of methanol addition on viscosity of the two types of organophilic clay dispersions.

same for both organophilic clays. The gel structure, therefore, stably developed at the optimal organic ion density in the clay interlayer.

In the low layer-charge region (<0.4 equivalent) of saponite dispersions (Figure 9), the μ values are sensitive to methanol concentration, and large quantities of methanol are needed to produce large μ values. This requirement is chiefly due to the large surface area that is uncovered by organic ions and that may be covered by the methanol molecule. In the high layer-charge region, changes of μ values with increasing methanol content are almost nil. Here, expansion of the interlayers appears to be less extensive, because the ammonium ions are crowded on the silicate surfaces and are not easily contacted by solvents.

The difference in maximum μ values of dispersions of hectorite and saponite organophilic products was probably due to the effect of negative charge sites in the silicate layers. The rheological features are not easily explained on the basis of different charge distributions, but other characteristics, e.g., particle size and shape and the density of interlayer organic ions, are almost the same for hectorite and saponite samples having maximum μ values. Saponite layers having negative charges in their tetrahedral sheets near the silicate surface apparently attached strongly to the organic ions; they inhibited the expansion of interlayers compared with hectorite layers, in which the charge was in the octahedral sheets. Partially expanded saponite platelets formed a gel structure, but they did not contribute

significantly to an increase of the μ value, because incompletely expanded particles were present in the dispersions.

On the other hand, excess polar molecules can act as a degellant, i.e., they break the edge-to-edge or edge-to-face hydrogen bonding of the gel structure (Gast and Mortland, 1971). For the amount of methanol, there appears to be a delicate balance between the effect of covering silicate surfaces to lift up the organic ions and the aggregation of particles by hydrogen-bonding followed by gellation and the effect of degellation. Hectorite clays existing as weakly attracted platelets expanded rapidly to form individual platelets in the presence of small amounts of methanol and formed gels. The methanol present in excess of that required for the gellation apparently acted as a degellant and resulted in a decrease of the μ values. Particles of the saponite clays expanded gradually and formed gel structure. Inasmuch as the expansion was slow, however, an excess of methanol destroyed hydrogen bonds in the structure. The effects of methanol on the gellation and the degellation probably compensated for each other (Figure 10). The gel structures of undeveloped saponite clay dispersions also harmonize with the fact that saponite samples had small n values compared with hectorite samples at the same μ values.

ACKNOWLEDGMENTS

REFERENCES

Barrer, R. M., Papadopoulos, R., and Rees, L. V. C. (1967) Exchange of sodium in clinoptilolite by organic cations: *J. Inorg. Nucl. Chem.* **29**, 2047–2063.

Burba, J. L., 3rd and McAtee, J. L., Jr. (1981) Adsorption of ethylene glycol on amine-substituted montmorillonites: *Clays & Clay Minerals* **29**, 60–66.

Cody, C. A. and Reichert, W. W. (1986) Studies of fundamental organoclay relationships: *NLGI Spokesman,* January 1986, 437–447.

Dekany, I., Szanto, F., Nagy, L. G., and Foti, G. (1975) Adsorption of liquid mixtures on bentonite and organophilic bentonite: *J. Colloid Interface Sci.* **50**, 265–271.

Dekany, I., Szanto, F., Weiss, A., and Lagaly, G. (1986) Interactions of hydrophobic layer silicates with alcohol-benzene mixtures. II. Structure and composition of the adsorption layer: *Ber. Bunsenges. Phys. Chem.* **90**, 427–431.

Fripiat, J., Cases, J., Francois, M., and Letellier, M. (1982) Thermodynamic and microdynamic behavior of water in clay suspensions and gels: *J. Colloid Interface Sci.* **89**, 378–400.

Gast, R. G. and Mortland, M. M. (1971) Self diffusion of alkylammonium ions in montmorillonite: *J. Colloid Interface Sci.* **37**, 80–92.

Jones, T. R. (1983) The properties and uses of clays which swell in organic solvents: *Clay Miner.* **18**, 399–410.

Jordan, J. W., Hook, B. J., and Finlayson, C. M. (1950) Organophilic bentonites. II: *J. Phys. Colloid Chem.* **54**, 1196–1208.

Konno, H. and Akizuki, M. (1982) Fluorine determination in topaz and relation between fluorine content and 2V value of topaz: *Neues Jahrb. Mineral. Monatsh.* **1982**, 465–470.

Lagaly, G. (1981) Characterization of clays by organic compounds: *Clay Miner.* **16**, 1–21.

Lagaly, G and Weiss, A. (1969) Determination of the layer charge in mica-type layer silicates: in *Proc. Int. Clay Conf., Tokyo, Vol. I,* L. Heller, ed., Israel Univ. Press, Jerusalem, 61–80.

Lagaly, G. and Weiss, A. (1975) The layer charge of smectitic layer silicates: in *Proc. Int. Clay Conf., Mexico City, 1975,* S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 157–172.

Mungan, N. and Jessen, F. W. (1963) Fractionated montmorillonite suspensions: in *Clays and Clay Minerals, Proc. 11th Natl. Conf., Ottawa, Ontario, 1962,* Ada Swineford, ed., Pergamon Press, New York, 282–294.

Pham Thi Hang and Brindley, G. W. (1970) Methylene blue absorption by clay minerals. Determination of surface areas and cation-exchange capacities (Clay-organic studies XVIII): *Clays & Clay Minerals* **18**, 203–212.

Slabaugh, W. H. and Hanson, D. B. (1969) Solvent selectivity by an organoclay complex: *J. Colloid Interface Sci.* **29**, 460–463.

Torii, K., Asaka, M., and Hotta, M. (1986) Synthesis method of silicate: *Jap. Patent* 61-12848.

van Olphen, H. (1977) *Clay Colloid Chemistry,* 2nd ed.: Wiley, New York, 318 pp.