INTERCALATION OF TETRAALKYLAMMONIUM CATIONS INTO SMECTITES AND ITS APPLICATION TO INTERNAL SURFACE AREA MEASUREMENTS

Louis Mercier and Christian Detellier

Ottawa-Carleton Chemistry Institute, University of Ottawa Campus
Ottawa, Ontario, Canada K1N 6N5

Abstract—Monolayer to bilayer (MTB) and bilayer to pseudotrimolecular (BTP) transitions were observed for smectites exchanged with symmetrical tetraalkylammonium cations of increasing sizes: $^+NR_4$, where $R = (CH_2)_nCH_3$, with $0 \leq n \leq 7$. In the case of SWy-1, SHCa-1 and SWa-1, the variation in layer spacing observed from intercalation of tetramethylammonium up to tetraoctylammonium cations showed a behavior characteristic of smectites with homogeneously distributed interlayer cations. In the case of STx-1, the change in interlayer spacing with the increase of the alkyl chain length was characteristic of a very high charge heterogeneity. Higher charge smectites (SAz-1 and SCa-3, CEC > 1.20 mmol/g) were found to have decreasing cation exchange with increasing cation size, resulting in a "leveling off" of the interlayer spacing toward larger cations. The MTB and BTP transitions were used to determine the internal surface area of various smectites. The proposed method was found to be a quicker and simpler alternative to the polar liquid sorption method for this measurement, but was ineffective for high-charge smectites (CEC > 1.20 mmol/g).

Key Words—Hectorite, Intercalation, Internal surface area, Montmorillonite, Quaternary ammonium cations, Smectite, Tetraalkylammonium cations.

INTRODUCTION

Tetraalkylammonium cations can readily replace the interlayer inorganic cations of smectites up to or near their cation exchange capacities, causing a significant "swelling" of the structures and, consequently, an increase in their interlamellar separation (Barrer and MacLeod, 1955; Barrer and Reay, 1957; Barrer and Hampton, 1957; Barrer and Perry, 1961; Barrer and Brummer, 1963; Barrer and Millington, 1967; Barrer, 1986, 1989a, 1989b; Lao *et al.,* 1991). This spacing changes as the size of the interlayer organic cations increases in such a way that one observes sudden jumps in the basal spacing of the clays due to the transition from monolayer to bilayer (Byrne, 1954; McAtee, 1958a, 1958b; Jonas and Roberson, 1966; Tettenhorst and Johns, 1966; Weiss *et al.,* 1969; Clementz and Mortland, 1974; Stul and Mortier, 1974; Lagaly and Weiss, 1975; Lagaly *et al.,* 1976; Lagaly, 1981, 1982; Rüehlicke and Kohler, 1981; Rüehlicke and Nieder-budde, 1985; Stanjek and Friedrich, 1986; Malla and Douglas, 1987; Laird *et al.,* 1987, 1988, 1989; Häusler and Stanjek, 1988; Chen *et al.,* 1989; Ghabru *et al.,* 1989; Olis *et al.,* 1990; Favre and Lagaly, 1991; Stanjek *et al.,* 1992), and to that of bilayer to pseudotrimolecular (Olis *et al.,* 1990; Favre and Lagaly, 1991). Most of the literature cited above pertaining to such transitions involve the exchange of n-alkylammonium cations (of the type $R-NH_3^+$). In this study, the intercalation behavior of a homologous series of tetraalkylammonium cations (of the type NR_4^+, quaternary ammonium cations) is investigated.

An important characteristic of smectites with regard to their intercalation properties is the area covered by the interlamellar regions of the clays, known as the internal surface area. Previously described means of measuring the internal surface area of lamellar minerals involved the sorption of polar liquids into their interlayer space. Ethylene glycol (Dyal and Hendricks, 1950) and ethylene glycol monoethyl ether (Carter *et al.,* 1965) were first used to gravimetrically determine the total surface area of clay minerals. The method involves treating a sample with the respective liquid, placing the mixture in an evacuated chamber over a desiccant ($CaCl_2$ or P_2O_5), and weighing it as a function of time. When a region of constant weight is reached, it is assumed that a stable saturated monolayer of the liquid is present in the interlayers and, knowing the mass of liquid adsorbed and the surface area covered by each molecule, the total surface area of the smectite may be calculated. BET measurements using nitrogen on a sample of the same clay must then be done in order to determine the external surface of the clay particles. The internal surface area S_i can then be calculated by subtracting the external surface from the total surface. Glycerol was also used to perform this measurement by treating montmorillonite with a 2% solution of glycerol in water and then heating the sample at 110°C until constant weight was reached (Diamond and Kinter, 1958). Nearly two decades later, this method was modified by heating the glycerol-smectite complexes in a thermoanalyzer under incremental heating (1°C min^{-1}) instead of using a preselected equilibrium temperature (Madsen, 1977).

In this study, a simpler and quicker method of determining the internal surface area (S_i) of smectites has been developed involving the intercalation of tetraalkylammonium cation into their interlamellar regions. Advantages and limitations of this method are also discussed with respect to the glycerol sorption method.

THEORY

Since tetraalkylammonium cations force an interlayer spacing of about 4–5 Å in monolayer smectites, it can be determined from molecular scale (CPK) models that these cations assume the flattest configuration possible, such that the alkyl chains lie parallel to the clay layers due to the compression between the lamellae (Barrer and MacLeod, 1955). The surface area covered by these "flat" cations can then be evaluated using the same models. The following empirical relationship can thus be derived from the measured surface areas:

$$\text{Cation area } (A_c) = n_c \times 26 \text{ Å}^2 \qquad (1)$$

where n_c is the number of carbons in each alkyl chain.

Thus, as the cations inserted into the clay interlayers get progressively larger by increasing the chain lengths, so does the surface area covered by the alkyl chains within the interlamellar space. At a certain point, the total surface coverage of the cations will exceed that of the available interlamellar space (internal surface area) and a second alkyl chain layer will begin to form. This is the monolayer to bilayer transition (MTB). As even larger cations are inserted, the bilayer to pseudotrimolecular (BTP) transition occurs when the total cation area exceeds twice that of the internal surface area.

The point of the MTB transition must, therefore, correspond to an organically saturated interlamellar space. In other words, each cation covers the surface area corresponding to a single charge on the clay layers: This surface is known as the unit charge area (S_c) and can be expressed as a function of the internal surface area and the cation exchange capacity (CEC) by the following relationship:

$$S_c = \frac{1000 \, S_i}{\text{CEC } N_A} \qquad (2)$$

where CEC is expressed in mmol/g, S_i in m²/g, S_c in m², and $N_A = 6.023 \times 10^{23}$ mol⁻¹.

It should be noted that the CEC of a smectite not only represents the number of exchangeable cations that are found inside the interlayer space but also those on the outside of the clay particles. By considering the usually very low external-surface-to-volume ratio of these particles, however, it can be extrapolated that the vast majority of these cations are located in the interlayer region of the smectites. Thus, CEC here is considered a value that reasonably represents the number of organic cations exchanged inside the interlayer space.

When observing a MTB transition, the value of S_c must be located between the last monolayer and first bilayer points. The value S_{mb} represents the middle area between these points, where the internal surface area would theoretically be entirely covered by the cations. Taking into account that each interlayer cation touches two smectite layers, the following equality exists at full surface coverage: $S_c = S_{mb}$. Thus, S_{mb} may be related to the internal surface area by rearrangement of Eq. 2:

$$S_i = \frac{\text{CEC} \times N_A \times S_{mb}}{1000}. \qquad (3)$$

The internal surface area may also be calculated using the BTP transition area, defined as S_{bp}, using the following equation:

$$S_i = \frac{\text{CEC} \times N_A \times (S_{bp}/2)}{1000}. \qquad (4)$$

Analogous equations relating cation size, layer charge, and smectite surface area (expressed as unit cell parameters a_0 and b_0) were derived using n-alkylammonium cations (Favre and Lagaly, 1991). In that work, however, those equations were used to calculate the interlayer charge density using given unit cell parameters and organic cation surface areas. In the work presented in this paper, the inverse is done: The surface area of the clay is determined by using the surface areas of intercalated cations and known interlayer charge (approximated as being close to the CEC values).

METHODS

Materials

Purification of clays (van Olphen, 1977; Villemure, 1987): the crude smectites (SWy-1, STx-1, SHCa-1, SAz-1, SWa-1, and SCa-3, obtained from the Clay Source Repository, University of Missouri) were purified in suspension by acidification to pH 3.5, washing by centrifugation with HCl pH 3.5, followed by overnight sedimentation at pH 8 to recover the fine particles ($<0.2 \mu$m) in the supernatant liquid. Excess NaCl was added to the suspension to form homoionic Na⁺ smectites. The mixture was then washed free of excess ions by dialysis and isolated by freeze-drying.

All of the tetraalkylammonium salts were obtained from Aldrich Chemicals either in the bromide or the iodide form (minimum 95% purity) and were used without further purification.

CEC determination of clay samples

A series of NaCl solutions were prepared ranging from 0.1 to 1.0 mM. A Na⁺ electrode was used to measure the potential of each solution. From these results, a standard plot was made relating log [Na⁺] to the measured voltage. Tetramethylammonium iodide (TMA, 0.4 mmole) was added to 0.1 g of each clay

Table 1.   Cation exchange capacities for studied smectites.

Smectite	CEC (meq/g) literary values	CEC measured by TMA displacement	CEC measured by TPA displacement
SWy-1	0.79	0.83	0.75
STx-1	0.80	0.85	0.60
SHCa-1	0.46	n.d.	n.d.
SWa-1	n/a	1.04	n.d.
SAz-1	1.20	1.26	0.53
SCa-3	1.53	1.70	0.70

Table 2.   Internal surface areas for smectites (in m^2/g).

Smectite	S_{mh} ($Å^2$)	$S_{bp}/2$ ($Å^2$)	Calculated S_i	Literature S_i (Madsen, 1977)
SWy-1	143 ± 13	—	646 ± 59	662 ± 22
STx-1	169 ± 13	—	611 ± 47	599 ± 24
SHCa-1	169 ± 13	—	468 ± 36	486 ± 12
SWa-1	91 ± 13	98 ± 7	611 ± 44	n.d.
SAz-1	65 ± 13	—	493 ± 99	820 ± 18
SCa-3	65 ± 13	—	670 ± 130	n.d.

The CEC values used for the calculations were obtained from TPA exchange, except for SHCa-1 and SWa-1, which used 0.46 and 1.04, respectively. For SAz-1 and SCa-3, the TMA exchange values were used because these transitions occurred before the TPA insertion.

(accurately weighed) and 50 ml of water was added. The suspension was stirred for 48 hr at room temperature and centrifuged, 25 ml of the supernatant was diluted with 50 ml water, and the potential was measured with the Na^+ electrode. Using the standard plot, the quantity of Na^+ released from the clay by cation exchange was determined and the CEC calculated. The above procedures were repeated using tetrapropylammonium iodide (TPA) to verify whether or not the exchange was dependent on cation size.

Internal surface area determination

To 0.1 g samples of clay were added about 0.4 mmol of each tetraalkylammonium cation (ranging from tetramethylammonium to tetraoctylammonium) and about 40 ml of a 70% methanol/water mixture. The samples were stirred for 48 hr at room temperature and centrifuged, discarding the supernatant liquid. The samples were then washed and centrifuged several times with 70% methanol in order to remove cations adsorbed in excess of the clay's CEC. The organo-clay

suspensions were then spread out on glass slides and studied by X-ray diffraction using a Philips 1710 automated diffractometer (CuKα radiation, wavelength = 1.54 Å). The layer separations (d) of the samples were calculated by averaging all of the visible d_{00n} contributions on the diffraction pattern, i.e., $d = (d_{001} + 2d_{002} + 3d_{003} + \ldots + nd_{00n})/n$. The interlayer separations (d_{is}) were then calculated for each sample by subtracting 9.6 Å (the thickness of a 2:1 smectite layer) from this average d value.

RESULTS

The results for the CEC determinations are presented in Table 1. The interlayer spacings of the substituted smectites are plotted as a function of the number of carbons in the alkyl chains in order to show the MTB and BTP transitions (Figures 1 and 2). Using the tran-
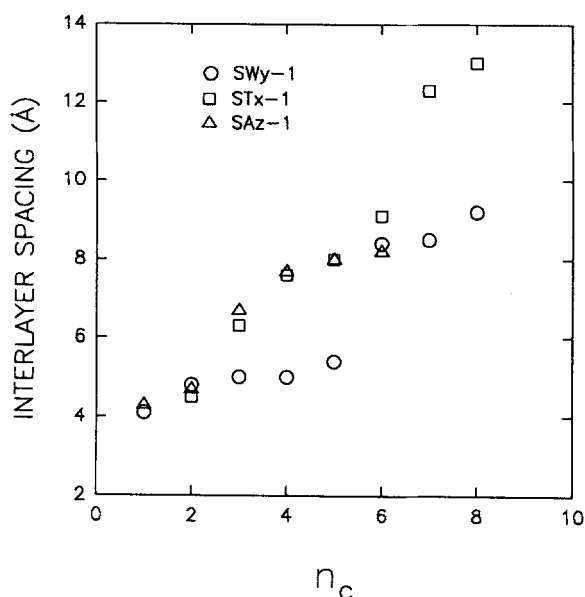

Figure 1.   Interlayer distance (d_{001} − 9.6 Å) of various organo-smectites (SWy-1, STx-1 and SAz-1) as a function of the number of carbons, n_c, of the alkyl groups of intercalated tetraalkylammonium, $^+N(CH_2)_{n-1}CH_3)_4$.
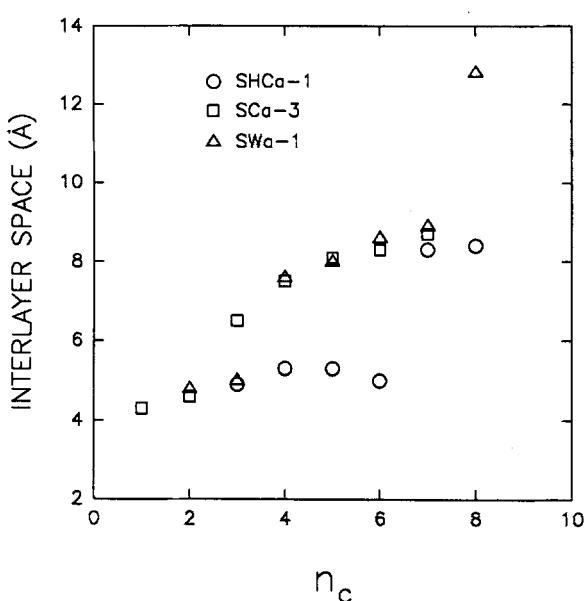

Figure 2.   Interlayer distance (d_{001} − 9.6 Å) of various organo-smectites (SHCa-1, SWa-1 and SCa-3) as a function of the number of carbons, n_c, of the alkyl groups of intercalated tetraalkylammonium, $^+N((CH_2)_{n-1}CH_3)_4$.

sition areas from these graphs and Eqs. 3 and 4, the internal surface areas of the smectites were calculated and are presented in Table 2.

DISCUSSION

X-ray diffraction data of smectites exchanged with tetraalkylammonium cations showed in most cases sharp MTB and BTP transitions from which the internal surface areas of SWy-1, STx-1, and SHCa-1 could be measured. These results were in excellent accordance with those obtained from the literature (see Table 2). The measurements for the high charge smectites (SAz-1 and SCa-3), however, had considerable uncertainties in their values and, in the case of SAz-1, did not concord with the previously determined value.

The theory behind the method follows two important assumptions: 1) that all of the exchangeable interlayer Na^+ be replaced with the organic cations of each tetraalkylammonium species (100% exchange), and 2) that the cations be placed in a homogeneous manner within the clay layers.

The first assumption was found to be correct in the case of SWy-1, where it has been shown that cation exchange is complete or nearly complete up to the tetraoctylammonium cation (Mercier, 1991). In SAz-1 and SCa-3, however, the cation exchange drops dramatically from the TMA cation to the TPA cation (see Table 1). It has indeed been reported that the reactivity of clays with tetraalkylammonium cations decreases with increasing clay layer charge (Laird *et al.,* 1989). The large tetraalkylammonium cations thus do not completely exchange the interlayer Na^+ of high charge clays (McAtee, 1962, 1963). The proposed method is, therefore, not reliable for high charge smectites (CEC > 1.20 meq/g) such as SAz-1 and SCa-3.

The second assumption is not quite factual since charge heterogeneity exists in the clay structure because of uneven isomorphic substitutions in the clay layers. As a consequence, the insertion of progressively larger n-alkylammonium cations (of type $R-NH_3^+$) does not produce any sudden MTB or BTP transitions. Rather, a gradual increase in the interlayer distance is seen in the transition zone (Byrne, 1954; McAtee 1958a, 1958b; Jonas and Roberson, 1966; Tettenhorst and Johns, 1966; Weiss *et al.,* 1969; Clementz and Mortland, 1974; Stul and Mortier, 1974; Lagaly and Weiss, 1975; Lagaly *et al.,* 1976; Lagaly, 1981, 1982; Rüehlicke and Kohler, 1981; Rüehlicke and Niederbudde, 1985; Stanjek and Friedrich, 1986; Malla and Douglas, 1987; Laird *et al.,* 1987, 1988, 1989; Häusler and Stanjek, 1988; Chen *et al.,* 1989; Ghabru *et al.,* 1989; Olis *et al.,* 1990; Favre and Lagaly, 1991; Stanjek *et al.,* 1992). The sharp transitions observed in the case of the tetraalkylammonium smectites suggest that the effect of charge heterogeneity has little effect for these species since the size increase from one such cation to the next larger is much greater than the size increase from one n-alkylammonium cat-

ion to the next. An exception to the previous statement is seen in the case of STx-1, where the interlayer space increases very strongly as the inserted cations get larger, presumably because the very high charge heterogeneity of the smectite results in the agglomeration of cations. The MTB transition for the STx-1 system is assumed to occur at the tetraheptylammonium cation, as this corresponds to the only appreciable jump in interlayer spacing.

Advantages of the discussed method with respect to the polar liquid adsorption methods are that it is quicker and requires no weighing or heating apparatus. Disadvantages of the tetraalkylammonium method include higher uncertainties in the calculated values than in the polar liquid adsorption method, the requirement of a precise CEC value (especially for the cations near the MTB transition), and the apparent ineffectiveness of the method for high-charge smectites (CEC > 1.20 meq/g). Another limitation about this method is that cations near the edge of the clay layers may have some of their alkyl chains "squeezed out" of the interlayer space (Favre and Lagaly, 1991), thus resulting in the calculation of too large an internal surface area. Considering the reasonably large size of the clay particles used here (average diameter of about 0.1 μm or more), this effect would fortunately not be very significant. Care should be taken, however, when applying this technique on ultrafine clay samples.

Qualitative observations seemed to be indicative of the MTB transition: When the substituted SWy-1 samples were washed with 70% methanol, the supernatant wash liquids were clear for the organo-clays inserted with cations up to tetrapentylammonium and cloudy for those inserted with larger cations. The formation of an organic bilayer indicates that the entire clay surface is covered with organophilic alkyl chains; thus, there is no contact between the solvent and the mineral clay surface, resulting in a sudden reduction in the flocculation ability of the clay in a largely organic solvent. This same observation is also valid for STx-1.

CONCLUSION

The internal surface areas of various smectites were calculated from the MTB and BTP transitions observed by exchanging the clays with tetraalkylammonium cations. Results thus obtained showed in many cases good accordance with literature values. The method was found to be a simple and quick alternative to the polar liquid sorption techniques previously described. It was, however, ineffective to measure that of smectites with high CEC values (> 1.20 meq/g) since cation exchange was incomplete for these species.

ACKNOWLEDGMENTS

REFERENCES

Barrer, R. M. and MacLeod, D. M. (1955) Activation of montmorillonite by ion exchange and sorption complexes of tetra-alkyl ammonium montmorillonite: *Trans. Farad. Soc.* **51**, 1290–1300.

Barrer, R. M. and Reay, J. S. S. (1957) Sorption and intercalation by methyl-ammonium montmorillonite: *Trans. Farad. Soc.* **53**, 1253–1261.

Barrer, R. M. and Hampton, M. G. (1957) Gas chromatography and mixtures isotherms in alkyl ammonium bentonites: *Trans. Farad. Soc.* **53**, 1462–1475.

Barrer, R. M. and Perry, G. S. (1961) Sorption of mixtures, and selectivity in alkylammonium montmorillonites. Parts I & II: *J. Chem. Soc.,* 842–849 and 850–858.

Barrer, R. M. and Brummer, K. (1963) Relations between partial ion exchange and interlamellar sorption in alkylammonium montmorillonites: *Trans. Farad. Soc.* **59**, 959–968.

Barrer, R. M. and Millington, A. D. (1967) Sorption and intracrystalline porosity in organo-clays: *J. Colloid Interface Sci.* **25**, 359–372.

Barrer, R. M. (1986) Expanded clay minerals: A major class of molecular sieves: *J. Inclusion Phen.* **4**, 109–119.

Barrer, R. M. (1989a) Clay minerals as selective and shape-selective sorbents: *Pure & Appl. Chem.* **61**, 1903–1912.

Barrer, R. M. (1989b) Shape-selective sorbents based on clay minerals: A review: *Clays & Clay Minerals* **37**, 385–395.

Byrne, P. J. S. (1954) Some observations on montmorillonite-organic complexes: *Clays & Clay Minerals* **2**, 241–253.

Carter, D. L., Heilman, M. D., and Gonzalez, C. L. (1965) Ethylene glycol monoethyl ether for determining surface area of silicate minerals: *Soil Sci.* **100**, 356–360.

Chen, C. C., Turner, F. T., and Dixon, J. B. (1989) Ammonium fixation by high-charge smectite in selected Texas Gulf Coast soils: *Soil Sci. Soc. Am. J.* **53**, 1035–1040.

Clementz, D. M. and Mortland, M. M. (1974) Properties of reduced charge montmorillonite: Tetra-alkylammonium ion exchange forms: *Clays & Clay Minerals* **22**, 223–229.

Diamond, S. and Kinter, E. B. (1958) Surface area of clay minerals as derived from measurements of glycerol retention: *Clays & Clay Minerals* **5**, 334–347.

Dyal, R. S. and Hendricks, S. B. (1950) Total surface of clays in polar liquids as a characteristic index: *Soil Sci.* **69**, 421–432.

Favre, H. and Lagaly, G. (1991) Organo-bentonites with quaternary alkylammonium ions: *Clay Miner.* **26**, 19–32.

Ghabru, S. K., Mermut, A. R., and St. Arnaud, R. J. (1989) Layer-charge and cation-exchange characteristics of vermiculite (weathered biotite) isolated from a gray luvisol in northeastern Saskatchewan: *Clays & Clay Minerals* **37**, 164–172.

Häusler, W. and Stanjek, H. (1988) A refined procedure for the determination of the layer charge with alkylammonium ions: *Clay Miner.* **23**, 333–337.

Jonas, E. C. and Roberson, H. E. (1966) Structural charge density as indicated by montmorillonite hydration: *Clays & Clay Minerals* **13**, 223–230.

Lagaly, G. and Weiss, A. (1975) The layer charge of smectitic layer silicates: *Proc. Int. Clay Conf. Mexico:* Applied Publishing Ltd., Willamette, Ill., 157–172.

Lagaly, G., Fernandez Gonzalez, M., and Weiss, A. (1976) Problems in layer-charge determination of montmorillonites: *Clay Miner.* **11**, 173–187.

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

Lagaly, G. (1982) Layer charge heterogeneity in vermiculites: *Clays & Clay Minerals* **30**, 215–222.

Laird, D. A., Scott, A. D., and Fenton, T. E. (1987) Interpretation of alkylammonium characterization of soil clays: *Soil Sci. Soc. Am. J.* **51**, 1659–1663.

Laird, D. A., Fenton, T. E., and Scott, A. D. (1988) Layer charge of smectites in an Argiaboll-Argiaquoll sequence: *Soil Sci. Soc. Am. J.* **52**, 463–467.

Laird, D. A., Scott, A. D., and Fenton, T. E. (1989) Evaluation of the alkylammonium method of determining layer charge: *Clays & Clay Minerals* **37**, 41–46.

Lao, H., Latieule, S., and Detellier, C. (1991) Molecular recognition in microporous organo-minerals. Shape-specific interactions of carbon dioxide in functionalized organo-montmorillonite microcavities: *Chem. Mater.* **3**, 1009–1011.

Madsen, F. T. (1977) Surface area measurements of clay minerals by glycerol sorption on a thermobalance: *Thermochimica Acta* **21**, 89–93.

Malla, P. B. and Douglas, L. A. (1987) Layer charge properties of smectites and vermiculites: Tetrahedral *vs.* octahedral: *Soil Sci. Soc. Am. J.* **51**, 1362–1366.

McAtee, J. L. (1958a) Heterogeneity in montmorillonite: *Clays & Clay Minerals* **5**, 279–288.

McAtee, J. L. (1958b) Random interstratification in organophilic bentonites: *Clays & Clay Minerals* **5**, 308–317.

McAtee, J. L. (1962) Cation exchange of organic compounds on montmorillonite in organic media: *Clays & Clay Minerals* **9**, 444–450.

McAtee, J. L. (1963) Organic cation exchange on montmorillonite as observed by ultraviolet analysis: *Clays & Clay Minerals* **10**, 53–162.

Mercier, L. (1991) Intercalation of tetraalkylammonium cations into smectites: Honours thesis, University of Ottawa, 55 pp.

Olis, A. C., Malla, P. B., and Douglas, L. A. (1990) The rapid estimation of the layer charges of 2:1 expanding clays from a single alkylammonium ion expansion: *Clay Miner.* **25**, 39–50.

Rüehlicke, G. and Kohler, E. E. (1981) A simplified procedure for determining layer charge by the n-alkylammonium method: *Clay Miner.* **16**, 305–307.

Rüehlicke, G. and Niederbudde, E. A. (1985) Determination of layer-charge density of expandable 2:1 clay minerals in soils and loess sediments using the alkylammonium method: *Clay Miner.* **20**, 291–300.

Stanjek, H. and Friedrich, R. (1986) The determination of layer charge by curve-fitting of Lorentz- and polarization-corrected X-ray diagrams: *Clay Miner.* **21**, 183–190.

Stanjek, H., Niederbudde, E. A., and Häusler, W. (1992) Improved evaluation of layer charge of n-alkylammonium-treated fine soil clays by Lorentz- and polarization-correction and curve fitting: *Clay Miner.* **27**, 3–19.

Stul, M. S. and Mortier, W. J. (1974) The heterogeneity of the charge density in montmorillonites: *Clays & Clay Minerals* **22**, 391–396.

Tettenhorst, R. and Johns, W. D. (1966) Interstratification in montmorillonites: *Clays & Clay Minerals* **25**, 85–93.

Val Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry:* Wiley Interscience, New York, 318 pp.

Villemure, G. (1987) Photochemical applications of the intercalation of organic cations in clay minerals: Ph.D. thesis, University of Ottawa, 238 pp.

Weiss, A., Becker, H. O., and Lagaly, G. (1969) Determination of charge density sequence in regular interstratified mica-type layer silicates by means of their n-alkylammonium derivatives: *Proc. Int. Clay Conf. Tokyo* **1**, 67–72.