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EVALUATION OF THE ALKYLAMMONIUM METHOD OF DETERMINING LAYER CHARGE[1]

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Abstract—The layer charge of five smectites, one vermiculitic material, and five reduced-charge clays was determined by the alkylammonium and structural formula methods. The two sets of results were found to be linearly correlated (r = .961); however, the values that were determined by the alkylammonium method were 20 to 30% lower than those determined by the structural formula method, and the regression slope for their linear relationship was 1.67. The fact that the structural formula method includes the effects of cations on the lateral edges of the clay particles probably accounted for some of the differences in the magnitude of the results but should not have caused the regression slope to deviate substantially from 1.00. Therefore, inaccurate estimates of the packing density of alkylammonium cations in the interlayer space of 2:1 phyllosilicates were deemed responsible for the systematic divergence of the results of the two methods. To satisfy the need for a relationship between the two methods of determining layer charge, an empirical means of adjusting the alkylammonium values has been proposed and shown to yield values of layer charge that are comparable to those determined by the structural formula method.

Key Words—Alkylammonium, Layer charge, Reduced charge, Smectite, Structural formula.

INTRODUCTION

Layer charge is a particularly important property of clay-size 2:1 phyllosilicates in that it determines the cation-retention capacity of clays, it influences the selectivity of clays for various cations during ion-exchange reactions, and it affects the ability of clays to adsorb water and various polar organic molecules. Furthermore, the magnitude of the layer charge serves as a criterion for the classification of 2:1 phyllosilicates (Bailey *et al.*, 1971). Thus, due regard needs to be given to the accuracy of the results obtained by different methods of determining the layer charge.

The alkylammonium method of determining the layer charge of smectites and vermiculites was introduced by Lagaly and Weiss (1969). This method offers certain advantages over methods based on chemical analyses: (1) information about the heterogeneity of the layer charge within a clay can be obtained with the alkylammonium method, (2) the alkylammonium method can be used to determine the layer charge of smectites in mixed mineral assemblages, and (3) the determinations are based on easily obtained X-ray powder diffraction (XRD) data. The procedure involved in the calculation of layer charges from XRD data, however, has been revised several times (Lagaly and Weiss, 1971; Stul and Mortier, 1974; Lagaly and Weiss, 1976) to cope with uncertainties about the packing density of alkylammonium cations in the interlayer space of 2:1 phyllosilicates. As a result, questions arise as to the accuracy of values of layer charge that have been determined by the alkylammonium method. For example, Maes *et al.* (1979) observed that differences between the permanent and total charge cannot account for the relative magnitudes of the layer charge determined by the alkylammonium method and the cation-exchange capacity of eight reference and reduced-charge clays.

Layer charge can also be estimated by deriving structural formulae from total elemental analyses of monomineralic clay samples. Unfortunately, the analytical difficulties, the long time, and the expense of obtaining accurate total elemental analyses have been major limitations in this use of structural formulae. This situation has been altered, however, by the availability of simultaneous multielement analyses of clay suspensions by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Spiers *et al.*, 1983). The development of this technique has made it much easier to determine the layer charge of minerals from their chemical composition and has, thereby, facilitated a comparison of the structural formula and alkylammonium methods.

The objectives of this study were to compare values of layer charge determined by the alkylammonium and structural formula methods and establish a means of obtaining similar results with the two methods.

MATERIALS AND METHODS

Five smectites and one vermiculitic material (a mixture of vermiculite, hydrobiotite, and biotite) were used in this investigation. Samples of Cheto montmorillonite (SAz-1), Washington State ferruginous smectite (SWa-1), and California hectorite (SHCa-1) were obtained from the Source Clays Repository of The Clay Minerals Society. A sample of Wyoming bentonite was

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obtained from the American Colloid Company, and a sample of South Carolina vermiculitic material from the Zonolite Company (now a part of W. R. Grace & Company). A sample of beidellite was separated from a sample of the Bt1 horizon of a Zwingle (fine, montmorillonitic, mesic Typic Albaqualfs) pedon located in Allamakee County, Iowa (Laird, 1987). Portions of the smectite samples and dry-ground vermiculitic material were mechanically dispersed in distilled water, and the < 1-μm size fractions were separated by sedimentation. The symbols used to designate the clays are B, C, F, H, V, and Z for the Wyoming bentonite, Cheto montmorillonite, Washington State ferruginous smectite, California hectorite, south Carolina vermiculitic material, and Zwingle beidellite, respectively.

Five reduced-charge smectites were also used in this investigation. Following the general procedure of Brindley and Etrem (1971), the preparation of these clays was initiated by washing portions of the < 1-μm Cheto sample three times in 1 M NaCl or LiCl solutions and then with a 50% (v/v) mixture of ethanol and water until the supernatant solutions were free of $AgNO_3$-detectable Cl^-. Stock suspensions (~50 g/liter) of these homoionic Li- and Na-clays were prepared and combined volumetrically to form various Li-Cheto : Na-Cheto mixtures. These mixed suspensions were mechanically shaken for 48 hr and dried in a vacuum oven at 60°C. The clay samples were then heated at 220°C in a vacuum (26 kPa) for 24 hr and designated RC0, RC1, RC2, RC3, and RC4 in accordance with their preparation from suspensions having Li-Cheto : Na-Cheto ratios of 0:10, 1:9, 2:8, 3:7, and 4:6, respectively.

Portions of each clay were treated with various alkylamine hydrochloride solutions and analyzed by XRD. The alkylamine hydrochlorides and the treatment solutions were prepared by the method of Rühlicke and Kohler (1981). For these alkylammonium treatments, the Na-saturated clay samples (~150 mg) were thoroughly mixed with 5 ml of the appropriate alkylamine hydrochloride solution, incubated at 60°C for 24 hr, and separated by centrifugation. The alkylammonium treatments were repeated once, and the samples were finally washed in 95% ethanol until the supernatant solutions were free of $AgNO_3$-detectable Cl^-. Oriented specimens of the treated clays were prepared on glass slides by the paste technique and dried at 60°C in a vacuum (26 kPa) for 24 hr. The XRD analyses were performed with the clay specimens in a desiccated atmosphere, and the results were used to calculate values of layer charge for each clay by the method of Lagaly (1981). For these calculations, it was assumed that the alkyl chains of interlayer alkylammonium cations did not protrude from the interlayer space (equivalent to assuming an infinitely large particle diameter).

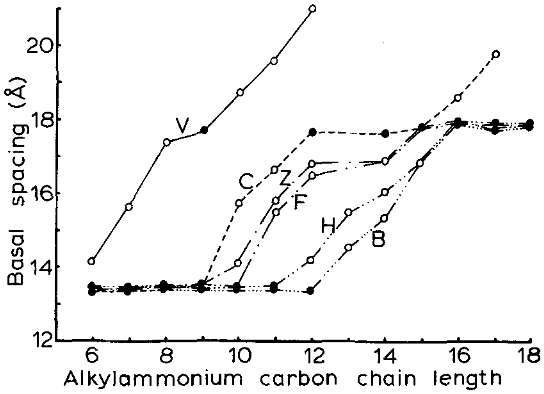

Figure 1. Relationship between basal spacing and the alkylammonium carbon chain length for the South Carolina vermiculitic material (V), Cheto montmorillonite (C), Zwingle beidellite (Z), Washington State ferruginous smectite (F), California hectorite (H), and Wyoming bentonite (B). Samples exhibiting rational higher-order X-ray power diffraction (XRD) peaks are shown with closed circles; samples exhibiting irrational higher-order XRD peaks are shown with open circles.

Replicate total elemental analyses of the eleven studied clays were performed by ICP-AES (Spiers *et al.*, 1983). For these analyses, portions of each clay were Ca-saturated by four centrifugal washings with 0.5 M $CaCl_2$ and then washed in distilled water until the supernatant solutions were free of $AgNO_3$-detectable Cl^-. Samples (~0.1 g) of the Ca-saturated clays were then sonified (1 min) in 100 ml of 0.16 M HNO_3 to obtain suspensions, which were introduced directly into the spectrometer. The suspensions were stirred continuously with a mechanical mixer to prevent settling during sample aspiration. Determinations of Si^{4+} in the hectorite and ferruginous smectite were also made by inductively coupled plasma-mass spectrometry. Ferrous iron measurements were carried out by the method of Amonette and Scott (1984). The results of the replicated elemental determinations were averaged for each clay, and the average values were used to calculate structural formulae (Gast, 1977). For these calculations, the clays were assumed to have 10 oxygens and 2 hydroxyls per formula unit, and all the Ca^{2+}, K^+, and Na^+ ions were assigned to interlayer positions.

RESULTS

The XRD patterns for the various alkylammonium derivatives of the smectites provided evidence for the existence of (1) monolayer forms which had 13.6-Å basal spacings, (2) bilayer forms which had 17.7-Å basal spacings, and (3) monolayer-bilayer transition forms which had irrational sequences of basal reflections and values of d(001) between 13.6 and 17.7 Å. The relationships between the carbon chain length of the alkylammonium cations and the basal spacings that they induced in the various clays are presented in Figures 1 and 2.

The South Carolina vermiculitic material consisted

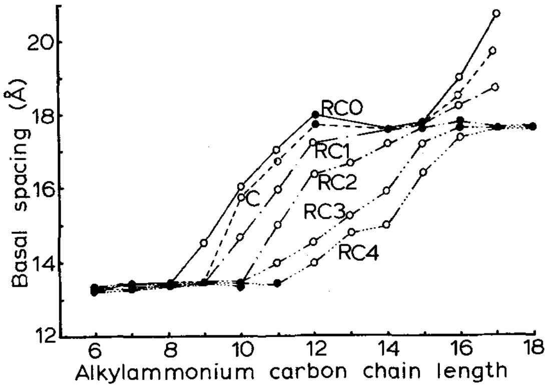

Figure 2. Relationship between basal spacing and the alkylammonium carbon chain length for the Cheto montmorillonite (C) and the reduced-charge clays (identified by symbols listed in Materials and Methods). Samples exhibiting rational higher-order X-ray powder diffraction (XRD) peaks are shown with closed circles; samples exhibiting irrational higher-order XRD peaks are shown with open circles.

of three phases; a fully contracted 9.4-Å phase, a regularly interstratified phase, and an expandable phase (Laird, 1987). The alkylamine hydrochloride treatments did not change the fully contracted phase, whereas the expandable and the regularly interstratified phases exhibited monolayer-bilayer transitions. An interpretation of the changes in the XRD peaks of the regularly interstratified phase was ruled out by the effects of mixed layering and the potential for an exchange of interlayer K^+. Therefore, only the XRD peaks for the expandable phase were used to estimate the layer charge of the vermiculitic material. In doing so, a bilayer configuration was identified with the nonylammonium derivative, and a monolayer configuration was assumed for the pentylammonium derivative. The contracted and the regularly interstratified phases may have had a higher average layer charge than the expandable phase. If so, the value of layer charge determined for the vermiculitic material by the alkylammonium method should have been less than the average charge of the entire sample.

The simultaneous multielement analyses of the clay suspensions by ICP-AES yielded reasonable results for most of the determinations; however, the Si^{4+} values seemed low for the hectorite and the ferruginous smectite and were replaced with those obtained by inductively coupled plasma-mass spectrometry. The results of the elemental analyses were tabulated by Laird (1987) and used here to calculate the structural formulae presented in Table 1.

The relationship between the values of layer charge determined by the alkylammonium (A1) and the structural formula (SF) methods is presented in Figure 3.

DISCUSSION

The comparison in Figure 3 describes a strong linear correlation between the A1 and SF values of layer charge, which affirms the general validity of both the alkylammonium and structural formula methods of determining layer charge. Ideally, both methods should yield estimates of the permanent layer charge and, therefore, ought to provide similar results. The A1 values, however, were 20 to 30% lower than the SF values, and the regression slope for their relationship was 1.67 rather than 1.00. These discrepancies between the A1 and SF values are indicative of systematic errors in one or both methods.

The accuracy of layer-charge values determined by the structural formula method is limited by three factors: (1) the applicability of the usual assumptions in the structural interpretations of chemical analyses (e.g., a clay may not have exactly 10 oxygens and 2 hydroxyls per formula unit), (2) the presence of contaminants or more than one species of clay mineral in the sample, and (3) the existence of cations adsorbed on the lateral edges of the clay particles. Factors 1 and 2 have variable effects on the results, whereas, because of factor 3 (the broken-bond effect) most values determined by the structural formula method exceed the permanent layer

Table 1. Cationic composition of the structural formulae of the studied clays (cations per $O_{10}(OH)_2$).

	Interlayer		Tetrahedral		Octahedral						
Clay[1]	Ca^{2+}	K^+	Si^{4+}	Al^{3+}	Mg^{2+}	Al^{3+}	Fe^{3+}	Fe^{2+}	Mn^{2+}	Ti^{4+}	Li^+
B	0.16	0.00	3.95	0.05	0.24	1.59	0.15	0.01	0.00	0.00	0.00
F	0.24	0.00	3.74	0.26	0.13	0.39	1.42	0.00	0.00	0.02	0.00
H	0.17	0.00	3.96	0.04	2.68	0.01	0.01	n.d.[2]	0.00	0.00	0.28
V	0.20	0.26	2.92	1.08	2.15	0.00	0.48	0.03	0.01	0.15	0.00
Z	0.15	0.09	3.66	0.34	0.22	1.29	0.52	0.02	0.00	0.01	0.00
C	0.23	0.01	4.00	0.00	0.58	1.37	0.07	n.d.	0.01	0.01	0.00
RC0	0.23	0.00	4.01	0.00	0.60	1.36	0.06	n.d.	0.00	0.01	0.00
RC1	0.22	0.00	4.01	0.00	0.59	1.36	0.06	n.d.	0.00	0.01	0.05
RC2	0.20	0.00	4.01	0.00	0.59	1.36	0.06	n.d.	0.00	0.01	0.09
RC3	0.18	0.00	4.01	0.00	0.59	1.36	0.06	n.d.	0.00	0.01	0.13
RC4	0.17	0.00	4.01	0.00	0.59	1.36	0.06	n.d.	0.00	0.01	0.16

[1] Symbols refer to clays specified in Materials and Methods.
[2] Not determined.

charge. The magnitude of this error is prescribed by the amount of cations on the lateral surfaces of the clay particles. Therefore, values of layer charge based on structural interpretations of chemical analyses usually depict the total layer charge.

The fundamental assumption of the alkylammonium method is that alkylammonium-clay derivatives will shift from a monolayer to a bilayer configuration when the average planar area associated with each interlayer alkylammonium cation (A_c) exceeds the average planar area available per charge site (A_e) in the interlayer space of a 2:1 phyllosilicate. To estimate values of A_c, Lagaly and Weiss (1969) assumed that each $-CH_2-$ group in an alkyl chain occupies 5.67 Å^2 and that the $-NH_3^+$ group occupies 9 Å^2 (later increased to 14 Å^2; Lagaly and Weiss, 1971). These values were based on estimates of C–H distances, van der Waals radii, and the assumption that the plane of the zig-zag arrangement of the carbon atoms in an interlayer alkylammonium cation is parallel to the plane of the silicate layers. Unfortunately, this approach does not provide an accurate estimate of values of A_c, because these values are influenced by the amount of unoccupied space between adjacent cations, the extent to which some cations protrude from the interlayer space, and possibly many other factors (Lagaly and Weiss, 1976). As a result, Lagaly and Weiss (1971) suggested that the values of A_c be corrected for particle-size effects. Stul and Mortier (1974) did so by assuming that half of each alkylammonium cation near the lateral edges of the clay particles is located outside the particle. These corrections for 'particle-size effects' are quite arbitrary, but without some kind of a correction factor, the alkylammonium method will yield values of layer charge that are lower than the permanent layer charge.

It is evident that most of the differences in the magnitude of the A1 and SF values can be attributed to a combination of the particle-size and broken-bond effects. Both these effects, however, are theoretically independent of the permanent layer charge and, therefore, cannot explain the observed regression slope of 1.67 for the A1-SF relationship. Indeed, the results in Figure 3 for the reduced-charge clays confirm this point. These five clay samples were derived from the same <1-μm Cheto material and, hence, should have imposed comparable particle size and broken bond effects, but their A1 and SF values still diverged as the layer charge increased. Likewise, because they have a unique role, none of the other factors limiting the accuracy of the structural formula method can account for this charge-dependent divergence of the results. On the other hand, at least two possible arrangements of interlayer alkylammonium cations exist that could produce a systematic change in the values of A_c. First, in high-charge clays, the alkylammonium cations located near the lateral edges of the clay particles can protrude out of the interlayer space to a greater extent than similarly positioned alkylammonium cations in low-charge clays (Maes *et al.*, 1979). Second, the small alkylammonium cations that cause monolayer-bilayer transitions in high-charge clays can be more densely packed than the large alkylammonium cations that cause monolayer-bilayer transitions in low-charge clays. As a result, the alkylammonium method is probably responsible for the A1-SF regression slope being 1.67 instead of 1.00.

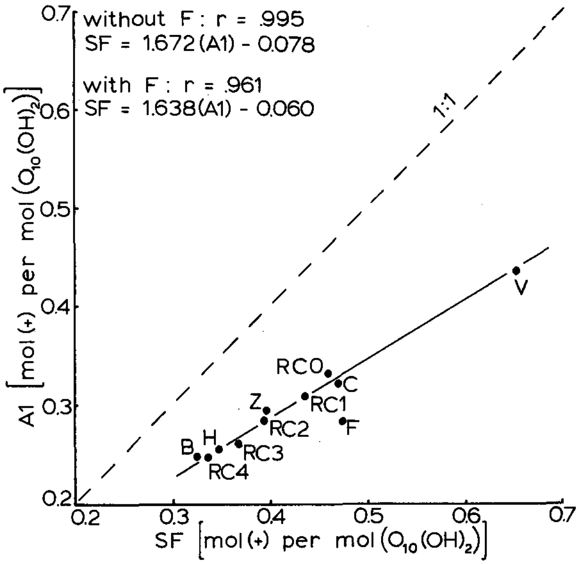

Figure 3. Relationship between values of layer charge determined by the structural formula (SF) and the alkylammonium (A1) methods for the studied clays (identified by symbols listed in Materials and Methods).

The development of the current classification scheme for 2:1 phyllosilicates was based on values of layer charge derived from structural formulae. On the other hand, increasing use of the alkylammonium method can be expected in the future, because it is the only method of determining the layer charge of smectites in mineral mixtures and of providing information about the layer-charge heterogeneity. Neither method, however, can be relied upon to obtain accurate estimates of the permanent layer charge. Indeed, under some circumstances substantial errors may be encountered with both methods. The errors associated with the alkylammonium method vary in an ill-defined manner with both the particle size and the magnitude of the permanent layer charge. By contrast, the errors introduced with the structural formula method can be confined to the broken bond effect. Therefore, an empirical means of relating the alkylammonium results to those obtained with the structural formula method was developed.

Lagaly (1981) suggested that values of A_c are related to the carbon chain length of the various alkylammonium cations (n_c) by Eq. (1),

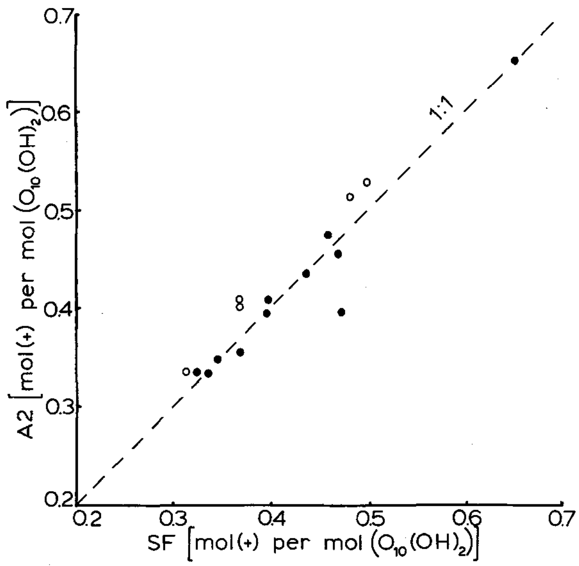

Figure 4. Relationship between values of layer charge determined by the structural formula (SF) and the empirically modified alkylammonium (A2) methods for the eleven clays used in this study (closed circles) and five reference smectites of Senkayi *et al.* (1985) (open circles).

$$A_c = 5.67(n_c) + 14, \qquad (1)$$

and that A_e is related to the charge per formula unit (σ) by Eq. (2),

$$A_e = \frac{d(100)d(010)}{2\sigma}, \qquad (2)$$

where d(100)d(010) is the planar area per unit cell. The relationship between the critical carbon-chain length that causes the monolayer-bilayer transition (n_c') and the related layer charge (σ'),

$$\sigma' = \frac{23.25}{5.67(n_c') + 14}, \qquad (3)$$

was obtained by equating A_c and A_e and by assuming that d(100)d(010) = 46.5 Å². Eq. (3) was used to calculate the A1 (weighted average σ' values for the n_c' values associated with the monolayer-bilayer transition) values of layer charge in Figure 3. Therefore, a combination of Eq. (3) and the A1-SF regression equation without F in Figure 3 was used to obtain the empirical relationship,

$$\sigma'' = \frac{38.88}{5.67(n_c') + 14} - 0.078, \qquad (4)$$

that should yield values of layer charge (σ'') comparable to those determined by the structural formula method.

Eq. (4) was used to calculate A2 (weighted average σ'' values for the n_c' values associated with the monolayer-bilayer transition) values of layer charge for the 11 clays used in this study. As expected, the agreement between the A2 and SF values for these clays was good (Figure 4). Because Eq. (4) was based on the SF values for these clays, however, an independent test of Eq. (4) was carried out with data of Senkayi *et al.* (1985), who presented both structural formulae and graphs depicting the relationship between n_c and d(001) and, hence, enough information to calculate SF and A2 values for five reference smectites. As shown in Figure 4, the A2 values based on the data of Senkayi *et al.* (1985) are slightly higher than their corresponding SF values, but they do demonstrate the general applicability of Eq. (4).

Layer-charge calculations based on Eq. (4) represent another modification of the alkylammonium method, but with monomineralic specimens this modification has been shown to yield layer-charge values similar to those obtained with the structural formula method. Furthermore, this modification appears to be reasonable for estimating the layer charge associated with the structural formulae of the smectite and vermiculite components of mineral mixtures.

The data for the South Carolina vermiculitic material were not essential for the establishment of the A1-SF relationship, because an exclusion of the V data from the regression analysis had relatively small effects on the correlation coefficient (.982 vs. .995) and slope (1.631 vs. 1.672). On the other hand, the results for this mineral fit the relationships prescribed by the other minerals in Figures 3 and 4, even though the A1 and A2 values depicted the layer charge of only the expandable phase, whereas the SF value gave an average layer charge for the entire sample. This observation suggests that all three phases of the mineral have nearly the same layer charge. If so, factors other than charge (e.g., hydroxyl dipole orientation) must be responsible for the interstratified character of the mineral.

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