LAYER CHARGE–CATION-EXCHANGE CAPACITY RELATIONSHIPS IN MONTMORILLONITE

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Abstract—The charge density distribution among different classes of a series of reduced charge montmorillonites is heterogeneous as in the parent Camp Berteau clay. In addition, charge reduction proceeds inhomogeneously. Up to 20% differences in charge density can be accounted for by alkyl chains extending at the edges of the clay particle. A realistic charge density–cation-exchange capacity relationship for hectorite, Otay montmorillonite, and a series of reduced charge montmorillonites of Camp Berteau is obtained by accounting for the influence of particle radius and for the extent of alkyl chains lying outside the clay layers in the charge density calculations.

Key Words—Cation-exchange capacity, Hectorite, Hofmann-Klemen effect, Layer charge, Montmorillonite.

INTRODUCTION

The surface charge density of highly dispersed solids is one of the most important parameters in understanding adsorption behavior. For example, it has recently been shown that, in montmorillonite, the exchange of simple inorganic ions is very much dependent upon charge density, not only in heterovalent (Maes and Cremers, 1977) but also in homovalent exchange equilibria (Maes and Cremers, 1978).

The surface charge density of montmorillonite may be obtained by various methods: the first method relies on the measurement of the specific surface area and the cation exchange capacity (CEC). Its value is dependent on pH (Peigneur *et al.*, 1975) and on the nature of the index cation and therefore leads to somewhat arbitrary values of the surface charge density. The isomorphic layer charge may be obtained from the unit-cell composition, the result being rather sensitive to small amounts of precipitated aluminum oxide which of course obscures the real composition (Glaeser *et al.*, 1972). A third method for measuring the isomorphic layer charge relies on the effect of the chain length of alkylammonium ions upon the monolayer–double layer transition in the interlamellar space (Lagaly and Weiss, 1969, 1971).

It is the purpose of the present study to examine the relationships between the cation-exchange capacity and the alkylammonium method on a series of isostructural samples of decreasing layer charge as obtained by the Hofmann-Klemen effect (Hofmann and Klemen, 1950).

EXPERIMENTAL

Five reduced charge montmorillonites (0.94 RCM, 0.72 RCM, 0.61 RCM, 0.55 RCM, and 0.34 RCM) were prepared from the <0.5-μm fraction of Camp Berteau montmorillonite (Maes and Cremers, 1977, 1978). Appropriate amounts of LiCl were added to 2% by weight sodium Camp Berteau clay suspensions in dialytic equilibrium with 0.01 N $NaNO_3$ so as to obtain about 25, 45, 50, and 75% Li exchange. Overnight equilibration was followed by freeze drying of the suspensions and heating to 220°C for 24 hr. The reference Na clay was submitted to the same heat treatment. Expansion of the layers was accomplished by ethylene glycol treatment followed by washing with ethanol and exchange with 1 mole/dm³ $NaNO_3$ solution. The samples are subsequently dialyzed to remove salt, freeze dried, and stored.

The sample name refers to the fractional cation-exchange capacity in water *vis-a-vis* the untreated parent Camp Berteau clay. The CEC of the samples was determined by isotopic dilution techniques in aqueous 0.01 M $NaNO_3$ at about pH 6 and in 1:1 95% ethanol/water also at 0.01 M $NaNO_3$. The charge density of the RCMs and of Otay montmorillonite (<0.5-μm fraction) was determined by the alkylammonium method (Lagaly and Weiss, 1969, 1971) following the procedure described by Stul and Mortier (1974).

RESULTS

The d001 spacings of the original Camp Berteau montmorillonite (Stul and Mortier, 1974) and the RCMs are shown in Figure 1 as a function of the number of carbon atoms in the alkyl chain. The apparent spacing increases from the monolayer complex (13.6 Å) to the double layer complex (17.6 Å) over a wide transition zone showing the heterogeneity of the charge density of the materials under study. Only first order reflections are given. With decreasing layer charge, broader reflections are observed while the second and third orders disappear. It could not be decided therefore whether
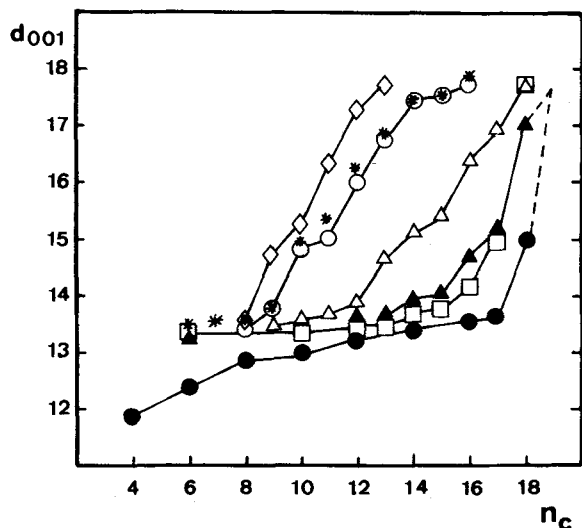
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Figure 1.   Basal spacings (Å) of the n-alkylammonium complexes of Otay (◇), original Camp Berteau montmorillonite (*) (Stul and Mortier, 1974), 0.94 RCM (○), 0.72 RCM (△), 0.61 RCM (▲), 0.55 RCM (□), and 0.34 RCM (●); n_c indicates the number of carbon atoms in the alkyl chain.
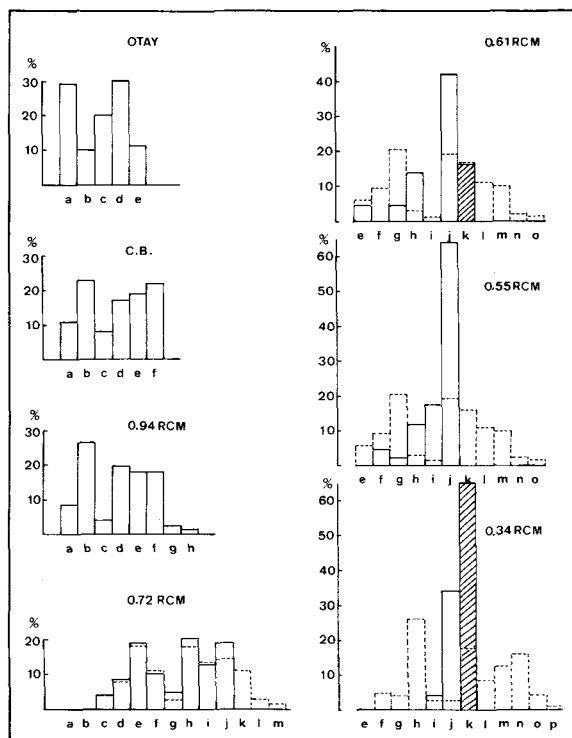

Figure 2.   Interlayer cation density distribution in different classes for Otay montmorillonite, Camp Berteau montmorillonite (C.B.) (Stul and Mortier, 1974), and different RCMs. Broken lines refer to calculated distributions (see text). Shaded classes refer to an approximation (see text).

the recorded 13.6- or 17.6-Å spacings were indeed integral or not.

In the 0.34 RCM sample, spacings as low as 12.3 Å (for hexylammonium) were observed indicating the presence of collapsed layers (9.6 Å). No separate line corresponding to 9.6 Å could, however, be detected. Spacings smaller than 13.6 Å were also observed in the 0.61 RCM and 0.55 RCM. Spacings between 13.4 and 13.6 Å were assigned to alkylammonium cations lying flat between the silicate layers (Lagaly and Weiss, 1971; Lagaly *et al.*, 1976). The theoretical thickness of the silicate layer being 9.4 Å (Brindley and Hoffmann, 1962), and since keying-in can occur—particularly in the case of low charged minerals—the appearance of 13.4-Å layers is not surprising. The slightly smaller spacings (13.2–13.3 Å) recorded for 0.55 RCM and 0.61 RCM result therefore from the interference of 9.6-Å layers.

Although 13.4 Å might be a more reasonable choice for the spacing of the monolayer complex, calculations were based on the 13.6- to 17.6-Å transition (Lagaly and Weiss, 1969, 1976; Stul and Mortier, 1974), the ensuing error in charge density being quite small (2–3% increase). From the data in Figure 1 the distributions of the interlayer cation density over different classes a to j (see Table 2) were obtained by the method of Stul and Mortier (1974) and are shown in Figure 2. Calculations were performed for a particle radius of 150 Å by assuming that half of the alkyl chains at the edges are lodged between the clay layers (Lagaly and Weiss, 1971; Stul and Mortier, 1974). In the case of 0.61 RCM and 0.34 RCM, the double layer complex is not formed at oc-

tadecylammonium. Since only alkylammonium cations up to C_{18} (corresponding to class j in Figure 2) were available, it was assumed that the remainder of the charge is present in class k. The extrapolations made for 0.61 RCM and 0.34 RCM can be seen in Figure 1 and are realistic in view of the data for 0.55 RCM and the fact that the charge densities in class k (0.229), l (0.22), etc. are barely different. The mean charge densities, given in Table 1, range from 0.359 (Otay montmorillonite) to smaller than 0.233 electrons per $Si_4Al_2O_{10}(OH)_2$ (0.34 RCM). The value for the Otay material agrees with the one (0.35) calculated from the data of Lagaly and Weiss (1976).

As already observed in the parent material (Stul and Mortier, 1974) the charge density distribution in the RCM clays remains also heterogeneous. The distributions in the 0.94 RCM material are barely different from those in the original Camp Berteau clay, taking into account the heating and re-expansion treatment (Maes and Cremers, 1977, 1978). The reduction in charge density of Camp Berteau montmorillonite by means of the Hofmann-Klemen effect results in charge density distributions which shift towards lower charge density classes.
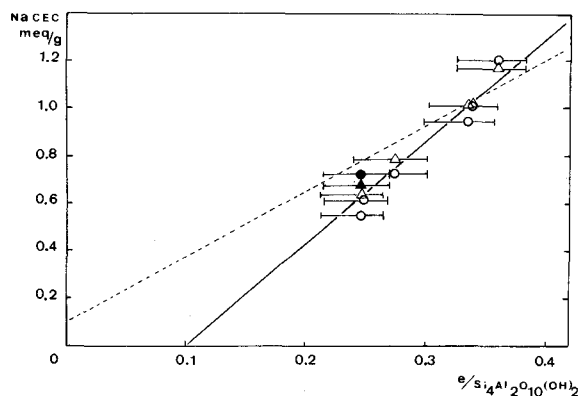
Figure 3. Relation between sodium CEC (meq/g) measured in water (circles) and in 1:1 95% ethanol/water (triangles) and the charge density (electrons/$Si_2Al_2O_{10}(OH)_2$) for montmorillonites (Otay, Camp Berteau, several RCMs) ($\bigcirc, \triangle$) and hectorite (Lagaly and Weiss, 1969) ($\blacktriangle, \bullet$). The charge density limits corresponding to the proportion alkyl chains extend at the edges of the clay (fully inside or completely outside) are incorporated. Full line corresponds to the linear regression equation (see text).

Table 2. Classes of interlayer cation density with varying degree of outer alkyl chains lying outside the clay plate.[1]

Class	Completely inside clay plate	Half inside[2] clay plate	Completely outside clay plate
a	0.375	0.409	0.434
b	0.344	0.378	0.402
c	0.317	0.351	0.375
d	0.294	0.328	0.352
e	0.274	0.308	0.331
f	0.257	0.291	0.314
g	0.242	0.276	0.298
h	0.229	0.263	0.284
i	0.217	0.250	0.271
j	0.206	0.239	0.260

[1] Electrons/$Si_4Al_2O_{10}(OH)_2$ calculated for a particle of 150-Å radius.
[2] Stul and Mortier (1974).

To verify if charge reduction proceeds homogeneously one may calculate the expected distributions from the composition of the 0.94 RCM. The latter is used as the reference material since it was subjected to the same treatments as the other RCM clays. The charge reductions are calculated as the ratios of the charge density in each RCM to the charge density in the 0.94 RCM. The reduction of 0.94 RCM to 0.72 RCM can be used as an illustration. All classes in 0.94 RCM should be reduced by a factor 0.27/0.335, e.g., the reduction of class a (0.409 e/half unit cell) of the 0.94 RCM by 0.27/0.335 results in a charge density (0.327) between class d (0.328) and e (0.308) (see Table 2). The

percentage of each of these classes can be calculated. Since the total amount of charge present in class a of 0.94 RCM is known, one can then find the respective charges in class d and e of 0.72 RCM. In Figure 2 the expected distributions are represented by broken lines. Calculated and observed distributions agree quite well in 0.72 RCM except for the absence of charge density classes k, l, and m. In 0.61, 0.55, and 0.34 RCM clays calculated and observed distributions disagree. The charge corresponding to these low charged classes (beyond class k) has in fact shifted towards the higher charge density classes. Respectively 15, 24, 40, and 42% of the charges in 0.72, 0.61, 0.55, and 0.34 RCM have moved to higher charge densities. This indicates that charge reduction proceeds *in*homogeneously.

Table 1 lists the CEC values for the RCMs, the Otay montmorillonite, the Camp Berteau montmorillonite,

Table 1. Sodium cation-exchange capacity in water (CEC 1) and in 1:1 ethanol/water (CEC 2) and charge density for smectites and reduced charge products.

Clay	CEC 1[1] (meq/g)	% of original CEC 1	CEC 2[1] (meq/g)	% of original CEC 2	Electrons per $Si_4Al_2O_{10}(OH)_2$	% of original charge
Otay montmorillonite	1.210[2]	—	1.178 ± 0.001 (2)	—	0.359	—
Hectorite	0.720[2]	—	0.670	—	0.245[3]	—
Camp Berteau montmorillonite	1.008 ± 0.011 (2)	—	1.010 ± 0.025 (4)	—	0.339[4]	—
0.94 RCM[5]	0.951 ± 0.029 (4)	94.2	1.012 ± 0.054 (4)	100	0.335	98.8
0.72 RCM	0.729 ± 0.024 (4)	72.2	0.786 ± 0.048 (4)	77.8	0.274	81
0.61 RCM	0.615 ± 0.009 (2)	61.0	—	—	<0.249	<73.5
0.55 RCM	0.547 ± 0.036 (6)	54.3	0.641 ± 0.052 (6)	63.5	0.246	72.6
0.34 RCM	0.346 ± 0.006 (2)	34.3	0.449 ± 0.025 (2)	44.5	<0.233	<68.7

[1] Numbers in parentheses = number of determinations.
[2] Maes and Cremers (1977).
[3] Lagaly and Weiss (1969).
[4] Stul and Mortier (1974).
[5] RCM = Reduced charge montmorillonite. See text for preparation procedure and discussion.

and hectorite, as measured in water and in a 1:1 mixture of ethanol and water. The range of capacities from 1.2 (Otay) to 0.34 (0.34 RCM) meq/g oven-dry clay (110°C) is covered. The capacities in ethanol-water generally agree with the values in water for the Otay and Camp Berteau materials. In the RCM series a tendency exists for larger differences at decreasing charge (Clementz *et al.*, 1974). The CEC in ethanol-water exceeds that in water by respectively 0.06 (0.95 RCM and 0.73 RCM), 0.09 (0.54 RCM), and 0.1 (0.34 RCM) meq/g.

Charge reduction by means of the Hofmann-Klemen effect results in sodium CEC reductions in disagreement with the decrease in charge density (see Table 1). Considering that the alkylammonium method measures only the isomorphic layer charge (Lagaly and Weiss, 1969; Stul and Mortier, 1974; Lagaly, 1977), the agreement between both methods for the measurement of the charge becomes even worse if a constant broken bond capacity is subtracted from the sodium CEC. The fraction of the original CEC measured in 1:1 ethanol-water is intermediate between the values obtained in water and those obtained from the charge density measurement.

The charge density of the 0.34 RCM is largely overestimated due to the interference of 9.6-Å layers. Correction of the data using a triangular diagram (Jonas and Brown, 1959; Mamy, 1968) is difficult since the combination of 9.6- and 17.6-Å layers using the method of Brown and MacEwan (1949) leads to spacings exceeding the latter.

DISCUSSION

The relation between the layer charge and the sodium CEC is shown in Figure 3 for the Otay clay and the RCMs along with literature data on the Camp Berteau montmorillonite (Stul and Mortier, 1974) and hectorite (Lagaly and Weiss, 1969). The 0.34 RCM is omitted since the interference of 9.6-Å layers results in an overestimate of charge density. The linear regression through all experimental points reads: CEC = 4.41σ − 0.4535 (r = 0.98) and corresponds to a zero CEC at about 0.1 e/half unit cell. This seems unrealistic and is at variance with expectation in view of the commonly accepted contribution (0.1–0.2 meq/g) of pH dependent sites in smectites.

The reason for the discrepancy can be due either to an underestimate of the CEC of the RCM samples or to an overestimation of the charge density. Hectorite and the Otay montmorillonite also fail to behave as expected.

According to the data of Clementz *et al.* (1974) and Brindley and Ertem (1972) on Wyoming bentonite, the fraction of collapsed layers (9.6 Å) increases with decreasing charge and can be estimated by a CEC determination in 1:1 ethanol-water mixtures, solvating all interlayer cations. In addition, Annabi *et al.* (1973) stat-

ed that in the Camp Berteau clay up to 70% reduction, homogeneous swelling occurs in ethanol and methanol. The CEC data in 1:1 ethanol-water are nevertheless insufficient to explain the deviation from the expected CEC–charge density relationship.

On the other hand several factors could be invoked which lead to an overestimation of the charge density. First, Li back-migration (Glaeser and Mering, 1971) during the exchange of the alkylammonium cations would result in a higher charge. However, unpublished data on hexylammonium exchange in RCMs show that no Li could be detected in the equilibrium solutions. Second, since on reduction the number of classes increases (instead of remaining constant), it is probable that the charge density within the individual clay plates is heterogeneous. The measured charge density will be overestimated since the intercalation of the whole clay plate will be determined by the most highly charged regions. However, charge delocalization over the surface oxygens in octahedrally substituted clays is believed to minimize this effect. Third, the packing and the unsymmetric charge distribution, two phenomena which are more likely to occur upon charge reduction, would give an overestimate but are believed to be quite small (Lagaly *et al.*, 1976). Finally, in the case of 0.61 and 0.55 RCMs, the small interference of 9.6-Å layers, judging from the appearance of 13.2–13.3 Å spacing for C_6, may give rise to a slight overestimate of the charge in these cases. The fact, however, that hectorite and Otay montmorillonite also deviate from the expected relation between isomorphic charge and sodium CEC requires an alternative explanation.

The charge densities as determined by the alkylammonium method are very much dependent on both the choice of the particle radius of the material under study and the extent of which the outer alkylammoniums are lying outside the clay plate. In Table 2 the charge densities in the different classes a to j are shown for the outer alkylammonium cations lying completely inside, half outside, and having only the NH_3^+-group between the clay plates. A particle radius of 150 Å was used throughout the calculations. For class "a" a charge density of 0.434 e/half unit cell is obtained if the outer alkylammonium cations have only the NH_3^+-group in the interlamellar region which, compared to the case of complete coverage (0.375 e/half unit cell), amounts to a 13.5% deviation. In the highest class j, values of respectively 0.26 and 0.206 are obtained which corresponds to a 20% difference.

The uncertainty limits due to this effect are shown in Figure 3. One may take for granted that the lowest charged minerals have no alkyl groups outside the platelet and that in the high charge-density mineral (Otay) alkyl chains are lying completely outside the clay. The dashed line in Figure 3 corresponds with this behavior and extrapolates through ~0.10 meq sodium

CEC which corresponds to the pH dependent site CEC. It appears that the under- or overestimation of the charge density, due to the extent which alkyl chains at the edges belong to the interlayer, can account for the observed effect. The persistent small discrepancy in the case of 0.61 and 0.55 RCMs is probably due to a small CEC underestimate as inferred from the increasing difference between the CEC in water and 1:1 ethanol/water and/or a slight charge overestimate caused by interference of 9.6-Å layers.

The value of the charge density is also a function of the particle dimensions. Increasing particle radii correspond to smaller charge densities (Stul and Mortier, 1974). One expects, however, that the different treatments to which the RCMs are subjected will result in equal or smaller particle radii than those of the original sample, which were taken to be 150 Å (Stul and Mortier, 1974). Accounting for this would give rise to even higher charge densities and concomitant larger deviations from the expected charge density–CEC relationship. Deviations observed in the case of hectorite and Otay montmorillonite can also partly be accounted for if the dimensions for particle radii used in the calculations are respectively higher or smaller than 150 Å. The particle dimensions observed for hectorite (Grim, 1968) exceed 1000 Å. Otay montmorillonite occurs as globular particles of about 100-Å radius (Grim and Güven, 1978). Both are in the expected direction.

Summarizing one can state that the agreement between the observed and expected charge density–CEC relationship depends on (a) the dimensions of the clay particles (particle radius), (b) the fraction of the alkyl chains extending at the edges which in turn depends on the charge density itself, and (c) the appearance (in the RCM clays) of 9.6-Å layers, which leads to underestimates of the CEC and overestimates of the charge density.

ACKNOWLEDGMENTS

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Резюме—Наблюдается гетерогенное распределение плотности зарядов среди различных классов серий монтмориллонитов с пониженными зарядами как в материнской глине Кэмп Бертю. Кроме того понижение запяда происходит неравномерно. Различие в плотности заряда до 20% может быть обусловлено алкильными цепями, протягивающимися на краях частиц глины. При вычислениях плотности зарядов достигаются реальные соотношения плотности зарядов и катионной обменной способности для гекторита, монтмориллонита Отэй и серии монтмориллонитов с пониженными зарядами из Кэмп Бертю, если учитывать влияние радиусов частиц и протяжения алкильных цепей, лежащих снаружи слоев глины.

Resümee—Die Verteilung der Ladungsdichte zwischen verschiedenen Arten von Montmorilloniten mit reduzierter Ladung ist genauso heterogen wie im ursprünglichen Camp Berteau Ton. Außerdem geht die Reduzierung der Ladung inhomogen vor sich. Ein Unterschied bis zu 20% in der Ladungsdichte kann durch die Alkylketten erklärt werden, die an den Ecken der Tonteilchen liegen. Eine realistische Ladungsdichte–Kationenaustauschkapazität für Hektorit, Otay Montmorillonit, und eine Reihe von Camp Berteau Montmorilloniten mit reduzierter Ladung ergibt sich, wenn man den Einfluß des Teilchenradius und die Länge der Alkylketten, die außerhalb der Tonschichten liegen, bei der Berechnung der Ladungsdichte berücksichtigt.

Résumé—La distribution de la densité de charge dans une série de montmorillonites à charge réduite est hétérogène comme dans l'argile originale de Camp Berteau. En plus la réduction de la charge procède d'une manière inhomogène. Des différences de 20% dans la densité de charge peuvent être expliquées comme dues aux chaines d'ions alkylammonium étendues aux bords des particules de l'argile. La relation réelle entre la densité de charge et la capacité d'échange pour l'hectorite, la montmorillonite Otay, et une série de montmorillonites à charge réduite est obtenue en tenant compte de l'influence du rayon des particules et de la proportion des ions alkylammonium débordants de la particule argileuse dans le calcul de la densité de charge.