

## THE NATURE OF THE SURFACE CHARGE OF KAOLINITE

**Key Words**—CEC, Kaolinite, Origin of surface charge, Surface charge density, Surface proton charge density.

It is well known that kaolinite has a heterogeneous surface charge. The basal surface of kaolinite is believed to carry a constant structural charge which is attributed to the isomorphous substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$ . The charge on the edges is due to the protonation/deprotonation of surface hydroxyl groups and therefore depends on the solution pH. This view was originally presented by van Olphen (1951) and supported by many other researchers in this field (Schofield and Samson, 1954; Flegmann *et al.*, 1969; Rand and Melton, 1977; van Olphen, 1977; Williams and Williams, 1978). For the convenience of discussion, we will call this model CBSC-Constant Basal Surface Charge in the following text. However, in their isotopically labelled ion exchange experiments, Ferris and Jepson (1975) found that the cation uptake by the kaolinite surface depends upon the cation chosen, the electrolyte concentration, and the solution pH. They concluded that a structural charge does not exist on the basal surface of their samples. In a later study, Bolland *et al.* (1976) showed that dissolved  $\text{Al}^{3+}$  may compete with index cations ( $\text{Na}^+$ ,  $\text{K}^+$ , etc.) and account for most of the cation exchange capacity at low pH. They concluded that “most of the negative surface charge on the kaolinites is pH independent and is likely to be due to isomorphous substitution.”

With respect to the current interests in the modelling of the electrophoretic behaviors (Fair and Anderson, 1989), the particle interactions (Chow, 1991; James and Williams, 1982), and the transport (Cerda, 1987) of kaolinite, the fundamental issue of the origin of the surface charge of kaolinite deserves more attention. Any attempt to model the behaviors of kaolinite, whether particle interaction or its transport in hydrocarbon reservoirs, requires a physical model to describe the charge distribution on the kaolinite surfaces. Thus, the nature of the charge on the basal surface of kaolinite becomes very important to each and all of the modelling efforts. In this note, the origin of the surface charge of kaolinite is discussed in the light of the surface charge density. We will show that the CBSC model can not account for the data on the cation exchange capacity (CEC) and net proton charge density of kaolinite.

### CHARGE DENSITY OF EDGE: CEC DATA

The charge density on the edges of kaolinite particles can be evaluated using the published and our own CEC data on kaolinite and the CBSC concept. Figure 1A shows the CEC of kaolinites as a function of pH. The

CEC of KGa-1 was measured using a method similar to that of Flegmann *et al.* (1969) and Bolland *et al.* (1976). In our method, a homoionic Na-kaolinite was first prepared using the method of Schofield and Samson (1954). For each desired pH, the kaolinite was brought to equilibrium with a NaCl solution of that pH through successive washings. Adsorbed cations ( $\text{Na}^+$ , and a tiny amount of  $\text{Al}^{3+}$ ) were then displaced with a 1.0 N  $\text{Mg}(\text{NO}_3)_2$  solution, and their concentrations were analyzed to determine the CEC. This procedure was repeated a number of times to determine the dependence of CEC on pH. The CEC of kaolinite tends to be lowest ( $\text{CEC}_m$ ) in acidic solutions. In the concept of the CBSC model,  $\text{CEC}_m$  represents the permanent structural charge of kaolinite (Flegmann *et al.*, 1969). Logically, if we define

$$\Delta\text{CEC} = \text{CEC} - \text{CEC}_m \quad (1)$$

the  $\Delta\text{CEC}$  should represent the contribution from the edges under the experimental conditions. This was graphically illustrated by Flegmann *et al.* (1969). The negative charge density on the edges can be calculated:

$$\sigma_e = \Delta\text{CEC} \times F/A_e \quad (2)$$

where  $F$  is the Faraday constant ( $96,485 \text{ C mol}^{-1}$ ),  $A_e$  is the specific surface area of the edges ( $\text{m}^2\text{g}^{-1}$ ),  $\Delta\text{CEC}$  is in equivalents per gram ( $\text{eq g}^{-1}$ ), and  $\sigma_e$  has units of Coulombs per square meter ( $\text{C m}^{-2}$ ).

The specific edge area of kaolinite is usually not known and has to be estimated. Morphologically, kaolinites exist as thin platelets whose edge area is small compared with their basal surfaces. The surface area of the edges was measured by Ferris and Jepson (1975) and found to be 12% of the total surface area. The edge area, calculated by using the dimensions of a kaolinite particle given by Sposito (1984) and James and Williams (1982), is 7% and 14%, respectively, of the total surface area. We assume an  $A_e$ , most favorable to the CBSC model, of 14% of the total surface area in our calculations when the edge area is not known.

Figure 1B shows the  $\sigma_e$  calculated from the CEC data in Figure 1A using Equation 2. Actual values of  $A_e$  used in the calculation are listed in Table 1. The charge densities of alumina (Sprycha, 1989b) and silica (Abendroth, 1970), as determined by cation exchange methods, are also shown in Figure 1B for comparison. The surface charge density of the edges of kaolinite is one of order magnitude greater than that of either alumina

Table 1. Surface charge densities on kaolinite edges.

Na-kaolinite	$A_c$ (m <sup>2</sup> /g)	Solution		$\sigma^1$ mC/m <sup>2</sup>	$\sigma^2$ mC/m <sup>2</sup>	$\sigma^3$ mC/m <sup>2</sup>	Reference
		pH	mM				
Cornwell	1.30	12	7	-2250	-290	-386	Ferris and Jepson (1975)
Greenbushes	3.36 <sup>4</sup>	9.5	10	-950	-51	-61	Bolland <i>et al.</i> (1976)
KGa-1, CEC	1.68 <sup>4</sup>	8.8	10	-689	-27	-30	this study
KGa-1, titration	1.68 <sup>4</sup>	9.0	10	-996	-33	-38	this study

<sup>1</sup> Charge densities, based on CBSC's interpretation of the experimental data.

<sup>2</sup> Charge densities for an amphoteric site ( $pK_1 = 5.7$ ,  $pK_2 = 8.7$ ,  $N_s = 5.0 \times 10^{18}/m^2$ ).

<sup>3</sup> Charge densities for an amphoteric site ( $pK_1 = 5.7$ ,  $pK_2 = 8.7$ ,  $N_s = 10.0 \times 10^{18}/m^2$ ).

<sup>4</sup> Estimated from total surface area:  $A_c = 0.14A_T$ .

or silica in the same solution conditions. As will be shown later, this charge density is not realistic.

### NET SURFACE PROTON CHARGE DENSITY

Figure 2 shows the results of the potentiometric titration of Na-kaolinite. The Na-kaolinite sample (KGa-1) was prepared following the procedures of Schofield and Samson (1954). The resolution of the titration curve is not sensitive enough to distinguish multiple end points as would be expected for a multiple site surface. However, our main concern is the surface charge density itself, and consequently the shape of the titration

curve need not be analyzed for this purpose. The net surface proton charge density ( $\sigma_H$ ) can be calculated by (Stumm and Morgan, 1981):

$$\sigma_H = (C_a - C_b - [H^+] + [OH^-]) \times F/A\phi \quad (3)$$

where  $C_a$  and  $C_b$  are the equivalent acid and base added during titration;  $[H^+]$  and  $[OH^-]$  are the concentrations of  $H^+$  and  $OH^-$  in the bulk solution;  $F$  is the Faraday constant;  $A$  is the surface area; and  $\phi$  is the solid concentration in grams per liter ( $g L^{-1}$ ). In the context of the CBSC model, only the kaolinite edges are ionizable. Thus, the surface area  $A$  in Equation 3 may be replaced by the surface area of the edge,  $A_c$ .

The net surface proton charge density of the edges of kaolinite, calculated using Equation 3, is shown in Figure 3. For comparison, the net surface proton charge densities of silica (Bolt, 1957) and alumina (Sprycha, 1989a) are also shown in Figure 3. The  $\sigma_H$  of the edges of kaolinite is an order of magnitude greater than that of either silica or alumina.

### DISCUSSION AND CONCLUSIONS

The edges of kaolinite are composed of exposed silica and alumina sheets. Thus, the surface charge density of the edges of kaolinite would be expected to be similar to that of alumina and silica (Williams and Williams, 1978). However, it is obvious from the above discus-

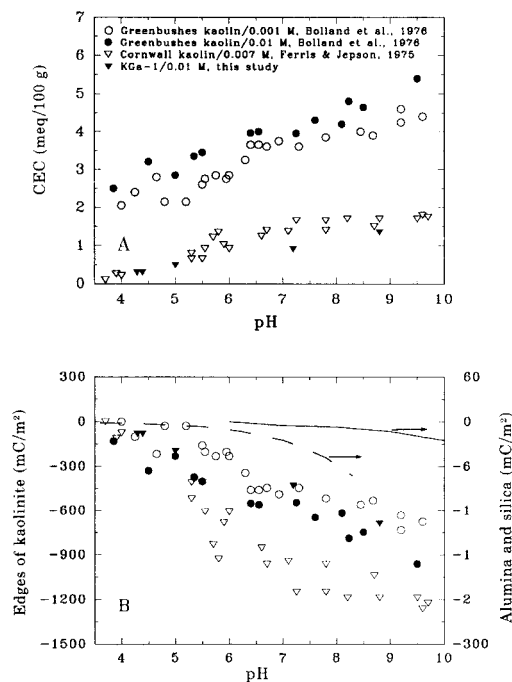


Figure 1. A: Cation exchange capacity (CEC) of various types of kaolinite. B: Charge densities of kaolinite edges, calculated by Equation (2). Symbols are the same as in Figure 1A. The solid curve is the charge density of alumina in 0.01 M CsCl solution (Sprycha, 1989b), and the dashed line is the charge density of silica in 0.01 M KCl solution (Abendroth, 1970). The arrows point to the ordinate at the right hand side for alumina and silica.

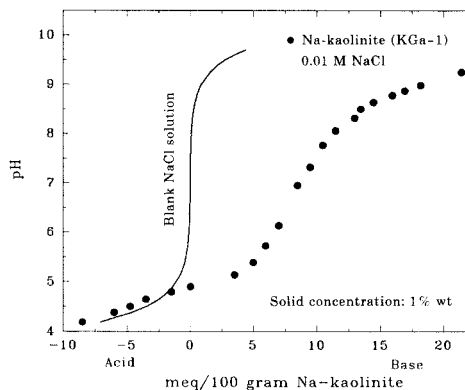


Figure 2. Potentiometric titration curve of Na-kaolinite (KGa-1). The titration cell was continuously purged with  $N_2$  gas during titration.

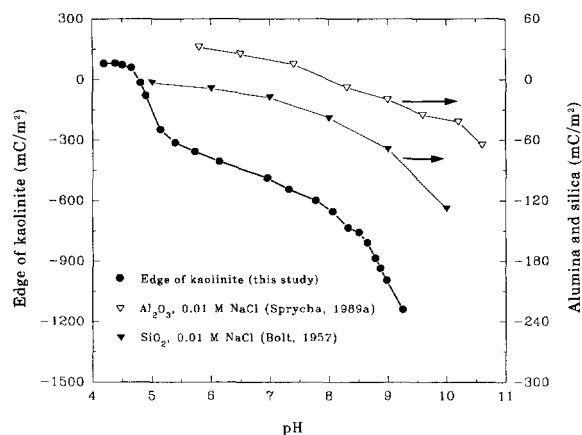


Figure 3. The net surface proton charge densities of kaolinite edges, in comparison with those of alumina and silica.

sion that a much higher surface charge density on the edges would result if a CBSC model were used to interpret the CEC and potentiometric titration data.

Furthermore, we may examine the CBSC model by considering the surface site concentration. The charge densities of various types of kaolinite under a number of solution conditions were calculated based on the CBSC model and are listed in Table 1 as  $\sigma^a$ . For a mineral surface with an amphoteric site, the charge density under any solution condition can be calculated if the total surface site concentration ( $N_s$ ) and surface equilibrium constants are known (Healy and White, 1978). The total number of surface sites available for silica and alumina is around  $2 \times 10^{18}$  to  $5 \times 10^{18} \text{ m}^{-2}$ , with the maximum less than  $10 \times 10^{18} \text{ m}^{-2}$  (Schindler, 1981). The  $\sigma^b$  and  $\sigma^c$  are the charge densities of an amphoteric surface with total surface site concentration of  $5 \times 10^{18}$  and  $10 \times 10^{18} \text{ m}^{-2}$  respectively. They are calculated with the surface group ionization model of Healy and White (1978). The surface equilibrium constants  $K_1$  and  $K_2$  were chosen to give the  $\text{pH}_{zpc}$  of the edge at 7.2 (Williams and Williams, 1978). The results indicate that even a surface with a maximum site concentration ( $N_s = 10 \times 10^{18} \text{ m}^{-2}$ ) can only generate charge densities one order of magnitude smaller than those required by CBSC. In other words, the total surface site concentration on the edges of kaolinite, required by the CBSC model, exceeds the physical limit imposed by kaolinite for the solution conditions under consideration.

As mentioned earlier, the edge area was assumed to be 14% of the total area for computational purposes. One may argue that this may not be correct and that it may be higher. However, even if this is doubled to 28% (corresponding to a disc with a radius of  $1.00 \mu\text{m}$  and a thickness of  $0.40 \mu\text{m}$ ), the  $\sigma^a$  in Table 1 would only be reduced by one half, which is still much too large compared with  $\sigma^b$  and  $\sigma^c$ .

From the consideration of surface charge density, it is obvious that the ionization of edges alone cannot explain the magnitude of the changes in the CEC and  $\sigma_H$  observed in many experiments. Thus, the basal surface must also contribute to these changes. Such a contribution from the basal faces may be described by a site dissociation model similar to that for mica surfaces (Scales *et al.*, 1990). The charges on the basal surfaces are always negative but the magnitude is pH-dependent. For well-crystallized kaolinite (KGa-1), the observed CEC and net surface proton charge density as presented in Figures 1 and 2 can be simulated by a site dissociation model for basal surfaces, along with amphoteric edges. Although the surface charge density itself cannot give molecular details on basal face ionization (e.g., the relative contributions of alumina side and silica side), it clearly indicates that the basal faces of kaolinite are ionizable in aqueous solutions.

#### ACKNOWLEDGMENTS

Earlier work by Ms. Pat Speyer in our laboratory formed a base which led us to seek alternatives to the CBSC model. The authors are grateful to Dr. G. W. Bird for his support for this study, and to Dr. R. E. Ferrell, Jr., Dr. H. van Olphen, and an anonymous reviewer for their constructive comments on this manuscript.

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(Received 4 September 1991; accepted 14 January 1992; Ms. 2142)