

## EXTENDED VERSION OF GOUY-CHAPMAN ELECTROSTATIC THEORY AS APPLIED TO THE EXCHANGE BEHAVIOR OF CLAY IN NATURAL WATERS

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**Abstract**—A model based on Gouy-Chapman theory, describing the ion exchange behavior of clays in mixed electrolyte solutions is presented. Computed ionic distributions, taking into account variations in relative permittivity, ion activity, and closeness of approach of ions to clay surfaces, are compared with experimental data for smectite and kaolinite in contact with river and saline waters. To obtain reasonable agreement between theoretical prediction and observation the most important extension of Gouy-Chapman theory involves the introduction of a closeness of approach term. Furthermore, the aggregated nature of smectites plays an important part in controlling its exchange properties, whereas a fixed-charge model provides a poor description for the ion exchange properties of kaolinite.

**Key Words**—Electrolyte, Gouy-Chapman theory, Ion exchange, Kaolinite, Smectite, Water.

### INTRODUCTION

Electrostatic theory can be used to describe element exchange behavior for many clay-water mixtures of environmental and theoretical importance, including soil salinization, pollutant transport through soil and groundwaters, major element budgets in the hydrosphere, soil and sediment stabilities, the structure of water and clay surfaces, and ion hydration. Here, the value of electrostatic theory is that it gives without prior determination of selectivity coefficients, the distribution of cations, anions, and neutral molecules in solution near clay surfaces on a molecular scale. This information can be compared with experimental evidence to provide insight into the molecular structure of clay surfaces, the hydration state of ions, and the structure of water in the intense electric fields near clay surfaces. Electrostatic theory also eliminates the need for arbitrary and limiting definitions of ion-exchange parameters and the experimentally unjustifiable simplification to monolayer adsorption of commonly used mechanistic models (Bolt, 1967; Sposito, 1981; Neal *et al.*, 1982; Thomas *et al.*, 1982; Truesdale *et al.*, 1982). Furthermore, electrostatic theory is complementary to, but distinct from, the well-developed, mass-action type, thermodynamic view of clay-electrolyte systems (cf. Bolt, 1967, 1979; Sposito, 1981a, 1981b); the latter is much simpler to evaluate than the former but can only be related on macroscopic scale in a non-mechanistic fashion to ion exchange (Neal *et al.*, 1982; Sposito, 1981).

Despite much progress (e.g., Bolt, 1955a, 1979; Bolt and Warkentin, 1958; Bolt and de Haan, 1965, 1979; Edwards and Quirk, 1962; Helmy *et al.*, 1980; Schofield, 1949), electrostatic models are not yet either sufficiently well developed or tested to describe clay-electrolyte solutions.

For example, homovalent selectivity coefficients are not close to unity for many clays in a wide variety of mixed electrolyte solutions (Bruggenwert and Kamphorst, 1979) in contradiction to Gouy-Chapman theory where ions are described as point charges (Joshi and Parsons, 1961; Bolt, 1979; Sposito, 1981). In addition, the Gouy-Chapman model does not allow for changes in the water structure near clay surfaces which can significantly affect the distribution both of neutral and charged molecules (Davis and Worrall, 1971; Bolt, 1979). Consequently the predictive capacity of the Gouy-Chapman model can be improved.

In an attempt to overcome some weaknesses of existing theory, an extended version of the Gouy-Chapman model is developed here. Predictions from this model are compared with experimental data for smectite and kaolinite in contact with mixed river and marine waters. The extended Gouy-Chapman model incorporates terms describing variations in the activity and hydration of ions and in the relative permittivity of water (Bolt, 1955a, 1955b, 1979; Grahame, 1952; Sparnaay, 1958; Ravina and Gur, 1978); these terms allow for ion-ion and ion-surface interactions to improve the prediction given by the basic Gouy-Chapman model. Following closely Oldham's (1975) analysis for a simplified Gouy-Chapman model for ion exchangers in contact with estuarine and marine waters, we show that the experimental and analytical results are compatible, provided that the closeness of approach of ions to the clay surface is considered.

### DEFINITIONS OF EXCHANGE PARAMETERS

Most of the variables which are of interest cannot be measured directly; the model predicts significant

changes in the concentration of ions and field strength within a region only a few tens of Ångströms from a charged surface, and these cannot be directly sampled. Consequently, an assessment of model performance can only be made indirectly by comparing experimentally determined "notional interfacial contents" (NIC) and computed G values as defined below.

For the laboratory studies the variables measured, NICs, are related to commonly used terms in the clay literature such as adsorbed and exchangeable cations (see Neal *et al.*, 1982, for discussion of the usage of NICs). NIC variables are defined by the general equation.

$$\text{NIC}_{i(j)} = T_i - T_j^i c_j,$$

where  $\text{NIC}_{i(j)}$  is the notional interfacial content of species  $i$  with respect to a reference species  $j$ ,  $T_i$  is the total amount of any species  $i$  in the system (both in units of meq/kg clay) and  $c_j$  is the concentration of  $i$  with respect to  $j$  in the bulk solution outside the influence of the clay charge (a dimensionless unit). For the laboratory study the reference species ( $j$ ) chosen was water; the subscript  $j$  is omitted, without ambiguity, in the remaining text, thus  $\text{NIC}_{i(\text{H}_2\text{O})} \equiv \text{NIC}_i$ . For the theoretical studies the quantities calculated (G) are similar to surface excesses defined by Bolt (1967) and are defined here by

$$G_i = \int (c_i - c_i^b) dx,$$

where  $c_i$  is the concentration of component  $i$  and  $x$  is the distance from the clay surface. As  $x$  tends to infinity  $c_i \equiv c_i^b$ , the bulk solution concentration of species  $i$ . The lower limit of integration is zero; when the upper limit is infinite,  $G_i \equiv G_i^b$ , the "overall ion excess."

An important feature of the experimental and theoretical results is that while the former refer to components related to water as a reference, the latter refer to molal concentrations. To make both sets of results comparable we have assumed the concentrations of water to be constant within the solution volume. Under this assumption the  $G_i^b$  values can be regarded as theoretical values of the observed  $\text{NIC}_i$ .

## CHEMICAL ANALYSIS

### Materials and methods

Samples of kaolinite (English china clay) and smectite (Wyoming bentonite), supplied by BDH Chemicals (UK) Ltd., were purified to give homoionic Na forms with a particle size of  $<2 \mu\text{m}$  using the method described by Neal (1977). They were converted to their "river" and "saline" counterparts by repeatedly washing ( $\sim 30$  times) and storing the clays ( $\sim 2$  days/wash) with mixtures of filtered water from the River Thames and artificial seawater prepared using the recipe of Lyman and Fleming (1940).

The notional interfacial content of the clays was determined for the treated clays using a multiple salt leach based on the method described by Neal (1977). To minimize analytical error, excess pore solution was removed using a porous asbestos tile, and subsequent determinations were made on well-mixed samples of the damp clay remaining. Exposure of the clay to the atmosphere was minimized to ensure that evaporative effects would be insignificant.

The total equivalents of cations (Na, K, Mg, Ca) per unit weight of dry clay,  $T_i$ , were determined by treating an accurately weighed sample of damp clay ( $\sim 0.2$  and  $0.5$  g portions of smectite and kaolinite, respectively) six or more times, depending upon extraction efficiency, with 10-ml portions of a 60% alcohol solution containing 0.25 M CsCl and 0.75 M LiCl. For each treatment the clay was continuously suspended for  $\sim 2$  hr in the extracting solution to maximize cation release. The major cation concentration of each solution was then determined by standard atomic absorption and emission spectroscopy (Slavin, 1968) and the  $T_i$  values calculated.

The water content  $T_{\text{H}_2\text{O}}$  was determined by drying weighed samples of damp clay at  $60^\circ\text{C}$  to constant weight and determining the weight loss (in accord with Thomas *et al.*, 1983). Drying times were  $\sim 6$  days. The amount of Cl ( $T_{\text{Cl}}$  - meq/kg of dry clay) was determined with the washing technique used for the cations except that the extraction solution contained no leaching salt. The concentration of Cl in each extract was determined using an automated colorimetric version of the method of Zall *et al.* (1956). Three washing steps were required to complete the extraction.

NIC values for Na, K, Mg, Ca, and Cl were subsequently determined for the saline and fresh-water clays by first determining the river and seawater molal end-member compositions and then calculating  $c_{\text{H}_2\text{O}}$ .

### Experimental results

Except for chloride, the variations in  $\text{NIC}_i$  values with changing salinity are similar for both clays (Table 1). Considering first, cation variations, with increasing salinity,  $\text{NIC}_{\text{Ca}}$  decreases and  $\text{NIC}_{\text{Na}}$  and  $\text{NIC}_{\text{K}}$  increase.  $\text{NIC}_{\text{Mg}}$  increases up to a salinity of  $\sim 4\%$  and then decreases slightly at higher salinities. For all cations the largest variation is in the 0 to 10% salinity range.

Cation NIC data for both clays are consistent with previous theoretical and experimental evidence for two reasons: (1) Because the river water contains mainly Ca in solution and the seawater contains relatively low Ca and high Na, Mg, and K concentrations,  $\text{NIC}_{\text{Ca}}$  should decrease with increasing salinity relative to  $\text{NIC}_{\text{Na}}$ ,  $\text{NIC}_{\text{K}}$ , and  $\text{NIC}_{\text{Mg}}$ . Such a trend has been observed for several studies of fresh and saline clays (Sayles and Manglesdorf, 1977, 1979; Zaytseva, 1966); (2) Be-

Table 1.  $NIC_i$  values for smectite and kaolinite in fresh and saline waters.

Salinity (%)	Na	K	Mg	Ca	Cl	Total
Smectite						
0.36	15	8	63	1039	0.0	1126
0.83	55	12	220	885	3.7	1169
1.30	72	15	275	521	1.5	1162
2.25	93	20	350	726	-2.5	1192
3.22	146	24	390	661	-9.7	1236
4.15	164	29	432	893	-19.3	1538
5.09	182	30	433	667	-19.1	1331
6.04	192	30	415	544	-20.0	1202
7.00	203	34	436	530	-27.3	1231
7.93	225	32	411	473	-35.2	1176
8.88	243	41	414	463	-38.8	1200
9.83	247	33	413	641	-42.3	1376
14.60	303	42	390	516	-63.4	1315
19.30	293	55	349	392	-82.9	1173
24.00	314	53	345	491	-85.6	1289
28.80	286	49	310	382	-116.1	1143
33.50	331	57	311	404	-130.2	1232
Kaolinite						
0.36	0.0	2.1	7.3	49.3	2.8	55.9
0.83	4.6	3.2	14.6	46.4	1.9	66.9
1.30	6.5	3.0	15.8	45.0	1.7	68.6
2.25	10.8	4.3	24.2	48.1	-0.1	87.6
3.22	11.2	5.1	23.7	40.3	-1.2	81.5
4.15	15.0	7.9	24.8	39.1	-1.8	88.6
5.09	14.9	6.4	26.3	26.6	0.6	73.6
6.04	13.8	6.9	25.7	20.4	0.6	66.1
7.00	17.8	7.5	28.2	28.0	-1.3	88.3
7.93	21.5	8.3	26.1	21.8	1.5	76.1
8.88	17.7	7.4	24.7	16.4	0.6	67.0
9.83	19.4	7.0	23.8	9.6	0.5	59.3
14.6	24.5	9.5	24.5	15.3	5.8	68.0
24.0	22.3	9.4	21.5	7.9	4.3	56.8
28.8	38.6	11.0	27.4	20.1	17.9	79.1
33.5	30.0	10.0	23.7	6.1	12.8	56.9

cause the main change in the proportion of cations in the bulk solution occurs in the 0 to 10‰ salinity range, the maximum change in  $NIC_i$  should also be in this range due to the freshwater salt component providing an insignificant contribution to the total salt content at high salinities. This prediction can be judged by comparing the proportions of ions at different salinities (Table 2); for example, the ratio of Na/K is 19.8 in the river water and 47.1 to 47.8 at salinities of 10‰ and above.

Despite these consistencies, the data are in part fairly variable. For smectite,  $NIC_{Na}$ ,  $NIC_K$ , and  $NIC_{Mg}$  change smoothly as salinity increases whilst  $NIC_{Ca}$  fluctuates. For kaolinite, the variations are probably due in part to the difficulty in analyzing for materials of low cation-exchange capacity in contact with solutions of high salt content; because both  $T_i$  and the product of  $T_{H_2O}$  and  $iC_{H_2O}$  will be of a similar size,  $NIC_i$  will be small and particularly sensitive to analytical errors in the component terms. For smectite, however, such errors are much less important because  $T_i \gg T_{H_2O}iC_{H_2O}$ . In con-

Table 2. Bulk solution chemical concentrations.

	River water	Mixedwater	Artificial seawater
Salinity (%)	0.36	10	20
33.5			
Ionic concentrations (mmole/liter)			
Na	1.72	136.0	276.0
K	0.087	2.89	5.78
Mg	0.215	15.3	31.0
Ca	2.60	4.75	6.98
Cl	1.75	157.0	318.0
HCO <sub>3</sub>	3.70	3.32	2.93
SO <sub>4</sub>	1.42	9.04	16.9
Ionic ratios			
Na/K	19.8	47.1	47.8
Na/Mg	8.0	8.9	8.9
Na/Ca	0.66	28.6	39.5
Na/Cl	0.983	0.866	0.868
			0.867

trast, the anion values differ for the two clays. For smectite, as previously noted by Thomas *et al.* (1982),  $NIC_{Cl}$  decreases uniformly with increasing salinity. For kaolinite, the variations were unexpectedly complicated because  $NIC_{Cl}$  decreases at very low salinities from a positive to a negative value and increases again to positive values at high salinities; as for the cations, the data do not vary smoothly, again probably due to analytical error.

### MODELING FRAMEWORK

Theoretical G-values have been computed for several models which are modified versions of the Gouy-Chapman model. The necessary additional notation is given in Table 3. The Poisson-Boltzmann equations of the basic Gouy-Chapman model for a system containing  $n$  ion species, are

$$c_i = c_i^b \exp\{z_i F \phi / RT\} \quad (1a)$$

$$i = 1, \dots, n, \text{ and}$$

$$d^2\phi/dx^2 = -F \sum z_i c_i / \epsilon_0 \epsilon, \quad (1b)$$

Table 3. Notation used for the mathematical analysis.

Symbol	Meaning	Units	Value of constant
F	Faraday constant	C mole <sup>-1</sup>	9.65 × 10 <sup>4</sup>
ε	Relative permittivity		
ε <sub>0</sub>	Permittivity of free space	Fm <sup>-1</sup>	8.85 × 10 <sup>-12</sup>
z <sub>i</sub>	Charge number of i <sup>th</sup> ion		
R	Gas constant	J K <sup>-1</sup> mole <sup>-1</sup>	8.32
T	Temperature	K	
φ	Potential	V	
E	Field strength	V m <sup>-1</sup>	
σ	Charge density	C m <sup>-2</sup>	
x	Distance	m	
I	Ionic strength	mole m <sup>-3</sup>	

where  $C_i \equiv C$  species  $i$ , the alternative notations being unambiguous. These equations have been modified in three different ways. First, the relative permittivity in the Poisson equation (1b) was allowed to vary with field strength. The functional relationship used was

$$\epsilon(E) = a_1/(1 + a_2E^2) + a_3,$$

where  $a_1$ ,  $a_2$  and  $a_3$  are constants taking values  $a_1 = -5.5$ ,  $a_2 = 1.2 \times 10^{-17} \text{ m}^2\text{v}^{-2}$ ,  $a_3 = 5.5$ . This choice of  $\epsilon(E)$  was suggested by Grahame (1951). Secondly, an activity term was introduced, modifying the exponent in the Boltzmann equation (1a). The full equation is

$$c_i = c_i^b \exp\{f_i(E, \phi, c_1 \dots c_n)\},$$

with

$$f_i(\cdot) = z_i F \phi / RT \\ - A z_i^2 \sqrt{I} / (1 + B L \sqrt{I}) \\ + A z_i^2 \sqrt{I^b} / (1 + B L \sqrt{I^b}),$$

where  $L$  is an ion-size parameter.

The additional extended Debye-Hückel activity terms approximate the difference in activity coefficients between ions in the bulk solution and those closer to the charged surface. Some justification for the choice of this functional form has been given by others (Berner, 1971; Pytkowicz, 1979a, 1979b; Whitfield, 1979; Moore 1968). Strictly,  $A$  and  $B$  should be regarded as functions of relative permittivity: here, this case was considered, but we also allowed  $A$  and  $B$  to be constant. Thirdly, certain ions were excluded from a region near the charged surface. If the charge on an ion is regarded as present at a point at its center, it cannot approach the surface closer than the radius of the ion. The surface concentration of any ion is therefore zero, unless it enters the structure of the clay surface. The effect of constraining ions to a position no closer than their hydrated radius is to increase the predicted concentration of smaller ions near the surface, compared with those given by models without this constraint. In the mathematical analysis the constraint was introduced by allowing the activity coefficient of each ion to be infinite in the exclusion zone. This third modification was included to allow for the selectivity of ions which is observed experimentally but not accounted for by the Gouy-Chapman model. It is an alternative to ideas suggested by other authors. The Stern triple layer model (Heald *et al.*, 1964; Bolt *et al.*, 1967; Westall and Hohl, 1980; Sposito, 1981b), for example, combines an adsorbed surface layer with given selectivity coefficient and a diffuse region extending into the bulk solution.

In summary, the models used were:

- (1) The Gouy-Chapman model.
- (2) The Gouy-Chapman model with the relative permittivity in the Poisson equation allowed to vary with field strength.

(3a) As in model (2), but with the extended Debye-Hückel activity term ( $A$  and  $B$  taken as constants) included in the exponent of the Boltzmann equations as described above.

(3b) As in model (3a), but with the terms  $A$  and  $B$  taken as functions of the relative permittivity.

(4) The Gouy-Chapman model with a minimum distance of approach for the ions introduced, with relative permittivity dependent on field strength. The minimum distances of approach for the ions in solution are taken to be 3 Å for  $\text{K}^+$ , and 4 Å for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and all anions. These values correspond approximately to the hydrated radii of the ions.

(5a) As in model (4), but using more appropriate values for the closeness of approach (McConnell, 1964; Grim, 1968; Berner, 1971). For kaolinite:  $\text{Na}^+$  and  $\text{K}^+$  = 2 Å,  $\text{Ca}^{2+}$  = 3 Å,  $\text{Mg}^{2+}$  and all anions = 4 Å; for smectite the values are the same except for  $\text{K}$  where a value of 0 Å is used to allow for this ion entering the surface of smectite particles (Dolcater *et al.*, 1968; Grim, 1968; Bruggenwert and Kamphorst, 1979).

(5b) As in model (5) for smectite, except the distances of approach are taken as zero for  $\text{K}$  and 4 Å for all other ions.

The method of computing  $G$ -values for each of the above models closely followed that of Oldham (1975). The surface potential  $\phi^s$  and surface field strength  $E^s$  were computed using the appropriate modified versions of Eq. (1a) and (1b) and the known value of the total charge density  $\sigma^b$ . First,  $E^s$  was found using the relationship.

$$d\sigma/dx = -\epsilon_0 \epsilon(E) dE/dx.$$

For simple functions  $\epsilon(E)$  this equation can be integrated analytically over  $[0, \sigma^b]$  to give a non-linear equation in  $E^s$ . For example, when  $\epsilon(E) = a_1/(1 + a_2E^2) + a_3$ , the relevant equation is

$$\sigma^b = \epsilon_0 [a_1 a_2^{-1/2} \tan^{-1}(a_2^{-1/2} E^s) + a_3 E^s]. \quad (2)$$

The surface potential  $\phi^s$  was found by solving numerically the equation

$$d\phi/d\{E^2\} = [-2F \sum z_i C_i / (\epsilon_0 \epsilon(E))]^{-1}.$$

Initially  $\phi \equiv \phi^b = 0$ , and numerical integration was carried out over the interval  $E^2 = [0, \{E^s\}^2]$ , giving as end point the surface potential  $\phi^s$ . Values of  $c_i$  were needed for this integration and were found by solving numerically the set of non-linear equations

$$c_i = c_i^b \exp\{f_i(1)\} \quad i = 1, \dots, n.$$

Having computed  $\phi^s$  and  $E^s$ , the equations

$$dG_T/dx = c_i - c_i^b,$$

$$d\phi/dx = E, \text{ and}$$

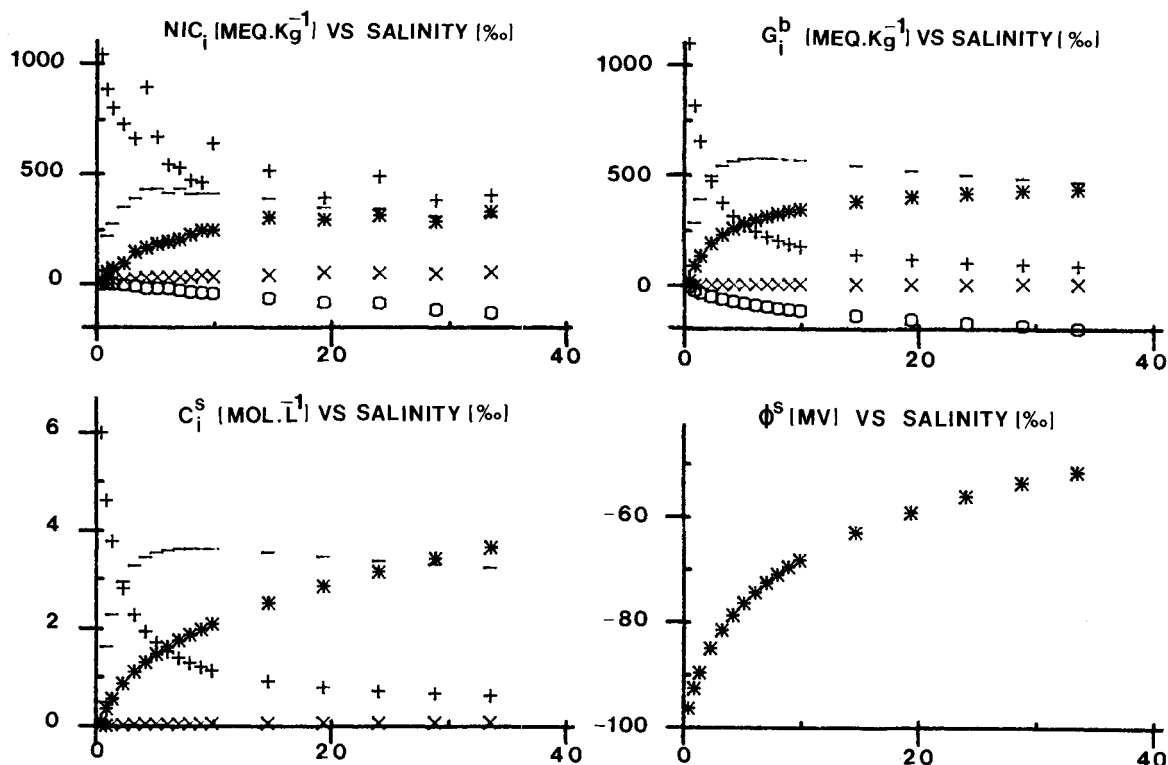


Figure 1. The variation in  $G_i$ , surface concentration, and surface potential as predicted by Gouy-Chapman theory (model 1) and  $NIC_i$  with change in salinity for smectite (+ = Ca, - = Mg, \* = Na, x = K, □ = Cl).

$$dE/dx = -F \sum z_i c_i / \epsilon_0 \epsilon(E)$$

can be solved numerically as an initial value problem, giving a profile of  $G_i$ ,  $\phi$ , and  $E$  adjacent to the charged surface. A more detailed account of a special case of our analysis is given by Oldham (1975).

## RESULTS

Results given here are for kaolinite and smectite in mixtures of river and seawater containing the ions Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>. The salinity of the mixture is in the range 0 to 35‰. Three sets of results are presented: (1) For the basic Gouy-Chapman model,  $G_i^b$ , and  $NIC_i$  values, surface concentrations of ions and surface potential are given for each mixture; (2) Values of these variables for the more complex models are given for seawater and fresh water only; (3) Profiles of  $G$ -values, ionic concentrations, and potential and field strength near a clay surface are given for smectite in seawater.

A comparison of  $G_i^b$  and  $NIC_i$  values for each mixture of waters (shown in Figures 1 and 2) is of interest because these are theoretical and observed measures of the same variable. A striking feature is the discrepancy for K<sup>+</sup> throughout the range of salinities for both clays. The low  $G_i^b$  values are to be expected because

the ratio of K<sup>+</sup> to Na<sup>+</sup> in the bulk solution was low, and in the Gouy-Chapman model this ratio was preserved throughout the double layer. For smectite, the  $G_{Ca^b}$  and  $NIC_{Ca}$  values also show discrepancies at high salinities which may be due to aggregation and the related difficulty of extracting Ca<sup>2+</sup> from the clay. The remaining important difference between theoretical and observed results is observed in the  $G_i^b$  and  $NIC_i$  values for both clays, particularly at high salinities. This difference could be explained by the presence of positively charged sites on the clay surface, especially for kaolinite, and aggregation, especially for smectite. Some evidence for this was given by Hofmann *et al.* (1958) and Grim (1968). Difficulties in providing a standard (fiduciary) drying temperature for damp clays (Thomas *et al.*, 1982) and complexation/hydrolysis of divalent ions near clay surfaces (Bache, 1976; Steger, 1973) may also be complicating factors.

Results for the more complex models are given in Tables 4–7. Although predicted surface concentrations are quite different for models 1 to 3, the  $G$ -values are much the same for any given ion. Comparison between predicted and measured values shows that the predictions are of variable quality; particularly poor are those for K<sup>+</sup> for both clays at both solution strengths, and also Ca<sup>2+</sup> for smectite in seawater. Of these models,

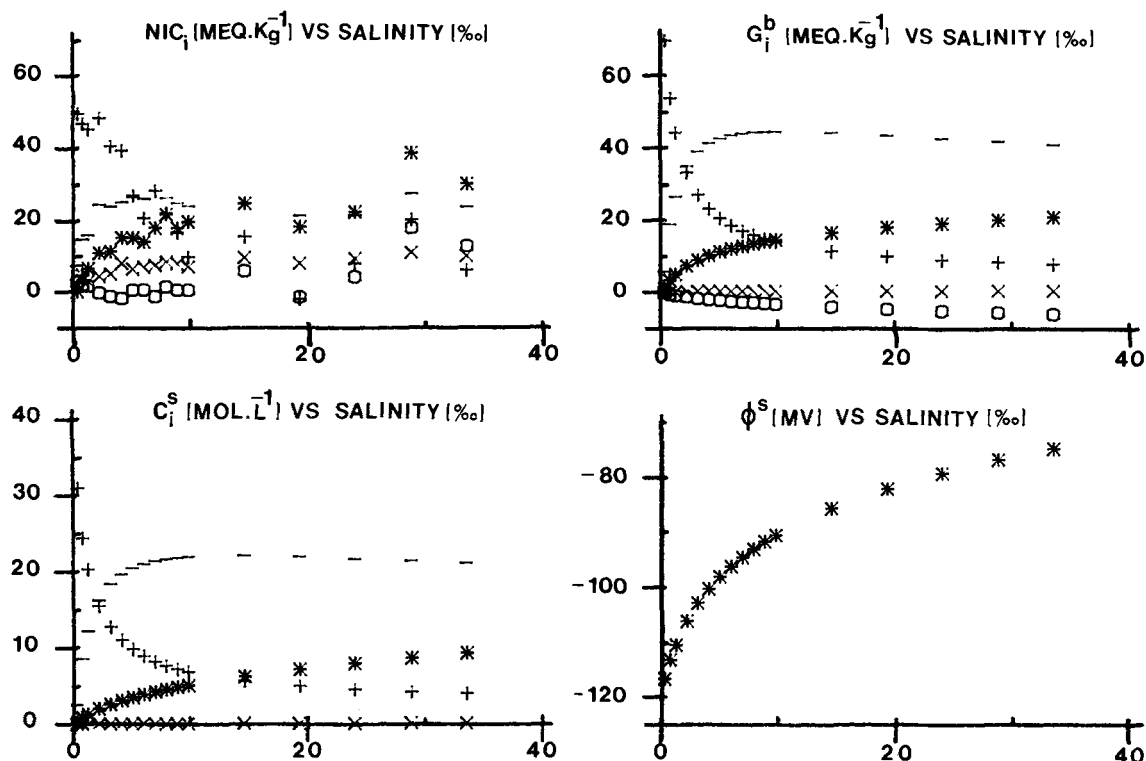


Figure 2. The variation in  $G_i$ , surface concentration, and surface potential as predicted by the basic Gouy-Chapman theory (Model 1) and  $NIC_i$  with change in salinity for kaolinite (+ = Ca, - = Mg, \* = Na, x = K, □ = Cl).

the one which included terms for relative permittivity in the activity equation (Model 3b) was unsatisfactory because unrealistic values of activity coefficients and surface concentrations were obtained. Indeed, for kaolinite,  $G$  values could not be determined for the

seawater example owing to this effect; surface ion concentrations were in excess of 1000 M. This concentration arose because within the model  $\epsilon$  varied by  $\sim 14$  fold ( $\epsilon \sim 6$  near the clay surface,  $\sim 80$  in the bulk solution) resulting in 52- and 4-fold changes, re-

Table 4. Smectite  $G_i^b$ -values for river and marine end members determined by various models.

Model	Na	K	Mg	Ca	Cl	SO <sub>4</sub>	HCO <sub>3</sub>
River water							
1	24.5	1.3	90.3	1096.2	-4.7	-11.0	-9.8
2	22.4	1.2	89.4	1084.4	-3.3	-6.9	-8.8
3a	19.0	1.1	66.4	1131.1	-3.5	-8.4	-7.5
3b	17.8	1.0	60.1	1140.3	-3.5	-8.5	-7.5
4	22.3	1.7	89.2	1082.9	-4.2	-9.0	-8.8
5a	33.7	8.2	45.3	1099.0	-3.7	-7.8	-7.8
5b	22.4	20.1	88.0	1068.4	-4.3	-9.3	-9.1
Measured	15.2	7.7	66.3	1039.5	0.0	—	—
Seawater							
1	422.9	9.3	474.3	90.7	-190.8	-29.7	-0.85
2	441.1	9.2	479.4	91.7	-189.5	-29.6	-0.84
3a	451.9	10.2	481.9	106.7	-162.3	-25.7	-0.74
3b	428.9	10.1	504.0	131.6	-141.3	-22.4	-0.70
4	282.0	16.8	435.9	83.4	-353.8	-45.8	-1.58
5a	600.6	75.5	135.0	68.3	-302.1	-40.3	-1.35
5b	234.2	187.0	342.4	65.5	-347.6	-45.2	-1.56
Measured	330.9	57.0	310.6	403.6	-130.2	—	—

Table 5. Kaolinite  $G_i^b$ -values for river and marine end members determined by various models.

Model	Na	K	Mg	Ca	Cl	SO <sub>4</sub>	HCO <sub>3</sub>
River water							
1	0.8	0.04	5.8	69.8	-0.13	-0.30	-0.28
2	0.8	0.04	5.7	69.5	-0.09	-0.19	-0.19
3a	0.6	0.04	3.9	72.2	-0.09	-0.20	-0.19
3b	0.5	0.03	2.1	76.8	-0.09	2.59	-0.20
4	0.7	1.7	5.5	66.3	-0.08	-0.15	-0.16
5a	7.1	4.4	1.5	61.1	-0.07	-0.15	-0.16
Measured	1.0	2.1	7.3	49.3	2.8	—	—
Seawater							
1	20.9	0.43	41.0	7.8	-6.0	-0.90	-0.03
2	19.7	0.41	42.6	8.0	-5.7	-0.90	-0.03
3a	20.5	0.48	40.7	9.8	-5.0	-0.80	-0.02
3b	—	—	—	—	—	—	—
4	14.6	9.4	34.5	6.6	-10.5	-1.4	-0.05
5a	48.4	6.2	7.3	4.8	-9.3	-1.4	-0.05
Measured	30.0	10.0	23.7	6.1	12.8	—	—

Table 6. Ratio of  $G_i^b/NIC_i$  values for smectite.

Salinity	Na	K	Mg	Ca	Cl
<i>Basic Gouy-Chapman model</i>					
0.36	1.60	0.16	1.43	1.05	-∞
0.83	1.65	0.21	1.31	0.92	-5.68
1.30	1.87	0.22	1.43	1.26	-21.6
2.25	2.08	0.22	1.43	0.65	19.6
3.22	1.58	0.21	1.40	0.57	6.3
4.15	1.58	0.20	1.31	0.35	3.7
5.09	1.54	0.20	1.33	0.41	4.2
6.04	1.56	0.21	1.40	0.45	4.4
7.00	1.55	0.20	1.32	0.42	3.5
7.93	1.45	0.22	1.41	0.43	2.9
8.88	1.39	0.18	1.39	0.41	2.7
9.83	1.40	0.22	1.38	0.29	2.7
14.60	1.27	0.19	1.41	0.27	2.1
19.30	1.39	0.15	1.51	0.31	1.8
24.00	1.34	0.17	1.18	0.22	2.0
28.00	1.52	0.19	1.58	0.26	1.6
33.50	1.33	0.16	1.52	0.22	1.5
<i>Alternative models</i>					
(a) River water					
Model					
1	1.60	0.16	1.43	1.05	-∞
2	1.49	0.15	1.42	1.04	-∞
3a	1.27	0.14	1.05	1.09	-∞
3b	1.17	0.13	0.94	1.00	-∞
4	1.49	0.21	1.41	1.04	-∞
5a	2.25	1.02	0.71	1.06	-∞
5b	1.49	2.51	1.39	1.03	-∞
(b) Seawater					
Model					
1	1.33	0.16	1.52	0.22	1.5
2	1.33	0.16	1.54	0.22	1.5
3	1.36	0.18	1.55	0.26	1.2
3a	1.30	0.18	1.62	0.33	1.1
4	0.85	0.29	1.40	0.21	2.7
5a	1.81	1.32	0.43	0.17	2.3
5b	0.71	3.20	1.10	0.16	2.7

Table 7. Ratio of  $G_i^b/NIC_i$  values for kaolinite.

Salinity	Na	K	Mg	Ca	Cl
<i>Basic Gouy-Chapman model</i>					
0.36	—	0.02	0.79	1.41	-0.1
0.83	0.69	0.03	1.30	1.14	-0.5
1.30	0.76	0.04	1.79	0.98	-0.6
2.25	0.66	0.04	1.43	0.68	14.0
3.22	0.79	0.04	1.63	0.67	1.4
4.15	0.67	0.03	1.67	0.59	1.2
5.09	0.74	0.04	1.80	0.77	-3.8
6.04	0.86	0.04	1.69	0.90	-4.3
7.00	0.71	0.04	1.56	0.60	2.1
7.93	0.62	0.03	1.70	0.72	-2.0
8.88	0.79	0.04	1.80	0.90	-5.2
9.83	0.74	0.04	1.87	1.46	-5.6
14.60	0.67	0.04	1.80	0.74	-0.7
24.00	0.86	0.04	1.98	1.13	-1.2
28.80	0.52	0.04	1.53	0.41	-0.3
33.50	0.70	0.04	1.73	1.29	-0.5
<i>Alternative models</i>					
(a) River water					
Model					
1	0.8	0.02	0.79	1.41	-0.04
2	0.8	0.02	0.79	1.41	-0.03
3a	0.6	0.02	0.53	1.46	-0.03
3b	0.5	0.01	0.29	1.56	-0.03
4	0.7	0.81	0.75	1.34	-0.03
5a	7.1	2.10	0.20	1.24	-0.03
(b) Seawater					
Model					
1	0.70	0.04	1.73	1.29	-0.5
2	0.66	0.04	1.80	1.31	0.4
3a	0.68	0.05	1.71	1.61	0.4
3b	—	—	—	—	—
4	0.49	0.94	1.46	1.08	0.8
5a	1.61	0.62	0.31	0.79	0.7

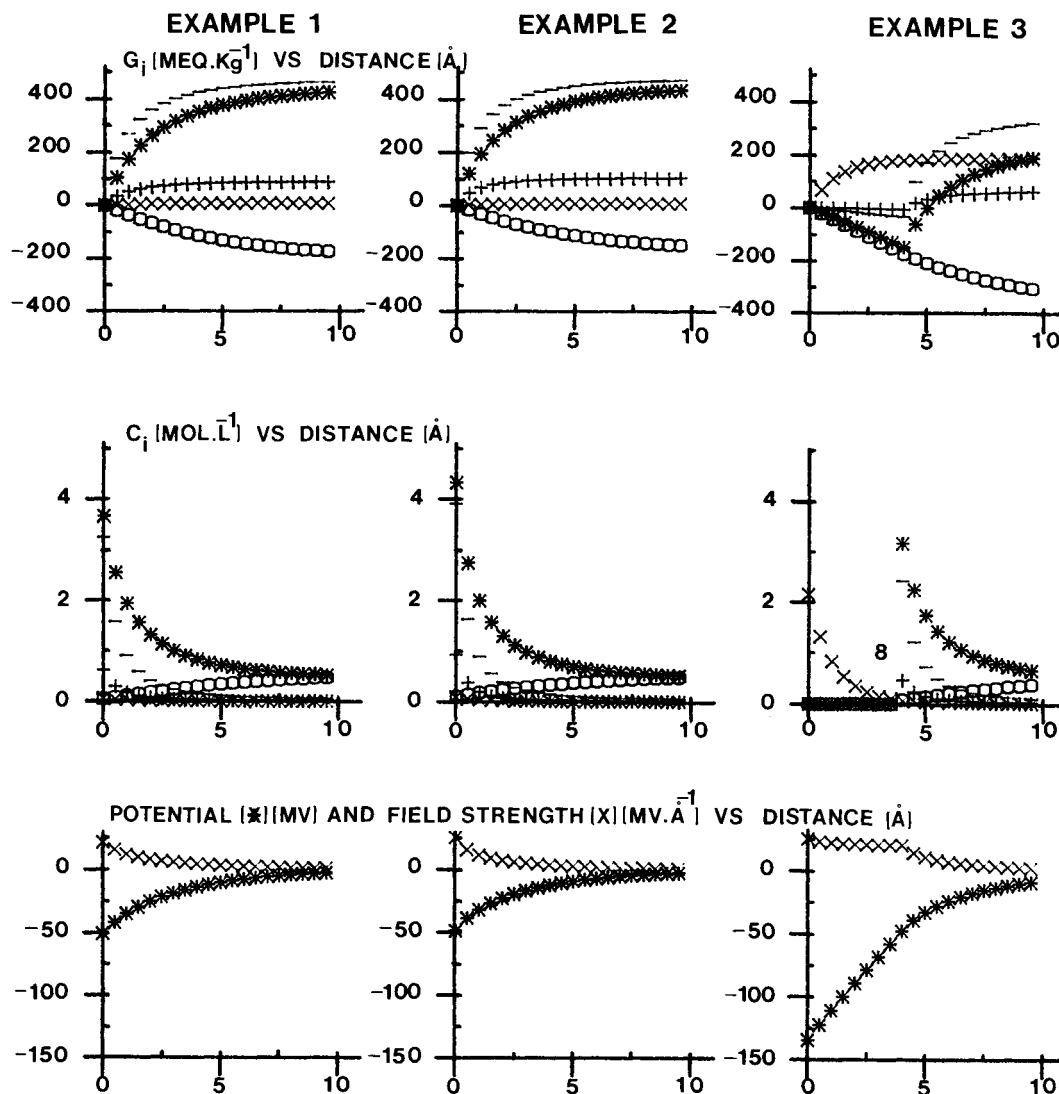


Figure 3. Numerical solutions to three electrostatic models for smectite in seawater. Example 1 = basic Gouy-Chapman model; example 2 = Gouy-Chapman model with dependence of the relative permittivity on field strength in the Poisson equation and an extended Debye-Hückel activity term included; example 3 = Gouy-Chapman model with all ions except potassium restricted to be at least 4 Å from the surface; potassium is unrestricted (+ = Ca, - = Mg, \* = Na, × = K, □ = Cl).

spectively, in the A and B terms in the activity coefficient expression. For example, within one molecular diameter of the clay surface, estimates of  $\gamma_i$  for monovalent and divalent ions ( $I = 4$ ,  $L = 4$ ) were  $2 \times 10^{-5}$  and  $1 \times 10^{-19}$ , respectively; these values compare with bulk solution values of  $5 \times 10^{-1}$  and  $7 \times 10^{-2}$ , respectively.

Models 4 and 5 show that large changes in G-values can be produced by using minimum distance constraints. For kaolinite, Model 4 gave  $G_K$  values which are considerably closer to observations than those for Models 1 to 3, whereas those for other cations were still of the correct order. Model 4 also gave quite good predictions for cation G-values for smectite, apart from

Ca. One effect of introducing distance constraints without also allowing the concentration of water to vary, however, was that G-values for anions became increasingly negative. This effect is clearly shown for Models 4 and 5, where the difference between experimental and predicted values were quite marked for both clays. The models certainly took no account of the possible presence of positively-charged sites on kaolinite which led to  $NIC_{Cl}$  values greater than zero, and aggregation in smectite which led to reductions in  $|NIC_{Cl}|$ . Models 5a and 5b showed that G-values may vary considerably when small changes are made in minimum distance constraints. The relative merits of these sub-models are difficult to judge. Surface concentrations of ions



given by Models 1, 2, and 3 were rather variable and in many cases unrealistic (e.g., 65 molar Ca). Models 4 and 5 gave zero surface concentrations in general, by definition.

Figure 3 shows profiles of ionic concentrations, G-values, potential, and field strength for smectite in seawater for a selection of the models used, namely Models 1, 3a, and 5b. The examples were chosen for the clarity with which the results could be presented graphically. The profiles show that the region in which there was most change in concentrations and G-values is for Models 1 to 3, of the order of 2 or 3 Å; smaller than most hydrated ionic radii.

### CONCLUSIONS

The incorporation of variable relative permittivity and activity coefficient terms in the basic Poisson-Boltzmann equations has little effect on G-values determined except where the relative permittivity term is inserted into the activity equation. Here, the large variation in relative permittivity results in extremely large variations in activity coefficients and surface concentrations which are unrealistic. Consequently, our results suggest that the incorporation of extra terms for relative permittivity and activity does not lead to a significant improvement in the performance of the model.

The inclusion of a closeness of approach constraint alters the determined  $G_i^p$  values to a far greater extent than any of the other modifications we tested and provides a better fit for the cation data. Indeed, the variation in closeness of approach may provide a sensitive means of adjusting the model to fit the observed data. Thus, inasmuch as our theoretical results were made more compatible by the incorporation of an ion hydration term and hydration effects were shown to be critical in controlling ion selectivity, this modification is an important extension to the Gouy Chapman model.

The more elaborate models, while providing better predictions of the clay-electrolyte system, show important differences between theory and observation which provide an insight on how the electrolyte-clay exchange system operates. Thus, it seems that the aggregated nature of smectite clays plays an important part in controlling its exchange properties. Correspondingly, for kaolinite it seems that a variable surface charge model is needed to describe its ion-exchange properties.

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**Резюме**—На основе теории Гюя-Чапмана представлена модель, описывающая ионообменное поведение глин в растворах смешанных электролитов. Принимая во внимание изменения диэлектрической проницаемости, активности ионов и близость доступа ионов к глинистым поверхностям, были рассчитаны ионовые распределения, которые сравнились с экспериментальными данными для смектита и каолинита, находившимися в контакте с речной и соленой водой. Наиболее значительное расширение теории Гюя-Чапмана включает в себя введение члена “близость доступа,” чтобы получить достаточное согласие между теоретическими предсказаниями и наблюдениями. Кроме того, сложная натура смектитов играет значительную роль в контроле свойств обмена, тогда как модель постоянного заряда неполностью описывает свойства обмена ионов для каолинита. [E.G.]

**Resümee**—Es wird ein Modell vorgestellt, das auf der Gouy-Chapman Theorie beruht, mit dem das Ionenaustauschverhalten von Tonen in gemischten Elektrolytlösungen beschrieben wird. Mittels Computerberechnete Ionenverteilungen, die Variationen der relativen Durlässigkeit, der Ionenaktivität und der Annäherung der Ionen an die Tonoberflächen berücksichtigen, wurden mit experimentellen Daten für Smektit und Kaolinit, die in Kontakt mit Flußwässern und salinen Wässern waren, verglichen. Um eine brauchbare Übereinstimmung zwischen der theoretischen Vorhersage und den Beobachtungen zu erzielen, war die Einführung eines Annäherungsterms die wichtigste Erweiterung der Gouy-Chapman Theorie. Darüberhinaus spielt das Aggregat-förmige Auftreten der Smektite eine wichtige Rolle, indem es die Austauschigenschaften beeinflusst, während ein Modell mit definierter Ladung nur eine ungenügende Beschreibung für die Ionenaustauschigenschaften des Kaolinitis liefert. [U.W.]

**Résumé**—On présente un modèle, basé sur la théorie Gouy-Chapman, décrivant le comportement d'échange d'ions d'argiles dans des solutions d'électrolytes mélangés. Des distributions ioniques calculées, qui tiennent compte des variations de permittivité relative, d'activité ionique et de la proximité d'approche des ions des surfaces argileuses, sont comparées avec des données expérimentales pour la smectite et la kaolinite en contact avec des eaux fraîches et salées. Pour obtenir un accord raisonnable entre la prédiction théorique et l'observation, l'extension la plus importante de la théorie de Gouy-Chapman implique le terme de proximité d'approche. De plus, la nature agrégate des smectites joue un rôle important dans le contrôle de ses propriétés d'échange, tandis qu'un modèle à charge fixe fournit une description pauvre pour les propriétés d'échange d'ions de la kaolinite. [D.J.]