

BORON ADSORPTION BY CLAY MINERALS USING A PHENOMENOLOGICAL EQUATION¹

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Abstract—Boron adsorption by Ca forms of montmorillonite, illite, and kaolinite was determined as a function of pH and boron concentration in solution. Data from batch experiments were compared with results computed for each clay according to fitted adsorption coefficients (maximum boron adsorption and affinity constants related to the binding energy). The agreement between calculated values and experimental results indicates that a phenomenological equation can be used to predict boron adsorption on clays as a function of both of these variables. For the solution-to-clay ratios examined, the water content does not affect the boron–surface interaction as expressed by the above adsorption parameters. Because the affinity of clays for $B(OH)_4^-$ is much stronger than for $B(OH)_3$, the adsorption maximum was obtained only under alkaline conditions at approximately pH 9.0 to 9.7. It is suggested that the pH of maximum adsorption is a function of the ratios of affinity coefficients of the three species $B(OH)_3$, $B(OH)_4^-$, and OH^- competing for the same adsorption sites. The adsorption coefficients indicate that in some cases the difference in the amount of adsorbed boron between montmorillonite and kaolinite could be either small or large, depending on the circumstances. The main factor that would affect this difference is the total amount of boron in the suspension. Estimated value of the adsorption maximum was 2.94, 11.8 and 15.1 $\mu\text{mole/g}$ for Ca-kaolinite, Ca-montmorillonite, and Ca-illite, respectively.

Key Words—Adsorption, Boron, Illite, Kaolinite, Montmorillonite.

INTRODUCTION

Several investigators have reported that boron can be adsorbed on clay minerals (Hingston, 1964; Fleet, 1965; Sims and Bingham, 1967) and on hydrous oxides of Fe and Al (Sims and Bingham, 1968a; McPhail *et al.*, 1972). Some of these investigators (Hingston, 1964; McPhail *et al.*, 1972) showed that the Langmuir adsorption equation describes the adsorption of boron from solution by clays as a function of concentration for a given pH. However, for a given adsorbent, the capacity and affinity factors in the Langmuir equation are not constant. The capacity factor increases with pH, whereas the affinity factor decreases (Hingston, 1964). Thus, the Langmuir equation cannot predict boron adsorption as a function of pH.

In contrast, Keren *et al.* (1981) found that a phenomenological equation described boron adsorption by Na-montmorillonite as a function of boron concentration and pH. This equation assumes that $B(OH)_3$, $B(OH)_4^-$, and OH^- compete for the same adsorption sites. The model was tested only for Na-montmorillonite; hence it is worthwhile to examine it for the Ca form of montmorillonite, illite, and kaolinite because the physical and chemical properties of these clays in suspension differ from those of Na-montmorillonite.

Several investigators (Couch and Grim, 1968; Bingham and Page, 1971) suggested that most of the clay's

adsorption sites are located on broken edges. If this is the case, boron adsorption in montmorillonite and illite should be the same regardless of the exchangeable ions, because the surface area of the broken edges of both clays is essentially the same. Hingston *et al.* (1970) found that the maximum adsorption of fluoride, sulphate, and phosphate on gibbsite and goethite occurs at pH values corresponding to their pKs. If the pH of maximum adsorption is a function of pK alone, boron adsorption on different clays should be maximized at the same pH.

The objectives of the present study were (1) to show that a phenomenological equation can be used to describe boron adsorption on different adsorbents as a function of boron concentration and pH; and (2) to determine the pH of maximum adsorption for several different clay minerals.

THEORY

Boron adsorption coefficients were estimated by Keren *et al.* (1981) from experimentally determined values of total amount of adsorbed boron (Q_{BT} , mole/g clay), as a function of equilibrium boron activity by using the equation:

$$Q_{BT} = \frac{T[K_{HB}(HB) + K_B(B)]}{1 + K_{HB}(HB) + K_B(B) + K_{OH}(OH)} \quad (1)$$

where T is the maximum boron adsorption (mole/g clay), K_{HB} , K_B , and K_{OH} are adsorption affinity coefficients (liter/mole) related to the binding energy for

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$B(OH)_3$, $B(OH)_4^-$, and OH^- , respectively, and (HB), (B), and (OH) are the solution activities of the above species.

Eq. (1) can be rearranged to relate Q_{BT} to total boron in the suspension, Q_T , (adsorbed boron + boron in solution, mole/g clay), and to solution-to-clay ratio, R (liter/g clay):

$$Q_{BT} = T \{1 + [PR/F(Q_T - Q_{BT})][1 + K_{OH}(OH)]\}^{-1}. \quad (2)$$

Here, $P = 1 + K_h \times 10^{14} \times (OH)$ and K_h is the hydrolysis constant of the reaction $B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$; $F = K_{HB} + K_B(P - 1)^{\dagger}$, the other terms have been defined.

MATERIALS AND METHODS

Clay preparation

The <2- μ m clay fractions of montmorillonite (Wyoming, API No. 25) and illite (Fithian, API No. 35) were obtained by allowing larger particles to settle out of a suspension and then decanting the suspension. The clays were saturated with Ca by washing them three times with 1 N $CaCl_2$. The clays were then washed with distilled water using a high-speed centrifuge until the equilibrium solution was free of chloride, as indicated by the $AgNO_3$ test. The <2- μ m fraction of Ca-kaolinite (Peerless No. 2) was obtained by the above procedure, modified during the fractionation step because too little of the <2- μ m fraction remained in suspension due to the highly flocculated condition of the clay. Instead, the kaolinite was fractionated by raising the pH of the clay suspension to 10 with NaOH. The salt-free clays were freeze-dried and stored in a desiccator over P_2O_5 . The cation-exchange capacities of the Ca-exchanged montmorillonite, kaolinite, and illite were 0.7, 0.03, and 0.2 meq/g, respectively.

Boron analysis

Boron analyses were conducted using the colorimetric azomethin-H method of Gupta and Stewart (1975).

Adsorption experiments

Three experiments were performed: A. Measurement of adsorption isotherms at constant pH; B. Measurement of the effect of pH on boron adsorption; and C. Determination of the effect of the solution-to-clay ratio on the amount of adsorbed boron.

Experiment A. To determine the adsorption coefficients, 1.5 g of montmorillonite, 1.5 g of illite, and 3 g of kaolinite were shaken in 50-ml polypropylene centrifuge tubes containing 15 ml of solution with boron in 0.01 N $CaCl_2$ solution at $24 \pm 2^\circ C$. To obtain a constant pH during the adsorption reaction, suspension pHs were adjusted prior to boron addition by successive washings with 0.01 N $CaCl_2$ adjusted to the appropriate pH with $Ca(OH)_2$ or HCl. The washings were repeated

until no change in pH was obtained after shaking for 24 hr.

The suspensions were centrifuged, and the solution was replaced with other solutions having the appropriate boron concentration, but with the same $CaCl_2$ concentration and pH. The boron concentration of the initial solutions (before adsorption took place) ranged from 1 to 15 ppm. The suspensions were then brought to final volume by adding an appropriate amount of 0.01 N $CaCl_2$ solution with the desired pH, taking into account the volume of solution remaining in the clay after centrifugation.

Preliminary experiments indicated that the adsorption equilibrium was established less than 2 hr after boron was added to the suspension of montmorillonite or kaolinite, and after 24 hr for illite. However, all the samples were shaken 24 hr for convenience. After 24 hr the suspensions were centrifuged, and aliquots of the supernatant were analyzed colorimetrically for boron.

Experiment B. The adsorption of boron by the Ca-clays as a function of pH was studied as described in Experiment A, except that a constant amount of boron was used in suspension: 9.25 μ mole/g for montmorillonite and illite; 7.0 μ mole/g for kaolinite.

Experiment C. The adsorption of boron by Ca-montmorillonite and Ca-kaolinite as a function of water-to-clay ratio (1 to 20) was studied by shaking 1.5 g of clay in a 0.01 N $CaCl_2$ solution and using a constant amount of boron (9.5 μ mole/g) in suspension. To obtain a constant pH during the adsorption, suspension pHs were adjusted as described above.

Computations

Adsorbed boron was calculated as the difference between the amount added and that found in solution at equilibrium. The negative adsorption of borate ions, $B(OH)_4^-$, was taken into account using the relationship given by Lahav and Banin (1968) for Ca-montmorillonite (1 ml/g clay). The negative adsorption for kaolinite and illite was neglected.

RESULTS AND DISCUSSION

Boron adsorption isotherms at several pHs for Ca forms of montmorillonite, illite, and kaolinite are presented in Figures 1, 2, and 3, respectively. The symbols in these figures represent experimental results, whereas the solid lines were calculated according to Eq. (1), using the adsorption coefficients T , K_{HB} , K_B , and K_{OH} , as summarized in Table 1. The agreement between the theoretical lines and the experimental results indicates that this equation does indeed describe boron adsorption on the Ca forms of these clays, as was shown previously for Na-montmorillonite (Keren *et al.*, 1981).

Evidence for the existence of polynuclear boron species, $B_3O_3(OH)_4^-$ and $B_4O_4(OH)_6^{-2}$, was obtained by Ingri *et al.* (1957), but these species are not present

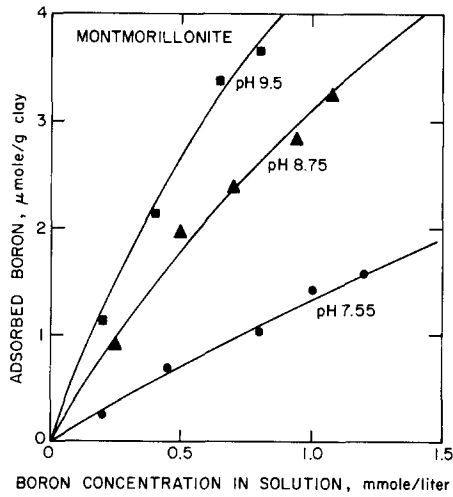


Figure 1. Boron adsorption isotherms on Ca-montmorillonite in 0.01 N CaCl₂ solution at various pHs. The lines were calculated according to $T = 1.18 \times 10^{-5}$ mole/g, and $K_{HB} = 105$, $K_B = 1034$, and $K_{OH} = 9188$ liter/mole.

in significant amounts at low boron concentrations (<0.025 M). It was also found that boron adsorption by Na- and Ca-montmorillonite is completely reversible (Keren and Gast, 1981) and that an insoluble salt of boron is not formed in the presence of CaCO₃ and Ca(HCO₃)₂ (Hingston, 1964). Thus, the suggested adsorption model for the two boron species can be used, if the boron concentration in solution is lower than 0.025 M.

Experimentally determined values of boron adsorption by montmorillonite, kaolinite, and illite, as a function of pH at a given total amount of boron in suspension (Experiment B), are given in Figure 4. The predicted lines were obtained by using Eq. (2) and the

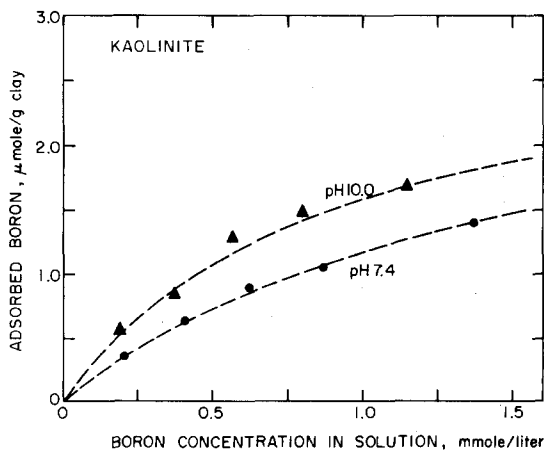


Figure 2. Boron adsorption isotherms on Ca-kaolinite in 0.01 N CaCl₂ solution at two pHs. The lines were calculated according to $T = 2.94 \times 10^{-6}$ mole/g, and $K_{HB} = 373$, $K_B = 17,428$, and $K_{OH} = 121,626$ liter/mole.

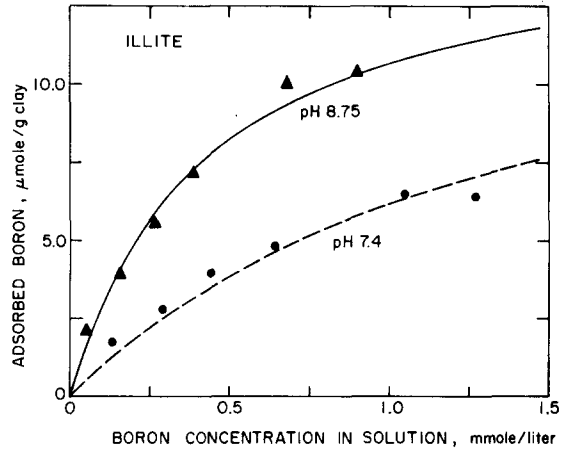


Figure 3. Boron adsorption isotherms on Ca-illite in 0.01 N CaCl₂ solution at two pH values. The lines were calculated according to $T = 1.51 \times 10^{-5}$ mole/g, and $K_{HB} = 348$, $K_B = 8727$, and $K_{OH} = 40,108$ liter/mole.

parameters given in Table 1. Here also, good agreement between the calculated and experimental results was found, indicating that the model can be used to predict boron adsorption on these clays as a function of boron concentration in solution and pH.

These calculated curves show adsorption maxima at pH 9.7, 9.3, and 9.0 for Ca-montmorillonite, Ca-illite, and Ca-kaolinite, respectively. Hingston *et al.* (1970) found that fluoride, sulphate, and phosphate ions have a specific affinity for gibbsite and goethite surfaces and that the maximum adsorption of these anions occurs at pH values corresponding to their pKs. If the pH of maximum adsorption is a function of pK alone, boron adsorption on these clays should be a maximum at the same pH for all of these clays. This contradicts the experimental results obtained for several clays (Sims and Bingham, 1967) and for hydroxy-ions, such as hydroxy-aluminum (Sims and Bingham, 1968a), in which the maxima of boron adsorption for different adsorbents occur over the pH range 7–11. Thus, contrary to the situation with fluoride, sulphate, and phosphate, the pH of maximum boron adsorption depended on the ratio of the affinity coefficients of the three species B(OH)₃,

Table 1. Adsorption coefficients of the competing adsorption equation for kaolinite, montmorillonite, and illite.

Clay	Ex-changeable ion	Maximum boron adsorption T (μmole/g)	Affinity coefficients		
			K_{HB}	K_B (liter/mole)	K_{OH}
Kaolinite	Ca	2.94	373	17,428	121,626
Montmorillonite ¹	Na	6.02	194	1745	25,803
Montmorillonite	Ca	11.8	105	1034	9188
Illite	Ca	15.1	348	8727	40,108

¹ From Keren *et al.* (1981).

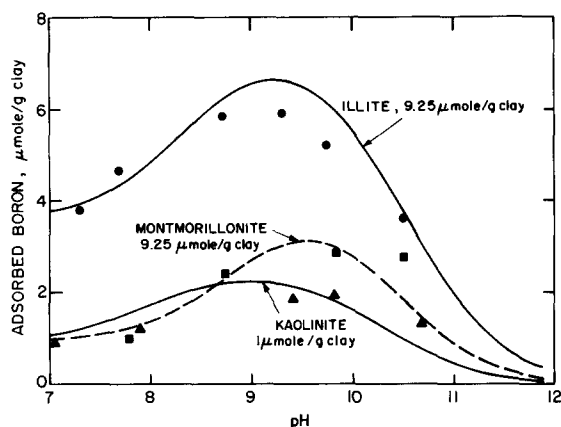


Figure 4. Boron adsorption on Ca forms of montmorillonite, kaolinite, and illite as a function of suspension pH at a given amount of boron. The lines were calculated according to the adsorption coefficients, expressed in terms of moles per gram of clay (Table 1).

$B(OH)_4^-$, and OH^- competing for the same adsorption sites.

On a weight basis, illite is the most reactive of the studied clay minerals. This observation is in agreement with those of Hingston (1964) and Fleet (1965). The difference in the amount of boron adsorbed by illite and montmorillonite at a given pH changes with pH (Figure 4). This change is related to the ratios among the affinity parameters. The ratio K_B/K_{HB} is about 10 and 16 for montmorillonite and illite, respectively. As the pH increased to about 9, the $B(OH)_4^-$ concentration increased rapidly, and the slope of the curve of both clays increased sharply, but not equally, according to the ratio K_B/K_{HB} . Thus, the difference in the amount of adsorbed boron between illite and montmorillonite increased. At this pH, the OH^- concentration was still relatively low and did not play an important role. Further increase in pH resulted in an increase in the OH^- concentration relative to $B(OH)_4^-$, and the difference in boron adsorption decreased rapidly (K_{OH} for illite is about four times higher than for montmorillonite).

Contrary to montmorillonite, kaolinite is characterized by a low value of maximum boron adsorption, but it has higher affinity coefficients (Table 1) indicating that the difference in the amount of adsorbed boron between montmorillonite and kaolinite could be small under certain circumstances and large under others. The main factor that affects this difference is the total amount of boron in the system. This was tested by calculating the amount of boron adsorbed by these two clays as a function of pH at three different total amounts of boron (Figure 5). The lines in Figure 5 were calculated according to Eq. (2), using the adsorption parameters given in Table 1. The results, at low content of total boron ($Q_T = 1 \times 10^{-6}$ or $Q_T = 5 \times 10^{-6}$ mole/g), show that boron adsorption by Ca-kaolinite is slightly

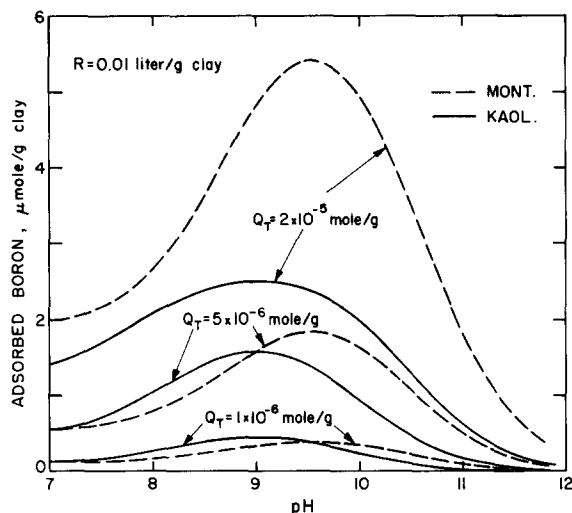


Figure 5. Calculated amount of adsorbed boron on Ca forms of montmorillonite and kaolinite as affected by changing the total amount of boron in suspension for various pHs.

greater than for Ca-montmorillonite at pHs below 9.5. As the pH increases, the opposite is true because of the higher values of K_{HB} , K_B , and K_{OH} for Ca-kaolinite. However, at a higher total boron content ($Q_T = 2 \times 10^{-5}$ mole/g), the boron adsorption by Ca-montmorillonite is greater than by Ca-kaolinite for all pHs. Because the maximum boron adsorption of Ca-kaolinite is much lower than that of Ca-montmorillonite, the saturation level was attained at lower pH than for montmorillonite. Thus, the effect of pH and boron concentration on boron adsorption by Ca-montmorillonite at high total boron content is much greater than by Ca-kaolinite.

The response of the systems to variations in pH can be explained as follows: Below pH 7, $B(OH)_3$ predominated, but because the affinity of the clay for this species was relatively low, the amount of adsorption was small. As the pH increased, the $B(OH)_4^-$ concentration increased rapidly. The amount of adsorbed boron increased rapidly because of the relatively strong affinity of the clays for $B(OH)_4^-$. Because OH^- concentration was still low at a pH below 9, this contribution to total boron adsorption was small despite its relatively strong affinity for the clays. Further increase in pH resulted in an enhanced OH^- concentration relative to $B(OH)_4^-$, and boron adsorption decreased rapidly due to the competition of OH^- for the adsorption sites.

Equilibrium amounts of adsorbed boron on the clay surface are given in Figures 6 and 7 as a function of solution-to-clay ratio at two pHs for montmorillonite and kaolinite (Experiment C), respectively. These two clays were chosen because of the big difference in their maximum adsorption and affinity coefficients. The symbols represent the experimental results, and the

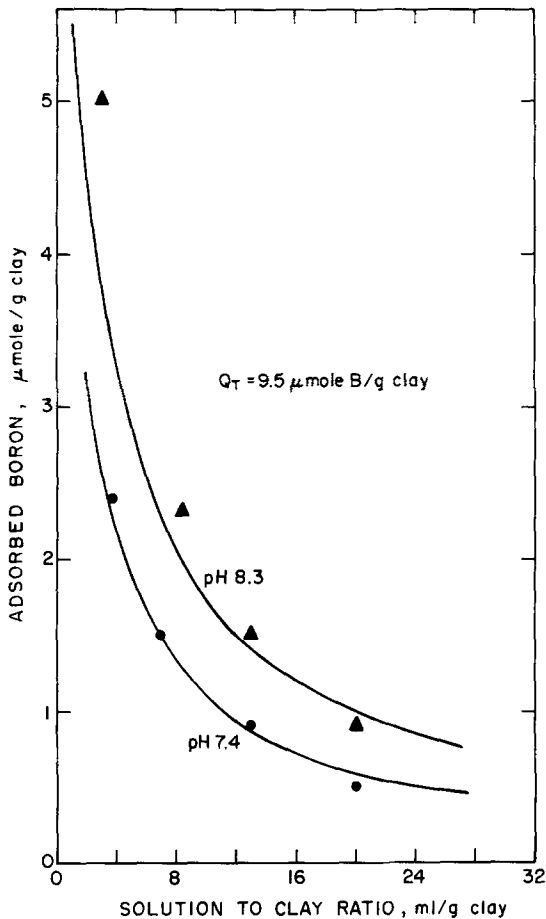


Figure 6. Boron adsorption on Ca-montmorillonite in 0.01 N CaCl_2 solution at two pHs as a function of solution-to-clay ratio at a given amount of boron. The lines were calculated according to $T = 1.18 \times 10^{-5}$ mole/g, and $K_{\text{HB}} = 105$, $K_{\text{B}} = 1034$, and $K_{\text{OH}} = 9188$ liter/mole.

solid lines represent the predicted values, obtained by using Eq. (2) and the adsorption parameters given in Table 1. The agreement between the predicted and experimental results indicates that within the tested range of R, the water content in both clays does not affect the boron-surface interaction as expressed by the adsorption parameters.

Assuming that the area of the boric acid molecule (or borate ion) is approximately 20 \AA^2 (Hingston, 1964), the total surface area covered by boron is only about 1.82, 1.42 and $0.35 \text{ m}^2/\text{g}$ for the Ca forms of illite, montmorillonite, and kaolinite, respectively. The amount of adsorption is very small per unit weight and could be very low per unit area of total surface. The coverage of boron becomes more significant if only the edge surface areas are considered (as suggested by Couch and Grim, 1968).

It is interesting to compare the maximum boron adsorption values of the different clays. From the data in

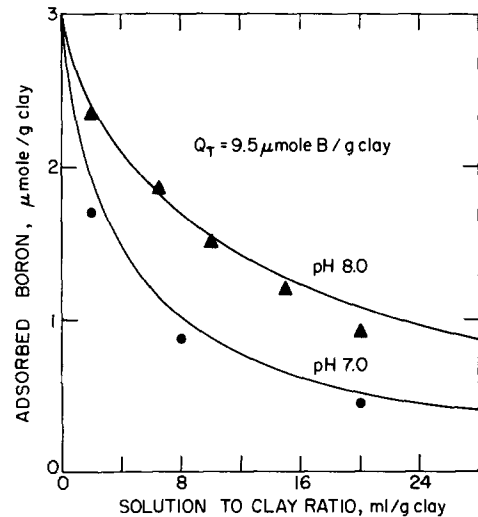


Figure 7. Boron adsorption on Ca-kaolinite in 0.01 N CaCl_2 solution at two pHs as a function of solution-to-clay ratios at a given amount of boron. The lines were calculated according to $T = 2.94 \times 10^{-6}$ mole/g, and $K_{\text{HB}} = 373$, $K_{\text{B}} = 17,428$, and $K_{\text{OH}} = 121,626$ liter/mole.

Table 1, boron adsorption on Ca-illite and Na- and Ca-montmorillonite is not the same, despite the similarity in the surface area of the edges. However, the maximum boron adsorption for Na-montmorillonite (6.02×10^{-6} mole/g, Keren *et al.*, 1981) is much lower than that for Ca-montmorillonite (1.18×10^{-5} mole/g) and Ca-illite (1.51×10^{-5} mole/g). Particles of Na-montmorillonite exist in suspension as single platelets (Shainberg and Otoh, 1968; Warkentin *et al.*, 1957), and the distance between the separate platelets is determined by the diffuse double-layer forces. Conversely, Ca-montmorillonite exists in tactoids consisting of several platelets each (Blackmore and Miller, 1961; Norrish and Quirk, 1954), and a similar structure exists for illite. Because the influence of the negative electric field of the clay particle on platelet edges is less in illite and Ca-montmorillonite than in Na-montmorillonite, it is possible that the ability of the negative borate ions to move close enough to interact with the adsorption sites may be hindered. It is also possible that different amounts of hydroxy-Al polymers are adsorbed on the clay surfaces, thereby increasing the number of adsorption sites for boron (Sims and Bingham, 1968b). These polymers may be formed as a result of clay dissolution in dilute salt solution (Shainberg, 1973).

Boron can be specifically adsorbed on mineral surfaces and hydroxy-Al polymers through a mechanism referred to as ligand exchange, whereby the adsorbed species displace OH^- (or H_2O) from the surface and form partly covalent bonds with the structural cations (Hingston *et al.*, 1972). Such specific adsorption, which occurs irrespective of the sign of the net surface charge, can occur theoretically for any species capable of co-

ordination with the surface metal ions. However, because oxygen is the ligand commonly coordinated to the metal ions in clay minerals, the boron species $B(OH)_3$ and $B(OH)_4^-$ are particularly involved in such reactions.

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REFERENCES

- Bingham, F. T. and Page, A. L. (1971) Specific character of boron adsorption by an amorphous soil: *Proc. Soil Sci. Soc. Amer.* **35**, 892–893.
- Blackmore, A. V. and Miller, R. D. (1961) Tactoid size and osmotic swelling in Ca-montmorillonite. *Proc. Soil Sci. Soc. Amer.* **25**, 169–173.
- Couch, E. L. and Grim, R. E. (1968) Boron fixation by illites: *Clays & Clay Minerals* **16**, 248–256.
- Fleet, M. G. L. (1965) Preliminary investigations into the sorption of boron by clay minerals: *Clay Minerals* **6**, 3–16.
- Gupta, S. K. and Stewart, H. W. B. (1975) The extraction and determination of plant-available boron in soils: *Schweiz. Landwirt. Monatsh.* **14**, 153–169.
- Hingston, F. J. (1964) Reactions between boron and clays: *Aust. J. Soil Res.* **2**, 83–95.
- Hingston, F. J., Posner, A. M., and Quirk, J. P. (1970) Anion binding at oxide surfaces—the adsorption envelope: *Search* **1**, 324–327.
- Hingston, F. J., Posner, A. M., and Quirk, J. P. (1972) Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes: *J. Soil Sci.* **23**, 177–192.
- Ingrì, N., Lagerstrom, G., Frydman, M., and Sillen, L. G. (1957) Equilibrium studies of poly-anions. II. Polyborates in $NaClO_4$ medium: *Acta Chem. Scand.* **11**, 1034–1058.
- Keren, R. and Gast, R. G. (1981) Effects of wetting and drying, and of exchangeable cations, on boron adsorption and release by montmorillonite: *Soil Sci. Soc. Amer. J.* (in press).
- Keren, R., Gast, R. G., and Bar-Yosef, B. (1981) pH-dependent boron adsorption by Na-montmorillonite: *Soil Sci. Soc. Amer. J.* **45**, 45–48.
- Lahav, N. and Banin, A. (1968) Effect of various treatments on the optical properties of montmorillonite suspensions: *Israel J. Chem.* **6**, 285–294.
- McPhail, M., Page, A. L., and Bingham, F. T. (1972) Adsorption interactions of monosilicic and boric acid on hydrous oxide of iron and aluminum: *Proc. Soil Sci. Soc. Amer.* **36**, 510–514.
- Norrish, K. and Quirk, J. P. (1954) Crystalline swelling of montmorillonite: *Nature* **173**, 255–256.
- Shainberg, I. (1973) Rate and mechanism of Na-montmorillonite hydrolysis in suspensions: *Proc. Soil Sci. Soc. Amer.* **37**, 689–694.
- Shainberg, I. and Otoh, H. (1968) Size and shape of montmorillonite particles saturated with Na/Ca ions: *Israel J. Chem.* **6**, 251–259.
- Sims, J. R. and Bingham, F. T. (1967) Retention of boron by layer silicates, sesquioxides and soil minerals: I. Layer silicates: *Proc. Soil Sci. Soc. Amer.* **31**, 728–732.
- Sims, J. R. and Bingham, F. T. (1968a) Retention of boron by layer silicates, sesquioxides and soil minerals: II. Sesquioxides: *Proc. Soil Sci. Soc. Amer.* **32**, 364–369.
- Sims, J. R. and Bingham, F. T. (1968b) Retention of boron by layer silicates, sesquioxides and soil minerals: III. Iron- and aluminum-coated layer silicates and soil materials: *Proc. Soil Sci. Soc. Amer.* **32**, 369–373.
- Warkentin, B. P., Bolt, G. H., and Miller, R. D. (1957) Swelling pressure of montmorillonite: *Proc. Soil Sci. Soc. Amer.* **21**, 495–497.

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Резюме—Адсорбция бора Са-формами монтмориллонита, иллита, и каолинита определялась как функция рН и концентрации бора в растворе. Данные предварительных экспериментов сравнивались с расчётными данными для каждой глины в соответствии с установленными коэффициентами адсорбции (максимальная адсорбция бора и константы химического сродства соответствующие энергии связи). Согласие между расчётными и экспериментальными данными указывает, что простое феноменологическое уравнение может быть использовано для предвидения адсорбции бора на глинах как функции этих двух переменных. Для исследованных соотношений раствор-глина содержание воды не влияет на взаимодействие бор-поверхность, как это выражается вышеуказанными параметрами адсорбции. В связи с тем, что химическое сродство глин с $B(OH)_4^-$ гораздо сильнее, чем с $B(OH)_3$, максимум адсорбции был получен только в щелочных условиях при рН приблизительно 9,0–9,7. Это указывает на то, что рН максимальной адсорбции является функцией соотношения коэффициентов химического сродства $B(OH)_3$, $B(OH)_4^-$, и OH^- , конкурирующих о занятие одних и тех же мест адсорбции. Коэффициенты адсорбции указывают, что в некоторых случаях разница в количестве бора, адсорбированного монтмориллонитом и каолинитом, может быть маленькой или большой в зависимости от обстоятельств. Главный фактор, который влияет на эту разницу, это целое количество бора в суспензии. Определённая величина максимальной адсорбции составляла 2,94, 11,8, и 15,1 моль/г для Са-каолинита, Са-монтмориллонита и Са-иллита соответственно. Адсорбция бора на Са-иллите и Na- и Са-монтмориллонитах неодинакова несмотря на подобие площадей поверхности краев. [E.C.]

Resümee—Die Bor-Adsorption durch Ca-Formen von Montmorillonit, Illit, und Kaolinit wurde als eine Funktion des pH-Wertes und der Bor-Konzentration in der Lösung bestimmt. Die Daten von "batch"-Versuchen wurden mit Ergebnissen verglichen, die für jeden Ton mittels Adsorptionskoeffizienten—via Ausgleichsrechnungen—(maximale Bor-Adsorption und Affinitätswerte entsprechend der Bindungsenergie) berechnet wurden. Die Übereinstimmung zwischen den berechneten Werten und den experimentellen Ergebnissen deutet darauf hin, daß eine einfache empirische Gleichung verwendet werden kann, um die Bor-Adsorption an Tone als eine Funktion beider Variablen voraussagen zu können. Für die untersuchten Lösung/Ton-Verhältnisse spielt der Wassergehalt für die Wechselwirkung Bor-Oberfläche keine Rolle, wie aus den o.a. Adsorptionsparametern hervorgeht. Da die Affinität der Tone für $B(OH)_4^-$ viel größer ist als für $B(OH)_3$, wurde das Adsorptionsmaximum nur unter alkalischen Bedingungen, bei etwa pH 9,0–9,7, erreicht. Es wird angenommen, daß der pH-Wert der maximalen Adsorption eine Funktion der Verhältnisse der Affinitätskoeffizienten der drei Arten, $B(OH)_3$, $B(OH)_4^-$ und OH^- , ist, die die gleichen Positionen besetzen wollen. Die Adsorptionskoeffizienten deuten darauf hin, daß in manchen Fällen der Unterschied im Betrag des adsorbierten Bor zwischen Montmorillonit und Kaolinit entweder klein oder groß sein kann, entsprechend den Umständen. Der wichtigste Faktor, der diesen Unterschied beeinflusst, ist der Gesamtgehalt an Bor in der Suspension. Der geschätzte Wert für die maximale Adsorption war 2,94, 11,8, bzw. 15,1 $\mu\text{Mol/g}$ für Ca-Kaolinit, Ca-Montmorillonit, bzw. Ca-Illit. Die Bor-Adsorption von Ca-Illit, und Na- und Ca-Montmorillonit ist trotz der Ähnlichkeit der Oberflächen an den Ecken nicht die gleiche. [U.W.]

Résumé—L'adsorption de boron par des formes Ca de montmorillonite, d'illite, et de kaolinite a été déterminée en fonction du pH et de la concentration du boron en solution. Les données d'expériences de fournée ont été comparées avec les résultats calculés pour chaque argile suivant des coefficients d'adsorption appropriés (adsorption maximum de boron et constantes d'affinités apparentées à l'énergie de liaison). L'accord entre les valeurs calculées et les résultats expérimentaux indique qu'une simple équation phénoménologique peut être utilisée pour prédire l'adsorption de boron sur des argiles en fonction de ces deux variables. Pour les proportions de solution-argile examinées, le contenu en eau n'affecte pas l'interaction boron-surface exprimée par les paramètres d'adsorption sus-mentionnés. Parce que l'affinité des argiles pour $B(OH)_4^-$ est plus forte que pour $B(OH)_3$, le maximum d'adsorption n'a été obtenu que sous des conditions alcalines à un pH d'approximativement 9,0 à 9,7. On a suggéré que le pH du maximum d'adsorption est une fonction des proportions des coefficients d'affinité des 3 espèces $B(OH)_3$, $B(OH)_4^-$, et OH^- en compétition pour les mêmes sites d'adsorption. Les coefficients d'adsorption indiquent que dans certains cas, la différence de quantité de boron adsorbé entre la montmorillonite et la kaolinite, pouvait être soit grande, soit petite, selon les circonstances. Le facteur majeur qui pourrait affecter cette différence est la quantité totale de boron dans la suspension. Les valeurs estimées pour le maximum d'adsorption étaient 2,94, 11,8, et 15,1 $\mu\text{mole/g}$ pour la kaolinite-Ca, la montmorillonite-Ca, et l'illite-Ca, respectivement. L'adsorption de boron sur l'illite-Ca et sur la montmorillonite-Na et -Ca n'est pas la même, malgré la similarité de l'aire de surface des bords. [D.J.]