

ADSORPTION OF MOLYBDATE ANION (MoO_4^{2-}) BY SODIUM-SATURATED KAOLINITE

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Abstract—Adsorption of Mo(VI) on 2–0.2- μm size fraction of sodium-saturated kaolinite at $25 \pm 2^\circ\text{C}$ and at a constant pH of 7.00 ± 0.05 was studied. The kaolinite sample was pretreated to remove any surface oxide and hydroxide coatings. The initial concentrations of Mo in solution ranged from 1 to 11 mg/liter in a NaClO_4 background electrolyte at a constant ionic strength of 0.09 ± 0.01 . Calculations of speciation using the GEOCHEM computer program indicated that under experimental conditions Mo(VI) was mainly in the MoO_4^{2-} form. The experimental conditions were also shown to fulfill the requirements for applying the Langmuir equation in interpreting adsorption data. The Langmuir parameter for the adsorption maximum, n^0 , and the affinity parameter, $K_{\text{MoO}_4^{2-}-\text{ClO}_4^-}$ were computed to be 3.33×10^{-4} mole/mole of adsorbent and 5.969×10^5 , respectively. The large affinity parameter indicated that the Na-saturated kaolinite surface has a very high affinity for MoO_4^{2-} ions relative to ClO_4^- ions.

Key Words—Adsorption, Electrolyte, Kaolinite, Molybdate ion, Speciation.

INTRODUCTION

Molybdenum is an essential trace element for plant and animal life; however, excessive amounts can have deleterious effects on various organisms. According to Aubert and Pinta (1977), total Mo concentrations in soils as high as 24 ppm have been found. A survey by Kopp and Kroner (1970) indicated that the surface waters in the United States contain Mo concentrations between 0.06 and 1.10 mg/liter. Concentrations of Mo in the environment are significantly enhanced by anthropogenic inputs from coal-resource development, fly ash, sewage sludge, and hard-rock mining activity. Sediments downstream from a molybdenum mine were reported to contain Mo concentrations as high as 2000 ppm (Vlek and Lindsay, 1977); the dissolved Mo in stream water was as high as 3.8 mg/liter (Jordan and Meglen, 1973). Therefore, it is essential to understand various Mo interactions in soils and sediments in order to assess the effects of anthropogenic inputs of this trace element into natural waters and soil systems.

An important aspect of Mo interaction in soils and sediments is its adsorption on to clay mineral surfaces. Relatively few studies of Mo adsorption on phyllosilicates have appeared in the literature, and only two studies have been published that involve the adsorption of Mo on kaolinite (Barshad, 1951; Jones, 1957). These studies were conducted using kaolinite samples that were not characterized, and background electrolytes were not used to maintain constant ionic strengths. In addition, these studies used a single initial concentration of Mo with variable pH. Therefore, a singular lack of data exists regarding Mo adsorption on well-characterized kaolinite with varying initial concentrations of Mo in constant ionic strength solutions. The objective of the present study was to obtain such data

under clearly defined conditions of Mo speciation in equilibrium solutions at constant pH.

MATERIALS AND METHODS

Preparation of kaolinite suspension

A sample of well-crystallized kaolinite from Georgia designated as KGa-1, obtained from the Source Clays Repository of The Clay Minerals Society, was dispersed in 0.1 M NaOH solution, and the 0.2–2- μm size fraction was separated by centrifugation. This size fraction was reacted with 0.001 M HClO_4 in 1.0 M NaClO_4 solution, washed several times with 0.1 M NaClO_4 solution at neutral pH, and stored as a suspension in the same electrolyte in a polyethylene container. This pretreatment procedure was used to remove any oxide and hydroxide coating on kaolinite surfaces. The Na-saturated kaolinite was used in all of the adsorption experiments. The weight of clay per unit volume of suspension was determined by drying known volumes of suspensions at 110°C for 24 hr and applying appropriate corrections for occluded salt. Quadruplicate measurements indicated that the suspension contained 373.14 ± 1.80 mg/ml of clay. A sample of suspension washed free of electrolyte was dissolved in aqua regia and hydrofluoric acid following the method of Bernas (1968). The analysis of the resulting solution indicated that the kaolinite sample contained no detectable molybdenum.

Adsorption experiments

To study the adsorption of Mo by Na-kaolinite, solutions of Na_2MoO_4 ranging from 1 to 11 mg/liter were added to polyethylene centrifuge tubes containing 15 ml of kaolinite suspensions. Aliquots of 0.1 M NaClO_4 solution were added to each centrifuge tube to maintain

Table 1. Association constants for aqueous molybdenum species at 25°C, and 1 atmosphere.

Reaction	log K
$\text{MoO}_4^{2-} + \text{H}^+ = \text{HMoO}_4^-$	4.3
$\text{MoO}_4^{2-} + 2\text{H}^+ = \text{H}_2\text{MoO}_4$	8.2
$7\text{MoO}_4^{2-} + 8\text{H}^+ = \text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O}$	52.8
$7\text{MoO}_4^{2-} + 9\text{H}^+ = \text{Mo}_7\text{O}_{23}(\text{OH})^{5-} + 4\text{H}_2\text{O}$	58.6
$7\text{MoO}_4^{2-} + 10\text{H}^+ = \text{Mo}_7\text{O}_{22}(\text{OH})_2^{4-} + 4\text{H}_2\text{O}$	63.6
$7\text{MoO}_4^{2-} + 11\text{H}^+ = \text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-} + 4\text{H}_2\text{O}$	66.5

Source: Baes and Mesmer (1976). Constants adjusted to zero ionic strength by the Davies equation.

a clay solution ratio of approximately 1:25 and an ionic strength of 0.09 ± 0.01 . The pH of these suspensions was 7.00 ± 0.05 . The choice of pH for these experiments was based upon calculations that indicated MoO_4^{2-} to be the dominant specie of Mo(VI) at neutral pH. The selection of NaClO_4 as the background electrolyte was based on two critical factors. First, the ClO_4^- ion does not form any soluble complexes (Cotton and Wilkinson, 1962) and thus precluded any influence of complex formation on adsorption. Second, MoO_4^{2-} and ClO_4^- ions are tetrahedral anions of comparable size, and, therefore, steric effects on competitive adsorption were expected to be at a minimum. The 25 ml of suspensions was equilibrated at $25 \pm 2^\circ\text{C}$ for 48 hr with continuous shaking. Preliminary experiments had shown that Mo adsorption reached a steady state at about 48 hr. After equilibration, the suspensions were centrifuged at $\sim 1100 g$ for 15 min. The concentration of Mo in the supernatant was measured using a Perkin-Elmer Model 5000 AA spectrometer. The pH values of supernatants showed no significant changes from initial values of 7.00 ± 0.05 . Al and Si in the supernatants were also determined by atomic absorption spectrometry to assess the extent of kaolinite dissolution during the experiment.

Calculation of Mo(VI) speciation in solution

The total amount of Mo adsorbed by Na-kaolinite was calculated from the difference between Mo concentrations in the initial and the equilibrium solutions. According to Baes and Mesmer (1976), Mo in solution can exist in valence states ranging from 3+ to 6+, with the 6+ state being the most stable form in the absence of complex-formation reactions. Mo(VI) can also exist in polymeric forms at higher concentrations and may form complexes. Therefore, Mo speciation in solution as a function of pH was computed by the chemical equilibrium computer program, GEOCHEM (Mattigod and Sposito, 1979). The ion-activity coefficients were calculated from the Davies equation (Davies, 1962). The association constants for various Mo(VI) species that were used in these calculations are listed in Table 1. The results (Figure 1) indicated that at pH

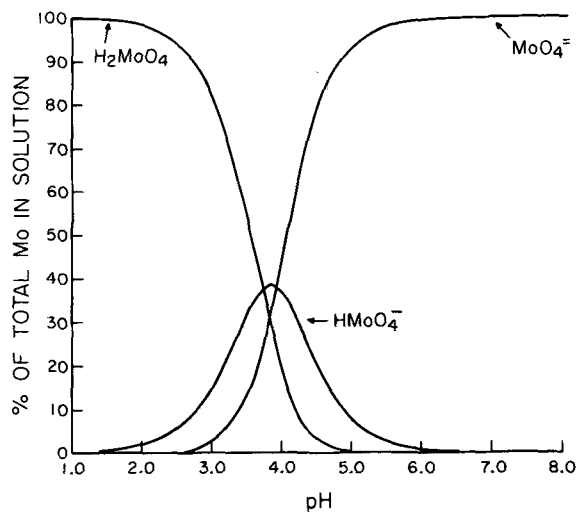


Figure 1. Distribution of Mo(VI) species in equilibrium solutions of 0.1 M NaClO_4 as a function of pH for total concentrations of Mo between 1 and 11 mg/liter.

7.00 and total concentrations ranging from 1 to 11 mg/liter in 0.1 M NaClO_4 solutions, Mo(VI) existed mainly as MoO_4^{2-} ions. No polymeric species or solid phases of Mo(VI) were predicted to be present under these conditions. Therefore, the data that were obtained in these experiments were interpreted on the basis of adsorption of MoO_4^{2-} ions on kaolinite surfaces.

The concentrations of Al and Si in the equilibrium solutions averaged 1.3 and 3.3 mg/liter, respectively, indicating that the dissolution of Na-kaolinite was insignificant during adsorption experiments. Inclusion of Al and Si concentrations in speciation calculations showed no changes either in speciation of Mo(VI), or the ionic strength.

Application of the Langmuir equation

The derivation of the Langmuir equation based on statistical thermodynamics was published by Sposito (1979). Recently, El Prince and Sposito (1981) outlined the critical assumptions that underlie the Langmuir equation. Sposito (1983) also showed that the Langmuir equation is a specific case of the following general adsorption equation:

$$n_A = \frac{n_A^0 K_{AB}^\beta (a_A/a_B)^\beta}{1 + K_{AB}^\beta (a_A/a_B)^\beta} \quad (1)$$

where, n_A = quantity of specie A adsorbed in competition with specie B, n_A^0 = maximum value of adsorption for specie A, K_{AB} = constant measure of affinity of specie A for the surface relative to specie B, β = surface heterogeneity parameter, a_A and a_B are the activities of A and B species in solution at equilibrium, and n_A and n_A^0 can have units: mg/g, mole/m², or mole/

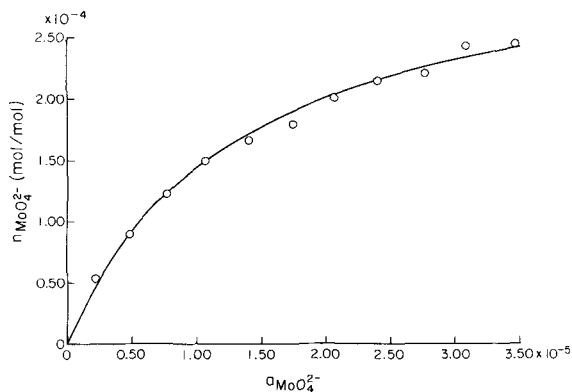


Figure 2. Adsorption isotherm with activity of MoO_4^{2-} in equilibrium solution and the quantity of Mo adsorbed on Na-kaolinite as variables. The curve was calculated from the Langmuir constants derived from Figure 3.

mole of adsorbent. The parameters: K_{AB} , β , a_A , and a_B are dimensionless.

If the surface heterogeneity parameter is unity, and if the activity of the specie B is held constant during an experiment, Eq. (1) can be expressed as:

$$n_A = \frac{n_A^0 K_{AB}^1 a_A}{1 + K_{AB}^1 a_A} \quad (2)$$

where $K_{AB}^1 = K_{AB}/a_B = \text{constant}$. Dividing both sides of the Eq. (2) by n_A and rearranging, gives rise to the traditional Langmuir equation:

$$\frac{a_A}{n_A} = \frac{1}{n_A^0 K_{AB}^1} + \frac{a_A}{n_A^0} \quad (3)$$

In the present experiments, the activity of ClO_4^- was maintained at a constant level by the use of 0.1 M NaClO_4 solution as background electrolyte. Because our computations showed that in equilibrium solutions, Mo(VI) existed as the MoO_4^{2-} species, it is valid to use the activity of MoO_4^{2-} ion in Eq. (3). The activity of OH^- was negligible at $\text{pH } 7.00 \pm 0.05$; therefore, MoO_4^{2-} ion adsorption on Na-kaolinite surfaces occurred mainly in competition with ClO_4^- ions—a clear justification for using the Langmuir Eq. (3) to describe MoO_4^{2-} ion-adsorption data obtained from these experiments.

RESULTS AND DISCUSSION

The activities of MoO_4^{2-} ions in equilibrium solutions in relation to the amount of MoO_4^{2-} adsorbed by Na-kaolinite are depicted in Figure 2. The Langmuir isotherm with $a_{\text{MoO}_4^{2-}}/n_{\text{MoO}_4^{2-}}$ as the dependent variable and $a_{\text{MoO}_4^{2-}}$ as the independent variable is illustrated in Figure 3 in which the relationship between these parameters is linear. From the slope and intercept of this isotherm, the adsorption maximum n^0 for the MoO_4^{2-}

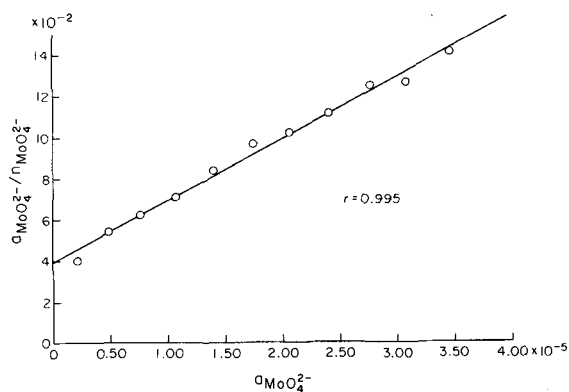


Figure 3. Langmuir isotherm depicting MoO_4^{2-} adsorption on Na-kaolinite in competition with ClO_4^- .

ion and the affinity parameter, $K_{\text{MoO}_4^{2-}-\text{ClO}_4^-}$ were calculated to be 3.33×10^{-4} mole/mole of kaolinite and 5.969×10^5 , respectively. This value of n^0 indicates that the highest adsorption attained in this experiment was approximately 74% of the predicted maximum. The large affinity parameter indicates that the Na-saturated kaolinite surface has a very high affinity for MoO_4^{2-} ions relative to ClO_4^- ions.

In these experiments, the kaolinite sample was pretreated to remove any oxide and hydroxide coatings and to ensure that adsorption occurred on kaolinite surfaces. Other experimental conditions were selected so that all of the Mo(VI) in solution was present in the MoO_4^{2-} form. In addition, the applicability of the Langmuir isotherm for the competitive adsorption data was established. Therefore, these data, collected under well-defined experimental conditions, are not comparable to the results of previous studies of Mo(VI) adsorption on kaolinite (Barshad, 1951; Jones, 1957) due to the following reasons. (1) Previous studies were conducted with kaolinite samples that were not fully characterized as to their physico-chemical properties. (2) The adsorption data of Barshad (1951) and Jones (1957) were based in each experiment on a single Mo(VI) concentration and without any background electrolyte to control the ionic strength. The MoO_4^{2-} adsorption data generated from the present experiment lead to two important conclusions. First, the steric factors being similar, the adsorption of MoO_4^{2-} ions on Na-kaolinite surfaces occurred even when the MoO_4^{2-} concentrations in equilibrium solutions were three to four orders of magnitude less than the concentrations of competing ClO_4^- ions. Second, the very high affinity of MoO_4^{2-} ions for the Na-kaolinite surfaces indicates probable specific adsorption. This phenomenon is similar to the commonly observed specific adsorption of other divalent anions on various types of oxide surfaces (Hings-ton, 1981).

The adsorption of Mo(VI) on well-characterized clay minerals and soils in the presence of different competing ligands and upon complex formation in media of known ionic strengths needs further study for a better understanding of Mo(VI) chemistry in natural systems.

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Резюме—Исследовалась адсорбция Mo(VI) на фракции размером 2–0,2 μm каолинита, насыщенного натрием при температуре $25 \pm 2^\circ\text{C}$ и при постоянной величине pH равной $7,00 \pm 0,05$. Образец каолинита обрабатывался так, чтобы удалить все окисные и гидроокисные поверхностные покрытия. Начальные концентрации Mo в растворе распределялись от 1 до 11 мг/литр в электролите NaClO_4 при постоянной ионной силе равной $0,09 \pm 0,01$. Вычисления количества новых виллов при помощи программы ГЭОХЕМ указывали на то, что в этих экспериментальных условиях Mo(VI) находился в основном в форме MoO_4^{2-} . Показано, что экспериментальные условия выполняли необходимые условия для использования уравнения Лангмюра для интерпретации данных адсорбции. Параметр Лангмюра для максимума адсорбции, n^0 , и параметр подобия, $K_{\text{MoO}_4^{2-}\text{-ClO}_4^-}$, были вычислены как $3,33 \times 10^{-4}$ моля/моль адсорбента и $5,969 \times 10^5$, соответственно. Значительный параметр подобия указывал на то, что поверхность каолинита, насыщенного Na, имеет очень высокое подобие для ионов MoO_4^{2-} по отношению к ионам ClO_4^- . [E.G.]

Resümee—Es wurde die Adsorption von Mo(VI) an die 2–0,2 μm Fraktion von Na-gesättigtem Kaolinit bei $25 \pm 2^\circ\text{C}$ und einem konstanten pH von $7,00 \pm 0,05$ untersucht. Die Kaolinitprobe wurde vorbehandelt, um oxidische und hydroxidische Oberflächenbeläge zu entfernen. Die ursprünglichen Konzentrationen an Mo in der Lösung reichten von 1–11 mg/Liter in einer NaClO_4 Elektrolytlösung mit einer konstanten Ionenstärke von $0,09 \pm 0,01$. Die Berechnungen mittels GEOCHEM-Programm deuten darauf hin, daß unter den experimentellen Bedingungen Mo(VI) hauptsächlich als MoO_4^{2-} vorlag. Es zeigte sich auch, daß die experimentellen Bedingungen so waren, daß sie die Anforderungen für die Anwendung der Langmuir-Gleichung bei der Interpretation der Adsorptionsdaten erfüllt haben. Der Langmuir-Parameter für das Adsorptionsmaximum, n^0 , und der Affinitätsparameter, $K_{\text{MoO}_4^{2-}\text{-ClO}_4^-}$, wurden, auf $3,33 \times 10^{-4}$ Mole/Mole für den Adsorbenten bzw. mit $5,969 \times 10^5$ berechnet. Der große Affinitätsparameter deutete darauf hin, daß die Na-gesättigte Kaolinitoberfläche eine große Affinität für MoO_4^{2-} -Ionen im Vergleich zu ClO_4^- -Ionen hat. [U.W.]

Résumé—On a étudié l'adsorption de Mo(VI) sur une fraction de kaolinite saturée de sodium de taille 2–0,2 μm à $25 \pm 2^\circ\text{C}$ et à un pH constant de $7,00 \pm 0,05$. L'échantillon de kaolinite avait été traité à l'avance pour enlever toutes couches oxydes et hydroxydes. Les concentrations de Mo initiales dans la solution s'étendaient de 1 à 11 mg/litre dans un électrolyte d'arrière plan de NaClO_4 à une force ionique constante de $0,09 \pm 0,01$. Des calculs de spéciation employant le programme GEOCHEM ont indiqué que sous les conditions expérimentales Mo(VI) était principalement dans la forme MoO_4^{2-} . On a aussi montré que les conditions expérimentales ont satisfait les exigences pour appliquer l'équation de Langmuir dans l'interprétation des données d'adsorption. Le paramètre de Langmuir pour le maximum d'adsorption, n^0 , et le paramètre d'affinité, $K_{\text{MoO}_4^{2-}\text{-ClO}_4^-}$, ont été calculés être $3,33 \times 10^{-4}$ mole/mole d'adsorbant et $5,969 \times 10^5$, respectivement. Le grand paramètre d'affinité a indiqué que la surface de kaolinite saturée de Na a une affinité très élevée pour les ions MoO_4^{2-} relativement aux ions ClO_4^- . [D.J.]