



Modeling competitive adsorption of molybdate, sulfate, selenate, and selenite using a Freundlich-type multi-component isotherm

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Abstract

This study examined the interactions of $\text{MoO}_4^{2-} + \text{SO}_4^{2-}$, $\text{MoO}_4^{2-} + \text{SeO}_4^{2-}$, and $\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$ systems on $\gamma\text{-Al}_2\text{O}_3$ to better understand the competitive adsorption of these anions in the natural environment. The Freundlich isotherms of anionic adsorption onto $\gamma\text{-Al}_2\text{O}_3$ in single and binary solutes were also investigated to estimate the competition between these anions. Experimental results indicate that a higher concentration of competitive solute yields a higher efficiency of the competitive solute's prevention of MoO_4^{2-} adsorption. The most significant result was found in the $\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$ system. The Freundlich isotherm constant (n) increases with the competitive solute concentration. The suitability of a Freundlich-type isotherm, the Sheindorf–Rebuhn–Sheintuch (SRS) equation, and the modified SRS equation in representing the competitive adsorption of MoO_4^{2-} , SO_4^{2-} , SeO_4^{2-} , and SeO_3^{2-} on $\gamma\text{-Al}_2\text{O}_3$ surface, was also examined. Each set of isotherm data was found to conform to linear SRS expressions, allowing competition coefficients to be derived on a concentration basis for each binary-solute system. The competition coefficient a_{ij} and relative affinity coefficients α_{ij} can be seen as a way to quantify competitive interactions. The proposed SRS and modified SRS equations are simple mathematical expressions accounting for competitive interactions of anions present in a mixture for the range of concentrations over which each individual component exhibits Freundlich behavior. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic adsorption; Binary-solute adsorption; SRS equation; Modified SRS equation; Competition coefficients; Relative affinity coefficients

1. Introduction

Colloids in the environment play a critical role in controlling anionic recycling and transport and stabilizing particles which influence the aquatic ecosystem. The mobility of anions in the aquatic environment is

typically regulated by adsorption at the solid/water interface and by competition among various anion species for surface binding sites. The magnitude of these competitive interactions must be determined to predict and model anion migration.

The adsorption of molybdate, sulfate, selenate, and selenite has been extensively studied (Roy et al., 1986; Hawke et al., 1989; Zhang and Sparks, 1989, 1990a,b; Bolan et al., 1993; Goldberg et al., 1996; Manning and Goldberg, 1996a,b; Wilkie and Hering, 1996; Wu et al.,

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1998, 1999, 2000, 2001). Zhang and Sparks (1989, 1990a,b) and Wu et al. (1998, 1999) have examined the kinetic processes of these anions on different oxide surfaces using the pressure-jump technique. Roy et al. (1986) demonstrated that the adsorption of arsenate and molybdate was noticeably reduced by the competitive adsorption of phosphate on the surfaces of Cecil clay (Typic Hapludults), EPA-14 (Ultisol), and Catlin silt loam (Typic Argiudolls). Sulfate decreased the adsorption of As(III), As(V), and phosphate on hydrous ferric oxide and goethite surfaces, while sulfate adsorption increased with increasing adsorption of Ca^{2+} on the goethite surface (Hawke et al., 1989; Bolan et al., 1993; Wilkie and Hering, 1996). Manning and Goldberg (1996b) demonstrated that the presence of molybdate decreased As(V) adsorption on the surfaces of α -FeOOH (goethite) and γ -Al(OH)₃ (gibbsit) when the pH was below 6. They further explored the presence of molybdate at equimolar with and at concentrations 10 times higher than that of As(V) and observed that only a slight decrease in As(V) adsorption on kaolinite, montmorillonite, and illite surfaces. Goldberg et al. (1996) revealed that competitive anion effects of B adsorption on the surfaces of kaolinite and montmorillonite increased in the order, phosphate > molybdate > sulfate.

Wu et al. (2000) further demonstrated that the order of the relative retention of anions on the γ -Al₂O₃ surface was molybdate > selenite > selenate > sulfate \approx chromate, corresponding to the magnitude of the overall proton coefficient of the corresponding anions. Wu et al. (2001) also showed that a higher pH reduces the efficiency with which molybdate inhibits sulfate and selenate adsorption; these researchers found similar results for the depression of sulfate adsorption by selenate. Systematic examination and quantitative information on the relative competition for sorption onto oxides among these anions with different binding affinities are rather scarce. Theoretically, multi-component mixture competition results in increasingly complex anion interactions at the water/oxide interface. Such complex systems frequently occur, and the magnitude of these competitive interactions must be clarified to better predict contaminant behavior and to identify anions whose transport is more likely to be affected by the presence of other anions. Accurately predicting the extent of anionic adsorption onto oxide surfaces involves: (i) an understanding of the competitive effects among anions; and (ii) a descriptive model which accurately describing adsorption characteristics in the presence or absence of competition.

Sheindorf et al. (1981) derived a Freundlich-type multi-component adsorption isotherm, the Sheindorf-Rebuhn-Sheintuch (SRS) equation, to represent experimental data. The assumptions incorporated in the derivation are: (i) each component individually obeys the Freundlich isotherm; and (ii) for each component in

a multi-component adsorption system, there exists an exponential distribution of site adsorption energies.

A general SRS equation can be written as

$$q_i = K_i C_i \left(\sum a_{ij} C_j \right)^{n_i-1}, \quad (1)$$

where q_i is the adsorption of component i per gram weight of sorbate in $\mu\text{mol/g}$; C_i and C_j are the concentrations of i and j in the equilibrium solution in μM ; K_i and n_i are the Freundlich constants obtained for i in a single-component system; and a_{ij} is the competition coefficient for the adsorption of component i in the presence of component j . The bicomponent isotherm can be written

$$\frac{C_1}{C_2} = \frac{\beta_1}{C_2} - a_{12}, \quad (2)$$

$$\frac{C_2}{C_1} = \frac{\beta_2}{C_1} - a_{21} \quad (3)$$

with

$$\beta_1 = \left(\frac{K_1 C_1}{q_1} \right)^{1/(1-n_1)} \quad \text{and} \quad \beta_2 = \left(\frac{K_2 C_2}{q_2} \right)^{1/(1-n_2)}. \quad (4)$$

If both concentrations vary during the experiment, then plotting C_1/C_2 vs β_1/C_2 yields a straight line-of-unity slope and the competition coefficient could be determined from the intercept. This SRS equation has been successfully applied to different types of contaminants (Sheindorf et al., 1981, 1982; Roy et al., 1986; Gutierrez and Fuentes, 1991, 1993; Susarla et al., 1992).

This research investigated the isotherms of the adsorption of molybdate, sulfate, selenate, and selenite onto γ -Al₂O₃ in single and binary mixture solutions to estimate the competitive adsorption among these anions. Both experimental and adsorption modeling results are discussed. This study aims: (i) to investigate the competitive adsorption of these anions in different concentration ratios; (ii) to determine the competition coefficients and explain the degree of competition in bicomponent systems; and (iii) to model the experimental results using the SRS equation and the triple-layer model (TLM).

2. Materials and methods

2.1. Materials

All solutions were prepared with deionized water (Milli-Q) and reagent-grade chemicals. Stock anion solutions (10^{-2} M) were prepared with Na₂MoO₄, Na₂SO₄, Na₂SeO₄, and Na₂SeO₃. Reagent grade HNO₃ and NaOH were used for adjusting the system pH. The adsorbent γ -Al₂O₃ obtained from Aerosil (Japan) was

purified by electrodialysis (1200 V, 3 mA) before use in the sorption experiments. The surface area of $\gamma\text{-Al}_2\text{O}_3$, determined by the manufacturer from the N₂ Brunauer–Emmett–Teller adsorption isotherm was equal to 100 m²/g.

2.2. Sorption experiments

In competitive adsorption experiments, MoO₄²⁻ (2000, 1500, 1000, and 700 μM) was equilibrated with $\gamma\text{-Al}_2\text{O}_3$ suspension (10 g/l), and the concentrations of competitive solutes (SO₄²⁻, SeO₄²⁻, and SeO₃²⁻) ranged from 300 to 7000 μM . A small amount of HNO₃ or NaOH was added to maintain the pH of the competitive systems at 5.7 ± 0.2. All experiments were performed in a tightly capped 15 ml polypropylene vial in an N₂ atmosphere at 25 ± 0.1 °C for 24 h. When equilibrium was reached, the pH of each suspension was determined. The suspensions were centrifuged at 9500 rpm for 10 min, and the supernatants were filtered through 0.2 μm filter paper (Gelman Sciences). All anion concentrations were determined by ion chromatography (Dionex 2000i SP). The adsorbed amounts q_i were calculated from

$$q_i = \frac{(C_i - C_0)}{m}, \quad (5)$$

where C_i and C_0 are the initial and equilibrium concentrations, respectively, in μM ; and m is the amount of $\gamma\text{-Al}_2\text{O}_3$ in 10 g/l suspension.

2.3. TLM simulation

Model analogous of two different types of surface complexes can be incorporated to TLM, either as inner-sphere or outer-sphere ion–pair complexes. The former corresponds to ions placed in the α -plane, the latter to ions placed in the β -plane.

Data were modeled with the TLM by assuming that: (i) homogeneous sites and (ii) the intrinsic surface complexation constants obtained for the adsorption of molybdate, sulfate, selenate, and selenite from a single anion system can be used to predict simultaneously, competitive adsorption from mixture of two of the anions. The intrinsic acidity surface hydrolysis constants

($\log K_{\text{al}}^{\text{int}}$ and $\log K_{\text{a2}}^{\text{int}}$) and binding constants ($\log K_{\text{Na}^+}^{\text{int}}$ and $\log K_{\text{NO}_3^-}^{\text{int}}$) of the background electrolyte (NaNO₃) with the $\gamma\text{-Al}_2\text{O}_3$ surface determined in our previous work were –6.9, –9.7, –8.3, and 6.9, respectively (Wu et al., 2000). Site density was reported by Peri (1965) to be 8 sites/nm². Inner- and outer-plane capacitances were assumed to be 80 and 20 $\mu\text{F}/\text{cm}^2$, respectively, as reported by Hayes et al. (1991). The TLM parameters, basic surface complexation constants and the equilibrium constants for anion/ $\gamma\text{-Al}_2\text{O}_3$ systems in Table 1 (Wu et al., 2000) were used in the model analysis to determine the anion partition for the competitive adsorption systems.

3. Results and discussion

3.1. Single-component adsorption

Fig. 1 displays the isotherms obtained for MoO₄²⁻ in a single-component system. Table 2 lists the adsorption isotherm constants derived from applying the Freundlich and Langmuir equations. Generally, the isotherm data were best described by the Freundlich equation. At low anion concentrations, the Freundlich equation closely represents adsorption results, as theoretically implied by many adsorption sites available to adsorb anions. At high concentrations, the Freundlich equation no longer represents adsorption, as the adsorption sites become saturated and the isotherm reaches a plateau.

Table 2 presents the Freundlich constant (n) and saturation adsorption constant (Q_m) of the Langmuir equation. Each constant is of the same order of magnitude for different anions. The order, MoO₄²⁻ > SeO₃²⁻ > SeO₄²⁻ > SO₄²⁻ is the same ordering as that of the relative retention of anions on oxide surfaces proposed by Wu et al. (2000). This finding implies that a greater saturation adsorption constant relates to increased affinity on the oxide surface.

3.2. Competitive adsorption

Anionic adsorbates in competitive systems directly compete for available binding sites and are indirectly

Table 1
Surface complexation reactions and equilibrium constants for anion/ $\gamma\text{-Al}_2\text{O}_3$ systems

Anions	Reactions in system ^a	$\log K_{\text{eq}}^{\text{int}}$
MoO ₄ ²⁻	SOH + H ⁺ + MoO ₄ ²⁻ = SMoO ₄ ⁻ + H ₂ O	6.5 ^a
SO ₄ ²⁻	SOH + H ⁺ + SO ₄ ²⁻ = SOH ₂ ⁺ – SO ₄ ²⁻	10.4 ^a
SeO ₄ ²⁻	SOH + H ⁺ + SeO ₄ ²⁻ = SOH ₂ ⁺ – SeO ₄ ²⁻	9.8 ^a
SeO ₃ ²⁻	SOH + H ⁺ + SeO ₃ ²⁻ = SSeO ₃ ⁻ + H ₂ O	9 ^a
	SOH + 2H ⁺ + SeO ₃ ²⁻ = SHSeO ₃ + H ₂ O	5 ^a

Note. $K_{\text{eq}}^{\text{int}}$ is the intrinsic equilibrium constant.

^a Wu et al. (2000).

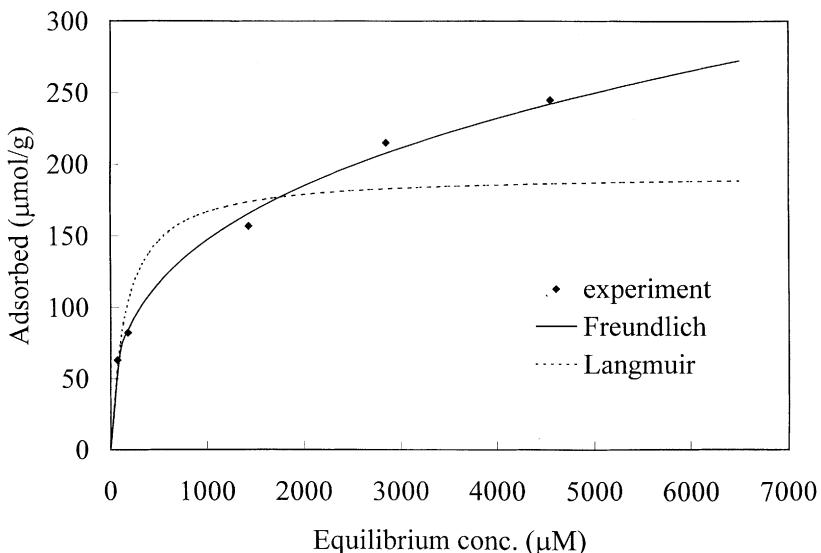


Fig. 1. Adsorption isotherm of MoO_4^{2-} by $\gamma\text{-Al}_2\text{O}_3$ at $\text{pH } 5.7 \pm 0.2$ and 25°C .

Table 2
Summary of adsorption isotherm constants and characteristics for single-solute isotherm

Anions	Freundlich			Langmuir		
	K	n	r^2*	Q_m (μmol/g)	K (l/μmol)	r^2*
MoO_4^{2-}	15.24	0.328	0.996	192.96	6.37×10^{-3}	0.915
SO_4^{2-}	28.87	0.123	0.918	80.17	1.09×10^{-2}	0.906
SeO_4^{2-}	21.43	0.179	0.944	86.03	1.50×10^{-2}	0.849
SeO_3^{2-}	24.12	0.246	0.995	164.19	1.07×10^{-2}	0.921

* Significant at the $\alpha = 0.05$ level.

influenced by the variation in the electrostatic charge at the solid surface. Both interactions are influenced by the concentration of competitive adsorbates and the intrinsic binding affinities of the adsorbates.

Competitive adsorption experiments were performed to determine the magnitude of the variations in adsorption due to competitive interactions among MoO_4^{2-} , SO_4^{2-} , SeO_4^{2-} , and SeO_3^{2-} . Figs. 2–4 show the influence of SO_4^{2-} , SeO_4^{2-} , and SeO_3^{2-} concentrations on the competitive adsorption of MoO_4^{2-} by $\gamma\text{-Al}_2\text{O}_3$. The experimental results indicate that a higher competitive solute concentration results in a more significant competitive effect on MoO_4^{2-} , suggesting that increasing the competitive adsorbate concentration enhances the opportunity of competitive adsorbate to occupy the binding sites on the oxide surface. Accordingly, the oxide surface tended to be more negatively charged than the original surface and resisted MoO_4^{2-} adsorption onto $\gamma\text{-Al}_2\text{O}_3$.

The summed concentrations of adsorbed solute in MoO_4^{2-} (1000 μM), SO_4^{2-} (1000 μM), SeO_4^{2-} (1000 μM), SeO_3^{2-} (1000 μM), MoO_4^{2-} (1000 μM) + SO_4^{2-} (1000 μM), MoO_4^{2-} (1000 μM) + SeO_4^{2-} (1000 μM), and MoO_4^{2-}

(1000 μM) + SeO_3^{2-} (1000 μM) systems were 82, 60, 59, 85, 90, 83, and 131 μmol/g, respectively. The competitive adsorption experiments demonstrated that the total amount of MoO_4^{2-} , SO_4^{2-} , SeO_4^{2-} or SeO_3^{2-} anions adsorbed in a binary-solute system in combination was usually higher than that adsorbed when added alone. Evidently, some sites were specific to only one or other anion. Similar results were obtained by Hingston et al. (1971) and Violante et al. (1991), who found that, in mixed phosphate and arsenite, phosphate and selenite, or phosphate and oxalate systems, more sites can be occupied by a mixture of anions than by either of the ions alone.

In all experiments, increasing the amount of SO_4^{2-} , SeO_4^{2-} , or SeO_3^{2-} in the binary-solute system caused less MoO_4^{2-} to be adsorbed. The general shapes of the isotherms for each anion were similar. The general shape of the binary-solute isotherms regressed according to the Freundlich equation (Table 3). The n values of Table 3 in each system exhibit an increasing trend with competitive solute concentration. A comparison of n in a single-solute system with that in a binary-solute system

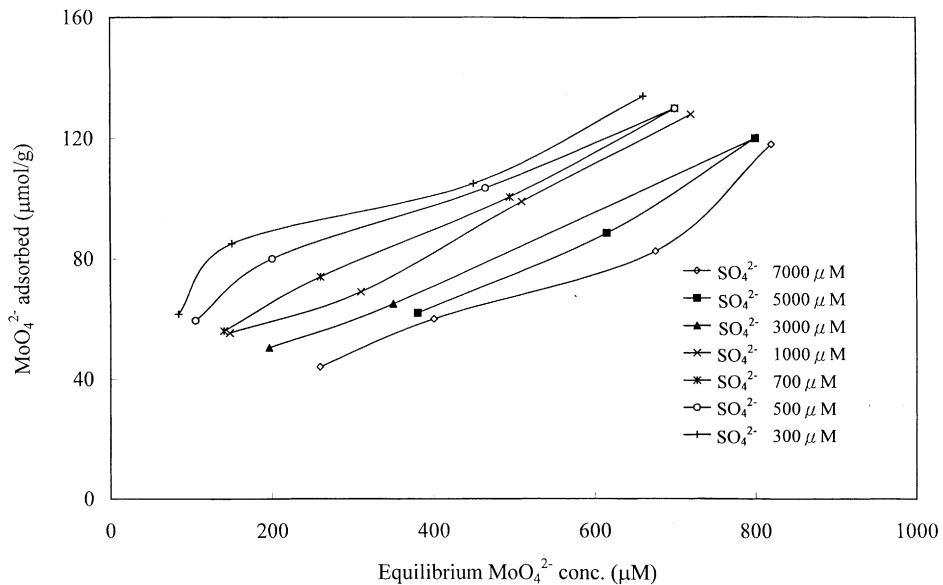


Fig. 2. Amount of MoO_4^{2-} adsorbed by $\gamma\text{-Al}_2\text{O}_3$ in the presence of SO_4^{2-} at pH 5.7 ± 0.2 and 25°C .

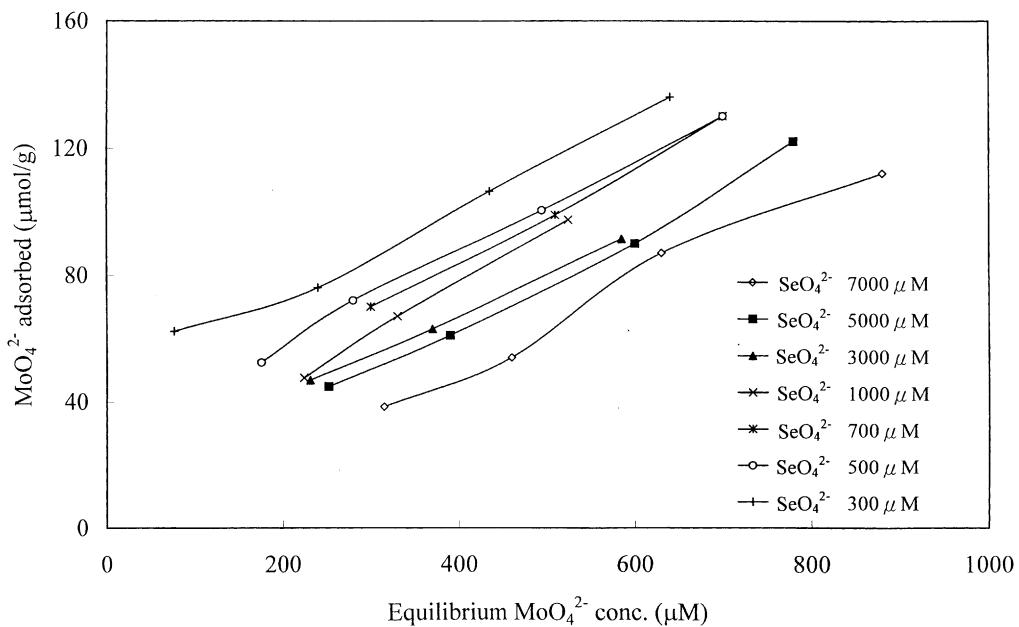


Fig. 3. Amount of MoO_4^{2-} adsorbed by $\gamma\text{-Al}_2\text{O}_3$ in the presence of SeO_4^{2-} at pH 5.7 ± 0.2 and 25°C .

shows that a more significant competitive effect yields a higher n value, but a lower K value. $\text{MoO}_4^{2-} + \text{SO}_4^{2-}$ and $\text{MoO}_4^{2-} + \text{SeO}_4^{2-}$ systems with the lowest competitive solute concentrations show similar n values to that of the MoO_4^{2-} single-solute system – 0.34, 0.36, and 0.33, respectively. This finding suggests that the competitive effect on MoO_4^{2-} is insignificant when SO_4^{2-} and SeO_4^{2-}

are added in low concentrations. Furthermore, SeO_4^{2-} demonstrates a higher affinity than SO_4^{2-} when competing with MoO_4^{2-} for binding sites. Table 3 shows that the competitive order: $\text{SeO}_3^{2-} > \text{SeO}_4^{2-} > \text{SO}_4^{2-}$. This observation resembles that of Wu et al. (2000), who concluded the same order of the relative retention of anions on $\gamma\text{-Al}_2\text{O}_3$.

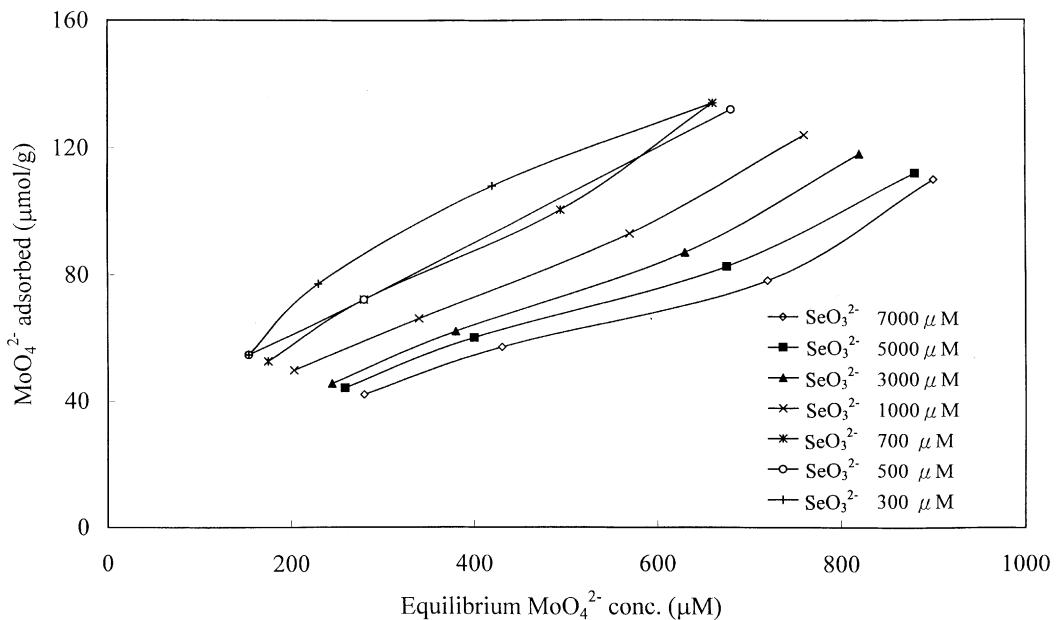


Fig. 4. Amount of MoO₄²⁻ adsorbed by γ-Al₂O₃ in the presence of SeO₃²⁻ at pH 5.7 ± 0.2 and 25 °C.

Table 3
Summary of MoO₄²⁻ adsorption isotherm constants and characteristics for the binary-solute Freundlich isotherm

Competitive solute concentration (μM)	7000	5000	3000	1000	700	500	300
$\text{MoO}_4^{2-} + \text{SO}_4^{2-}$							
K	0.52	0.06	2.60	3.73	4.39	9.63	14.51
n	0.794	1.140	0.555	0.528	0.511	0.394	0.336
r ^{2*}	0.960	0.935	0.919	0.952	0.990	0.990	0.951
$\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$							
K	0.08	0.33	0.34	0.31	0.18	1.89	12.25
n	1.081	0.880	0.894	0.927	1.012	0.644	0.359
r ^{2*}	0.985	0.990	0.942	0.990	0.883	0.998	0.910
$\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$							
K	0.52	0.74	0.67	1.30	1.53	2.29	2.69
n	0.777	0.733	0.765	0.680	0.683	0.627	0.607
r ^{2*}	0.971	0.987	0.989	0.986	0.991	0.960	0.985

* Significant at the $\alpha = 0.05$ level.

3.3. Application of the SRS equation

Eqs. (2) and (3) were used to determine competition coefficients on a concentration basis. These coefficients were obtained from experimental data of bicomponent systems. The magnitude of sulfate competition on molybdate adsorption by γ-Al₂O₃ was insignificant and this data set conformed to the linear SRS isotherm (Fig. 5), yielding a competition coefficient ($a_{\text{MoO}_4^{2-}-\text{SO}_4^{2-}}$) of 0.11. Table 4 summarizes the competition coefficients for each system. Sheindorf et al. (1982) proposed that the values

for a_{ij} range from zero (complete lack of competition) to greater than zero (normally <10) for a high degree of competition. This research defines a relative affinity coefficient assuming that a high competition coefficient is caused by a high degree of competition. Wu et al. (2000) showed that the order of the relative retention of anions on an oxide surface corresponds to the magnitude of the overall proton coefficient of the corresponding anions. The overall proton coefficient is the slope of the Kurbatov plot, which has been defined in Wu et al. (2000). Hence, this research consolidates the results of

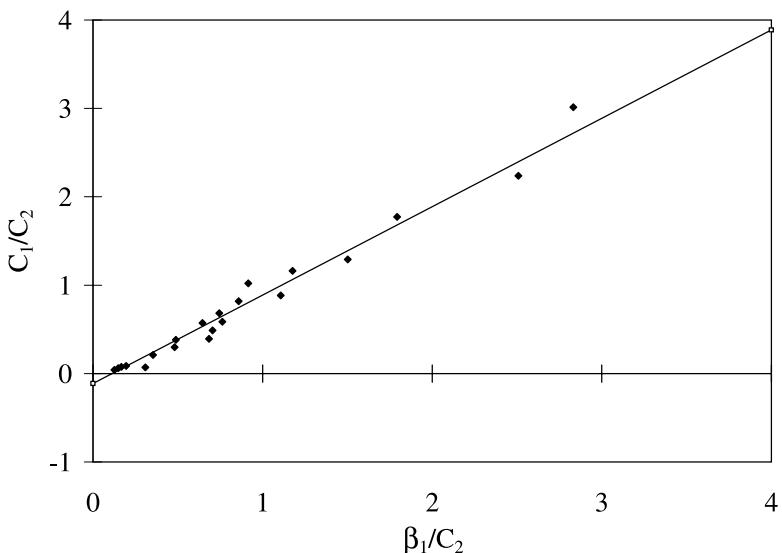
Fig. 5. Graphic determination of the competition coefficient $a_{\text{MoO}_4^{2-}-\text{SO}_4^{2-}}$.

Table 4
Summary of competition coefficients and relative affinity coefficients for binary-solute systems

$i + j$	a_{ij}	a_{ji}	α_{ij}	α_{ji}
$\text{MoO}_4^{2-} + \text{SO}_4^{2-}$	0.11	6.79	0.25	4.00
r^{2*}	0.979	0.928	—	—
$\text{MoO}_4^{2-} + \text{SeO}_4^{2-}$	0.19	14.49	0.32	3.09
r^{2*}	0.933	0.935	—	—
$\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$	0.56	2.67	0.56	1.79
r^{2*}	0.881	0.727	—	—

a – competition coefficients; α – relative affinity coefficients.

* Significant at the $\alpha = 0.05$ level.

Sheindorf et al. (1982) and Wu et al. (2000) to define the relative affinity coefficient as

α_{ij} = the overall proton coefficient of component j
/the overall proton coefficient of component i

(6)

and, the SRS equation is modified to:

$$q_1 = K_1 C_1 (C_1 + \alpha_{12} C_2)^{n_1-1}, \quad (7)$$

$$q_2 = K_2 C_2 (C_2 + \alpha_{21} C_1)^{n_2-1}. \quad (8)$$

Sheindorf et al. (1982) and Susarla et al. (1992) asserted that the competitive adsorption data were usually too scattered to calibrate using a single line to estimate the competition coefficients. This research simplified the competition coefficients to relative affinity coefficients. The latter are ratios of overall proton coefficients of anions. Table 4 summarizes the relative affinity coefficients for binary-solute systems. Competition coefficients

(a_{ij}) and relative affinity coefficients (α_{ij}) exhibit the same trend in all experimental data, which is $(\text{MoO}_4^{2-} + \text{SeO}_4^{2-}) > (\text{MoO}_4^{2-} + \text{SeO}_3^{2-}) > (\text{MoO}_4^{2-} + \text{SO}_4^{2-})$. The adsorbed MoO_4^{2-} in the systems MoO_4^{2-} (2000 μM), MoO_4^{2-} (2000 μM) + SO_4^{2-} (7000 μM), MoO_4^{2-} (2000 μM) + SeO_4^{2-} (7000 μM), and MoO_4^{2-} (2000 μM) + SeO_3^{2-} (7000 μM) are 131, 118, 112, and 110 $\mu\text{mol/g}$, respectively. These results indicate that the competitive effects in these systems are insignificant, since the values of the competition coefficient and relative affinity coefficient are below unity and the adsorption of MoO_4^{2-} is slightly influenced by competition of these anions. Restated, the affinity of these anions on the $\gamma\text{-Al}_2\text{O}_3$ surface is $\text{MoO}_4^{2-} > \text{SeO}_3^{2-} > \text{SeO}_4^{2-} > \text{SO}_4^{2-}$. Therefore, the competition coefficients and relative affinity coefficients can be considered as measurements of the relative affinity of anions on oxide surfaces. The competitive equations are evaluated after substituting a_{ij} and α_{ij} in the SRS and modified SRS equations. A “calculated” adsorption value was then generated for each set of

conditions. These calculations were compared to the experimentally measured adsorption values to examine the applicability of the SRS and modified SRS equations.

Not all of the binary-solute systems conformed well to the SRS and modified SRS equations. For the adsorption of mixtures represented in Figs. 6–8, the calculated data were similar to the observed values only at

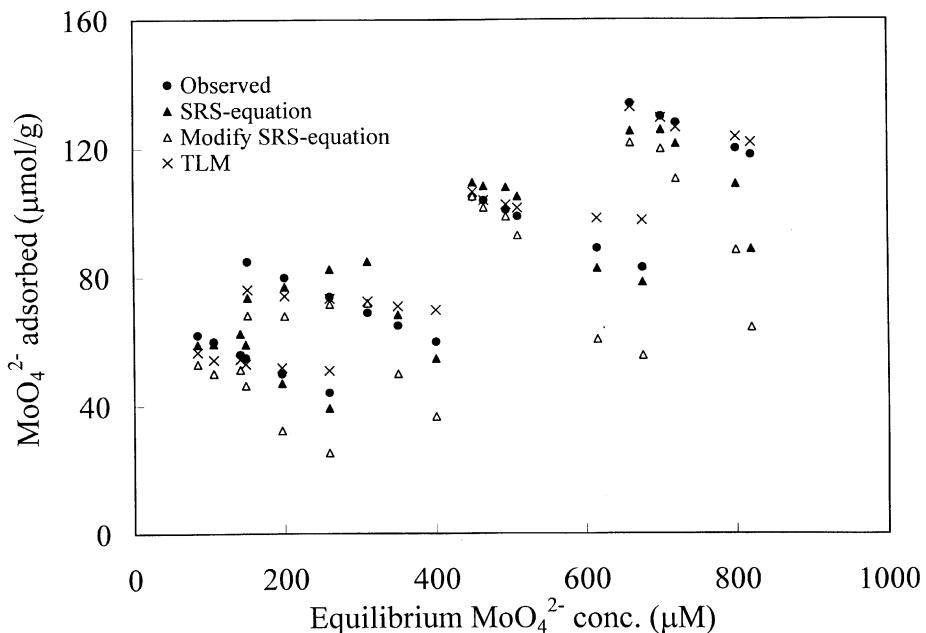


Fig. 6. Comparison between predicted (SRS equation, modified SRS equation, and TLM) and observed values for the competitive sorption of MoO_4^{2-} in the $\text{MoO}_4^{2-} + \text{SO}_4^{2-}$ system.

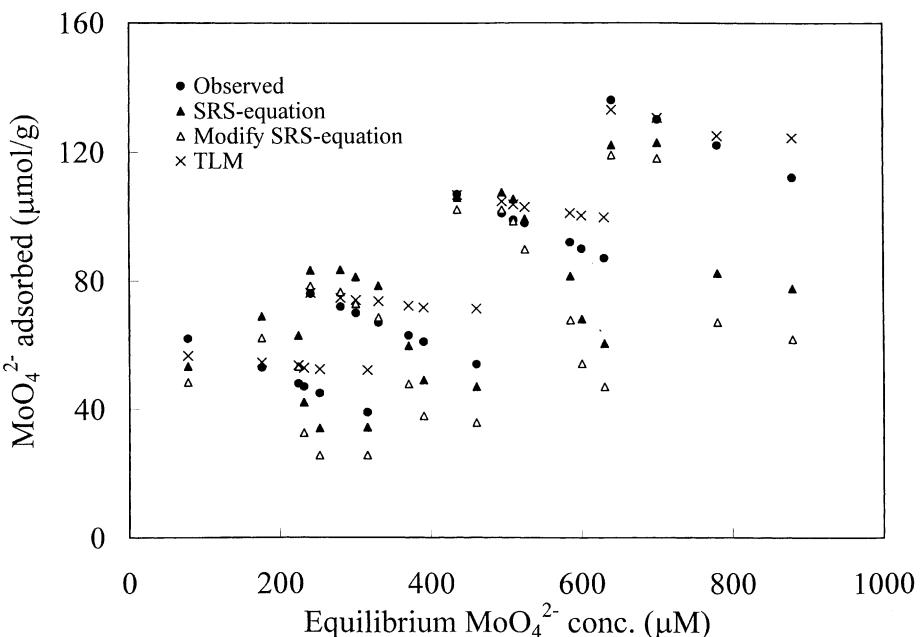


Fig. 7. Comparison between predicted (SRS equation, modified SRS equation, and TLM) and observed values for the competitive sorption of MoO_4^{2-} in the $\text{MoO}_4^{2-} + \text{SeO}_4^{2-}$ system.

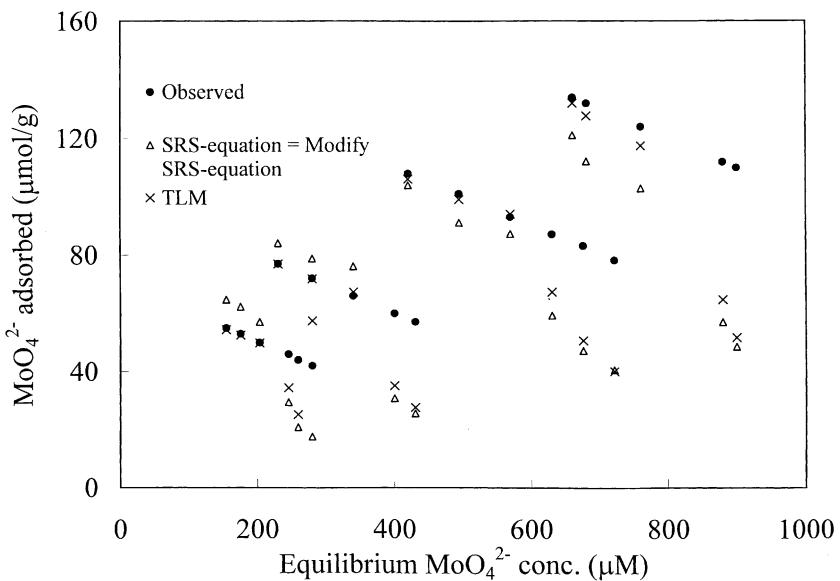


Fig. 8. Comparison between predicted (SRS equation, modified SRS equation, and TLM) and observed values for the competitive sorption of MoO_4^{2-} in the $\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$ system.

low concentrations of competitive solute. It should be stressed that the SRS equation represents competitive adsorption only at those concentrations in which single-component systems follow Freundlich behavior. At higher concentrations, the calculated SRS and modified SRS values start deviating from the observed values, since the SRS and modified SRS equations at those concentrations no longer apply. Other adsorption models such as surface complexation models more flexibly represent adsorption processes as they account for changes in pH, competing ions, and concentrations. Figs. 6–8 also display the TLM simulation results of the $\text{MoO}_4^{2-} + \text{SO}_4^{2-}$, $\text{MoO}_4^{2-} + \text{SeO}_4^{2-}$, and $\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$ systems. The TLM simulation results of MoO_4^{2-} in binary adsorbate systems were more closed to the experimental observations than the simulation results of SRS and modified SRS equations. The TLM is based on the assumption that adsorption occurs on only one type of site. While this assumption has been adequate for modeling of single anion systems, our previous study (Wu et al., 2001) has indicated that it is very likely an oversimplification. Oxide surface contain features such as steps and irregularly broken edges that will contribute to site heterogeneity and, thus, specific binding energies at different surface sites. Therefore, the differences between TLM simulations and experimental observations in $\text{MoO}_4^{2-} + \text{SO}_4^{2-}$, $\text{MoO}_4^{2-} + \text{SeO}_4^{2-}$, and $\text{MoO}_4^{2-} + \text{SeO}_3^{2-}$ competitive adsorption systems may be attributed to the site heterogeneity on $\gamma\text{-Al}_2\text{O}_3$ surfaces. Such models involve mathematical expressions which are far

more complex than the SRS and modified SRS equations. This research provides relatively simple mathematical representation of the SRS and modified SRS equations to model experimental data without resorting to more complex equations.

4. Conclusions

Competitive adsorption experiments were conducted to determine the magnitude of concentration variations in adsorption due to competitive interactions between MoO_4^{2-} , SO_4^{2-} , SeO_4^{2-} , and SeO_3^{2-} , introduced to a system in binary mixtures. The results indicate that a higher competitive solute concentration addition results in a more significant competitive effect on MoO_4^{2-} . The Freundlich constant (n) in each binary-solute system increases with the competitive solute concentration. Two valuable parameters specified in this study were the determined competition coefficient a_{ij} and the relative affinity coefficient α_{ij} , which express the intensity of the competitive interactions between anions in a manner that can easily be visualized and compared way. The proposed SRS and modified SRS equations are successfully employed to describe competitive adsorption data in the range of concentrations over which Freundlich behavior is followed. This study provides relatively simple expressions of the SRS and modified SRS equations to model experimental data without the need for more complex equations.

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