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Adsorption of Anionic Dye and Surfactant from Water onto Organomontmorillonite

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ABSTRACT

Single- and bisolute competitive adsorptions were carried out to investigate the adsorption behavior of an anionic dye, Orange II, and an anionic surfactant, dodecylbenzenesulfonate (DBS), from water at 25°C onto montmorillonite treated with hexadecyltrimethylammonium (HDTMA) cation. The monovalent HDTMA cation was exchanged for the metal cations on the montmorillonite to prepare HDTMA–montmorillonite, changing its surface property from hydrophilic to organophilic. Adsorption affinity of DBS on HDTMA–montmorillonite was found to be slightly higher than that of Orange II, probably due to hydrophobic or nonpolar interactions between the long hydrocarbon chains of the HDTMA with an anion. The single-solute adsorption data were fitted to the Langmuir and the Redlich–Peterson (RP) adsorption models. The competitive Langmuir model and the ideal adsorbed solution theory (IAST) coupled with the single-solute adsorption models were used to predict the bisolute competitive adsorption equilibria. Among the models, the IAST coupled with the Langmuir and the RP models for DBS and Orange II, respectively, yielded the most favorable representation of the bisolute competitive adsorption behavior.

INTRODUCTION

Removal of organic contaminants from wastewater has been extensively studied by using various physicochemical and biological techniques. Among

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these techniques, removal of organic contaminants using organically modified clays has drawn much attention. Natural clays are inherently hydrophilic due to hydration of the exchangeable inorganic sodium, calcium, and/or magnesium cations on the surface of the clay. They become organophilic by ion-exchanging quaternary amine cations having short or long hydrocarbon chains for the inorganic cations on the clay.

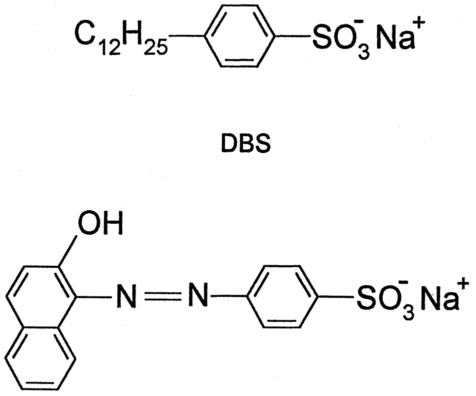
Many investigators have studied adsorption of nonionic organic contaminants in aqueous solution using clays modified with quaternary amine cations (1–7). However, studies on sorption of anions by organoclays have rarely been reported. Haggerty and Bowman (8) studied the sorption of inorganic divalent oxyanions, such as chromate, selenate, and sulfate, from aqueous solution on natural zeolite (about 60% clinoptilolite) modified with the monovalent hexadecyltrimethylammonium (HDTMA) cation from HDTMA bromide. The adsorption of HDTMA cation was limited to external surfaces of zeolite particles due to the channel size of the natural zeolite. Li and Bowman (9) studied the sorption of chromate on natural zeolites (about 74% clinoptilolite) modified with HDTMA cations coupled with three different counterions (Cl^-, Br^-, and HSO_4^-) to reveal the effect of counterions on chromate sorption. The sorption affinity of chromate on HDTMA-zeolite decreased in the order HDTMA–HSO_4 $>$ HDTMA–Cl $>$ HDTMA–Br. In a separate paper, Bowman and coworkers (10) studied the possible mechanism of chromate sorption onto HDTMA-modified natural zeolite using Fourier Transform Raman spectroscopy. They attributed the sorption of divalent chromate predominantly to anion-exchange with the bromide counterions on the external portion of the HDTMA bilayer. In addition to the anion-exchange mechanism, they asserted that surface-enhanced Lewis acid–base interactions (i.e., Lewis acid sites present in zeolite vs penetrating chromate acting as an electron donor) were also responsible for the chromate sorption.

In this work we studied the single- and bisolute competitive adsorption of two organic anions onto montmorillonite modified with HDTMA chloride. Two monovalent organic anions from a surfactant and a dye were selected as model solutes to simulate wastewater from textile-dyeing industries. Experimental isotherms and analyses that quantify the single- and bisolute competitive adsorption from water onto the HDTMA–montmorillonite will be presented.

EXPERIMENTAL

Materials

Montmorillonite-KSF was purchased from Aldrich Chemical Co. and washed with distilled water five times to remove any impurities contained during manufacturing. The washed montmorillonite particles were collected by



DBS

Orange II

FIG. 1 Molecular structures of DBS and Orange II.

gravity settling after washing with distilled water. According to Kim et al. (6), the CEC and BET surface area were found to be 50.4 meq/100 g-clay and 97 m^2/g-clay, respectively. The cation used as an organic modifier, hexadecyltrimethylammonium (HDTMA) chloride (25 wt%) aqueous solution, was obtained from Aldrich Chemical Co. and used as received. An anionic surfactant, dodecylbenzenesulfonate (DBS), and an anionic dye, Orange II [4-(2-hydroxy-1-naphthylazo)benzenesulfonic acid, sodium salt], were both purchased in sodium salt form from Aldrich Chemical Co. Figure 1 and Table 1 show the molecular structures and physicochemical properties of the two organic anions, respectively. All reagents were used as received without further purification.

Preparation of HDTMA–Montmorillonite

HDTMA–montmorillonites were prepared following the procedures employed by Kim et al. (6) and were utilized in the subsequent adsorption experiments. According to Kim et al. (6), maximum uptake of HDTMA was found to be about 152 mg/g-clay which corresponds to approximately 95% of the CEC of the montmorillonite used in this study.

TABLE 1
Physicochemical Properties of Dodecylbenzenesulfonate (DBS) and Orange II

Solute	Molecular weight	UV maximum wavelength (nm)
DBS	325.48	224
Orange II	327.33	486

Single- and Bisolute Adsorption

Single-solute adsorption isotherms on HDTMA–montmorillonite were obtained for each solute dissolved in water at 25°C. Through the time study of adsorption for each solute, it was observed that adsorption equilibrium was reached in about 24 hours on an orbit shaker revolving at 250 rpm.

Each 20 mL solution with a different initial concentration was poured into a capped 50 mL flask containing 0.500 g of HDTMA–montmorillonite, and then vigorously shaken on an orbit shaker for 24 hours at 25°C. The solutions were then centrifuged at 2000 rpm for 20 minutes. The equilibrium concentration of each solution was determined at the UV wavelength maxima using a UV-Visible spectrophotometer (Hewlett-Packard 8453, USA). Single-solute adsorptions for Orange II and DBS were carried out in duplicate and triplicate, respectively.

A bisolute system of DBS/Orange II with several different initial concentrations was made by mixing each solution of the same mass concentration in a 1:1 volume ratio into a 20-mL solution. We performed bisolute adsorption experiments for the various initial concentrations with the fixed amount of HDTMA–montmorillonite (0.500 g) by following the same procedures as described for the single-solute adsorption experiment. Equilibrium concentrations were also determined using the UV-Visible spectrophotometer which correlated absorbances at different wavelengths to the concentrations of the two solutes involved. Bisolute adsorptions were performed in duplicate.

SINGLE- AND MULTISOLUTE COMPETITIVE ADSORPTION MODELS USED

The adsorption isotherms frequently employed for single-solute systems are the 2-parameter Langmuir and the 3-parameter Redlich–Peterson (RP) (11) models. Langmuir and RP models obey the correct thermodynamic boundary condition of Henry's law over an infinitely dilute concentration range. The Langmuir and RP models for liquid-phase adsorption are written respectively as follows.

$$q = \frac{q_{\max} bC}{1 + bC} = \frac{aC}{1 + bC} \tag{1}$$

$$q = \frac{\alpha C}{1 + \beta C^{\nu}} \tag{2}$$

where C is the equilibrium solute concentration in the solution phase and q is the equilibrium sorbed concentration of solute per unit weight of adsorbent. $q_{\max}$ and b in the Langmuir model represent monolayer adsorption capacity and a constant related to adsorption equilibrium constant, respectively, and α, β, and ν in the RP model are empirical constants.

To analyze multisolute competitive adsorption behaviors, the competitive Langmuir model (CLM) (12) and the ideal adsorbed solution theory (IAST) (13) were used in this study. The CLM is an extended form of the Langmuir model which allows predictions of the amount of a solute i sorbed per unit weight of an adsorbent, $q_{\mathrm{m},i}$ in the presence of other solutes.

$$q_{\mathrm{m},i} = \frac{q_{\max,i} b_i C_{\mathrm{m},i}}{1 + \sum_{j=1}^{N} b_j C_{\mathrm{m},j}} \tag{3}$$

where $C_{\mathrm{m},i}$ is the equilibrium concentration of solute i in a mixture consisting of N solutes, and constants b_i and $q_{\max,i}$ are parameters determined by fitting the Langmuir model to the single-solute adsorption data of solute i.

The IAST proposed by Radke and Prausnitz (13) is of a descriptive nature and requires experimental equilibrium concentrations in the liquid phase to predict sorbed solid-phase concentrations. To utilize the full predictive power and to simplify the calculation, we followed modifications made by Yen (14, 15). The equivalence of spreading pressure in a mixture containing N solutes leads to

$$\int_0^{q_1^*} \frac{d \log C_1}{d \log q_1} dq_1 = \int_0^{q_2^*} \frac{d \log C_2}{d \log q_2} dq_2 = \cdots = \int_0^{q_N^*} \frac{d \log C_N}{d \log q_N} dq_N \tag{4}$$

Other equations involved in IAST calculation are

$$\begin{gathered} C_{\mathrm{m},i} = z_i C_i^*, \qquad \sum_{l=1}^{N} z_i = 1, \qquad q_i^* = f(C_i^*), \\ \frac{1}{q_\mathrm{T}} = \sum_{i=1}^{N} \frac{z_i}{q_i^*}, \qquad q_{\mathrm{m},i} = z_i q_\mathrm{T} = \frac{V(C^0{}_{\mathrm{m},i} - C_{\mathrm{m},i})}{W} \end{gathered} \tag{5}$$

In the above equations, z_i represents the mole fraction of solute i in the adsorbed phase, and C_i^* and q_i^* refer to equilibrium concentrations in the liquid and solid phases of solute i that adsorbs singly from solution at the same temperature and spreading pressure as those of the mixture, respectively. The function f in $q_i^* = f(C_i^*)$ denotes a single-solute adsorption model for solute i, $C_{\mathrm{m},i}^0$ is the initial concentration of solute i in a mixture, and q_T is the total adsorbed concentration of all solutes in the mixture. V and W represent the solution volume and the adsorbent weight, respectively. Therefore, we can predict the multisolute adsorption equilibria, $q_{\mathrm{m},i}$ vs $C_{\mathrm{m},i}$, by solving these equations simultaneously.

RESULTS AND DISCUSSION

Single-Solute Adsorption

The single-solute adsorption of DBS and Orange II was carried out using HDTMA–montmorillonite as an adsorbent. Adsorption isotherms for DBS and Orange II are shown in Figs. 2 and 3, respectively. Both anions exhibited isotherms of type I (16), which were very close to irreversible adsorption. Such isotherms are characteristic of strong adsorbate–adsorbent interactions, probably due to hydrophobic or nonpolar interactions between the hydrophobic tail group of the anion and the long hydrocarbon tail group of the HDTMA cation on the montmorillonite. The long hydrophobic chain of the anion is solubilized in the organic medium formed by conglomeration of HDTMA hydrocarbon tails, and the negatively charged head of the anion is presented to the surrounding solution sorbed in the interlayer spacing, not being solubilized in the organic medium due to the hydrophilicity of hydrated ionic head. In view of the similarity in hydrophobicity, DBS having a C_{12} hydrocarbon tail is expected to interact more strongly with the C_{16} hydrocarbon groups of the HDTMA cation than Orange II. Adsorbate–solvent (water) interactions and shape/size of the penetrating anion may also have effected differences in adsorption affinity. As a result of these interactions, the adsorption affinity of DBS on HDTMA–montmorillonite was found to be slightly higher than that of Orange II. To al-

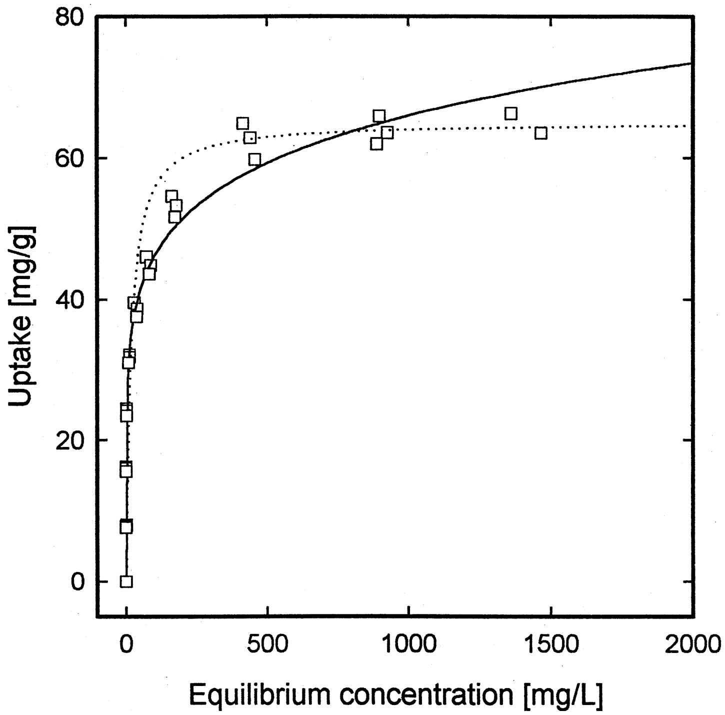


FIG. 2 Single-solute adsorption isotherm of DBS on HDTMA–montmorillonite. Solid and dotted lines represent Redlich–Peterson and Langmuir models, respectively.

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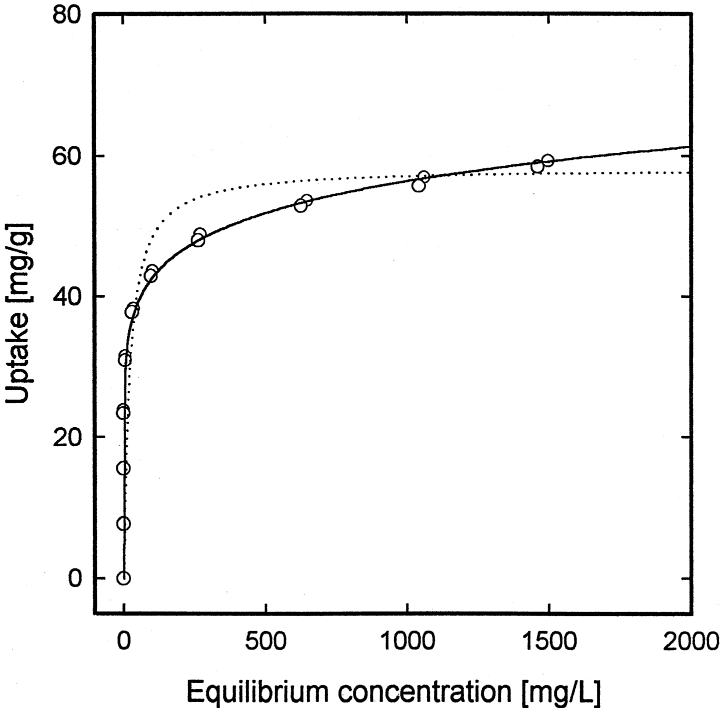

FIG. 3 Single-solute adsorption isotherm of Orange II on HDTMA–montmorillonite. Solid and dotted lines represent Redlich–Peterson and Langmuir models, respectively.

low better comparison of adsorption between the two anions, units of measurement can be converted from mg to mmol. However, we could not find the merits of this conversion since the molecular weights of DBS and Orange II anions are nearly the same (325.48 and 327.33, respectively).

The 2-parameter Langmuir model was fitted to the single-solute adsorption data by linearizing it as follows.

$$\frac{C}{q} = \frac{1}{q_{\max} b} + \frac{1}{q_{\max}} C \tag{6}$$

The 3-parameter RP model was fitted to the adsorption data of each solute using the nonlinear regression method. Fitted curves of the Langmuir and RP models are shown in Figs. 2 and 3 for comparison with the adsorption data, and the parameters of both adsorption models are tabulated in Tables 2 and 3,

TABLE 2
Langmuir Parameters of Each Solute on HDTMA – Montmorillonite

Solute	$q_{\max}$ (mg/g)	b (L/mg)	a (L/g)	R^2
DBS	65.1	5.99×10^{-2}	3.90	0.9536
Orange II	58.2	4.83×10^{-2}	2.81	0.9750

TABLE 3
Redlich–Peterson Parameters of Each Solute on HDTMA–Montmorillonite

Solute	α (L/g)	β (L/mg)$^{\nu}$	ν	R^2
DBS	153	6.70	0.846	0.9888
Orange II	515	21.1	0.879	0.9905

respectively. The values of the parameter $q_{\max}$, which appears in the Langmuir model, roughly reflect the order of adsorption affinity between the two anions, again. As a measure of the degree of fitness, the R^2 values for the single-solute adsorption were computed from the following equation (17).

$$R^2 = \frac{\sum q_i^2 - \sum (q_i - \hat{q}_i)^2}{\sum q_i^2} \tag{7}$$

In the above equations, q_i and $\hat{q}_i$ denote the experimental adsorption data and the fitted results of each single-solute adsorption model for a solute, respectively. In view of the R^2 values listed in Tables 2 and 3, the 3-parameter RP model exhibited a little better fit to the adsorption data than the 2-parameter Langmuir model as expected from the number of parameters involved in the model.

Bisolute Competitive Adsorption

Bisolute competitive adsorptions were performed for the DBS/Orange II binary system dissolved in water at 25°C. The competitive adsorption data are shown in Fig. 4. DBS competitively displaces Orange II from the finite adsorption sites available on HDTMA–montmorillonite at higher concentrations. One of the main features of adsorption is that adsorption capacity of a solute is reduced when multiple solutes are present due to sharing of the finite adsorption sites with other solutes on a competitive basis. Figures 5(a) and (b) show adsorption isotherms for the single- and bisolute competitive adsorptions of DBS and Orange II, respectively. Adsorption capacities of DBS (Orange II) decrease when Orange II (DBS) is present due to the competition for the available sites between adsorbable components. The amount of decrease in adsorption capacity was found to be greater for Orange II than for DBS. This point also establishes the fact that sorption of the anions onto HDTMA–montmorillonite occurs by an adsorptionlike, not a partitionlike, mechanism.

To predict the competitive adsorptions, we tried CLM, and IAST coupled with single-solute adsorption models (i.e., Langmuir/Langmuir, Langmuir/

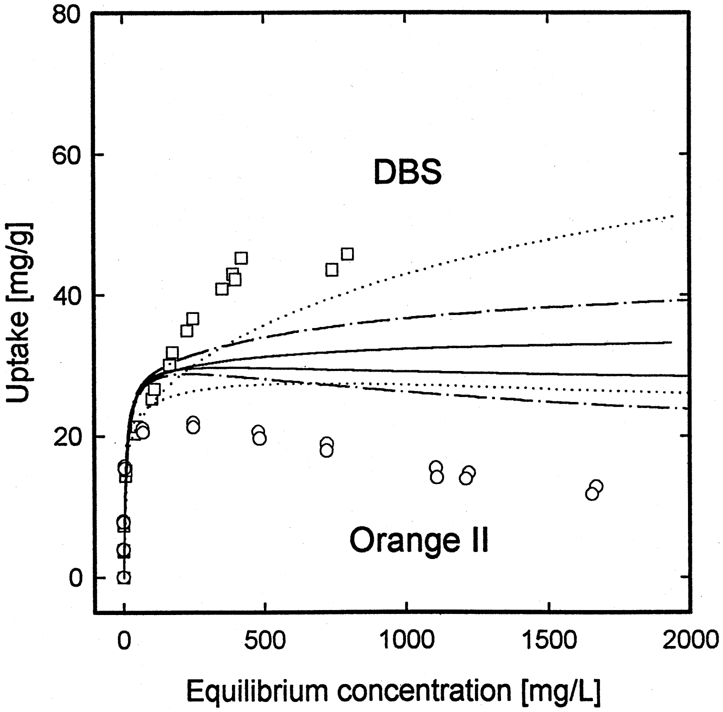

FIG. 4 Bisolute adsorption isotherms of DBS/Orange II system on HDTMA–moutmorillonite. Solid lines represent CLM predictions, dot-dashed and dotted lines are IAST predictions based on Langmuir and RP models for both anions, respectively.

RP, RP/Langmuir, or RP/RP models for DBS/Orange II, respectively). The parameters of each model were determined for each solute in the previous section, and they are listed in Tables 2 and 3.

To assess the predictive performances of the competitive adsorption models considered in this study, both the R^2 values and the sum of the squares of the errors (SSE) for the multisolute adsorption were utilized (17).

$$R^2 = \frac{\sum q_{\mathrm{m},i}^2 - \sum (q_{\mathrm{m},i} - \hat{q}_{\mathrm{m},i})^2}{\sum q_{\mathrm{m},i}^2} \tag{8}$$

$$\mathrm{SSE} = \sum (q_{\mathrm{m},i} - \hat{q}_{\mathrm{m},i})^2 \tag{9}$$

In the above equations, $q_{\mathrm{m},i}$ and $\hat{q}_{\mathrm{m},i}$ denote the experimental adsorption data and the predictions of a competitive adsorption model for a solute, respectively. The SSE and R^2 values of the bisolute competitive models are given in Table 4.

Predictions from the CLM, IAST coupled with Langmuir models for both solutes (IAST coupled with L/L), and IAST coupled with RP models for both solutes (IAST coupled with RP/RP) are shown in Fig. 4, together with the experimental data for comparison. In view of the SSE and R^2 values, predictions

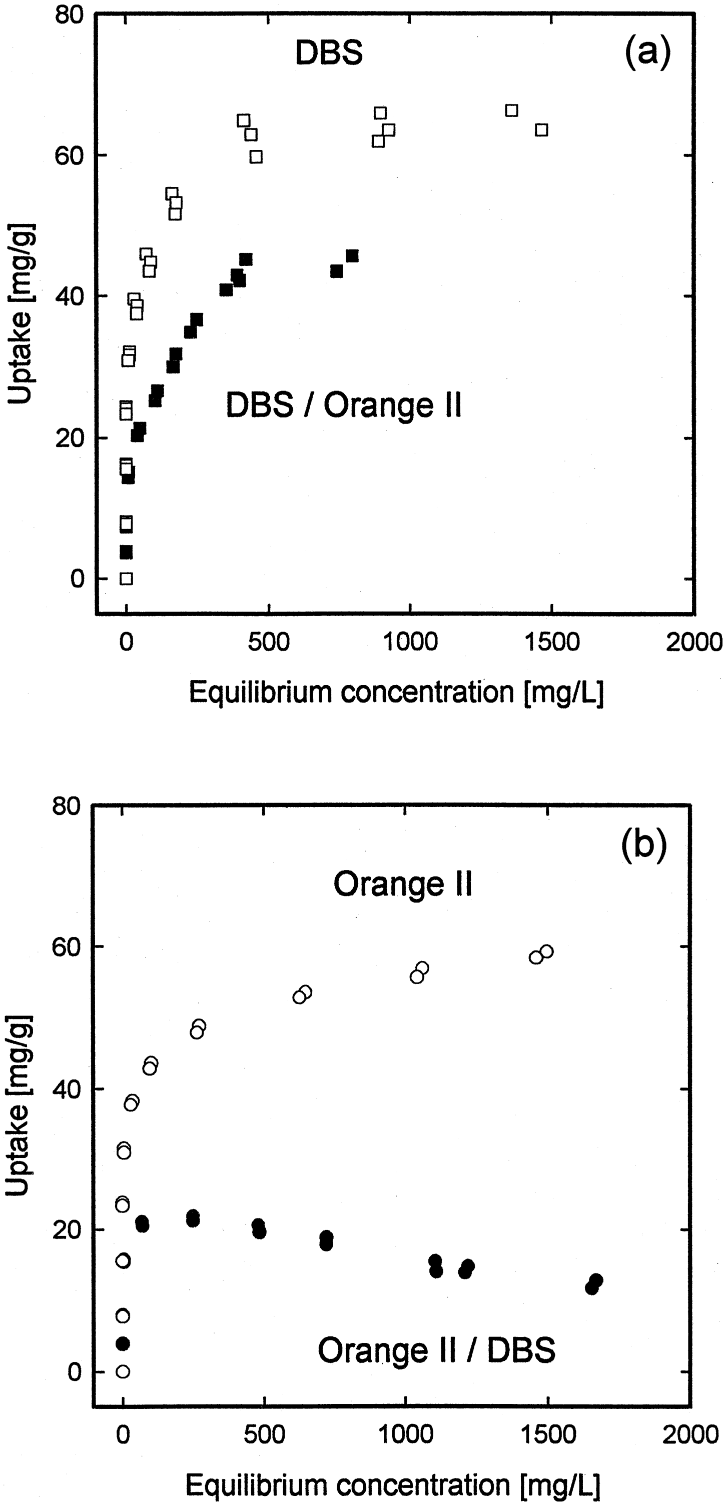

FIG. 5 Single- and bisolute competitive adsorption isotherms of (a) DBS and (b) Orange II on HDTMA–montmorillonite.

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TABLE 4
SSE and R^2 Values for Bisolute Competitive Adsorption Predictions from Competitive Models

			IAST (single-solute model for DBS/Orange II)			
	System	CLM	L*/L	L/RP	RP/L	RP/RP
SSE	DBS/Orange II	1127/2196	746/1465	388/632	1417/2703	620/1522
R^2	DBS/Orange II	0.9393/0.5664	0.9598/0.7107	0.9790/0.8752	0.9236/0.4664	0.9665/0.6995

* Langmuir model.

from the CLM were worst among the three sets of predictions shown in Fig. 4, and those from the IAST based on L/L or RP/RP models for both anions were both in poor agreement with the data quantitatively, although general trends of the competitive adsorption behavior were all correct in a qualitative sense. Predictions from IAST based on RP/L models for DBS/Orange II, respectively, were also poor in describing competitive adsorption behavior (graph not shown). Figure 6 shows predictions from IAST coupled with L/RP models for DBS/Orange II, respectively. The IAST coupled with the single-

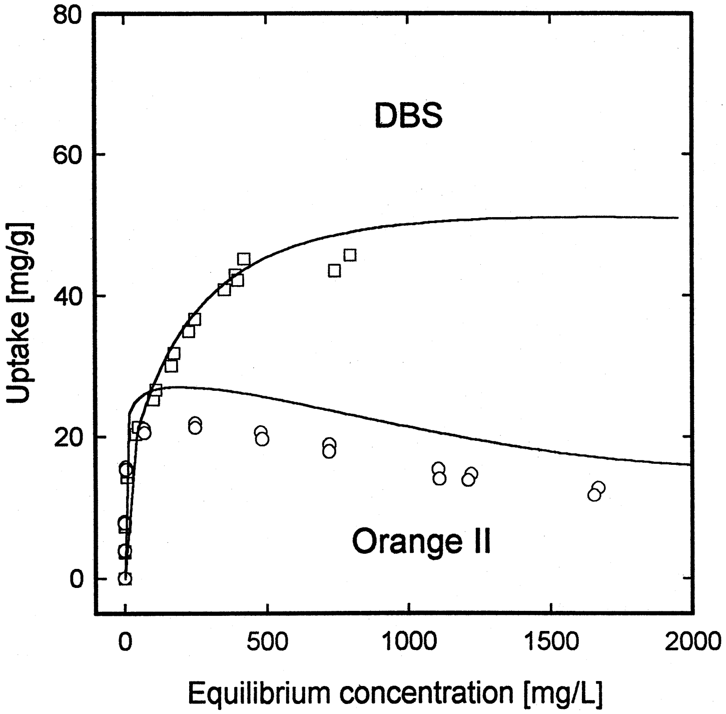

FIG. 6 Bisolute adsorption isotherms of DBS/Orange II system on HDTMA–montmorillonite. Solid lines represent predictions from IAST coupled with Langmuir and RP models for DBS and Orange II, respectively.

solute Langmuir and RP models for DBS and Orange II, respectively, provided the most favorable predictions for the bisolute competitive adsorption of the organic anions on HDTMA–montmorillonite, at least for these data, although a rather poor Langmuir model, instead of a RP model, was used as a single-solute model for DBS.

CONCLUSIONS

Single- and bisolute competitive adsorptions were carried out to investigate the adsorption behavior of an anionic dye, Orange II, and an anionic surfactant, dodecylbenzencsulfonate (DBS) from water at 25°C onto hexadecyltrimethylammonium (HDTMA)-treated montmorillonite. The monovalent HDTMA cation was exchanged for the inorganic metal cations on the montmorillonite to prepare HDTMA–montmorillonite, changing its surface property from hydrophilic to organophilic. Sorptive affinity of the two anions on HDTMA–montmorillonite was found to be in the order DBS $>$ Orange II. The single-solute adsorption data were fitted to the Langmuir and the Redlich–Peterson (RP) adsorption models. The main mode of adsorption was probably the hydrophobic or nonpolar interactions between the long hydrocarbon chains of the HDTMA with an anion. The competitive Langmuir model and the ideal adsorbed solution theory (IAST) coupled with the single-solute adsorption models were used to predict the bisolute competitive adsorption equilibria. Among the predictive models for bisolute competitive adsorptions, the IAST coupled with the Langmuir and RP models for DBS and Orange II, respectively, yielded the most favorable representations of competitive adsorption behaviors.

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