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Summary

U(VI) sorption on a purified Na-bentonite was investigated from 298±2 to 353±2 K by using a batch experimental method as a function of pH, U(VI) concentration, carbonate concentration and solid-to-liquid ratio (*m/V*). The data at 298±2 K could be well described by a surface complexation model (SCM) with a complex located on layer sites (X_2UO_2) and three complexes located on edge sites ($\equiv SOUO_2^+$, $\equiv SO(UO_2)_3(OH)_5$, and $\equiv SO(UO_2)_3(OH)_7^{2-}$). The intrinsic equilibrium constants (K^{int}) of the surface reactions at 333±2 K and 353±2 K were obtained by fitting U(VI) sorption curves versus pH on the Na-bentonite. The model enables U(VI) sorption in the presence of carbonate (P_{CO_2} =$10^{-3.58}$ atm) to be described without considering any ternary surface complexes involving carbonate, except for underestimation around pH 7 (6 < pH < 7.5). The standard enthalpy changes ($\Delta_r H_m^\theta$) of the surface reactions were evaluated from the K^{int} values obtained at three temperatures (298±2, 333±2

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and 353±2 K) via the van't Hoff equation. The proposed SCM and $\Delta_r H_m^\theta$ of the surface reactions enable U(VI) sorption on the Na-bentonite at other temperatures to be predicted.

1. Introduction

Because of its excellent physicochemical properties such as high specific surface area, large cation exchange and sorption capacity, and good swelling and sealing nature, bentonite has been considered as a backfilling material for deep geological repository of high-level radioactive waste in many countries. Uranium(VI) is an important contaminant to be considered in nuclear waste management and the sorption of U(VI) on bentonite/montmorillonite has received special attentions [1-9]. Different surface complexation models (SCMs) have been proposed to quantitatively describe macroscopic sorption of U(VI) on bentonite/montmorillonite using two main approaches. The first one treats montmorillonite as an aggregate of fixed-charge sites and edge sites analogous to gibbsite and silica [1]. The surface complexation constants for uranyl binding to gibbsite and silica were used for the edge sites. Different electrostatic models were chosen, for example, a triple-layer model was used by Turner et al. [2], whereas a constant capacitance model was used by Kowal-Fouchard et al [6]. Another approach is to consider montmorillonite as a specific sorbent. The capacity of layer sites is estimated by CEC measurement, while the densities of edge sites as well as the protonation and deprotonation constants are obtained by fitting the acid-base titration data at variable ionic strengths [10-14].

It is well known that the near-field temperature in deep geological repository for high-level radioactive waste may be higher than the ambient temperature and vary with time because of radionuclide decay [15-17]. However, most sorption data reported up to date were collected at ambient temperature and studies on temperature effect are still lacking [15]. In this paper, U(VI) sorption on a purified Na-bentonite at 298±2 K was studied as a function of pH, U(VI) concentration, solid-to-liquid ratio (*m*/*V*) and carbonate concentration by batch sorption experiments, and a SCM was constructed based on the sorption data collected at 298±2 K. Then, U(VI) sorption curves versus pH on the Na-bentonite at elevated temperatures (333±2 K and 353±2 K) were collected and the proposed SCM was fitted to these sorption data at elevated temperatures, respectively, to obtain the intrinsic equilibrium constants (K^{int}) of the surface complexation reactions at elevated temperatures. Finally, the K^{int} at three temperatures (298±2, 333±2 and 353±2 K) were used to assess $\Delta_r H_m^{\theta}$ of the surface complexation reactions via the van't Hoff equation.

2. Experimental

2.1 Materials

The Na-bentonite used in this work was obtained from Jinchuan Bentonite Company (Jinchuan, Gansu Province, China). The protocols of purification and characterization of the purified Na-bentonite have been described in our previous paper [14]. The purified Na-bentonite is mainly composed of 12 wt.% quartz and 88 wt.% montmorillonite with a calculated structural formula of $[Si(IV)_8](Al(III)_{3.19}$,

$Fe(III)_{0.29}$, $Fe(II)_{0.38}$,$Mg(II)_{0.14})O_{20}(OH)_4(Ca(II)_{0.023}$,$Na(I)_{0.35}$,$K(I)_{0.127}$). The CEC was experimentally found to be 623±12 meq/kg and is consistent with the value calculated according to the structural formula. The specific surface area obtained by B.E.T. analyses using N_2 was found to be 53.6 m^2/g. A uranium(VI) stock solution was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ (A.R. grade, made in China). All other chemicals used were at least analytical grade. All solutions were prepared with deionized water (18MΩ/cm).

2.2 Sorption

Sorption experiments were carried out in a nitrogen atmosphere glove box, except for the sorption in the presence of carbonate. The Na-bentonite was dispersed with NaCl solution (0.1mol/L) in polyethylene tubes and the pH of the suspension was adjusted by adding small amounts of HCl or NaOH solutions. Proper amounts of the uranium stock solution were added and the suspension was shaken for 2 days before analysis. The elevated temperature was controlled by a water bath. Our prior sorption experiments demonstrated that sorption steady state can be reached within 2 days. The pH of the suspension was recorded at the experimental temperature on a Metrohm 781 pH/ion Meter with a combined glass electrode (Metrohm No.6.0234.100) which was calibrated with three standard buffers. Phase separation was carried out by centrifugation at 18000g for 30 min. The concentration of U(VI) in the aqueous phase was analyzed by spectrophotometry at a wavelength of 652 nm by using U(VI) and Arsenazo-III complex. The relative errors of spectrophotometric measurements were less than 5%. The sorption on the tube walls was negligible. The

amount of U(VI) sorbed (q, mol/g) was calculated by the difference of the initial and final concentrations in the aqueous phase (C_0 and C_{eq}, respectively, mol/L):

$$q = \frac{V}{m}(C_0 - C_{eq}) \quad (1)$$

where V (L) is the volume of aqueous phase and m (g) the mass of Na-bentonite. The sorption percentage of U(VI) was calculated by

$$Sorption \quad (\%) = \frac{C_0 - C_{eq}}{C_0} \times 100 \quad . \quad (2)$$

The sorption experiment in the presence of carbonate was performed at the normal atmospheric condition (P_{CO_2} =$10^{-3.58}$ atm). The pH of Na-bentonite suspension was adjusted with HCl or $NaHCO_3$/Na_2CO_3 solutions. The tubes were opened regularly during sorption until the pH values were stable. The analytical methods were the same as described above.

2.3 Modeling

The sorption of U(VI) was interpreted by a double layer model (DLM), based on the acid-base chemistry of the Na-bentonite which has been reported in detail in our previous paper [14]. Two types of sorption sites were considered: layer sites (X^-) and edge sites. Both aluminol (≡SOH) and silanol (≡YOH) edge sites were included for the acid-base chemistry of the Na-bentonite. The capacities of the sites as well as the constants of protonation and deprotonation were summarized in Table 1. The code PHREEQC [18] was used for modeling calculations. Activity correction of the aqueous species was made by the Davies equation. U(VI) thermodynamic data used

in modeling were taken from the NEA (Nuclear Energy Agency) database [19], except for those of $UO_2(OH)_2$(aq) which were taken from the Nagra/PSI Chemical Thermodynamic Data Base [20]; in the NEA database, only a maximum limit of the equilibrium constant was given for this species. The U(VI) thermodynamic data used in the modeling are listed in Table 2.

3. Results and Discussion

3.1 U(VI) sorption on Na-bentonite at T = 298±2 K

Sorption curves of U(VI) versus pH on the Na-bentonite at 298±2 K and different U(VI) concentrations (4.01×10^{-5} and 8.02×10^{-5} mol/L) are presented in Fig. 1. The sorption of U(VI) on Na-bentonite is strongly pH-dependent; the sorption percentage of U(VI) increases slightly up to pH 4 and then increases significantly in the pH range of 4—8. This is consistent with previous observations of U(VI) sorption on montmorillonite/bentonite [2, 6]. The sorption curve of U(VI) versus pH at 8.02×10^{-5} mol/L is shifted somewhat to higher pH in comparison with that at 4.01×10^{-5} mol/L, indicating that U(VI) sorption percentage decreases with U(VI) concentration at a given pH. The inflection of sorption curves of U(VI) against pH results from a variation of sorption mechanisms. In the low pH range, U(VI) sorption on bentonite/montmorillonite has been interpreted by cation exchange on layer sites, whereas U(VI) surface complexation reactions on edge sites occur at pH > 4 [3, 6, 11]. The two types of U(VI) surface species have been supported by spectroscopic studies. Extended X-ray absorption fine structure (EXAFS) studies on U(VI)

sorption on montmorillonite have suggested that U(VI) adsorption on montmorillonite is most likely through an outer-sphere cation-exchange mechanism at low pH, whereas a transition to an inner-sphere surface complexation mechanism occurs at near neutral pH [7-8]. However, the detailed nature of the surface species formed at the edge sites can not be simply deduced from these spectroscopic studies [3]. Surface complexes are usually supposed based on analogous speciation in the aqueous phase [3, 11]. U(VI) speciation in the aqueous phase strongly depends on experimental conditions such as pH, U(VI) concentration, and the presence of ligands [21]. For comparison, both U(VI) speciations in the absence and presence of CO_2 (P_{CO_2} = $10^{-3.58}$ atm) at $C^0_{U(VI)}$ = 4.0×10^{-5} mol/L and I = 0.1 mol/L NaCl are shown in Fig. 2. UO_2^{2+} is the dominant species at pH ≤ 5 in both CO_2 conditions and U(VI) polynuclear hydrolysis products, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_7^-$, become major species in the high pH range in the absence of CO_2. Therefore, UO_2^{2+}, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_7^-$ are considered as the U(VI) species sorbed at the surface in the present study.

The first surface reaction considered in the modeling is the binding of UO_2^{2+} on the layer sites (X^-) :

$$2XNa + UO_2^{2+} \rightleftharpoons X_2UO_2 + 2Na^+ \quad (3)$$

$$K_1 = \frac{[X_2UO_2][Na^+]^2}{[XNa]^2[UO_2^{2+}]} \cdot \frac{\gamma^2_{Na^+}}{\gamma_{UO_2^{2+}}} \quad (4)$$

As expected, U(VI) sorption in the low pH range can be described by reaction (3), other surface reactions on edge sites must be considered to interpret the sharp

increase in the high pH range. Inner-sphere surface complexes of UO_2^{2+} and $(UO_2)_3(OH)_5^+$ on both aluminol and silanol edge sites are commonly considered [1-3, 6, 9]. Since aluminol sites are much more reactive than silanol sites [4, 16] and cations primarily sorb on octahedral sites such as $Al(O, OH)_6$ and $Fe(O, OH)_6$ [8], only surface complexation reactions on aluminol sites (≡SOH) were considered in the present paper. Similar modeling strategies have been used to interpret Eu(III) sorption on montmorillonite/bentonite [14, 16]. Surface complexation reactions of UO_2^{2+}, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_7^-$ on ≡SOH can be respectively expressed as:

$$\equiv SOH + UO_2^{2+} \rightleftharpoons \equiv SOUO_2^+ + H^+ \quad (5)$$

$$\equiv SOH + 3UO_2^{2+} + 5H_2O \rightleftharpoons \equiv SO(UO_2)_3(OH)_5 + 6H^+ \quad (6)$$

$$\equiv SOH + 3UO_2^{2+} + 7H_2O \rightleftharpoons \equiv SO(UO_2)_3(OH)_7^{2-} + 8H^+ \quad (7)$$

The corresponding intrinsic equilibrium constants of reactions (5)—(7) are as follows:

$$K_2^{int} = \frac{[\equiv SOUO_2^+][H^+]}{[\equiv SOH][UO_2^{2+}]} \cdot \frac{\gamma_{H^+}}{\gamma_{UO_2^{2+}}} \exp(F\Psi / RT) \quad (8)$$

$$K_3 = \frac{[\equiv SO(UO_2)_3(OH)_5][H^+]^6}{[\equiv SOH][UO_2^{2+}]^3} \cdot \frac{\gamma_{H^+}^6}{\gamma_{UO_2^{2+}}^3} \quad (9)$$

$$K_4^{int} = \frac{[\equiv SO(UO_2)_3(OH)_7^{2-}][H^+]^8}{[\equiv SOH][UO_2^{2+}]^3} \cdot \frac{\gamma_{H^+}^8}{\gamma_{UO_2^{2+}}^3} \exp(-2F\Psi / RT) \quad (10)$$

A stepwise fitting approach [11] was used to evaluate the equilibrium constants of the surface reactions by fitting U(VI) sorption curves versus pH at 298±2 K (Fig. 1). Surface reactions (3) and (5)-(7) were sequentially considered to describe the

sorption curves of U(VI) against pH from low to high pH and finally the equilibrium constants at 298±2 K were estimated (Table 3). The calculated results are shown as lines in Fig. 1.

The model was then used as a predictive tool to describe experimental data measured as a function of U(VI) concentration and *m/V*. Two U(VI) sorption isotherms at 298±2 K and different pH (4.78±0.10 and 5.76±0.10) were collected (Fig. 3). The two isotherms are almost parallel and are well described by the model. Moreover, U(VI) sorption dependence on *m/V* was carried out at T = 298±2 K, $C^{0}_{U(VI)}$ = 8.02×10^{-5} mol/L, pH 5.00±0.10 and I = 0.1 mol/L NaCl. As seen in Fig. 4, the sorption percentage of U(VI) increases with *m/V*, due to the increase of available sites, which is well reproduced by the model. The good interpretation for the U(VI) sorption isotherms and the sorption dependence on *m/V* imply that the proposed model is reasonable.

3.2 U(VI) sorption at P_{CO_2} = $10^{-3.58}$ atm and T = 298±2 K

Carbonate is an extensive ligand in the environment and the partial pressure of CO_2 in aquifers commonly reaches values of 1—5% [22]. Since carbonate has a strong binding affinity for uranyl, the effect of carbonate on U(VI) sorption is of importance. A sorption curve of U(VI) versus pH on the Na-bentonite in the presence of CO_2 (P_{CO_2} =$10^{-3.58}$ atm) was also collected in this study to evaluate the effect of carbonate and to test the performance of the proposed model. For comparison, U(VI) sorption data in the absence and presence of CO_2 as a function of pH are simultaneously shown in Fig. 5. At pH < 6.0, the two series of sorption data are identical, suggesting that in the low pH range the presence of CO_2 has a negligible influence on U(VI) sorption. At pH around 7 (6 < pH < 7.5), U(VI) sorption increases somewhat in the presence of

CO_2, whereas at pH > 7.5 U(VI) sorption decreases compared to that in the absence of CO_2. Since the concentration of carbonate in the aqueous phase increases significantly with increasing pH at a constant CO_2 partial pressure, the difference between the sorption curves of U(VI) versus pH in the absence and presence of CO_2 may be related to an effect of carbonate on U(VI) speciation in the aqueous phase [3, 9]. As seen in Fig. 2, in the presence of CO_2 (P_{CO_2} =$10^{-3.58}$ atm), the importance of $(UO_2)_3(OH)_5^+$ in the alkaline pH range is to some extent decreased and the content of $(UO_2)_3(OH)_7^-$ is completely suppressed, due to the formation of $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. Considering that the montmorillonite surface at a pH near 7 and in alkaline pH region is negatively charged [13, 14], the affinity of high negatively charged uranyl complexes of carbonate, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, for the surface may be weaker than the U(VI) hydrolysis products, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_7^-$, because of higher electrostatic repulsion. Thus, the sorption of U(VI) decreases sharply in the presence of CO_2 at pH > 7.5 compared to that in the absence of CO_2. This is in agreement with the carbonate effect on U(VI) sorption on other minerals such as ferrihydrite [23] and hematite [24]. A similar decrease of Eu(III) sorption on the Na-bentonite was also observed in the presence of CO_2 [14]. The higher U(VI) sorption around pH 7 (6 < pH < 7.5) in the presence of CO_2 may be due to the binding of $(UO_2)_2CO_3(OH)_3^-$ on the surface because $(UO_2)_2CO_3(OH)_3^-$ is the dominant U(VI) aqueous species around pH 7 in additional to $(UO_2)_3(OH)_5^+$.

As a first estimation, the proposed model without considering any ternary surface complexes of carbonate was used to predict the U(VI) sorption curve versus pH in the presence of CO_2 at P_{CO_2} =$10^{-3.58}$ atm, $C^{0}_{U(VI)}$ = 8.02×10^{-5} mol/L, I = 0.1M NaCl, and m/V = 1 g/L. As can be seen in Fig. 5, the model could readily interpret the identical sorption at pH < 6 and the lower sorption at pH > 7.5. However, it underestimates U(VI) sorption around pH 7 (6.0 < pH < 7.5). To improve the agreement, the binding of $(UO_2)_2CO_3(OH)_3^-$ on ≡SOH was considered:

$$\equiv SOH + 2UO_2^{2+} + 3H_2O + CO_3^{2-} \rightleftharpoons \equiv SO(UO_2)_2CO_3(OH)_3^{2-} + 4H^+ \quad (11)$$

Although ternary surface complexes of U(VI) and carbonate on montmorillonite have been suggested by a recent EXAFS study [8], modeling exercises indicated that reaction (11) could not improve the fitting goodness for the sorption curve of U(VI) versus pH in the presence of CO_2 (Fig. 5). The reason is not clear and further investigation is still needed.

3.3 Effect of temperature on U(VI) sorption onto Na-bentonite

The influence of temperature on chemical reactions can be described by the van't Hoff equation:

$$\log K^{\theta} = -\frac{\Delta_r H_m^{\theta}}{2.303\,R} \cdot \frac{1}{T} + \frac{\Delta_r S_m^{\theta}}{2.303\,R} \quad (12)$$

where K^{θ} is the standard equilibrium constant of the reaction at absolute temperature T, R the gas constant, $\Delta_r H_m^{\theta}$ the standard enthalpy change and $\Delta_r S_m^{\theta}$ the standard entropy change. When $\Delta_r H_m^{\theta}$ and $\Delta_r S_m^{\theta}$ are considered as constants with temperature, $\Delta_r H_m^{\theta}$ can be evaluated by the slope of $\log K^{\theta}$ against $1/T$ plot. The relationship between K_1^{θ} at T_1 and K_2^{θ} at T_2 can be described by

$$\ln\left(\frac{K_2^{\theta}}{K_1^{\theta}}\right) = \frac{-\Delta_r H_m^{\theta}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (13)$$

With a known $\Delta_r H_m^{\theta}$ and K_1^{θ} at T_1, Eq. (13) can be used to estimate K_2^{θ} at any other T_2. Considering the temporal and spatial variation of temperature in the near field of deep geological repository for high-level radioactive waste, $\Delta_r H_m^{\theta}$ of

surface reactions involving radionuclide sorption on back-filling materials (e.g. bentonite) are necessary for nuclear waste management [15-17]. In this study, U(VI) sorption curves versus pH on the Na-bentonite measured at $C^{0}_{U(VI)}$ = 8.02×10^{-5} mol/L, I = 0.1mol/L NaCl, m/V = 1 g/L and three temperatures (298±2, 333±2 and 353±2 K) were collected to evaluate the $\Delta_r H^{\theta}_m$ of surface reactions in the proposed model. As shown in Fig. 6, U(VI) sorption on the Na-bentonite does not vary with temperature at pH < 3.5, suggesting that the temperature effect on U(VI) binding to the layer sites is negligible. Above pH 3.5, U(VI) sorption on the solid phase increases with increasing temperature, indicating that U(VI) surface complexation reactions on edge sites are endothermic. Similar observations have been reported for Eu(III)/montmorillonite and Eu(III)/kaolinite sorption systems [16].

In principle, the equilibrium constants deduced in this study could be considered as intrinsic constants, although the electrostatic correction for clays is still a matter of discussion [11, 16, 25]. To assess $\Delta_r H^{\theta}_m$ of the surface reactions in the model, K^{int} at 298±2, 333±2 and 353±2 K should be first obtained. The K^{int} of surface reactions at 333±2 and 353±2 K were obtained by fitting the SCM to the sorption data at the respective temperatures. The prerequisite information for these fittings is that all $\Delta_r H^{\theta}_m$ of the related reactions, either in the aqueous phase or at the surface, should be known, because both the standard equilibrium constants at 298.15 K and the $\Delta_r H^{\theta}_m$ of these reactions are needed to calculate the equilibration constants at elevated temperatures. The $\Delta_r H^{\theta}_m$ of some U(VI) hydrolysis reactions were not available in both the NEA [19] and the Nagra/PSI databases [20], and were assumed

to be 0 in calculations. This implies that the standard equilibrium constants at 298.15 K were used in the whole temperature range. The $\Delta_r H_m^\theta$ of surface reactions responsible for the acid-base chemistry of the Na-bentonite were also assumed to be 0. This assumption is reasonable according to the work by Duc et al. [17], which indicated that the protonation and deprotonation reactions on edge sites of montmorillonite are not significantly temperature-dependent. Moreover, according to the negligible temperature effect upon U(VI) sorption at low pH (Fig. 6), the $\Delta_r H_m^\theta$ of UO_2^{2+} binding on the layer sites was directly assumed to be 0. Similar assumptions have been made for Eu(III) sorption on montmorillonite and kaolinite [16]. Based on the above assumptions, the K^{int} of surface reactions (5)—(7) at 333±2 and 353±2 K were estimated by using the geochemical modeling code PHREEQC [18]. The obtained K^{int} values are listed in Table 3 and the calculated results by the model are presented as lines in Fig. 6. The K^{int} values of reactions (5)—(7) increase with increasing temperature.

According to the van't Hoff equation, logK^{int} values are plotted against 1/T, and the plots for reactions (5)—(7) are illustrated in Fig. 7. Good correlation coefficients are obtained in all cases, which may imply that the assumptions made above are to some extent reasonable. From the slopes of these plots, $\Delta_r H_m^\theta$ of reactions (5)—(7) are calculated and listed also in Table 3. The positive $\Delta_r H_m^\theta$ indicate that the surface complexation reactions (5)—(7) are endothermic processes, which are consistent with the experimental observations. In principle, the proposed SCM and $\Delta_r H_m^\theta$ of the surface reactions may enable U(VI) sorption on the Na-bentonite at other

temperatures to be predicted. Finally, it should be pointed out that complementary $\Delta_r H_m^\theta$ of U(VI) aqueous reactions which are not listed in the databases are necessary to carry out reliable predictions of U(VI) sorption at variable temperatures.

4. Conclusions

Based on the experimental and modeling results in the present study, the following conclusions can be made:

(1) U(VI) sorption on the purified Na-bentonite at different temperatures (298±2, 333±2 and 353±2 K) could be quantitatively described by the SCM with a complex on layer sites (X_2UO_2) and three complexes on edge sites ($\equiv SOUO_2^+$, $\equiv SO(UO_2)_3(OH)_5$, and $\equiv SO(UO_2)_3(OH)_7^{2-}$). It seems that the nature of the surface species is governed by U(VI) speciation in solution.

(2) U(VI) sorption on the Na-bentonite in the presence of CO_2 (P_{CO_2} =$10^{-3.58}$ atm) is identical to that in the absence of CO_2 at pH < 6. The SCM could interpret the identical sorption at pH < 6 and the lower sorption at pH > 7.5. However, it underestimates to some extent the sorption of U(VI) around pH 7 in the presence of CO_2.

(3) The binding of UO_2^{2+} on the layer sites is apparently independent of temperature, whereas the surface complexation reactions on edge sites are endothermic. The $\Delta_r H_m^\theta$ of surface complexation reactions of UO_2^+, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_7^-$ on the edge sites are 52, 158, and 188 kJ/mol, respectively.

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Table 1. Modeling parameters for the acid-base chemistry of the Na-bentonite [14].

Description of the purified Na-bentonite	
Specific surface area	53.6 m^2/g
Sites	***Site density***
X^-	1.16×10^{-5} mol/m^2 (623 meq/kg)
≡SOH	5.88×10^{-7} mol/m^2
≡YOH	1.18×10^{-6} mol/m^2
Aqueous solution/solid equilibria: Reactions involved in acid-base titration	
Reactions	$\log K^{int}$ (T = 298 K)
$XNa \rightleftharpoons X^- + Na^+$	-1.3
$XNa + H^+ \rightleftharpoons XH + Na^+$	0.79
$\equiv SOH + H^+ \rightleftharpoons \equiv SOH_2^+$	3.23
$\equiv SOH \rightleftharpoons \equiv SO^- + H^+$	-3.89
$\equiv YOH \rightleftharpoons \equiv YO^- + H^+$	-6.57

Table 2. Thermodynamic data for aqueous reactions of U(VI) used in modeling (I = 0, T = 298.15K) [19, 20].

Reactions	log$K$	$\Delta_r H_m^o$ (kJ/mol)
$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$	-5.20	58
$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2\,(aq) + 2H^+$	-12.0	20
$UO_2^{2+} + 3H_2O \rightleftharpoons UO_2(OH)_3^- + 3H^+$	-19.2	—
$UO_2^{2+} + 4H_2O \rightleftharpoons UO_2(OH)_4^{2-} + 4H^+$	-33.0	—
$2UO_2^{2+} + H_2O \rightleftharpoons (UO_2)_2OH^{3+} + H^+$	-2.70	—
$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$	-5.62	54
$3UO_2^{2+} + 4H_2O \rightleftharpoons (UO_2)_3(OH)_4^{2+} + 4H^+$	-11.9	—
$3UO_2^{2+} + 5H_2O \rightleftharpoons (UO_2)_3(OH)_5^+ + 5H^+$	-15.55	105
$3UO_2^{2+} + 7H_2O \rightleftharpoons (UO_2)_3(OH)_7^- + 7H^+$	-31.0	—
$4UO_2^{2+} + 7H_2O \rightleftharpoons (UO_2)_4(OH)_7^+ + 7H^+$	-21.9	—
$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2CO_3(aq)$	9.68	5.0
$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_2^{2-}$	16.94	18.5
$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$	21.60	-39.2
$3UO_2^{2+} + 6CO_3^{2-} \rightleftharpoons (UO_2)_3(CO_3)_6^{6-}$	54.00	-62.7
$2UO_2^{2+} + CO_2(g) + 4H_2O(l) \rightleftharpoons (UO_2)_2CO_3(OH)_3^- + 5H^+$	-19.01	—
$3UO_2^{2+} + CO_2(g) + 4H_2O(l) \rightleftharpoons (UO_2)_3O(OH)_2(HCO_3)^+ + 5H^+$	-17.5	—
$11UO_2^{2+} + 6CO_2(g) + 18H_2O(l) \rightleftharpoons (UO_2)_{11}(CO_3)_6\,(OH)_{12}^{2-} + 24H^+$	-72.5	—
$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+$	0.17	8.0
$UO_2^{2+} + 2Cl^- \rightleftharpoons UO_2Cl_2(aq)$	-1.10	15

Table 3. Surface complexation reactions of U(VI) on Na-bentonite and corresponding intrinsic equilibrium constants (I = 0 mol/L).

U(VI) surface complexation reactions	$\log K^{int}$			$\Delta_r H_m^\theta$ (kJ/mol)
	298±2 K	333±2 K	353±2 K	
$2XNa + UO_2^{2+} \rightleftharpoons X_2(UO_2)_2 + 2Na^+$	0.6	0.6	0.6	0
$\equiv SOH + UO_2^{2+} \rightleftharpoons \equiv SOUO_2^+ + H^+$	-0.9	0.1	0.5	52
$\equiv SOH + 3UO_2^{2+} + 5H_2O \rightleftharpoons \equiv SO(UO_2)_3(OH)_5 + 6H^+$	-15.7	-13.1	-11.3	158
$\equiv SOH + 3UO_2^{2+} + 7H_2O \rightleftharpoons \equiv SO(UO_2)_3(OH)_7^{2-} + 8H^+$	-26.2	-23.0	-21.0	188

Figure Captions

Fig. 1. Sorption curves of U(VI) versus pH on the Na-bentonite at different initial U(VI) concentrations; T = 298±2 K, I = 0.1 mol/L NaCl and m/V = 1 g/L. The points show the experimental data and the solid lines represent the results calculated by the proposed model. The dash lines illustrate the contributions of different surface complexes to U(VI) sorption at $C^0_{U(VI)}$ = 8.02×10^{-5} mol/L: (A) X_2UO_2; (B) ≡$SOUO_2^+$; (C) ≡$SO(UO_2)_3(OH)_5$; (D) ≡$SO(UO_2)_3(OH)_7^{2-}$.

Fig. 2. Speciation of U(VI) in NaCl solution; T = 298.15K, $C^0_{U(VI)}$ = 4.0×10^{-5} mol/L and I = 0.1 mol/L NaCl; (a) P_{CO_2} = 0; (b) P_{CO_2} = 10$^{-3.58}$ atm; Solids are not allowed to precipitate.

Fig. 3. Sorption isotherms of U(VI) on the Na-bentonite; T = 298±2 K, I = 0.1mol/L NaCl and m/V = 1 g/L. The points show the experimental data and the lines represent the results calculated by the proposed model.

Fig. 4. Effect of m/V upon U(VI) sorption on the Na-bentonite; T = 298±2 K, $C^0_{U(VI)}$ = 8.02×10^{-5} mol/L, pH = 5.00±0.10 and I = 0.1 mol/L NaCl. The points show the experimental data and the line represents the results calculated by the proposed model.

Fig. 5. Sorption curves of U(VI) versus pH on the Na-bentonite in the presence and absence of CO_2; T = 298±2 K, $C^0_{U(VI)}$ = 8.02×10^{-5} mol/L, I = 0.1 mol/L NaCl and m/V = 1 g/L. The points show the experimental data, the solid line represents the results calculated by the proposed model for the sorption system at P_{CO_2} =10$^{-3.58}$ atm. The dash lines illustrate the contributions of different surface complexes to U(VI) sorption at P_{CO_2} =10$^{-3.58}$ atm: (A) X_2UO_2; (B) ≡$SOUO_2^+$; (C) ≡$SO(UO_2)_3(OH)_5$; (D) ≡$SO(UO_2)_3(OH)_7^{2-}$.

Fig. 6. Sorption curves of U(VI) versus pH on the Na-bentonite at different

temperatures; $C^{0}_{U(VI)}$ = 8.02×10^{-5}mol/L, I = 0.1 mol/L NaCl, m/V = 1 g/L. The points show the experimental data and the lines represent the results calculated by the proposed model with the equilibrium constants listed in Table 3.

Fig. 7. The dependence of equilibrium constants (K^{int}) of U(VI) surface complexation reactions on temperature according to the van't Hoff equation; (a) ≡SOUO_2^+ ; (b) ≡S$O(UO_2)_3(OH)_5$; (c) ≡S$O(UO_2)_3(OH)_7^{2-}$.

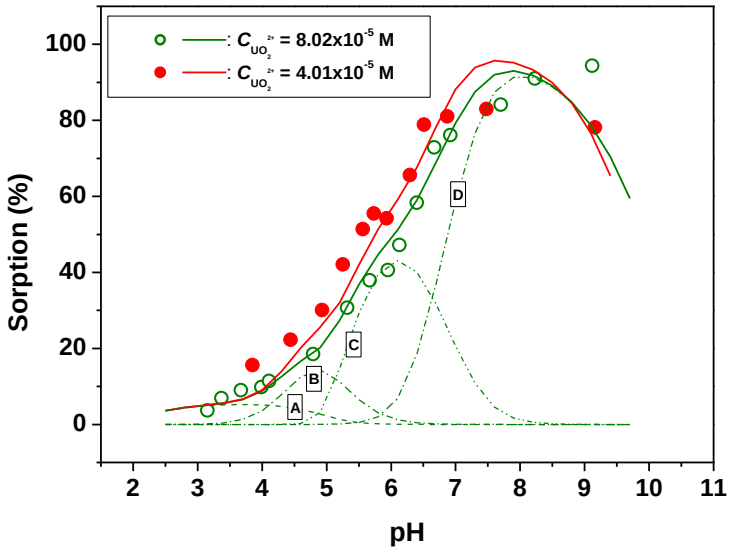


Fig. 1. Sorption curves of U(VI) versus pH on the Na-bentonite at different initial U(VI) concentrations; T = 298±2 K, I = 0.1 mol/L NaCl and m/V = 1 g/L. The points show the experimental data and the solid lines represent the results calculated by the proposed model. The dash lines illustrate the contributions of different surface complexes to U(VI) sorption at $C^{0}_{U(VI)}$ = 8.02×10^{-5} mol/L: (A) X_2UO_2; (B) ≡$SOUO_2^+$; (C) ≡$SO(UO_2)_3(OH)_5$; (D) ≡$SO(UO_2)_3(OH)_7^{2-}$.

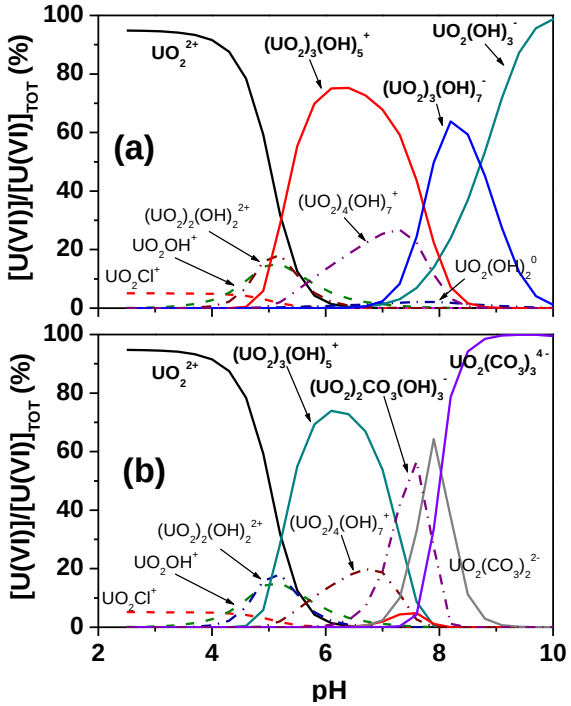
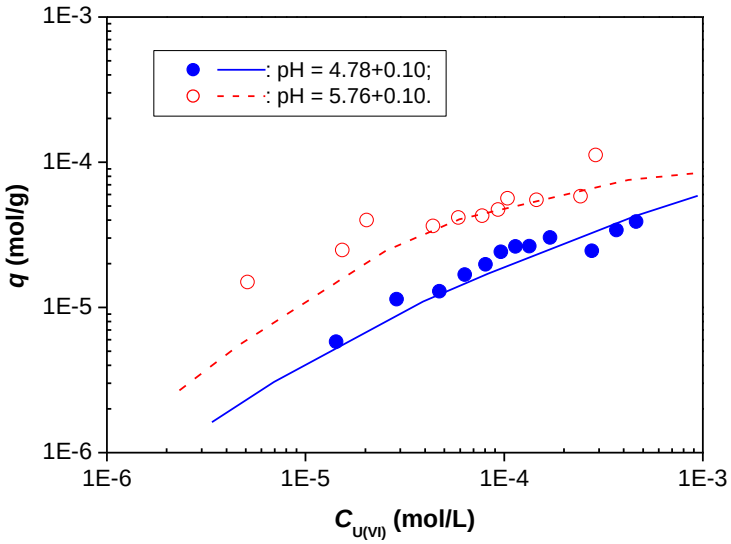


Fig. 2. Speciation of U(VI) in NaCl solution; T = 298.15K, $C^{0}_{U(VI)}$ = 4.0×10^{-5} mol/L and I = 0.1 mol/L NaCl; (a) P_{CO_2} = 0; (b) P_{CO_2} = 10$^{-3.58}$ atm; Solids are not allowed to precipitate.



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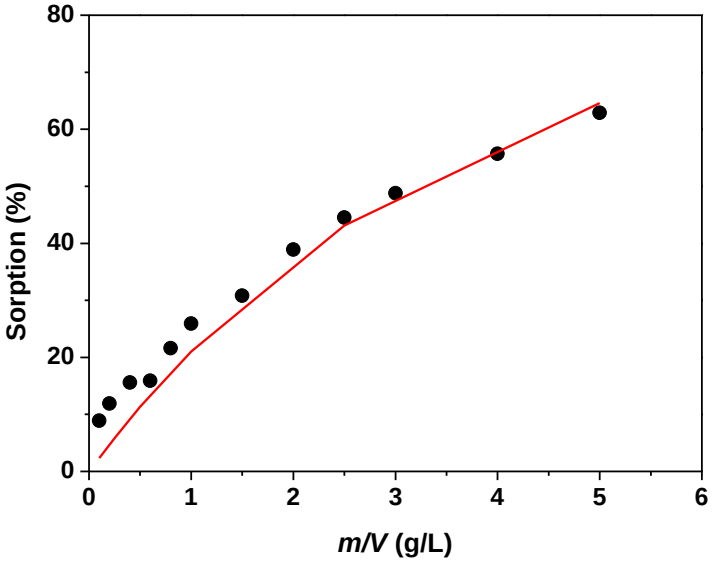
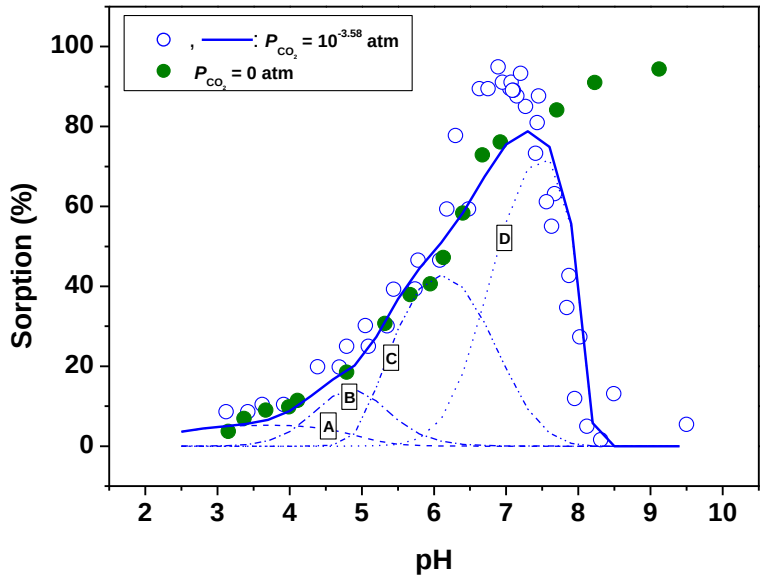


Fig. 4. Effect of *m/V* upon U(VI) sorption on the Na-bentonite; T = 298±2 K, $C^{0}_{U(VI)}$ = 8.02×10^{-5} mol/L, pH = 5.00±0.10 and I = 0.1 mol/L NaCl. The points show the experimental data and the line represents the results calculated by the proposed model.



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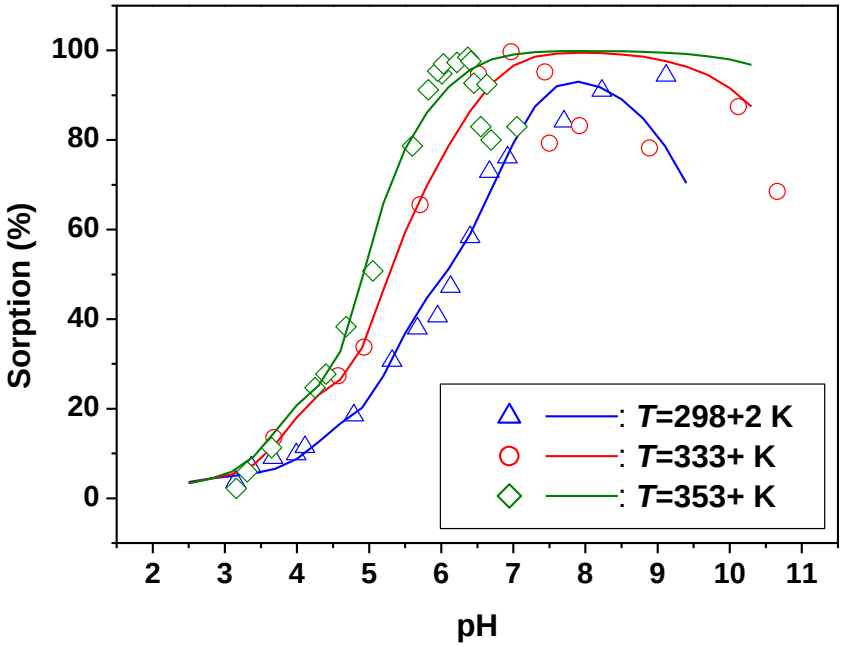
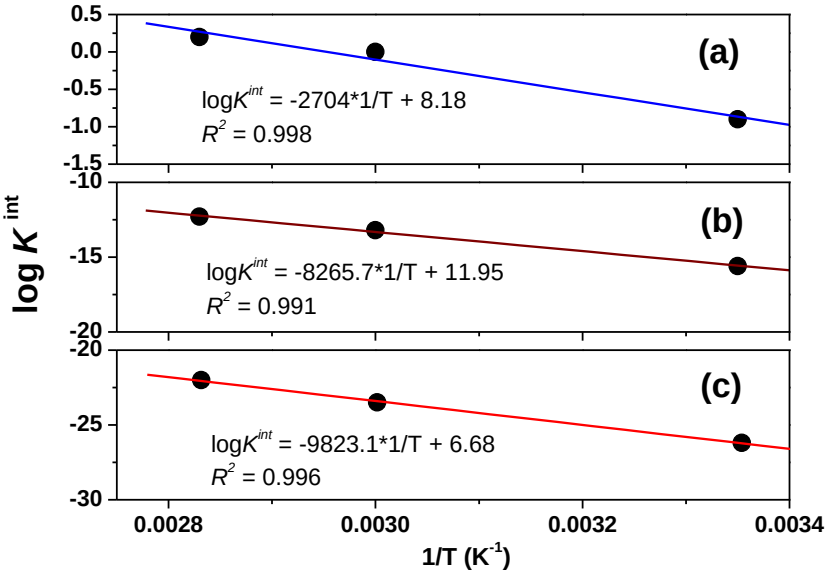


Fig. 6. Sorption curves of U(VI) versus pH on the Na-bentonite at different temperatures; $C^{0}_{U(VI)}$ = 8.02×10^{-5}mol/L, I = 0.1 mol/L NaCl, m/V = 1 g/L. The points show the experimental data and the lines represent the results calculated by the proposed model with the equilibrium constants listed in Table 3.



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