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MODELS FOR THE ADSORPTION OF URANIUM ON TITANIUM DIOXIDE

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SUMMARY

A hydrated titanium oxide whose acid-base properties are well defined has been used to study the retention mechanism of uranium as UO_2^{2+} (in acidic media) and as $\text{UO}_2(\text{CO}_3)_3^{4-}$ (in carbonate media). The influence of various parameters on the distribution coefficient of uranium (pH, $[\text{CO}_3^{2-}]$) and of the adsorption of uranium on the electrophoretic mobilities of the titanium oxide have been investigated. It is shown that, in both media, coordinative TiO-UO₂ bonds are formed. These strong bonds explain the high affinity of the titanium oxide for uranium.

INTRODUCTION

In Great Britain^{1,2} and in Japan³, previous studies have shown that titanium dioxide presents a high affinity for uranium and that it may be used as an adsorbant in the process of extraction of uranium from sea-water.

Using a hydrated titanium oxide whose acid-base properties are well defined⁴⁻⁶, we have studied the retention mechanism of uranium as UO_2^{2+} and $\text{UO}_2(\text{CO}_3)_3^{4-}$. Owing to the high stability constant of the tricarbonato-uranyl complex^{7,8} and to the relatively high carbonate concentration in sea-water, uranium should occur predominantly as the tricarbonato-uranyl complex (74%). We have studied the influence of various parameters on the distribution coefficient of uranium (pH, $[\text{CO}_3^{2-}]$). Our experimental results are in good agreement with adsorption models of the electrophoretic mobilities.

EXPERIMENTAL

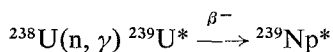
Syntheses

Titanium dioxide was prepared by hydrolysis of titanium tetrachloride with ammonia in acetate media as previously described⁴.

Sodium tricarbonato-uranate was prepared by the method of Bachelet *et al.*⁹ by dissolution of a mixture of UO_3 and NaHCO_3 in distilled water followed by evaporation of the solution. The chemical composition of the product was in good agreement with the formula $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ (ref. 5).

Determination of distribution coefficients (D)

The retention of uranium was studied by shaking 50 ml of a buffered solution (pH = 1.5–3.2 or 8–9) containing a low concentration of uranyl nitrate or uranyl tricarbonate (10^{-4} M) at a constant ionic strength ($I = 0.8$), with 500 mg of titanium dioxide for 3 h at $20 \pm 1^\circ\text{C}$. After separation of solid from liquid, the uranium was titrated by non-destructive neutron activation analysis: the sample and an uranium standard were irradiated for 2 h in the EL3 reactor of the C.E.N.-Saclay (France). The nuclear reaction which occurred was:



After 1 week, the gamma radioactivity of $^{239}\text{Np}^*$ was detected with a Ge(Li) detector and was compared to those of standard samples. The distribution coefficient was calculated as:

$$D = \frac{\text{Quantity of retained uranium per gram of dry TiO}_2}{\text{Quantity of uranium remaining per ml of solution}}$$

Electrophoresis measurements^{10,11}

These "free electrophoresis" measurements were performed with a commercial microelectrophoresis apparatus (Rank-Brothers, Cambridge, Great Britain), in which particles are observed to move in a flat cell.

All the solutions were prepared using analytical reagents and twice distilled water. Titanium dioxide (granulometry $\leq 10 \mu\text{m}$) was dispersed in 10^{-2} M KNO_3 solutions; its concentration was 5 mg/l. pH measurements and adjustments were made out of the cell. Concentrations of 10^{-5} M uranyl nitrate and $4 \cdot 10^{-6}$ M uranyl tricarbonate were used to study the adsorption of uranium.

At least ten particles were observed at each stationary level, with the polarity of the platinum black electrodes being reversed between successive observations to minimize polarization effects. The average deviation in the measured electrophoretic mobilities varied from 0.5 to 0.1 $\mu\text{m} \cdot \text{sec}^{-1}/\text{V} \cdot \text{cm}^{-1}$, the larger relative deviations occurring when mobilities were small ($< 1 \mu\text{m} \cdot \text{sec}^{-1}/\text{V} \cdot \text{cm}^{-1}$).

RESULTS AND DISCUSSION

Characteristics of titanium dioxide

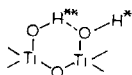
The oxide obtained is a granular gel; its granulometry is inferior to 20 mesh. Its chemical composition is 73% TiO_2 and 27% H_2O . The principal impurities are chlorine (30 ppm) and ammonia (less than 10 ppm).

Its ion-exchange characteristics are^{5,6}:

At pH 1.6, 0.4 mequiv. OH^- per gram of dry TiO_2 are exchangeable for Cl^- . The basic constant has been found to be equal to 2.9.

At pH 11.0, 2.9 mequiv. H^+ per gram of dry TiO_2 are exchangeable for Na^+ . The two acidic constants are $\text{p}K_1 = 4.9$ and $\text{p}K_2 = 9.3$.

These two acidities are attributed to two different types of protons H^* and H^{**} , schematized as follows:



The pH of the isoelectric point is found to be 3.9. Its retention capacity for uranium is found to be 0.11 mequiv. UO_2^{2+} per gram of dry TiO_2 at pH 8.4.

The electrophoretic mobilities of TiO_2 in $10^{-2} M KNO_3$ solution are presented in Fig. 1 (●). The value of point of zero charge is 3.8, very near the isoelectric point determined from the adsorption isotherms of Na^+ and Cl^- (ref. 5). This figure shows that, at pH values less than 3.8, the positive forms $>TiOH_2^+$ are predominant, but are negligible compared to the negative forms $>TiO^-$ which exist at pH values greater than 3.8.

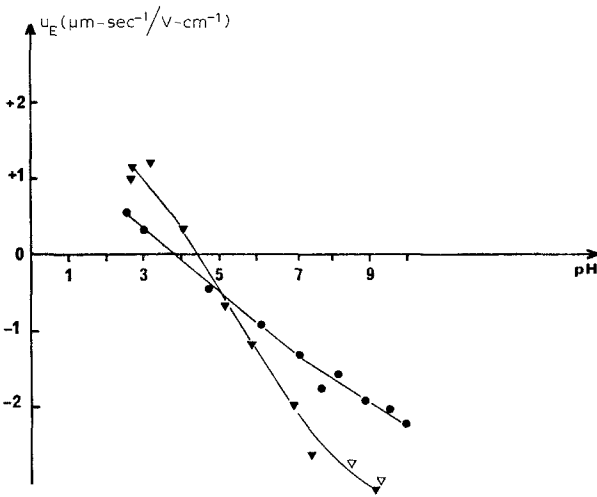
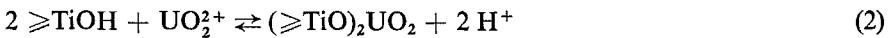
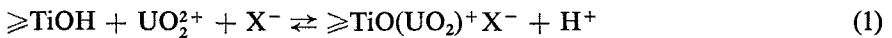


Fig. 1. Electrophoretic mobilities of TiO_2 versus pH of the solution. ●, $10^{-2} M KNO_3$; ▲, $10^{-2} M KNO_3 + 10^{-5} M UO_2(NO_3)_2$; △, $10^{-2} M KNO_3 + 4 \cdot 10^{-6} M Na_4UO_2(CO_3)_3$.

Model for the adsorption of UO_2^{2+} in acidic media

We have studied the behaviour of the uranyl ion in the pH range (1.5–3.2) where only UO_2^{2+} exists¹⁰. In this pH range, the titanium oxide retains monovalent anions on the $\geq TiOH_2^+$ groups but also retains divalent cations as UO_2^{2+} . The protonated hydroxyl groups are $\geq TiOH^{*+}$. We suggest that the hydroxyl groups $\geq TiOH^*$, which are not protonated, allow the retention of the divalent cations. Two equilibria are proposed to explain this retention:



According to eqn. 1, the distribution coefficient would follow the expression:

$$\log D = \text{constant} + \text{pH}$$

According to eqn. 2, the distribution coefficient would be expressed as:

$$\log D = \text{constant} + 2 \text{pH}$$

Our experimental results show that the retention equilibrium is reversible and the distribution coefficient follows the expression

$$\log D = apH - b$$

with $a = 1.08 \pm 0.10$, $b = 2.09 \pm 0.08$ and r (regression coefficient) = 0.99. Thus this result shows that in the pH range 1.5–3.2, the stoichiometry of the retention equilibrium is one \geq TiOH per UO_2^{2+} .

The electrophoretic mobilities observed after the adsorption of the uranyl ion are also presented in Fig. 1 (\blacktriangle). We can see that the surface charge becomes more positive in the pH range 2.5–5.0. This may be explained by our retention model if the bond TiO– UO_2 is coordinative; the UO_2^{2+} ion is specifically adsorbed on titanium dioxide and its adsorption leads to a shifting of the point of zero charge to 4.5.

From these results, we propose a model for the double layer at the surface of titanium oxide at pH 2.5, similar to that of Bockris *et al.*¹² (*cf.*, Fig. 2). This simple ion-exchange model has been verified only in the acidic pH range. At pH > 5, hydrolysed species are formed and hydrolytic adsorption would explain the high retention of uranium as has been shown by Sakodinskii and Lederer¹³ in LiCl, NaCl, Na_2SO_4 and $(NH_4)_2SO_4$ media.

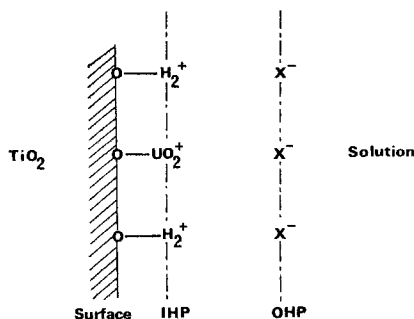
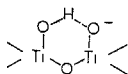


Fig. 2. Model for the double layer at TiO_2 surface (pH = 2.5). IHP = inner Helmholtz plane; OHP = outer Helmholtz plane.

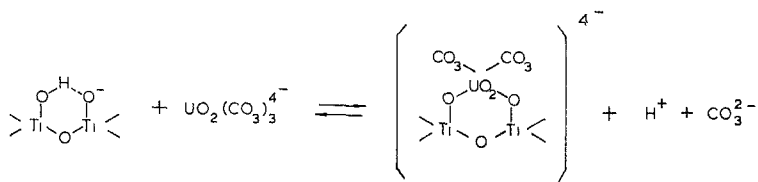
Model for the adsorption of $UO_2(CO_3)_3^{4-}$ in carbonate media

The first question is: is the uranyl retained as a carbonate complex or not? We have followed the retention of the carbonate with ^{14}C -labelled sodium tricarbonato-uranate. We found that the ratio $(CO_3^{2-} \text{ retained})/(\text{uranium retained})$ remained equal to 2.0 whatever the concentration of uranium. Also, that the carbonate ion alone was not retained.

We noticed that at pH = 8–9 all the hydroxyl groups having $pK_1 = 4.9$ are exchanged with Na^+ present in excess⁵; under our experimental conditions, the bonding of the hydroxyl groups is:



We propose the following complexation of uranyl to explain its adsorption:



This model gives the distribution coefficient as:

$$\log D = \text{constant} - \log [\text{H}^+] [\text{CO}_3^{2-}]$$

Our experimental results show that the retention equilibrium is reversible and the distribution coefficient follows the expression

$$\log D = (-10.00 \pm 1.6) - (1.0 \pm 0.1) \log [\text{H}^+] [\text{CO}_3^{2-}]$$

with r (regression coefficient) = 0.94, which is in good agreement with our model.

The electrophoretic mobilities observed after the adsorption of the uranyl carbonate in the pH range 8–10 are presented in Fig. 1 (Δ). We can see that the surface charge becomes more negative, in good agreement with the model of adsorption described. The bonds $\text{TiO}_2\text{-UO}_2$ and $\text{UO}_2\text{-CO}_3$ are coordinative. From these results, we propose a model for the double layer at the surface of titanium dioxide (*cf.*, Fig. 3)

The electrophoretic measurements show the adsorption of a negative form. These results are not in agreement with the model proposed by Davies *et al.*¹ and Schenk *et al.*¹⁴ where uranium would be retained as uranyl ion in carbonate media. Schenk *et al.*¹⁴ have shown that the uranyl-adsorbent bond is stronger than the uranyl-carbonate bond in the carbonate complex; this result is in agreement with the formation of strong $\text{UO}_2\text{-OTi}$ bonds but not with the adsorption of the carbonate complex as proposed by Ogata *et al.*³

The desorption of uranyl from TiO_2 is performed with highly concentrated solutions of carbonate¹; this is explained by the stabilization of the tricarbonato-uranyl complex in solution which prevents the formation of the TiO-UO_2 bonds.

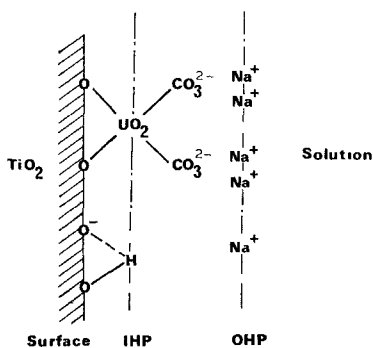


Fig. 3. Model for the double layer at TiO_2 surface (pH = 8).

These results obtained in carbonate-buffered media cannot be extrapolated to sea-water which is not a buffered medium. But we have shown the strong TiO–UO₂ bonds can displace any strong ligand–uranyl bond present in sea-water.

CONCLUSION

After preparing a titanium oxide whose acid–base properties are well defined, we have proposed models for the adsorption of uranium as uranyl ion (in acidic media) or as a carbonato-uranyl complex (in carbonate media): coordinative TiO–UO₂ bonds are formed in both media. These strong bonds explain the high affinity of titanium dioxide for uranium. Nevertheless, the carbonato-uranyl complex keeps part of its carbonate ligands (2 CO₃²⁻ per UO₂²⁺).

We have quantified the variation of the distribution coefficient of uranium *versus* pH and carbonate concentration, so that the behaviour of uranium during its extraction from carbonate effluents can be predicted.

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