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Sorption of Uranyl Ions on Hydrous Oxides. A New Surface Hydrolysis Model

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Sorption of uranyl ions on hydrous titanium oxide(HTiO), magnetite(MAG), and hydrous thorium oxide(HThO) has been studied as a function of pH. Hydrous oxides have been characterized by their pH-titration curves, intrinsic dissociation constants(pK_{ai}^*) and point of zero charge (pH_{pzc}). The fraction of protonated surface hydroxyl groups as well as the surface pH(pH_{surf}) as a function of solution pH have been computed. The distribution of various hydrolyzed species of uranyl ions with solution pH have been compared with uranyl sorption isotherm on these oxides. Sorption edge in all the cases occurs when free hydroxyl groups are available on the surface and pH_{surf} is sufficiently high to favor the formation of dimer-like species on the surface. A new model for the sorption process, called surface hydrolysis model, which explains these and other features of uranyl sorption on hydrous oxides has been proposed. The model visualizes the sorption process as linking of uranyl ions with two adjacent free surface hydroxyl groups without deprotonation (provided the surface pH is high for the hydrolysis of uranyl ions) and formation of dimer-like structures on the surface. The new model has been successfully applied to the present and other available data on uranyl ion sorption on hydrous oxides.

There has been a great interest in the study of the sorption of hydrolysable metal ions on hydrous oxides. Though many features of the sorption behavior are well-understood, a complete picture is still not available. The sorption process depends upon the properties of the metal ions (e.g. hydrolysability), characteristics of the oxide surface (e.g. point of zero charge, pzc) and experimental conditions (e.g. pH of the solution) Dugger et al.[1] viewed the sorption of transition metal ions on hydrous oxides as an ion exchange reaction between the surface hydroxyl groups and the metal ions:

$$m(\mathrm{SOH})+\mathrm{M}^{m+}\rightleftharpoons(\mathrm{SO})_m\,\mathrm{M}+m\mathrm{H}^+, \qquad (1)$$

where (SOH) is the surface hydroxyl group and M is the metal ion being sorbed. The variation in the sorption of different metal ions was attributed to the strength of the M-O bond which was correlated with the stability constants of monohydroxo complexes of cations.[1] This was applicable when the solution pH was such that hydrolysis of metal ions did not take place. In the sorption isotherms, an abrupt increase was observed as a function of pH, James and Healy[2] suggested that ionic charge on the sorbing metal ion was lowered by hydrolysis or ligand complex formation, facilitating closer approach to the interface and the sorption process.

More recently, the sorption process has been looked upon as surface complexation of metal ions by suface hydroxyl groups, so that the hydrolysis of metal ions in solution was not a pre-requisite of the sorption mechanism.[3,4] The deprotonation of the surface groups accompanied the sorption of the metal ions. In general, the soption of metal ions is viewed[5] as a competition between the surface hydroxyl groups and any ligand present in solution for the complexation of free metal ion. The sorption of ligands or anions of the oxide surface is also taken into consideration[6] to explain the sorption data. Recently, a precipitation model[7] for the sorption of metal ions on hydrous oxides has been proposed to account for the non-limiting sorption capacities of the oxides. Essentially the model is based on Eq. 1 but allows for precipitation of sorbing metal ion and solid solution formation, provided the solubility product of the sorbing metal cation is exceeded on the surface.

The above models, however, do not explain satisfactorily the observation that the abrupt increase in the sorption of metal ions on hydrous oxides occurs at a pH where the oxide surface is positively charged. These models also fail to explain the observed incease in the positive charge and the shift in pzc of the oxide as a result of sorption.[2,8] With a view to understand the sorption process on hydrous oxides, we had undertaken a detailed study of the sorption of metal cations on different hydrous oxides. In this communication we are presenting our results on the sorption of uranyl ions on hydrous titanium and thorium oxides and hydrous magnetite. A new sorption mechanism which accounts for all the features of the sorption process (including the hitherto unexplained ones) is proposed.

Experimental

Peparation of the Hydrous Oxides. Hydrous Titanium Oxide (HTiO): HTiO was prepared by adding 2 mol dm^{-3} NaOH to a hot solution of Ti(IV) in concd H_2SO_4 under constant stirring. The precipitate was digested in the mother liquor at 353 K for 4 h, allowed to cool and stand for 2 d. It was then filtered, washed free of alkali and air dried. The product, which is the same used in an earlier study,[9] did not contain any sulfate but sodium ions were present making the material alkaline. The sodium ions incorporated in it were removed by repeatedly treating it with dil $HClO_4$ and washing with water. This was continued till the pH of the water in contact with HTiO was neutral.

Hydrous Thorium Oxide (HThO): HThO was prepared by adding 1 mol dm^{-3} NaOH to a hot solution of thorium (IV) nitrate in HNO_3. The precipitate was later digested in

Table 1. Characteristics of the Hydrous Oxides

Hydrous oxide	Capacity (C) mmol g^{-1}	$pK_a = pK_a^* + m \cdot q$	$pH_{pzc} = \frac{1}{2}(pK_{a1}^* + pK_{a2}^*)$
HTiO	0.65	$pK_{a1} = 4.79 - 0.43 \times 10^4 q$ $pK_{a2} = 8.3 - 0.26 \times 10^4 q$	6.55
HThO	0.23	$pK_{a1} = 3.18 + 0.88 \times 10^3 q$ $pK_{a1} = 10.4 - 0.35 \times 10^4 q$	6.79
MAG	0.14	$pK_{a1} = 2.88 + 0.48 \times 10^4 q$ $pK_{a1} = 10.05 - 0.45 \times 10^4 q$	6.47

hot condition, aged for 2 d, filtered, washed, and air dried.

Hydrous Magnetite (MAG): MAG was prepared by the method of Benton and Horsfall.[10] To a hot 5L solution containing sulfuric acid, 25 g KNO_3 and 90 g $FeSO_4 \cdot 7H_2O$, NaOH was added under constant stirring. The green precipetate initially formed turned black. The precipitate was digested in hot condition, aged for 2 d, filtered, washed and air dried.

All the air dried hydrous oxides were broken in water, washed, dried and finally crushed and sieved. For sorption experiments −100 BSS samples were used. X-Ray analysis of the oxides showed that HTiO and HThO were amorphous; and MAG was crystalline.

pH Titration. Continuous pH titration were carried out with 0.4 g of the air dried samples in 50 cm^3 of 0.1 mol dm^{-3} $NaNO_3$ with 0.1 mol dm^{-3} HNO_3 or NaOH. The pH of the slurry was measured using Elico Digital pH-meter. After the addition of acid or alkali, solutions were stirred continuously for 10 min before pH measuement.

Sorption Experiments. All sorption experiments were done at a total ionic strength of about 0.1 mol dm^{-3} $NaClO_4$. 0.1 g of the oxide was equilibrated with 25 cm^3 of the solution of 10^{-4} mol dm^{-3} uranyl nitrate in $NaClO_4$, preadjusted to a known pH using $HClO_4$ or NaOH. The solid-solution mixture was equilibrated for 4 h at constant room temperature (298±1 K). Later the pH of the supernatant solution was measured. The uranium in the equilibrated solution was estimated spectrophotometrically using H_2O_2 at 400 nm.[11] The difference in the uranium concentration before and after equilibration gave the amount sorbed on the oxide.

Results and Discussion

Characteristics of the Hydrous Oxides. Capacity Determination: The capacity of the hydrous oxide is the ion sorption capacity of the material (mmol g^{-1}). It is equal to the total number of hydroxyl groups taking part either in Reaction 2 or 3. It has been determined as the limiting value of H^+ ions consumed in the acid region of the pH-titration curve or the limiting value of OH^- ions consumed in the alkaline region of the titration curve. Its value has also been estimated from the limiting amounts of Na^+ or Cl^- ions sorbed by the oxides. The values for capacities obtained by different procedures were in reasonable agreement with one another and are listed in Table 1.

Analysis of pH-Titration Curves: The pH-titration curves of the three oxides in the acidic as well as alkaline regions are given in Fig. 1. The steep rise (alkaline region) and decline (acidic region) of pH in the titration curve of HThO and MAG compared to HTiO reflect their lower capacities vis-a-vis HTiO. As the hydrous oxides are amphoteric in character, the following reactons take place:

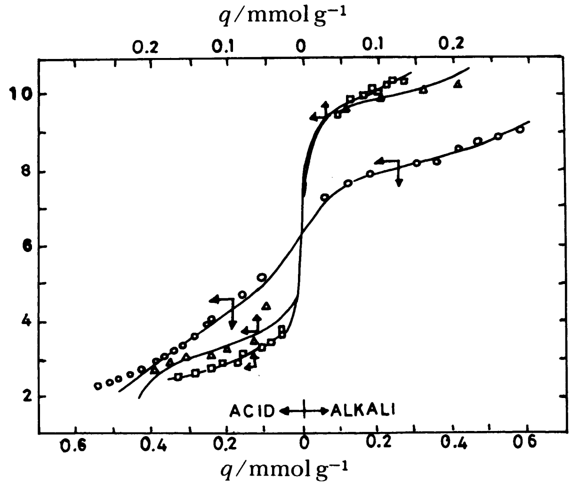

Fig. 1. pH-titration curves of hydrous oxides (○): HTiO; (△): HThO; (□): Magnetite. Solid lines based on pK_{a1} and its dependence on q (Table 1).

$$\text{acidic rigion: } SOH_2^+ \rightleftarrows SOH + H^+, \tag{2}$$

$$\text{alkaline region: } SOH \rightleftarrows SO^- + H^+. \tag{3}$$

The coresponding equilibrium constants are given by:

$$K_{a1} = N_{(SOH)}\, m_{H^+} / N_{(SOH_2^+)}, \tag{4}$$

$$K_{a2} = N_{(SO^-)}\, m_{H^+} / N_{(SOH)}, \tag{5}$$

where m_{H^+}, $N_{(SOH_2^+)}$, $N_{(SOH)}$, and $N_{(SO^-)}$ are molality of H^+ in solution and mole fractions of protonated, undissociated and dissociated surface hydroxyl groups in the oxide.

These equilibrium constants can be computed from the pH-titration curves by the method given by Schindler and Gamsjaeger.[12] Similar procedures have been recommended by other workers also.[13] The function q defined by $q = [SOH_2^+] - [SO^-]$, is computed from:

$$q = \frac{V(H-h)}{a} \quad (\text{mol g}^{-1}). \tag{6}$$

Where V is the volume of the solution taken for titration (dm^3); H is the amount of acid or base added (mol dm^{-3}); h is the equilibrium H^+ concentration in solution (mol dm^{-3}); and a is the amount of hydrous oxides used (g). Assuming that SOH_2^+ is zero in alkaline region and SO^- is zero in acidic region, the equilibrium constants are:

$$K_{a1}=\frac{h(C-q)}{q}=\frac{h(1-\alpha)}{\alpha}\qquad\text{(acidic region)},\qquad(7)$$

$$K_{a2}=\frac{h\cdot q}{C-q}=\frac{h(\alpha)}{(1-\alpha)}\qquad\text{(alkaline region)},\qquad(8)$$

where C(mol g^{-1}) is the capacity of the hydrous oxide, and $\alpha=q/C$, is the fraction of the surface hydroxyl groups in either SOH_2^+ (Eq. 7) or SO^- (Eq. 8) form. The values of the equilibrium constants vary with q. A plot of pK_{ai} ($=-\log_{10} K_{ai}$, i=1 or 2) versus q were straight lines. The y-intercept gives the intrinsic dissociation constant (pK_{ai}^*) of the surface groups of the hydrous oxides. The slopes of the linear plots ('m') were either positive or negative. The equations describing the linear relationship between pK_{a1} and q are given in Table 1. Using these equations the pH-titration curves of the three hydrous oxides were calculated, which were in good agreement with experimental data (Fig. 1). The point of zero charge, pH$_{pzc}$, is the pH where the net surface charge is zero, implying that [SOH_2^+] and [SO^-] are equal at this point. pH$_{pzc}$ is calculated from the relation:

$$\mathrm{pH}_{pzc}=\frac{1}{2}\,(\mathrm{p}K_{a1}^*+\mathrm{p}K_{a2}^*).\qquad(9)$$

The values of pK_{ai}^* and pH$_{pzc}$ for HTiO and MAG are in the range reported for these oxides.[2,12-17]

The surface hydrogen ion concentration, h^*, is given by the relations:

$$K_{a1}^*=\frac{h^*(C-q)}{q}=\frac{h^*(1-\alpha)}{\alpha}\qquad\text{(acidic region)},\qquad(10)$$

$$K_{a2}^*=\frac{h^*q}{C-q}=\frac{h^*(\alpha)}{(1-\alpha)}\qquad\text{(alkaline region)}.\qquad(11)$$

Using these equations surface pH, pH$_{surf}$, ($=-\log_{10} h^*$) for different α values have been evaluated.

Sorption of Uranium. Sorption isotherms of uranium as a function of pH on the three hydrous oxides are given in Fig. 2(A). An abrupt increase in the sorption within a narrow pH range is observed in all the three cases. The sorption edge, however, occurs at different solution pH (pH$_{soln}$) for the three hydrous oxides. As pH$_{pzc}$ of these oxides are higher than the sorption edge pH, the sorption of uranyl ions occurs on positively charged surfaces.

For a particular value of $\alpha(=q/C)$, the value of K_{a1} can be calculated with the help of data given in Table 1. Using this value of K_{a1}, the value of the solution pH ($=-\log_{10} h$) was calculated from Eq. 7. Plots of α vs. solution pH for the SOH_2^+ group present on the three hydrous oxides are given in Fig. 2(C). The plots clearly show that the sorption edge for HTiO (Fig. 2A) occurs when 90% of the surface hydroxyl groups are in SOH_2^+ form. In HThO and MAG, 20% and 15% of surface hydroxyl groups, respectively, are in SOH_2^+ form at the sorption edge.

Earlier models[18] regarded the sorption process as surface complexation accompanied by the dissociation of surface hydroxyl groups, even at pH lower than their pH$_{pzc}$, just as the deprotonation of hydroxyl groups of the ligands on complex formation with metal cations. Such a model does not account for the data in Fig. 2, in particular for HTiO where more than one proton per hydroxyl group has to be released for forming a single SO-UO_2^{2+} link, i.e. the formation of oxo bridges between uranyl ions and the surface is ruled out. Another aspect of the earlier models, namely the participation of hydrolyzed metal ion species in the sorption process, was also examined. For this purpose, the distribution of hydrolyzed species of uranium as a function of pH at a total uranium concentration of 10^{-4} mol dm^{-3}, was computed using the following stability constants:[1]

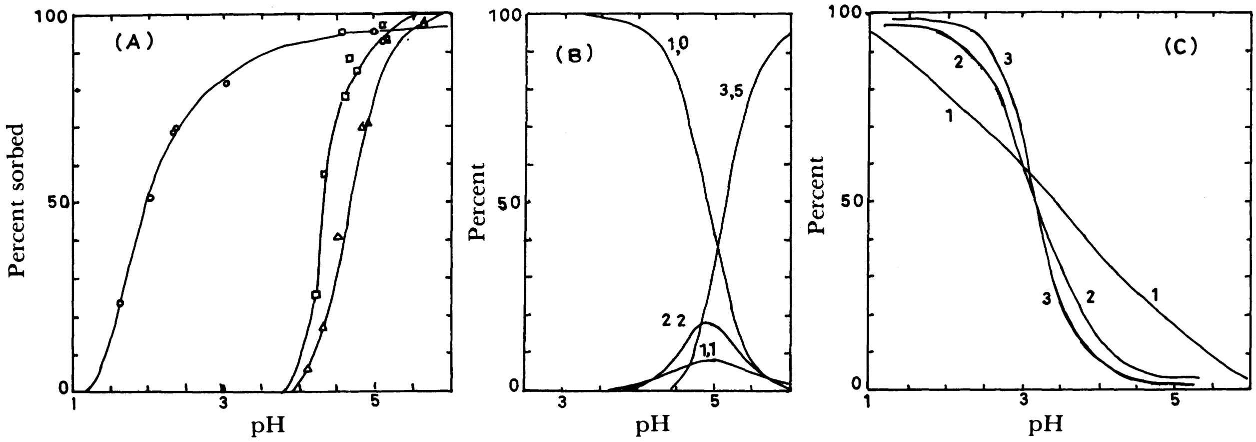

Fig. 2. (A) Uranyl sorption isotherm on hydrous oxides $\sum U=10^{-4}$ mol dm^{-3}. (O) HTiO; (□) HThO; (Δ) Magnetite. (B) Distribution of hydrolyzed uranyl species vs. pH. (1,0)=UO_2^{2+}; (1,1)=$(UO_2)(OH)^+$; (2,2)=$(UO_2)_2(OH)_2^{2+}$; (3,5)=$(UO_2)_3(OH)_5^+$. (C) Percent of SOH_2^+ groups vs. pH; (1) HTiO; (2) HThO; (3) Magnetite.

$$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+;\ \log\beta_{11} = -5.7, \tag{12}$$

$$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+;\ \log\beta_{22} = -5.92, \tag{13}$$

$$3UO_2^{2+} + 5H_2O \rightleftharpoons (UO_2)_3(OH)_5^+ + 5H^+;\ \log\beta_{35} = -16.5. \tag{14}$$

Distribution plots for various species in Fig. 2(B) demonstrate that uranium is present only as UO_2^{2+} at the sorption edge for HTiO and hydrolysis of uranyl ions starts only after 90% of uranium has been absorbed. In the case of HThO and MAG sorption edge occurs at a pH where the hydrolysis of uranium has not started and uranium is essentially present as uranyl ions.

The New Model-Surface Hydrolysis Model. The above analysis clearly demonstrates that the sorption of uranium on the three hydrous oxides, studied in this investigation, can not be accounted for by the existing models. Neither the hydrolyzed species of uranium participate in the sorption process nor does the sorption takes place under conditions where the surface complexation and conversion of surface hydroxyl groups to oxo groups would be a likely process. Sorption occurs on positively charged surfaces which are, as in HTiO, predominantly in SOH_2^+ form. Besides another feature of the sorption process observed in earlier studies,[2,18,20] namely, the increase in the positive charge of the oxide surface as a result of the sorption of metal ions, can not be explained by any of the existing models. In order to account for these features of the sorption process, a new model for the sorption of hydrolyzable metal cations on hydrous oxides is proposed.

Essential Features of the Model Are: 1) The main postulate of the model is that the sorption of metal ions on the surface of hydrous oxides occurs by attachment to surface hydroxyl groups without deprotonation of hydroxyl groups. On positively charged surfaces having SOH_2^+ groups, sorption of metal ions occurs only on free hydroxyl groups, i.e. SOH groups. The availability of free SOH groups is, thus, an essential requirement of the sorption process. (Fig. 3, A)

Schematically, the sorption process according to the new surface hydrolysis model is shown in Fig. 3.

2) In order to overcome the coulombic repulsion between positively charged metal ions and positively charged surfaces as well as to make the sorption process to be energetically favorable in comparison with the protonation of surface hydroxyl groups, it is further postulated that metal ion is simultaneously attached to two adjacent surface hydroxyl groups forming bridged hydroxo complexes with the surface in much the same manner as in dimerized hydroxo species, $(M^{+z} \genfrac{}{}{0pt}{}{\diagup OH \diagdown}{\diagdown OH \diagup} M^{+z})^{2z-2}$ formed during the hydrolysis of metal cations (B).

3) For the sorption process described in postulate (2), to be thermodynamically feasible, the model requires that the surface pH of the oxide at the sorption edge, as distinct from the solution pH, which defines the sorption edge, should correspond to the pH where dimerized hydroxo species are formed in solution, i.e. pH_D.

4) As surface pH increases, dimer or trimer-like species can be formed on the surface (C). pH_T is the pH at which trimeric species are formed in solution. In the limit when pH_{surf} approaches precipitation pH, i.e. pH_{ppt}, precipitation of the metal cation on the surface and solid solution formation takes place (E).

5) When $pH_{surf} \geqslant pH_{pzc}$, sorption process is governed by Eq. 1 (D). (In Fig. 3, pH_{surf} is indicated as pH_{su}).

The model thus predicts that the surface becomes more positively charged as a consequence of the adsorption process—a feature hitherto unexplained by the existing models of the sorption process. The validity of the various postulates of the model has been tested by analyzing the present data on the sorption of uranyl ions on the three hydrous oxides. Subse-

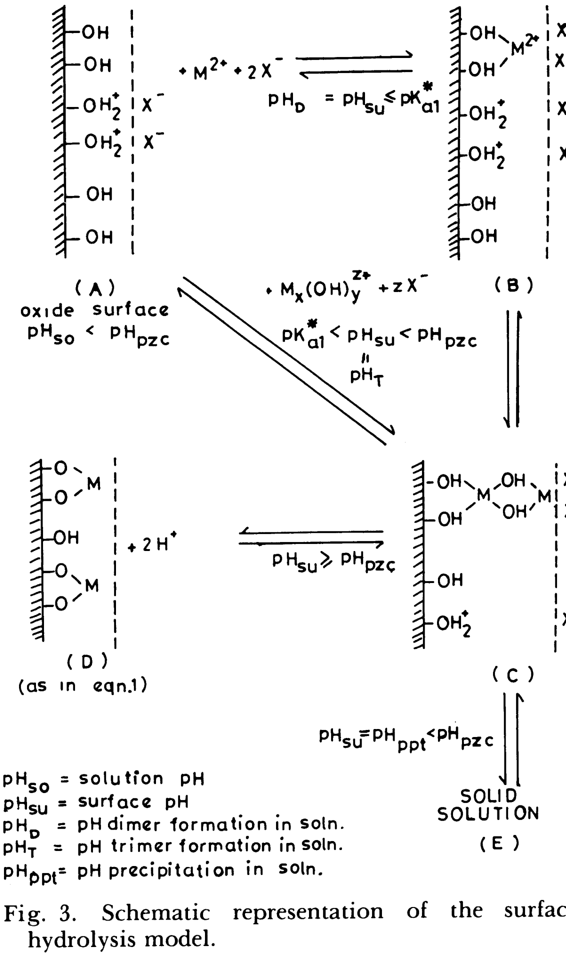

Fig. 3. Schematic representation of the surface hydrolysis model.

(A) Positively charged oxide surface having SOH_2^+ groups. (B) Dimer-like structure formed by the unhydrolyzed metal ion on the surface. (C) Trimer-like structure formed by the hydrolyzed dimeric species on the surface. (D) Negatively charged oxide surface. (E) Solid solution formation.

quently, the model has been applied to those studies on uranyl sorption on other hydrous oxides where data required for the application of the model are available.

Hydrous Titanium Oxide. Besides the sorption isotherms of uranyl ions as a function of solution pH, the model also requires information about the variation of the fraction of surface hydroxyl groups in SOH_2^+ form with solution pH. Such data plotted in Fig. 2(C) clearly show that at sorption edge pH (1.3) free SOH groups are available for the sorption of uranyl ion. Then the oxide surface corresponds to A in Fig 3. At this pH, uranyl ions in the solution phase exist only as unhydrolyzed uranyl ions. In order to apply the model, surface pH, pH_{surf}, is also required. This has been computed using Eq. 10. pH_{soln} as a function of α were calculated using Eq. 7. Table 2 lists values of pH_{surf} and pH_{soln} for various values of α. It is seen that pH_{surf} for HTiO is considerably higher than pH_{soln}. For this oxide, at the sorption edge pH_{soln} is 1.3, SOH_2^+ is 90%, and pH_{surf} is 3.9. The distribution diagram of various hydrolyzed uranium species shows that the hydrolysis of uranyl ions starts at pH 3.5 (formation of monomeric $UO_2(OH)^+$ (1, 1) in Fig. 2(B)) and at pH 3.8, (pH_D in Fig. 3) formation of dimeric species ((2, 2) in Fig. 2(B)), $(UO_2)_2(OH)_2^{2+}$, starts. At the sorption edge, pH_{surf} is very close to this. Thus, at the sorption edge, when solution pH is 1.3 and only free UO_2^{2+} (aq) ions exists in solution, conditions on the surface are favorable for the process A→B to occur (Fig. 3), which results in the formation of dimer-like species on the surface. In the dimeric species in solution, two OH groups form two bridges between two uranyl ions, $[UO_2{<}^{OH}_{OH}{>}UO_2]_{sol}$. In the dimer-like species on the surface, two OH groups form two bridges between a uranyl ion and the surface $[^{-OH}_{-OH}{>}UO_2]_{surf}$. Thus the uranyl ions are sorbed without the dissociation of OH groups, with the formation of dimer-like structures on the surface.

The fact that sorption edge occurs when pH_{surf} is 3.9 and not at 3.5, when UO_2OH^+ species or structures resembling such species (in the same sense as dimer-like structures) could exist on surface implies that sorption process corresponds to A→B (Fig. 3). Such a sorption mechanism, that is, attachment of uranyl ions on hydroxyl groups to form dimer-like structures, is supported by a recent Raman study of the interaction of uranyl ions with Th(IV) hydrolyzed polymer networks[21] in homogeneous systems.

As the solution pH increases, the solution contains hydrolyzed (dimeric) species of uranyl ions and pH_{surf} approaches pH_T (solution pH when trimecic species are formed in solution) and the condition on surface becomes favorable for A→C or B→C (Fig. 3) $[^{-OH}_{-OH}{>}UO_2{<}^{OH}_{OH}{>}UO_2]_{surf}$. If precipitation pH, pH_{ppt}, is less than pH_{pzc}, process C→E can occur, otherwise, C→E occurs when pH_{surf} exceeds pH_{pzc}.

Table 2. pH_{sol} and pH_{surf} as a Function of α

α	HTiO		HThO		MAG	
	pH_{sol}	pH_{surf}	pH_{sol}	pH_{surf}	pH_{sol}	pH_{surf}
0.1	5.4	5.7	4.1	4.13	3.95	3.83
0.2	4.8	5.39	3.8	3.78	3.6	3.48
0.3	4.3	5.16	3.6	3.55	3.45	3.25
0.4	3.8	4.97	3.4	3.36		
0.5	3.4	4.79				
0.6	2.95	4.61				
0.7	2.4	4.42				
0.8	1.9	4.19				
0.9	1.3	3.89				

Hydrous Thorium Oxide and Magnetite. The sorption isotherms of uranyl ions on these two oxides are very similar. The data (Fig. 2(A)) show that the sorption edge in both the oxides occur at about pH_{soln} 3.9, which is also the pH at which dimeric species, $(UO_2)_2\ (OH)_2^{2+}$, are formed in solution. The surface pH for both the oxides (Table 2) is nearly equal to solution pH. On both the oxides nearly 90% of the surface groups are in the undissociated SOH form (Fig. 2(C)). Thus, in these oxides A→C (Fig. 3) is likely to be the preferred process.

To summarize, the present data indicate that uranyl ions are sorbed on positively charged oxide surface. The sorption edge occurs when pH_{surf} is favorable for the formation of dimer-like or trimer-like structures on the oxide surface. At the sorption edge, undissociated surface hydroxyl groups are present and sorption of uranyl ion involves simultaneous attachment to two adjacent undissociated surface groups. Thus, our data conforms to the basic postulates of the surface hydrolysis model.

Application of the Model to Other Oxides. Haematite: In a recent study of the sorption of uranyl ions on haematite,[22] Ho and Doern correlated the sorption edge at pH ≈5.0 with the marked increase of $(UO_2)_3(OH)_5^+$ species in solution phase at that pH and concluded that the trimer species are the sorbed species on the surface.

Their electrophoretic mobillity data on pure haematite (no uranyl sorption) clearly show that electrophoretic mobility remains constant between pH 3 and 5 and decreases beyond pH 5. This indicates that below pH 5 surface hydroxyl groups are totally in SOH_2^+ form and only after pH 5 free SOH groups become available on the surface. Even at pH 4 the dimeric species of uranyl ions will be present in solution.

The striking feature of the data of Ho and Doern.[22] is that though solution conditions are favorable for the sorption of uranyl ions even at pH 4, the sorption edge on haematite occurs only after pH 5.0 due to nonavailability of free surface hydroxyl groups at $pH<5.0$ thus satisfying one of the prime requirement of the surface hydrolysis model for the sorption of uranyl ions. In this case, reaction A→C (Fig. 3) is likely to be the preferred process.

γ-Alumina: In another study,[23] Mikami et al. have studied the sorption of uranyl ions on γ-alumina by pressure jump technique. γ-Alumina used had a $pK_{a1}^*=6.8$, $pH_{pzc}=8.5$ and sorption edge was at $pH_{soln} \geqslant 4.0$. They also concluded that $(UO_2)_3(OH)_5^+$ species are sorbed on the oxide.

Based on their pK_{a1}^* value, it is found that for all values of α between 0.9—0.1, pH_{surf} is greater than 6.0. This indicates that the surface pH conditions are favorable for the formation of trimer-like species (reaction A→C Fig. 3). The sorption edge occurs in the decreasing part of the ξ-potential curve, which indicates that some SOH_2^+ groups have already deprotonated to give free SOH groups. Though the solution pH conditions are not favorable for trimeric species, the pH_{surf} favors the formation of trimer-like species on the surface (reaction A→C in Fig. 3) as soon as free surface hydroxyl groups become available.

Conclusion

In contrast to the above two oxides, free surface hydroxyl groups are available on MAG and HThO even at pH 3 (Fig. 2(C)), but sorption of uranyl ions on MAG and HThO occrts only when pH_{surf} approaches 4 when dimer-like species can be formed on the surface. Hence it is the characteristics of the oxide surface, (pK_{a1}^*, pH_{surf}) and availability of free SOH groups which govern the sorption of uranyl ions. Sorption is not governed by the presence or absence of hydrolyzed uranyl species in the solution. This point is strikingly demonstrated by HTiO where the sorption edge occurs when uranium is present only as unhydrolyzed uranyl ion in solution.

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