

Sorption properties of oxides IX: Effect of anions on the sorption of uranium (VI) on hydrous oxides

H S MAHAL*, B VENKATARAMANI and
K S VENKATESWARLU**

Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

** Reactor Chemistry Section, Chemistry Division, Chemical Group,
BARC, Bombay 400085, India

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Abstract. Effect of anions such as nitrate, chloride, sulphate and carbonate on the sorption of U(VI), from aqueous solutions on hydrous oxides of Ti(IV), Ce(IV) Zr(IV) and Th(IV) has been studied. The sorption of U(VI) is markedly reduced in the presence of anions, like carbonate, which form strong complexes with UO_2^{2+} in solution. The results are explained in terms of a competition for free UO_2^{2+} between surface hydroxyl groups and ligands (anions) present in solution. The sorption of U(VI) on these hydrous oxides was also studied from a bicarbonate-carbonate mixture. Sorption was less under conditions when tricarbonato complex of U(VI) was formed, but increased at higher pH values (> 9), presumably due to the formation and sorption of hydroxo complexes of U(VI).

Keywords. Quadrivalent hydrous oxides; U(VI) sorption; competitive complexation ; U(VI) carbonato complex.

1. Introduction

Sorption of U(VI) from nitrate solution on hydrous oxides of quadrivalent Ti, Ce, Zr and Th (represented as TiO_2 , CeO_2 , ZrO_2 and ThO_2) was shown to depend on the nature of the hydrous oxides, that is, the acidity of the hydrous oxide (Mahal *et al* 1981). It was shown that sorption process involved uranyl ions in the case of hydrous TiO_2 and CeO_2 and electrolyte sorption predominated in the case of less acidic hydrous oxides of Zr and Th. The effect of several anions on the sorption of U(VI) on the above hydrous oxides was investigated. The anions chosen for these studies were nitrate, chloride, sulphate and carbonate since they have varying abilities to form complexes with uranyl ion in solution. The results of these studies are presented in this paper.

2. Experimental

Preparation and characterisation of the hydrous oxides are described in detail elsewhere (Mahal *et al* 1981). Hydrous oxides precipitated using NH_4OH are

* To whom all correspondence should be sent.

designated $\text{Me}_2\text{O}_2(\text{NH})$ and those prepared using NaOH , $\text{MeO}_2(\text{Na})$, where $\text{Me} = \text{Ti, Ce, Zr or Th}$. Hydrrous TiO_2 prepared by homogeneous precipitation is designated $\text{TiO}_2(\text{hp})$.

Sorption experiments were carried out at room temperature (300 K) using 0.3g of the oxide and 25 ml of the solution containing known amounts of uranyl ion as respective salts. The mixture was kept in a mechanical shaker for 24 hr to ensure complete equilibration. Uranyl ion in solution was estimated spectrophotometrically by the peroxide method at 400 nm (Sandell 1959).

Tetrasodium tricarbonato uranilate (tr碳酸盐 complex) was prepared by mixing uranyl nitrate and sodium carbonate solution and precipitating the tr碳酸盐 complex formed by adding excess of methanol and washing the resultant precipitate with methanol. An aqueous solution of the tr碳酸盐 complex thus prepared gave a spectrum which was identical with that reported in literature (Scanlan 1977).

The pH of the uranyl salt solutions was in the region of 3.5; in the case of tr碳酸盐 complex the solution pH was around 9.

Sorption of U(VI) was also studied from a mixture of NaHCO_3 and Na_2CO_3 keeping the concentration of $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3 \sim 0.2 \text{ N}$. Initial U(VI) concentration in these solutions was 0.01 M and was added as a nitrate. The initial pH of these solutions varied between 7.3 and 10.7.

3. Results and discussion

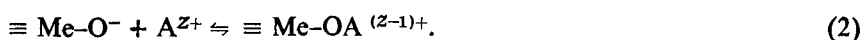
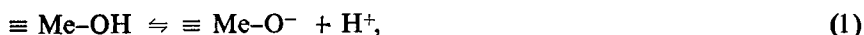
The uptake of U(VI) by hydrrous oxides from a 0.01 M solution of different (uranyl) salts is given in table 1. The uptake decreased in the series: nitrate > chloride > sulphate > tr碳酸盐, with the exception of sulphate where in some cases slightly increased sorption was noted. The reverse of the above sequence parallels the ability of the anions to complex uranyl ion (Chernyaev 1966, p. 515).

Table 1. Sorption of U(VI) on hydrrous oxides from different uranyl salt solutions (Initial $\text{UO}_2^{2+} = 0.01 \text{ M}$).

Hydrrous oxide	Salts used \rightarrow	Uptake of uranium, mg U/g of oxide			
		Nitrate	Chloride	Sulphate	Tr碳酸盐
$\text{TiO}_2(\text{hp})$		205	180	185	107
$\text{TiO}_2(\text{NH})$		158	126	135	83
$\text{TiO}_2(\text{Na})$		195	164	143	64
$\text{CeO}_2(\text{NH})$		75	39	100	42
$\text{CeO}_2(\text{Na})$		104	70	79	60
$\text{ZrO}_2(\text{NH})$		48	30	71	31
$\text{ZrO}_2(\text{Na})$		79	35	88	42
$\text{ThO}_2(\text{NH})$		13	6	23	4
$\text{ThO}_2(\text{Na})$		38	23	21	14

This indicates that the sorption of U(VI) decreases with increase in the ability of the anions to complex uranyl ion in solution. The higher sorption in the case of sulphate salts could be because sulphate ion itself was being sorbed (resulting in electrolyte sorption, as uranyl sulphate). It is generally known that the quadrivalent ions (Ti^{4+} , Ce^{4+} , Zr^{4+} and Th^{4+}) have a strong affinity for sulphate ions and forms sulphate complexes. IR spectra of the hydrous oxide equilibrated with uranyl sulphate showed absorption characteristic of sulphate ions, thus confirming the above view that sulphate ions are being sorbed.

The observed results on the effect of anions on the sorption of uranium could be explained with the help of surface complex approach proposed to describe the sorption of metal ions on hydrous oxides (Stumm *et al* 1976). If the surface hydroxyl groups of the hydrous oxide, MeO_2 , is represented as $\equiv \text{Me-OH}$, then the sorption of metal ion A^{z+} can be written as :



It has been postulated (Stumm *et al* 1976) that $\equiv \text{Me-O}^-$ acts as a ligand and complexes sorbing metal ion, A^{z+} , in a way similar to the complexation of A^{z+} in solution by ligands. In situations when anions (L^-) capable of forming complexes with A^{z+} , are present in solution, as



there is a competition for the free A^{z+} between the surface ($\equiv \text{Me-O}^-$ groups) and the ligand (L^-) present in the solution (Theis and Richter 1980).

In the present investigation the hydrous oxides have varying acidities (Fuller, 1971) that is, the reaction represented by (1) occurs to varying degrees in each of the hydrous oxides and also the electron donor properties of $\equiv \text{Me-O}^-$ of the oxides vary, decreasing from TiO_2 to ThO_2 . In solution the anions having varying abilities to complex uranyl ion are present. For a given hydrous oxide the sorption decreases as the tendency of the anion to complex uranyl ion increases (from nitrate to carbonate), along the row in table 1. For a given anion in solution, the sorption decreases as the electron donor property of the $\equiv \text{Me-O}^-$ group or the acidity of the hydrous oxide decreases, down the column in table 1. The differences in the sorption of hydrous oxides prepared using NH_4OH and NaOH are due to the amount of hydroxyl groups present in the hydrous oxide, which depends on the alkali used for precipitation (Mahal *et al* 1981 ; Venkataramani *et al* 1978).

The above explanation is supported by the IR spectra of the hydrous oxides equilibrated with different uranyl salts. The vibration frequencies of UO_2^{2+} group observed in pure salts were 945, 943, 930 and 853 cm^{-1} , respectively, for nitrate, chloride, sulphate and tricarbonatate and the corresponding values, for hydrous TiO_2 were 900, 915, 910 and 895 cm^{-1} . A lowering of the vibration frequency of UO_2^{2+} group indicates an increase in the donor strength of the ligand (Chernyaev 1966, p. 362). In the case of hydrous TiO_2 (all the three preparations), the vibration frequency of UO_2^{2+} group decreased as a result of sorption (see above). This shows that the complexation at the surface due to $\equiv \text{Me-O}^-$ group is stronger

than with anions present in solution. In the case of tricarbonat complex, the shift in the vibration frequency of UO_2^{2+} is not as pronounced as in other salts. This shows that the carbonate ion forms a much stronger complex with UO_2^{2+} in solution than those formed by $\equiv\text{Me}-\text{O}^-$ groups at the surface.

The absorption of UO_2^{2+} in the IR spectra were diffuse in other hydrous oxides. The shift in the vibration frequencies of UO_2^{2+} were, however, marginal for other hydrous oxides as compared to hydrous TiO_2 . It is clear that among the quadri-valent metal hydrous oxides investigated, UO_2^{2+} forms a stronger bond with the surface hydroxyl groups of hydrous TiO_2 in contrast to other oxides.

Sorption of U(VI) from solutions containing a mixture of bicarbonate and carbonate (at a total concentration of $\sim 0.2\text{ N}$) on different hydrous oxides is given in table 2. In general, the amount of uranium sorbed is much lower than that from a solution of the salt of tricarbonat complex (table 1). In solutions containing a mixture of bicarbonate and carbonate, the concept of competitive complexation of the free metal ion, referred to earlier (Theis and Richter 1980), between the surface $\equiv\text{Me}-\text{O}^-$ groups (equation (2)) and the carbonate ions in solution (equation (3)) is more valid than for the aqueous solution of the salt

Table 2. Sorption of U(VI) on hydrous oxides from bicarbonate-carbonate mixture (Initial $\text{UO}_2^{2+} = 0.01\text{ M}$).

Initial CO_3^{2-} (N)	0.0	0.01	0.05	0.06	0.08	0.11	0.15
Initial HCO_3^- (N)	0.22	0.2	0.16	0.15	0.12	0.09	0.04
Initial pH	7.35	8.2	9.0	9.2	9.4	9.8	10.7
Hydrous oxide	Uptake of uranium, mg U/g of oxide						
TiO_2 (hp)	25 (8.3)	22 (8.4)	14 (8.7)	14 (8.9)	14 (9.1)	14 (9.5)	25 (9.95)
TiO_2 (NH)	13 (8.35)	11 (8.75)	11 (8.9)	13 (9.1)	13 (9.3)	13 (9.65)	25 (10.15)
TiO_2 (Na)	9 (8.4)	2 (8.7)	2 (8.9)	2 (9.1)	2 (9.3)	2 (9.7)	22 (10.1)
CeO_2 (NH)	1 (8.6)	1 (8.8)	1 (9.0)	1 (9.2)	2 (9.4)	2 (9.7)	22 (10.3)
CeO_2 (Na)	*	*	*	3 (9.2)	3 (9.4)	5 (9.7)	30 (10.3)
ZrO_2 (NH)	*	*	*	*	*	2 (9.8)	12 (10.4)
ZrO_2 (Na)	*	*	*	*	*	*	6 (10.4)
ThO_2 (NH)	*	*	*	*	*	*	*
ThO_2 (Na)	*	*	*	*	*	*	*

* uptake negligible. Values in parenthesis refer to equilibrium pH.

of tricarbonat complex (table 1). In the case of bicarbonate-carbonate mixtures the ligand capable of forming a (strong and) soluble complex (that is, CO_3^{2-}) is present to a greater extent than in the aqueous solution containing the salt of the tricarbonat complex alone. The reduced sorption of uranium from as mixture of bicarbonate and carbonate (table 2) is due to the extensive complexation of U(VI) in solution by the CO_3^{2-} .

The sorption of U(VI) was higher when the initial pH was below 8.0, was minimum and nearly constant in the pH range 8.2–9.8, and increased when the pH was above 10.0 (table 2). The pH, bicarbonate and carbonate content of the equilibrated solution were determined for all hydrous oxides. The equilibrium pH values are given in table 2 and the bicarbonate and carbonate concentrations for $\text{TiO}_2(\text{hp})$, $\text{TiO}_2(\text{NH})$, $\text{TiO}_2(\text{Na})$ and $\text{CeO}_2(\text{NH})$ are presented in table 3. There was a reduction in the total alkalinity of the solution. The reduction was significant in $\text{TiO}_2(\text{hp})$ and $\text{CeO}_2(\text{NH})$. The decrease in the alkalinity indicates the release of H^+ ion, which either could be from the hydrous oxide (see equation 1) or, be a result of hydrolysis of UO_2^{2+} ion.

Based on the stability constant values of different U(VI) species, it has been estimated (Yamashita *et al* 1980), that in the pH region 8 to 10, both hydrolysed species and carbonate complexes of UO_2^{2+} coexist, the latter predominating up to a pH of 9 (Bezborodov *et al* 1976). It is also known that mixed hydroxo carbonates of UO_2^{2+} are formed at higher pH values or in weakly acidic solutions (Chernyaev 1966, chapter 2; Ciavatta *et al* 1979).

Table 3. Equilibrium concentrations of bicarbonate-carbonate mixtures for hydrous oxides of Ti and Ce.

Initial CO_3^{2-} (N)	0.0	0.01	0.05	0.06	0.08	0.11	0.15
Initial HCO_3^- (N)	0.22	0.20	0.16	0.15	0.12	0.09	0.04
Equilibrium concentration, N							
$\text{TiO}_2(\text{hp})$							
CO_3^{2-}	0.016	0.016	0.023	0.034	0.045	0.070	0.095
HCO_3^-	0.182	0.175	0.164	0.151	0.136	0.108	0.079
$\text{TiO}_2(\text{NH})$							
CO_3^{2-}	0.029	0.036	0.047	0.059	0.070	0.099	0.131
HCO_3^-	0.181	0.171	0.156	0.142	0.128	0.095	0.065
$\text{TiO}_2(\text{Na})$							
CO_3^{2-}	0.018	0.032	0.043	0.059	0.07	0.099	0.131
HCO_3^-	0.196	0.181	0.165	0.147	0.133	0.100	0.062
$\text{CeO}_2(\text{NH})$							
CO_3^{2-}	0.025	0.027	0.032	0.050	0.06	0.088	0.091
HCO_3^-	0.170	0.165	0.157	0.139	0.128	0.093	0.059

The higher sorption of U(VI) in low carbonate solutions (up to 0.01 N) (table 2) could be due to the presence to a lesser extent of tricarbonat complex, the sorption of U(VI) probably occurring with the breaking of the carbonate complex, releasing carbonate into the solution (table 3) and thus increasing the pH of the equilibrated solution (table 2). The nearly constant and minimum sorption could be explained as due to the predominance of tricarbonat complex in the pH range 9-10. The increased uranium sorption at carbonate concentration above 0.1N is probably due to the sorption of hydrolysed species of UO_2^{2+} (Yamashita *et al* 1980).

Different mechanisms have been proposed to explain the sorption of uranium on hydrous oxides from tricarbonat complex. It is proposed that the tricarbonat complex breaks down and the uranyl ion is sorbed on the hydrous oxides (Davies *et al* 1965; Yamashita *et al* 1980). Another mechanism involves the partial breaking of the tricarbonat complex and the sorption of a dicarbonat complex on the oxide (Jaffrezic-Renault *et al* 1980). Our results indicate that the sorption of uranium from carbonate solutions involves only a partial breaking of the tricarbonat complex. However, the data obtained in the present study (tables 2 and 3) could not be fitted into suitable mathematical relations describing the sorption process, as has been attempted by others (Davies *et al* 1965; Jaffrezic-Renault *et al* 1980). This is because, apart from the sorption of U(VI), other reactions (such as hydrolysis) taking place in solution also have altered the carbonate-bicarbonat equilibrium.

4. Conclusion

There is a growing interest in selecting a sorbent for the recovery of uranium from sea water (Davies *et al* 1965; Jaffrezic-Renault *et al* 1980; Schwochau *et al* 1977; Yamashita *et al* 1980). Uranium is present in trace levels (about 3 ppb) in sea water as tricarbonat complex. The present study indicates that the $\equiv\text{Me}-\text{O}^-$ groups of the hydrous oxides do not possess enough electron donor properties to compete with carbonate ion to complex uranyl ion, so that uranium could be selectively sorbed on hydrous oxides. In addition under actual sea water conditions, the alkaline earth metal ions, which are present in much larger amounts, would compete for the sorption sites on hydrous oxides and still reduce the sorption of uranium. If hydrous oxides are to be used on a large scale for the recovery of uranium from sea water, their sorption capabilities should be modified and improved by orders of magnitude by suitable preparative techniques.

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