Course Name: Nuclear and Radiochemistry
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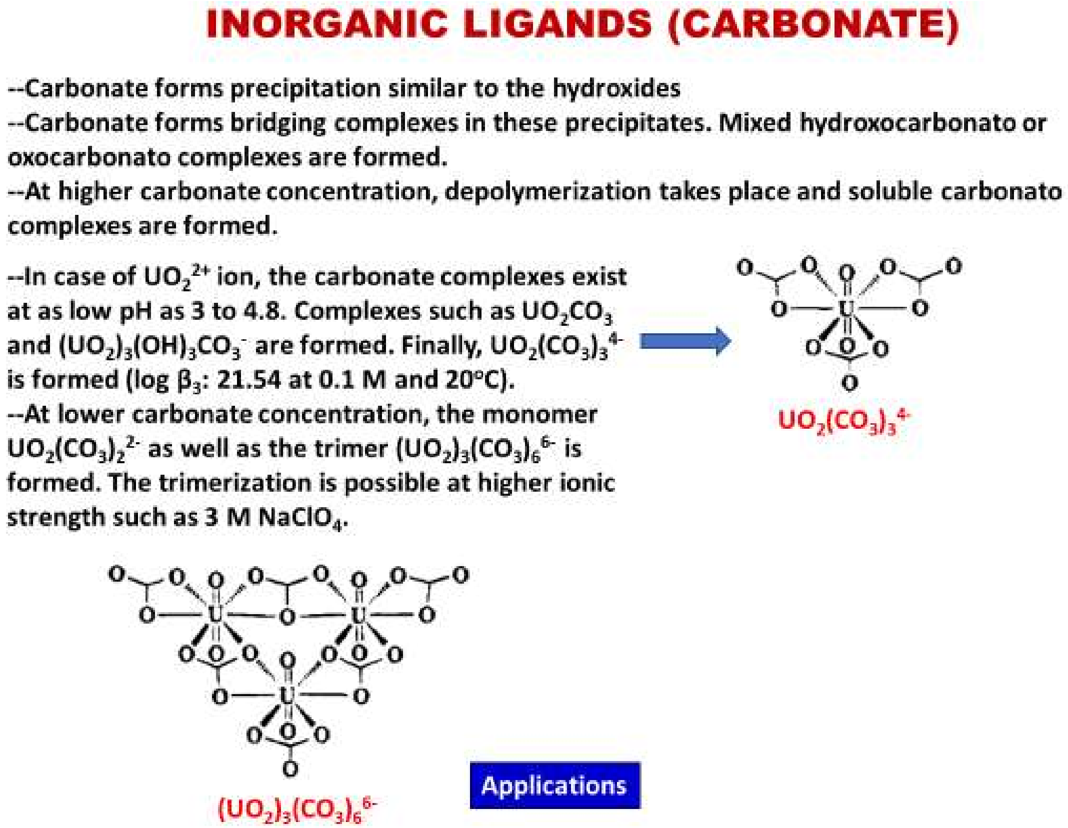
Week – 10
Lecture - 47

So, we were discussing the complexation of actinide ions with inorganic ligands. We have already covered inorganic ligands like fluoride, bromide, chloride and also nitrate. The complexation of hydroxide, I have not discussed, but that will be discussed in a separate lecture. So, the hydrolysis of actinides will be covered and followed by its migration in environment. That will be a separate lecture. Now, coming to the remaining inorganic ligands of relevance are carbonate and phosphate.



INORGANIC LIGANDS (CARBONATE)

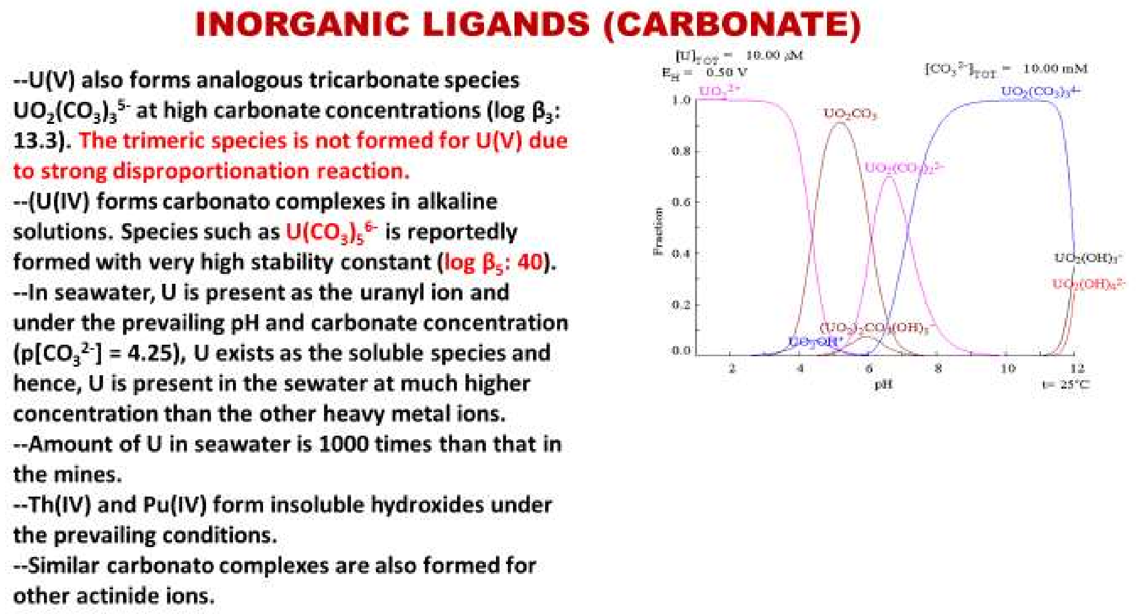
--Carbonate forms precipitation similar to the hydroxides
--Carbonate forms bridging complexes in these precipitates. Mixed hydroxocarbonato or oxocarbonato complexes are formed.
--At higher carbonate concentration, depolymerization takes place and soluble carbonato complexes are formed.

--In case of UO_2^{2+} ion, the carbonate complexes exist at as low pH as 3 to 4.8. Complexes such as UO_2CO_3 and $(UO_2)_3(OH)_3CO_3^-$ are formed. Finally, $UO_2(CO_3)_3^{4-}$ is formed (log β_3: 21.54 at 0.1 M and 20°C).
--At lower carbonate concentration, the monomer $UO_2(CO_3)_2^{2-}$ as well as the trimer $(UO_2)_3(CO_3)_6^{6-}$ is formed. The trimerization is possible at higher ionic strength such as 3 M $NaClO_4$.

$UO_2(CO_3)_3^{4-}$

$(UO_2)_3(CO_3)_6^{6-}$

So now, these carbonates are very, very important because of the fact that it forms very strong complexes with some of the actinides, particularly the uranyl ion or the actinyl ion. So, the carbonates form precipitation similar to the hydroxide. There are mixed hydroxy as well as carbonato species formed, which I will be showing in the speciation diagram of uranium(VI) ion or the uranyl ion. The carbonates form bridging complexes in these precipitates and at higher carbonate concentrations, we can have depolymerization and we have the soluble carbonato complexes. In case of the uranyl ion, the carbonato complexes exist at as low as pH 3 to 4.8. The different types of carbonate complexes are formed such as UO_2CO_3 and trimeric species that is, $(UO_2)_3(OH)_3(CO_3)^-$ type of species are formed. Finally, you get the soluble complex, that is, the monomeric soluble complex, $UO_2(CO_3)_3^{4-}$ and the structure of this complex is given here. You see that in this case, all the three carbonates are forming bidentate coordination with the uranyl ion and they are in the equatorial plane, while the oxygens of the uranyl ion are perpendicular to this plane and are termed as the axial oxygen atoms. At lower carbonate concentrations, the monomer, $(UO_2)(CO_3)_2^{2-}$, as well as the trimeric, $(UO_2)_3(CO_3)_6^{6-}$ type species are formed. Now this structure of this trimeric carbonate species is given here. You can see that three carbonates are independently coordinating to the uranyl ions. So they are bound, binding to the uranium atom in the equatorial plane, which they have in the bidentate manner, while three other carbonates, they are forming bridging complexes. The bonds are bridging type. You can see that one of the oxygen of this carbonate is actually shared by this uranium as well as this uranium and the other two oxygens of the carbonate are binding to the uranium in the monodentated fashion. So same is there for all the three uranium atoms. Now the stability constants of these carbonate complexes are very, very high. As we see that the tris carbonate complex of monomeric uranyl ion is very high, the log beta 3 value is 21.54 at 0.1 M and 20 degrees Celsius. Now the application of this carbonate complexation that we will be discussing separately. The uranium leaching from the ores by the alkaline leaching process. So in that case, you have these carbonate complexes which are making the soluble complexes from the ores and this is coming out of the solid ore phase. Now as I was discussing the speciation diagram of uranyl ion, as you can see here, given as a function of pH. You see that at lower pH, there is a possibility of the carbonate not being stable, but at higher pH, the carbonate is stable and it at higher pH also because of the presence of the hydroxide ion, you have hydroxide complexes of uranyl ion. So at very low pH, as I have already mentioned, pH less than 4, you get the only uranyl ion and at higher pH, you have the uranyl hydroxide complexes and in the presence of carbonate, you also have UO_2CO_3 and also $UO_2(CO_3)_2^{2-}$ and at pH 10, (more specifically) in the pH 8 to 10 region, you have this $UO_2(CO_3)_3^{4-}$ type of species which is a soluble species and beyond that you have the hydroxide species as indicated here.



INORGANIC LIGANDS (CARBONATE)

--U(V) also forms analogous tricarbonate species $UO_2(CO_3)_3^{5-}$ at high carbonate concentrations (log β_3: 13.3). The trimeric species is not formed for U(V) due to strong disproportionation reaction.

--(U(IV) forms carbonato complexes in alkaline solutions. Species such as $U(CO_3)_5^{6-}$ is reportedly formed with very high stability constant (log β_5: 40).

--In seawater, U is present as the uranyl ion and under the prevailing pH and carbonate concentration ($p[CO_3^{2-}]$ = 4.25), U exists as the soluble species and hence, U is present in the sewater at much higher concentration than the other heavy metal ions.

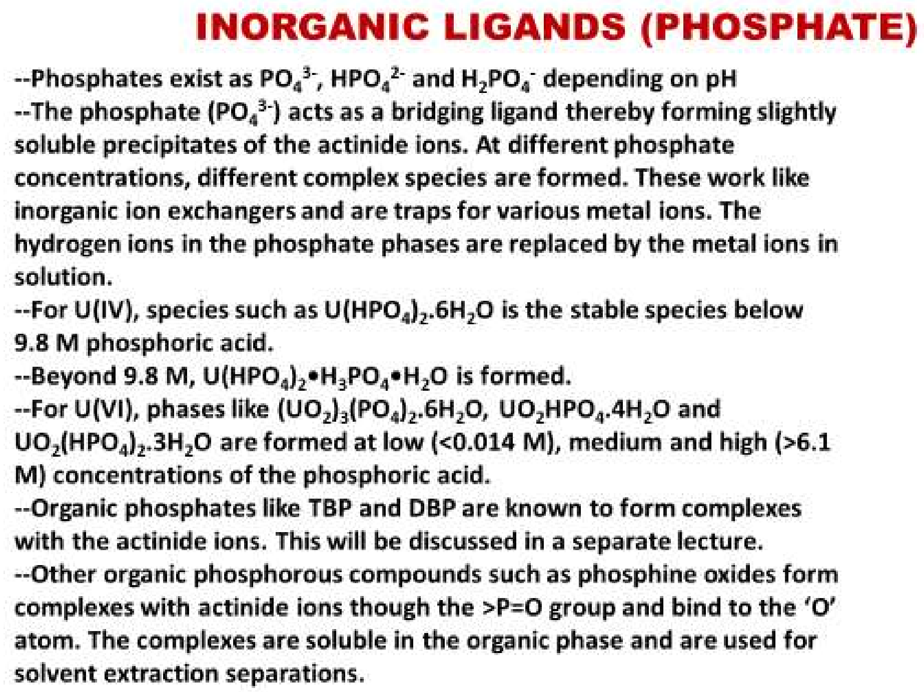
--Amount of U in seawater is 1000 times than that in the mines.

--Th(IV) and Pu(IV) form insoluble hydroxides under the prevailing conditions.

--Similar carbonato complexes are also formed for other actinide ions.

Now U(V) also forms the analogous carbonate species similar to what I have shown for the U(VI), i.e., the uranyl ion. So, that is $UO_2(CO_3)_3^{5-}$ and this type of species have formed with the uranyl (plus 5) species, that is UO_2^+ ionic species, but then this occurs only at a very high carbonate concentration, that is the log β_3 value is around 13.3. Nevertheless, this is much lower than that has been reported with the U(VI), that is UO_2^{2+} ion, so it is more than 7 orders of magnitude lower and the trimeric species is not formed for the U(V) because of the strong disproportion reaction prevalent in case of the U(V).

U(IV) also forms carbonato complexes in alkaline solutions. Species such as $U(CO_3)_5^{6-}$ is reportedly formed, which has a very (very) high stability constant log β_5 value is around 40. One interesting consequence of this carbonate complexation of uranium is that in seawater, uranium is present as the carbonate complexes in its soluble form. As you know that seawater pH conditions and what is the carbonate concentration prevailing under the seawater condition, that is the $p[CO_3^{2-}]$ around 4.25. In this case, uranium exists as a soluble species and hence uranium is present in the seawater at a much higher concentration than the other heavy metal ions like thorium. So, the amount of uranium in seawater is around 4 gigatons and it is about 1000 times higher than that in the mines. Th(IV) and Pu(IV) can also form insoluble hydroxides and if the carbonate concentration is very high, they can form the soluble carbonate species but for that you need very (very) high concentrations of carbonate which is not available under the seawater conditions. That is why thorium(IV) and plutonium(IV), if it is there in the seawater, that is due to discharging of some plutonium activity into the seawater, they are forming insoluble precipitates under the prevailing conditions. Other carbonate complexes are also formed for other actinide ions but I will not be discussing those here.

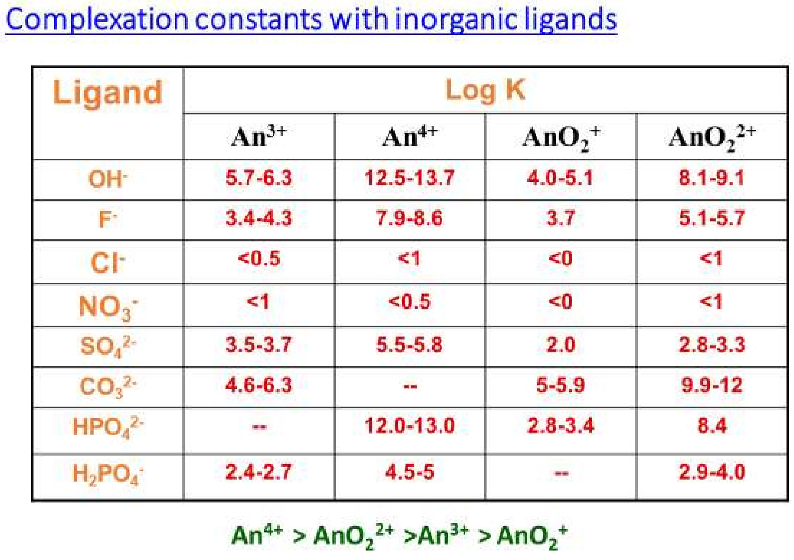


INORGANIC LIGANDS (PHOSPHATE)

--Phosphates exist as PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ depending on pH
--The phosphate (PO_4^{3-}) acts as a bridging ligand thereby forming slightly soluble precipitates of the actinide ions. At different phosphate concentrations, different complex species are formed. These work like inorganic ion exchangers and are traps for various metal ions. The hydrogen ions in the phosphate phases are replaced by the metal ions in solution.
--For U(IV), species such as $U(HPO_4)_2.6H_2O$ is the stable species below 9.8 M phosphoric acid.
--Beyond 9.8 M, $U(HPO_4)_2{\bullet}H_3PO_4{\bullet}H_2O$ is formed.
--For U(VI), phases like $(UO_2)_3(PO_4)_2.6H_2O$, $UO_2HPO_4.4H_2O$ and $UO_2(HPO_4)_2.3H_2O$ are formed at low (<0.014 M), medium and high (>6.1 M) concentrations of the phosphoric acid.
--Organic phosphates like TBP and DBP are known to form complexes with the actinide ions. This will be discussed in a separate lecture.
--Other organic phosphorous compounds such as phosphine oxides form complexes with actinide ions though the >P=O group and bind to the 'O' atom. The complexes are soluble in the organic phase and are used for solvent extraction separations.

Another important inorganic complexing agent is the phosphate. The phosphates exist as different species like PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$. This depends on the phosphate concentration as well as on the pH value. The phosphate that is PO_4^{3-}, can act as a bridging ligand and thereby forming slightly soluble precipitates of the actinide ions. At different phosphate concentrations, you can find different actinide complex species and these complexes, they work like inorganic ion exchangers. You may be knowing some of these tetra-valent phosphates like Ce(IV)phosphate and Zr(IV) phosphates. They are used as inorganic ion exchangers. So, similarly, the U(IV) phosphates can be used as inorganic ion exchangers and in the natural environment, the U(IV) phosphate complexes are present in the rocks and they can act as inorganic ion exchangers and trap different metal ions from aquatic conditions. Now the U(IV) species like $U(HPO_4)_2.6H_2O$ is a stable species below 9.8 M molar phosphoric acid and beyond 9.8 molar concentration of phosphoric acid, you have the species like $U(HPO_4)_2.H_3PO_4.H_2O$ type of species are formed. For U(VI), phases like $(UO_2)_3(PO_4)_2.6H_2O$, $UO_2(HPO_4).4H_2O$ and $UO_2(HPO_4)_2.3H_2O$ are formed at low concentrations of phosphoric acid, low means (I mean) here less than 0.014 M and medium and high, that is greater than 6.1 M concentrations of phosphoric acid. Now when we are talking about this phosphoric acid and the complexation of phosphate with a uranyl ion, there are some applications like the uranium estimation by the Davis Gray method where actually there is a reversal of the U(VI) - U(IV) couple and Fe(III) - Fe(II) couple taking place and that is the key of this estimation method, that is by the Davis Gray method. And also in the phosphoric acid medium, uranium which is present in the wet process phosphoric acid, (a secondary source of uranium) around 100 to 150 ppm of uranium is present and from this medium also uranium separation is done. This is another application of the phosphate complexes for uranium.

Another application is the organic phosphates. (Up to) this what I was discussing are the inorganic phosphates. Now the organic phosphates, they are very important and it will be discussed subsequently where the extractants or ligands like tributyphosphate, that is TBP and dibutyphosphoric acid, that is DBP, they are known to form complexes with the actinide ions and as will be discussed later, this is the mainstay of the PUREX process where the complexation of uranium(VI), that is the uranyl ion and plutonium(IV) takes place with TBP and it is extracted into the organic phase leaving behind all the fission products and all trans plutonium elements. Now other organic phosphorus compounds such as phosphine oxides, they form complexes with actinide ions through the phosphoryl group and bind to the uranium atom. So, the complexes are soluble in the organic phase and that is how the metal ion extraction is done from a variety of mediums. Now the application of this is the extraction of uranium from the wet process phosphoric acid where a mixture of di-2-ethyl-hexyl phosphoric acid, that is DEHPA and tri-octyl phosphine oxide, that is TOPO, they are used as the extractant mixture. Now, I will summarize the complexation of these inorganic ligands with actinides. Now this hydroxide ion I have not covered here, but in a detailed manner it will be covered in a subsequent lecture where the hydrolysis of actinides will be discussed.



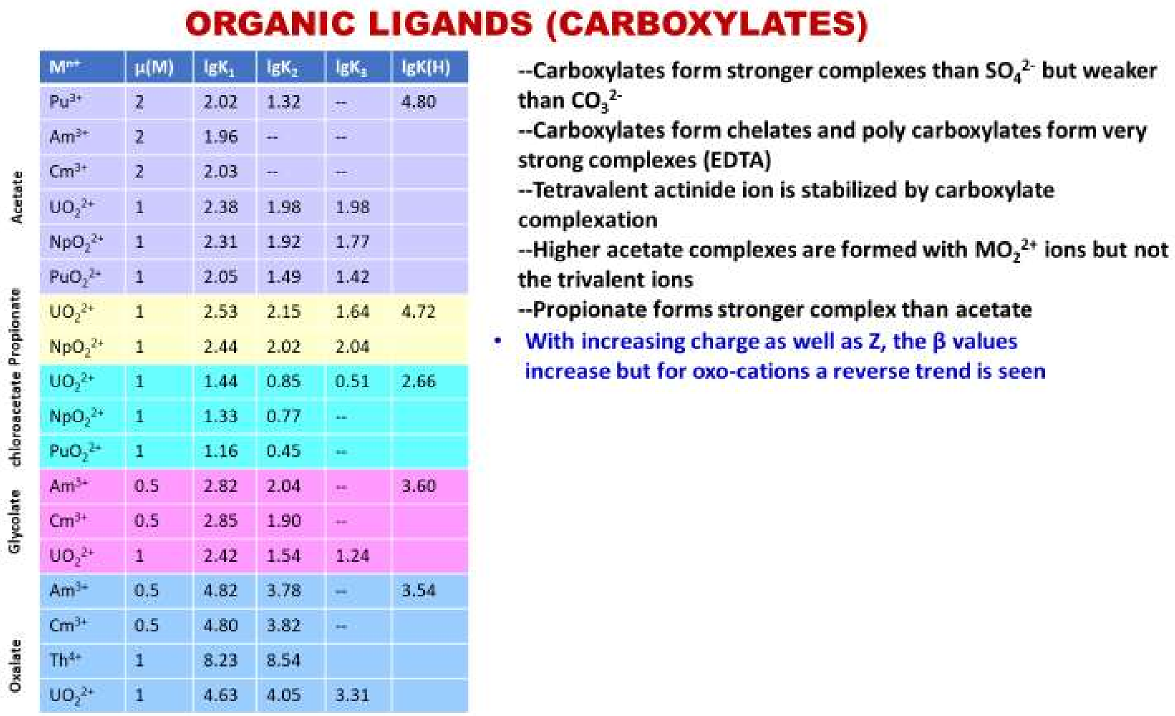
Complexation constants with inorganic ligands

Ligand	Log K			
	An^{3+}	An^{4+}	AnO_2^{+}	AnO_2^{2+}
OH^-	5.7-6.3	12.5-13.7	4.0-5.1	8.1-9.1
F^-	3.4-4.3	7.9-8.6	3.7	5.1-5.7
Cl^-	<0.5	<1	<0	<1
NO_3^-	<1	<0.5	<0	<1
SO_4^{2-}	3.5-3.7	5.5-5.8	2.0	2.8-3.3
CO_3^{2-}	4.6-6.3	--	5-5.9	9.9-12
HPO_4^{2-}	--	12.0-13.0	2.8-3.4	8.4
$H_2PO_4^-$	2.4-2.7	4.5-5	--	2.9-4.0

$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$

Now the fluoride, chloride, etc I have already discussed. Now you can see here I have given a range of their complex formation constants, that is for the trivalent actinides, I have noted as An^{3+}.

There the fluoride complex formation constants are in a range of 3 to 4 and that of chloride are less than 0.5, nitrate less than 1, sulfates 3.5 to 3.7, carbonates 4.6 to 6.3 and phosphate, that is the dihydrogen phosphate 2.4 to 2.7. Similarly, for the actinide 4 plus ion, that is An^{4+}, the complexation constants are higher for each of these complexing agents as you can see. Now coming to the pentavalent actinyl ion, that is AnO_2^{+}, the complex formation constants are in between that of An^{3+} and An^{4+} for certain cases and in certain other cases like nitrate and sulfate, they become even less than that of the trivalent ion. Now for the actinyl (6 plus) ion, that is AnO_2^{2+}, the complex formation constants, mostly they lie in between that of the +3 as well as +4 actinide ions.



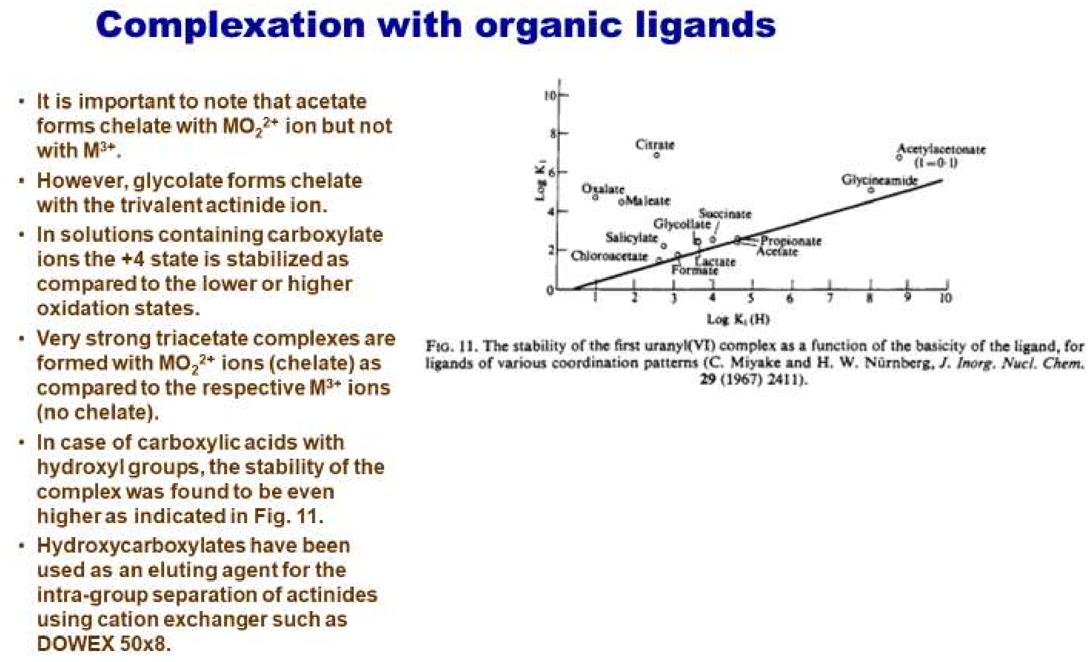
ORGANIC LIGANDS (CARBOXYLATES)

	M^{n+}	μ(M)	lgK_1	lgK_2	lgK_3	lgK(H)
Acetate	Pu^{3+}	2	2.02	1.32	--	4.80
	Am^{3+}	2	1.96	--	--	
	Cm^{3+}	2	2.03	--	--	
	UO_2^{2+}	1	2.38	1.98	1.98	
	NpO_2^{2+}	1	2.31	1.92	1.77	
	PuO_2^{2+}	1	2.05	1.49	1.42	
Propionate	UO_2^{2+}	1	2.53	2.15	1.64	4.72
	NpO_2^{2+}	1	2.44	2.02	2.04	
chloroacetate	UO_2^{2+}	1	1.44	0.85	0.51	2.66
	NpO_2^{2+}	1	1.33	0.77	--	
	PuO_2^{2+}	1	1.16	0.45	--	
Glycolate	Am^{3+}	0.5	2.82	2.04	--	3.60
	Cm^{3+}	0.5	2.85	1.90	--	
	UO_2^{2+}	1	2.42	1.54	1.24	
Oxalate	Am^{3+}	0.5	4.82	3.78	--	3.54
	Cm^{3+}	0.5	4.80	3.82	--	
	Th^{4+}	1	8.23	8.54		
	UO_2^{2+}	1	4.63	4.05	3.31	

--Carboxylates form stronger complexes than SO_4^{2-} but weaker than CO_3^{2-}
--Carboxylates form chelates and poly carboxylates form very strong complexes (EDTA)
--Tetravalent actinide ion is stabilized by carboxylate complexation
--Higher acetate complexes are formed with MO_2^{2+} ions but not the trivalent ions
--Propionate forms stronger complex than acetate

- **With increasing charge as well as Z, the β values increase but for oxo-cations a reverse trend is seen**

Now I come to the organic ligands. The first thing I would like to cover, the carboxylate ligands. These carboxylates, they are actually having a single charge like acetate, which is a dissociated form of the acetic acid and it forms stronger complexes than sulfate, which is having two negative charges but weaker than that of carbonate, which is having 2 minus charges as well. I have given some complex formation constants of the actinide ions in this table. You can see here the ionic strength values are given in the second column and the log K values for the first complex, second complex as well as the third complex formation for the successive complex formation values are given here. Now for comparison purpose, the log K_H values also are given of the ligand. That is the proton association constant of the ligand is given. So that is how we can compare the complexation of the actinides with the ligand basicity. Now coming to the trivalent actinide ions like Pu^{3+}, Am^{3+}, Cm^{3+}, Bk^{3+}, and Cf^{3+}, with the acetate ion. You can see there is a steady increase in the complex formation constants when you go in this series. That is, with increasing Z, the complex formation constants increase. But there is also an ionic strength effect. But that is not that significant when you have this complex formation constants of Am^{3+}, with 0.5 M ionic strength. You have the acetate complex formation constant log K_1 is 1.99. And at 2 M ionic strength, the log K_1 is 1.96. So that is very marginally (it is) decreasing. And same also is there for the Cm^{3+}. Now coming to the actinyl ions, the 3 actinyl ions are given here are the uranyl, neptunyl, plutonyl ions, all in their plus 6 oxidation states. And you can see that the complex formation constant of neptunyl ion is somewhat lower than that of uranyl ion. And then for plutonyl ion, it increases as this has been the trend as discussed previously also with other complexing agents. Now for the plutonyl ion, there is ionic strength, there is some difference as what we have been studying for uranyl as well as neptunyl ions, that is 1 M ionic strength. However, as I mentioned, the ionic strength effect is not that much significant. So, you can say that going from uranyl to neptunyl, the log K value decreases. And from neptunyl to plutonyl, the log K value increases. Coming to the propionate, compared to the acetate, it gives slightly higher complex formation constants. For propionate, I have the values here for the uranyl and neptunyl ions only. You can see that for 1 M ionic strength, the complex formation constants are higher for propionate as compared to that with acetate that is for uranyl, it was 2.38 (acetate) at 1 molar ionic strength and it has been increased to 2.53 (propionate). Similarly, for the neptunyl ion, the log K value was 2.31 for acetate, which increased to 2.44 for the propionate. So that means by increasing the carbon chain length, the complex formation constant has slightly increased, that is because of the relaxation of the chelate ring in this case. And also, when we have the monochloroacetate, that case you have actually the log K_H values lower than that of acetate, that is because of the chlorine atom, which is an electron withdrawing group. And because of that, the complex formation constants also are becoming slightly lower. You can see from 2.38 for acetate, with monochloroacetate, it has become 1.44 for (the) uranyl ion under the same condition of ionic strength. Now the log K_2 values, they become less as it is expected because after the first complexation, that is the second complex formation constant becomes always less because of the statistical factor and also because some part of the metal ion charge is also neutralized by the first ligand.

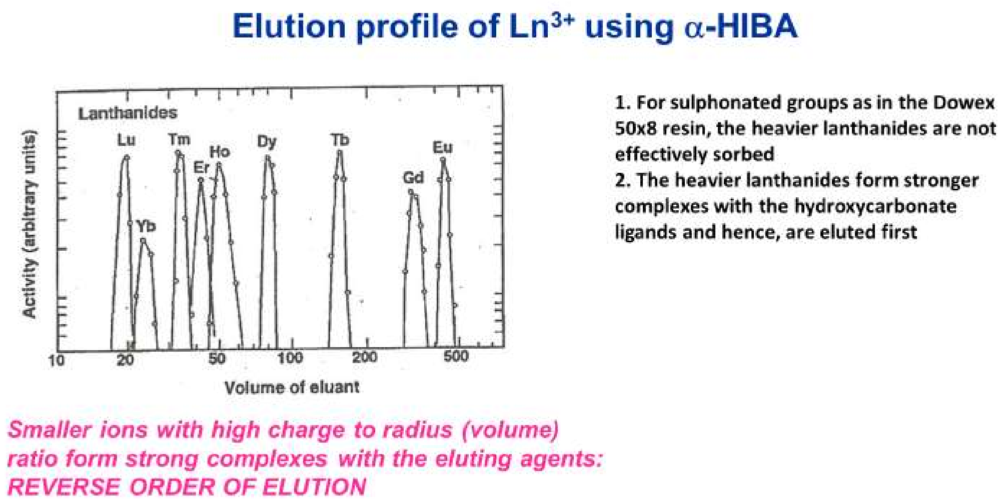


Complexation with organic ligands

- It is important to note that acetate forms chelate with MO_2^{2+} ion but not with M^{3+}.
- However, glycolate forms chelate with the trivalent actinide ion.
- In solutions containing carboxylate ions the +4 state is stabilized as compared to the lower or higher oxidation states.
- Very strong triacetate complexes are formed with MO_2^{2+} ions (chelate) as compared to the respective M^{3+} ions (no chelate).
- In case of carboxylic acids with hydroxyl groups, the stability of the complex was found to be even higher as indicated in Fig. 11.
- Hydroxycarboxylates have been used as an eluting agent for the intra-group separation of actinides using cation exchanger such as DOWEX 50x8.

FIG. 11. The stability of the first uranyl(VI) complex as a function of the basicity of the ligand, for ligands of various coordination patterns (C. Miyake and H. W. Nürnberg, *J. Inorg. Nucl. Chem.* 29 (1967) 2411).

Now coming to the glycolate, which is having a hydroxide group, the values for Am(III), we can compare with that of acetate ion, we see that the values are significantly higher, close to one order magnitude higher for americium and curium. And also for the uranyl and plutonyl ions, you can see that the stability constant with the glycolate ion is becoming slightly lower compared to that what we have seen in case of the acetate ion. That is because of the steric hindrance, which is observed for the uranyl ion because the complexation is taking place in the equatorial plane. So, the higher acetate complex formation constants are obtained with the actinyl ion, but not with the trivalent ion. We have the just opposite trend when you have the hydroxycarbonates like the glycolate. Now, the tetravalent actinide ions are stabilized by the carboxylate complexation because of the higher charge on the metal ion. Now finally we come to the oxalate ion complexation. We see because of the 2 minus charge in case of the oxalate ion, the complex formation constants are significantly larger as compared to that of the acetate ion. This is for all the trivalent, tetravalent as well as the hextravalent actinide ion (uranyl ion). Now if you have a correlation of this complexation constant of these organic ligands, that is the log K_1 values with the acid association constant or the basicity constant of the ligand (log K_H), then you get a linear behavior as shown here in the figure. This is for the ligands I have discussed, that is acetate and propionate. They have a very close log K_H values, around 4.76 for acetate and 4.88 for the propionate. You find that their log K values are also more or less same. Now this type of linear behavior is there for the carboxylate ligands. We have this monocarboxylate like chloroacetate and this lactate, formate, they also fall in this line. But when you have this dicarboxylates like oxalate, then you find that this is falling out of this line and it is much higher. Oxalate has this log K_H value close to 1, around 1.1 or so. But you find that the log K values for the uranyl ion is much, much higher in this case. This glycolate, they form chelate complexes so also the oxalate (both form chelate complexes). In case of the uranyl ion, the acetate forms chelates, but not the trivalent actinide ions. That is how the acetate complexation of the uranyl ion is much higher in stability than that of the trivalent actinide ions. Now, in solutions containing carboxylates, the plus four state is stabilized as compared to the lower or higher oxidation states. Very strong triacetate complexes are formed with the actinyl ions compared to the trivalent ions. In case of the carboxylic acids with hydroxy group, the stability of the complex was found to be higher as indicated in this figure.



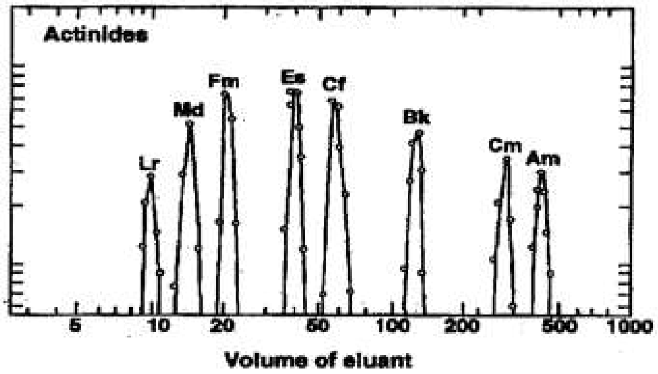
Elution profile of Ln^{3+} using α-HIBA

1. For sulphonated groups as in the Dowex 50x8 resin, the heavier lanthanides are not effectively sorbed
2. The heavier lanthanides form stronger complexes with the hydroxycarbonate ligands and hence, are eluted first

Smaller ions with high charge to radius (volume) ratio form strong complexes with the eluting agents: REVERSE ORDER OF ELUTION

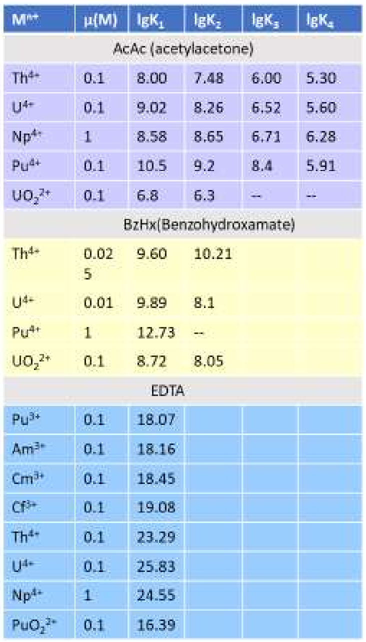
Also, this hydroxycarboxylates have been used as an eluting agent for the intra-group separation of actinides using cation exchangers such as the DOWEX 50 × 8 as shown in the next slide. See this elution profile of the lanthanide ions using a hydroxycarboxylate ligand that is alpha hydroxy isobutyric acid. So, here the heavier actinide is eluted first and the lighter actinide is eluted later. See the trend here, lutetium comes out first, then ytterbium, then thulium, then erbium, then holmium like that it goes on and it goes up to europium. Same also the trend for the actinides I will be showing. Now for the reason for this is for the sulfonated groups present in the DOWEX 50 × 8 resin which is used for this separation, the heavier lanthanides are not effectively soft. On the other hand, the heavier lanthanides form stronger complexes with the hydroxycarbonate ligand that is alpha hydroxy isobutyric acid here and hence, are eluted first.

Elution profile of An^{3+} using α-HIBA



Smaller ions with high charge to radius (volume) ratio form strong complexes with the eluting agents: REVERSE ORDER OF ELUTION

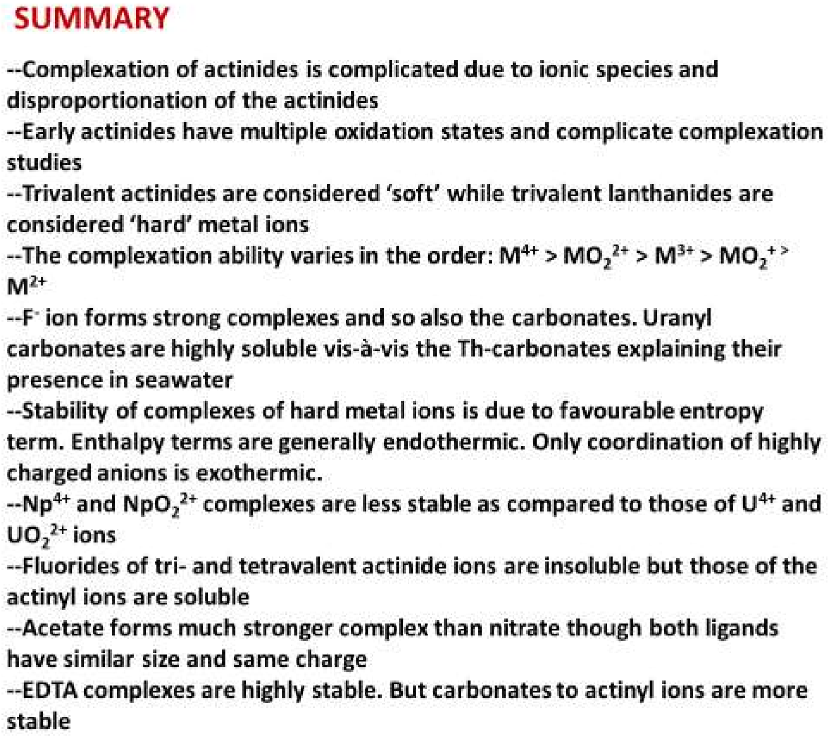
Same is the trend for the actinide ions using the alpha hydroxy isobutyric acid. See that lawrencium coming out first, then mandelevium, then fermium, like that and americium comes last, out of the trivalent actinide ions.



M^{n+}	μ(M)	$\lg K_1$	$\lg K_2$	$\lg K_3$	$\lg K_4$
AcAc (acetylacetone)					
Th^{4+}	0.1	8.00	7.48	6.00	5.30
U^{4+}	0.1	9.02	8.26	6.52	5.60
Np^{4+}	1	8.58	8.65	6.71	6.28
Pu^{4+}	0.1	10.5	9.2	8.4	5.91
UO_2^{2+}	0.1	6.8	6.3	--	--
BzHx(Benzohydroxamate)					
Th^{4+}	0.025	9.60	10.21		
U^{4+}	0.01	9.89	8.1		
Pu^{4+}	1	12.73	--		
UO_2^{2+}	0.1	8.72	8.05		
EDTA					
Pu^{3+}	0.1	18.07			
Am^{3+}	0.1	18.16			
Cm^{3+}	0.1	18.45			
Cf^{3+}	0.1	19.08			
Th^{4+}	0.1	23.29			
U^{4+}	0.1	25.83			
Np^{4+}	1	24.55			
PuO_2^{2+}	0.1	16.39			

- **AcAc forms strong 6 membered chelates and BzHx forms even stronger complexes with 5 member rings**
- **EDTA forms very strong complex with the actinides. Strongest with +4 ions but much lower with MO_2^{2+}**

Now, we go to the stronger chelating ligands like acetylacetone, benzohydroxamate. So in these cases, we have actually the stability constants of some of the complexes shown here in the table. See here that the complex formation constants are much much larger than what has been reported with the carboxylic ligands. And that is because of the very strong chelate formation in this type of ligands. And their application is that this acetylacetone as well as this benzohydroxamic acid, they form these complexes which can be easily extracted into the organic phase and that is how the separation of actinides can be done. And also, ethylene diamine tetraacetic acid or EDTA which is a multipodant chelating ligand and it forms a very very strong complex. And you can see here that the trivalent actinide ions like Pu^{3+}, Am^{3+}, Cm^{3+}, Bk^{3+}, and Cf^{3+}. They form the stability constant very close to 18. Now you also find slight increase in the stability constant values with the ionic potential that is with increasing Z of this actinide ion. Now for this, tetravalent actinide ions, you find the value is around 23 to 25 as seen here. For the Th^{4+}, U^{4+}, and Np^{4+}. And again, for U^{4+}, the log beta value with EDTA is around 25.83. And for Np^{4+}, the value is lower as already we have seen for the other complexing agents as well. And we have a value of 24.55. And for the plutonyl ion, the log β value or the log K_1 value in this case because ethylene diamond forms only 1 : 1 complex. So, this value is 16.39 which is significantly lower than that has been reported for the other actinide ions. That is because of the steric requirement of this actinyl ion where the complexing agent necessarily has to bind in the equatorial plane. Now in summary, this complexation of actinide is very complicated due to the different ionic species and disproportionation of the actinides. We have seen that the early actinides like uranium, plutonium, neptunium, they have multiple oxidation states and they complicate the complexation studies. And for these actinide ions, what we have to do is we have to necessarily stabilize the oxidation state in a given oxidation state and then carry out the complexation studies. For example, plutonium in the +4 oxidation state can be stabilized and then we carry out the complex formation studies such that there is no Pu(V) or Pu(VI) or Pu(III) present in the aqueous medium. In case of trivalent actinides (i.e., Am and beyond), there is no such ambiguity. Mostly they are present in the plus 3 oxidation state. However, many of these trivalent actinides are considered soft metal ions compared to the lanthanides which are the hard metal ions and this is the basis of the separation of trivalent actinides from lanthanides in the nuclear fuel cycle which I will be discussing in a separate lecture.



SUMMARY

--Complexation of actinides is complicated due to ionic species and disproportionation of the actinides

--Early actinides have multiple oxidation states and complicate complexation studies

--Trivalent actinides are considered 'soft' while trivalent lanthanides are considered 'hard' metal ions

--The complexation ability varies in the order: $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+} > M^{2+}$

--F^- ion forms strong complexes and so also the carbonates. Uranyl carbonates are highly soluble vis-à-vis the Th-carbonates explaining their presence in seawater

--Stability of complexes of hard metal ions is due to favourable entropy term. Enthalpy terms are generally endothermic. Only coordination of highly charged anions is exothermic.

--Np^{4+} and NpO_2^{2+} complexes are less stable as compared to those of U^{4+} and UO_2^{2+} ions

--Fluorides of tri- and tetravalent actinide ions are insoluble but those of the actinyl ions are soluble

--Acetate forms much stronger complex than nitrate though both ligands have similar size and same charge

--EDTA complexes are highly stable. But carbonates to actinyl ions are more stable

The complexation ability of the actinides they vary in the order: the tetravalent forming the strongest complex with a given ligand as compared to the hexavalent followed by trivalent followed by pentavalent and followed by the bivalent actinide. Out of the monovalent ligands, or the single charged ligands, the halides generally form very weak complexes, but fluoride ion forms a stronger complex. On the other hand, the carbonates form very very strong complexes and we have seen that the uranyl carbonates form very strong complexes in the +6 oxidation state. Also, in +4 oxidation state of uranium, we have seen how the log β value is very high around 40 for U(IV)-carbonate complex species. The stability of the complexes of hard metal ions, it is due to the very favorable entropy term and the enthalpy terms are generally endothermic. Only coordination of highly charged anions is exothermic. So, that is to say that in most of the cases for the actinide complexation you find that the complex formation is endothermic process and this is because of the favorable entropy term because while forming the complexes the inner sphere hydration is actually broken that is the water molecules are released and that contribute very large entropy and that is how the complex formation is taking place. For Np^{4+} and neptunyl ion that is NpO_2^{2+}, the complexes are less stable as compared to those of U^{4+} and UO_2^{2+} ions. Fluorides of tri and tetravalent actinide ions are insoluble, but those of the actinyl ions are soluble. So this is one of the very interesting observation of the actinide complexation and this has been used for the separation science for actinide ions. Acetate forms stronger complexes than the nitrate though both ligands have similar size and same charge. EDTA complexes are highly stable but the carbonate complexes of the actinyl ions are much more stable. Thank you.

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