Chapter VII

Summary & Conclusions
In the present thesis complexation and sorption behaviour of actinides/lanthanides on oxide surfaces have been investigated using batch sorption, molecular level spectroscopic techniques, LAM and SCM. The work presented in this thesis is divided into three parts: (i) the complexation of lanthanides with LMCA of environmental relevance and naturally occurring HA (ii) sorption of actinides/lanthanides onto mineral oxides (iii) the effect of complexing anions on sorption of actinides/lanthanides onto mineral oxides. The results of these studies are summarized in this chapter.

1. Complexation of Eu(III) by different complexing anions, viz., HIBA, SA, PA and MA has been studied using TRFS as a tool. The results have been compared with the observations obtained with Eu(III)-HA complexation. The small organic molecules, such as, HIBA, SA, PA and MA form 1: n complexes with Eu(III), with the values of ‘n’ varying depending upon the denticity of the ligand. The formation of different stoichiometric complexes between Eu(III) and these small organic molecules was evident from the increase in the asymmetric ratio ($I_{616}/I_{592}$) in the emission spectra with increasing ligand to metal ion concentration ratio. These observations were further corroborated with the life time data which showed increase in the life time with increasing ligand to metal ion concentration ratio. The stoichiometry of the complexes was obtained from the life time data using an empirical relation, between the life time and the number of water molecules coordinated to Eu$^{3+}$ ion, available in the literature. The stability constant of the different Eu(III) complexes was obtained from the measured asymmetry ratio as a function of ligand to metal ion concentration ratio. Similar experiments were also carried out with the Eu(III)-HA system. In this case the life time values
were found to remain constant at least upto the HA/Eu(III) ratio of 8, above which quenching of the fluorescence was observed as evident from the reduced emission intensity. Thus the stability constant for Eu(III)-HA complexes could not be obtained. Nevertheless, these studies provided the information that the large macromolecular anions, such as, behave differently from the small organic anions.

2. Sorption of Cm(III) by silica was found to be greatly influenced by the presence of HA in the suspension. The sorption of Cm(III) by silica increases with the pH of the suspension, which can be explained in terms of the electrostatic attraction between the positively charged Cm$^{3+}$ ions and the negatively charged surface sites of the type $\equiv$Si-O$^-$ on silica, as well as the surface complexation of the metal ion by the surface sites. In presence of HA, the sorption of Cm(III) by silica is enhanced at lower pH values (3-5) and decreased at higher pH values (6-8), and thereafter the sorption was found to increase with pH. These observations could be explained in terms of the sorption of HA by silica. HA is strongly sorbed by the silica at lower pH and the sorption decreases with increasing pH of the suspension becoming negligible at pH $> 6$. Thus the surface bound HA at lower pH results in increased sorption of Cm(III) by silica. On the other hand, in the intermediate pH range the HA is predominantly present in the solution and hence strong complexation of Cm(III) by HA in the solution results in decreased sorption. At higher pH values ($> 8$), the increases in the sorption with pH could plausibly be due to the formation of hydrolysed Cm(III) species which might have higher sorption tendency towards the silica surface. The above observation of the effect of HA on the sorption of Cm(III) by silica could be
quantitatively explained in terms of the linear additive model, by incorporating the modifications to take into account the different binding affinity of surface bound HA from the HA in solution. With a view to obtain more insight into the mechanism of the sorption of Cm(III) by silica in presence of HA, TRFS studies were carried out using Eu(III) as the chemical analogue of Cm(III) and alpha hydroxy iso-butyric acid (HIBA) as a small organic molecule to study if it could be used as an analogue of HA. The TRFS measurements helped in identifying the surface complexes. Further the sorption data could be modeled successfully with the help of SCM. It was observed that the effect of small organic molecules like HIBA was quite different from that of HA, indicating the different binding characteristics of the two complexing anions.

3. Sorption of U(VI) by silica has been studied in presence of two important complexing anions, namely, carbonate and citrate, which are ubiquitous in geosphere. U(VI) sorption by silica increases with the pH of the suspension, with the sorption edge, that is, the pH at 50% sorption, shifting to higher pH with increasing concentration of the metal ion. In presence of carbonate, there was negligible change in the sorption profile, while citrate was found to have significant effect on the sorption of U(VI) by silica, with the sorption decreasing in presence of citrate at higher pH values compared to the binary U(VI)-silica system. The sorption profile for the binary U(VI)-silica and ternary U(VI)-silica-citrate system were fitted using the surface complexation model. SCM using DLM showed the evolution of different surface complexes as a function of U(VI) concentration. The bidentate mono nuclear surface complex was able to fit the sorption data in entire concentration range. The two modeling approaches were applied to some of the literature data for their
evaluation and mononuclear mono-dentate complexes were able to explain the sorption data better than mononuclear bidentate complexes. Moreover, TRFS revealed the existence of two surface complexes at $[U] = 5 \times 10^{-5}$ M, which was used to constrain the SCM. In case of ternary systems, U(VI) is sorbed as $(\equiv\text{SiO})_2\text{UO}_2$ and $(\equiv\text{SiO})_2\text{UO}_2\text{CO}_3^{2-}$ in presence of carbonate and as $(\equiv\text{SiO})_2\text{UO}_2\text{Cit}^{3-}$ in presence of citrate.

4. Sorption of neptunium by hematite colloids was studied both in absence and presence of HA. Hematite colloids were prepared by precipitation of hydroxide from aqueous solution of ferric chloride followed by heating of the precipitate at high temperatures and grinding in a ball mill. Sorption experiments were carried out using $^{239}\text{Np}$, the short lived gamma emitting isotope of neptunium. Under aerobic conditions, Np(V) is the dominant species and its sorption by hematite increases slowly with the pH of the suspension, which could be explained in terms of the low ionic potential of the NpO$_2^+$ ions. The stability constant of Np(V)-humate complex was determined using the Schubert’s method. Under reducing conditions, Np(IV) is the dominant species and its sorption increases significantly with the pH of the suspension. In presence of HA the sorption was found to increase at lower pH with respect to the binary Np(IV)-hematite system. These studies showed that the migration of neptunium on hematite is greatly influenced in presence of HA under anaerobic conditions.

The work carried out as a part of this thesis has shown that colloids based on mineral oxides of Si, Fe, etc., greatly influence the speciation of actinides under the conditions prevailing in natural waters. Presence of complexing anions, such as, HA has drastic effect on the sorption of trivalent actinides, which in turn is influenced by
the presence of natural organic matter containing HS. TRFS provided valuable information on the complexation of trivalent rare earths by small organic molecules, which can be used to infer about the complexation of trivalent actinides by the small organic molecules present in natural waters. This technique could also provide information about the sorbed metal ions on the surface of mineral oxides, and thereby help in validating the predictions of the SCM. Attempt has also been made to understand the sorbed uranyl species on the surfaces of silica, though the information obtained was limited owing to the lower sensitivity of the TRFS system based on xenon flash lamp as the excitation source. With the induction of dye laser based TRLFS system, it would be possible to study the uranium speciation on the surface of mineral oxides at much lower metal ion concentrations. In the case of neptunium, the studies provided information about the speciation of the metal ion under aerobic and anaerobic conditions in absence and presence of HA. The modeling of the sorption data by SCM needs to be carried out for which the spectroscopic information has to be obtained using techniques, such as LIPAS.

The present work is a small step towards understanding the migration behaviour of actinides and long lived fission products in the geosphere, which is a frontier area of research by the radiochemists worldwide. With the availability of intense synchrotron sources and laser based spectroscopic instruments, the molecular structure of the actinides can be obtained, which in turn would help in validating the models proposed to predict the migration pathways of these long lived radionuclides in the geosphere upon their release from the deep geological repository.