Chapter IV

Sorption of

Trivalent Actinides/Lanthanides:

Effect of Complexing Anions
4.1. Introduction:

In the present chapter the effect of HA and HIBA on sorption of Cm(III) by silica colloids was studied by employing batch sorption, LAM (in case of HA) and SCM (in case of HIBA). Moreover, the effect of changing the order of addition of the metal ion and HA/ HIBA on sorption was also investigated. Further, similar sorption studies, using HIBA, were carried out with Eu(III) at higher concentration (5 X 10^{-5} M) so as to characterize the surface complexes by TRFS and information obtained from TRFS was used in the SCM. The results obtained for Eu(III) and Cm(III) systems have been compared. Also, the use of small organic molecules as model compounds of HA has been evaluated by comparing the influence of HA and HIBA on sorption of Cm(III) by silica.

Trivalent actinides such as, americium (\textsuperscript{241}Am, \textsuperscript{243}Am) and curium (\textsuperscript{245}Cm, \textsuperscript{246}Cm) constitute a major fraction of the minor actinides present in the high level liquid waste generated during the reprocessing of spent nuclear fuel. Though partitioning and transmutation is being considered as one of the options to incinerate these minor actinides in accelerator driven sub-critical reactor system (ADS), presently the HLW is being managed by immobilizing it in solid form (glass, synroc), which may be buried in deep geological repositories in near future. Thus, these long-lived isotopes, such as, \textsuperscript{241}Am, \textsuperscript{243}Am, \textsuperscript{245}Cm and \textsuperscript{246}Cm will be present in the earth (deep geological repositories) for thousands of years and over this time period, it is possible that these minor actinides might enter the geosphere, through earthquakes, volcanic eruptions, leaching and corrosion of waste form and underground water movement. The major concern during the release of the minor actinides and long lived fission products from the vitrified waste buried in a deep geological repository is the migration of long lived radionuclides in aquatic environment which is known to be
influenced by the presence of colloids and complexing anions (Kepak, 1971; Penrose et al., 1990; Kersting et al., 1999). Moreover, organic complexing anions affect the dissolution of glass containing vitrified waste (Gin et al., 1994). Hence it is imperative to know the mechanism of interaction of the radioactive elements with colloids and complexing anions. The complexing anions include simple organic molecules, viz., carboxylic acids, amino polycarboxylic acids as well as complex molecules, such as, FA and HA.

The common colloids present in natural waters are based on oxides of Si, Al and Fe. Extensive studies have been carried out on the sorption of trivalent actinides/lanthanides on different colloids (Piasecki and Sverjensky, 2008; Rabung et al. 1998, 2000, 2004, 2006; Kumar et al., 2013; Fairhurst et al., 1995a; Takahashi et al., 2006; Pathak et al., 2006, 2007a). Silica is one of the most common constituents of the mineral oxides, viz., feldspar, quartz, etc. as well as clays, viz., bentonite, which are being proposed as backfill material in the deep geological repositories. The granitic rocks which contain silica rich minerals are preferred host rocks for depositing the immobilized HLW. Various literature reports exist in which sorption of Eu(III) on silica follows typical S shaped sorption profile and role of various parameters such as pH, ionic strength and silica dissolution has been evaluated (Fairhurst et al., 1995a; Takahashi et al., 2006; Pathak and Choppin, 2006, 2007a).

The concentration of HA in natural waters is observed to be in the range of few parts per million which is sufficient to affect the sorption behaviour of multivalent cations such as Am(III) and Cm(III). Several studies exist in literature in which the effect of HA on the sorption of Eu(III) and Am(III) on colloids are reported (Macasek et al., 1999; Ledin et al., 1994; Fairhurst et al. 1995b; Sakuragi et al., 2004; Samadfam et al. 2000). Presence of HA enhances the sorption of
Eu(III)/Am(III) on colloids at low pH and decrease the same at high pH, compared to the binary metal ion-colloid system.

Although attempts are being made to understand the sorption behaviour of radionuclides in presence of HS (Macasek et al., 1999; Ledin et al., 1994; Fairhurst et al., 1995b; Sakuragi et al., 2004; Samadfam et al., 2000; Tan et al., 2008, 2009; Wang et al., 2004; Chen et al., 2013), the complex structure and poly functionality of HS make it extremely difficult to understand the sorption phenomena from fundamental point of view. However, the sorption phenomena in systems containing simple molecules are easier to explain, as complexation of metal ions with such molecules is well understood (Jain et al., 2008). Further, the small molecules have well defined structure and thus are helpful in understanding the sorption phenomena from mechanistic point of view. Various literature reports exist in which effect of LMCA on sorption of trivalent lanthanides and actinides have been studied (Alliot et al., 2005a, 2005b, 2006; Pathak and Choppin, 2007a; Tits et al., 2005).

The sorption profile is dependent upon the interaction of the complexing anions with the metal ion as well as the surface sites in the case of ternary metal ion-ligand-mineral oxide systems. The formation of synergic surface complexes has also been proposed to explain the sorption profile of Eu(III)/Am(III) sorption on alumina in presence of complexing anions (acetic, oxalic and carbonic acids) (Alliot et al., 2005a; Alliot et al., 2005b; Alliot et al., 2006). A synergistic enhancement in the sorption of Eu(III) on suspended silica was observed for oxalate and phosphate ligands and formation of ternary Eu/silica/ligand complexes were confirmed by TRLFS (Pathak and Choppin, 2007a). On the other hand the retention of Eu(III), Am(III) and Th(IV) on calcite was not affected by gluconic acid and isosaccharinic acid (Tits et al., 2005).
Spectroscopic techniques such as TRLFS and EXAFS have been employed to characterize the sorbed species in both binary and ternary systems containing complexing anions (Tan et al., 2008, 2009; Wang et al., 2004; Chen et al. 2013, Rabung et al., 2000, 2005; Fouchard et al., 2004a; Hartmann et al., 2008; Ishida et al., 2009; Schlegel et al., 2004; Stumpf et al., 2007). Though TRLFS and EXAFS are the most widely used spectroscopic techniques for characterization of the sorbed metal ions, other techniques, such as, XPS and SEM-EDS has also been used in a few cases (Fouchard et al., 2004a; Mercier et al., 2006). These studies provide valuable information about the structure of the surface complexes and thereby help in validation of SCM hypothesis.

SCMs provide molecular description using equilibrium approach and are designed to calculate the interaction constants mathematically by taking into account the aqueous distribution of species, the reactivity and the electrostatic properties of the surface. SCM has been widely used to model sorption data of actinides and fission products on various mineral oxides and clays (Kar et al., 2012; Bradbury and Baeyens 2006; Grambow et al., 2006; Bradbury et al., 2005; Gaskova and Bukaty, 2008). In addition to the modeling of binary systems, the modeling of the sorption data for the ternary, actinide-complexing anions- mineral oxides, systems has also been attempted (Guo et al., 2009a; Stamberg et al., 2006; Singh et al., 2010). Recently the sorption of Eu(III) on rectorite in the presence of HA has been successfully modeled by SCM (Chen et al., 2013).

The aim of the present work was to study the effect of HA on the sorption of Cm(III) by silica. LAM was used to qualitatively explain the sorption profile. To the best of our knowledge, there are no studies in the literature on the effect of HA on sorption of Cm(III) by silica colloids. The effect of ionic strength and HA
concentration on Cm(III) sorption was also investigated. Further, the studies were also carried out on the effect of addition order of Cm(III) and HA to the silica suspensions.

In addition, the effect of varying concentration of HIBA and addition order of the Cm(III) and HIBA on the sorption of Cm(III) by silica was also studied using batch sorption experiments and SCM. HIBA has been used as a simple organic complexant. SCM for both binary and ternary system was done using the DLM. Though there exist large number of studies in literature in which SCM of effect of complexing anions have been dealt (Guo et al., 2009a; Stamberg et al., 2006; Singh et al., 2010), SCM of Cm(III) in presence of small organic molecules has been attempted for the first time. Moreover, the comparison of the effect of HIBA and HA on Cm(III) sorption on to silica has been made so as to ascertain whether simple molecules can be used as analogue of HS when it comes to study the influence of organics on the sorption of metals.

Furthermore, the spectroscopic characterization of the sorbed species was also carried out using TRFS with Eu(III) as a probe. The effect of HIBA on the sorption of Eu(III) by silica was investigated using batch sorption experiments, TRFS and SCM. Both, batch sorption experiments as well as TRFS measurements, were carried out in the case of binary (Eu(III)-Silica) and ternary (Eu(III)-silica-HIBA) systems. The complexation of Eu(III) by HIBA has been studied in our laboratory using TRFS, wherein the fluorescence emission spectra were found to be sensitive to the complexation of Eu(III) by HIBA as described in chapter 3 (Jain et al., 2008). The TRFS of sorbed Eu(III) have been used to infer about the surface complexes during the modeling for both binary and ternary system using the DLM.
4.2. Experimental:

4.2.1 Materials and characterization:

Silica powder (Aerosil Belgium) was used as received. Its surface area and point of zero charge was determined by methods described in Chapter 2. The number of surface sites on the silica powder was determined by titrating the 300 mg of silica in 50 ml 0.1 M NaClO\(_4\) with standard 0.01 M HClO\(_4\) / 0.1 M NaOH.

\(^{244}\text{Cm}\) (\(T_{1/2} = 18.1\) years) was used as a tracer for curium so as to attain low concentration (\(2.2 \times 10^{-10}\) M) encountered in natural water conditions. For sorption studies of Eu(III), \(^{152}\text{Eu}\) was used as a radiotracer.

HA (Aldrich) having proton exchange capacity of 7.1 meq/g was used (Boily and Fein, 2000). AR grade HIBA (Alfa Aesar) was used as received. All solutions were prepared in low conductivity Millipore water having resistivity of 18 M\(\Omega\)cm and HA solutions were stored in dark.

4.2.2. Batch Sorption Experiments:

Sorption studies were carried out by using batch sorption method to investigate the sorption of \(^{244}\text{Cm}\) (III) on silica. The sorption of Cm(III) is influenced by several factors such as contact time, pH, ionic strength, HA concentration and order of addition of HA/HIBA and Cm(III). The effect of these different experimental parameters on Cm(III) sorption by silica has been studied. Furthermore, batch sorption studies were also carried out with Eu(III) in presence and absence of HIBA.

The details of the batch sorption experiments have been discussed in Chapter 2. The concentration of silica suspensions was 5 g/L in case of Cm(III) and 10 g/L for experiments with Eu(III). Ionic strength was maintained at 0.1 M using NaClO\(_4\).
In order to determine the time required to achieve equilibrium in the sorption, kinetic sorption study at pH 6.5 was carried out which showed that the equilibrium in the percentage sorption was achieved in 24 hours. Hence the equilibration time for sorption of $^{244}\text{Cm}$ by silica was fixed as 24 hours.

In the case of experiments in presence of HA, the suspensions were first equilibrated with 2 mg/L HA for 48 hours and subsequently $^{244}\text{Cm}$ activity was added for further equilibration for another 24 hours. This order is hereafter referred to as Silica-HA-Cm. The 48 hours of contact time for silica and HA was based on the literature reports for the Eu(III)-silica system (Fairhurst et al., 1995 b).

The experiments with the reverse order of addition of $^{244}\text{Cm}$ and HA (referred to as Silica-Cm-HA) were carried out by first equilibrating the silica suspensions (20 mL containing 5 g/L silica) at varying pH with the $^{244}\text{Cm}$ activity for 24 hours and later adding the HA solution (2 mg/L), which was then equilibrated for another 48 hours. 1 mL aliquots were drawn from the supernatant (after centrifugation) after equilibration with HA to obtain the sorption data for ternary (silica-Cm-HA) system.

The effect of ionic strength was studied by measuring sorption at different ionic strengths, 0.005-0.2 M NaClO$_4$ and at a fixed pH of 6.5. This pH value was chosen as the percentage sorption was found to be close to 100% at this pH. Effect of HA concentration (2-20 mg/L) on sorption of Cm by silica was also studied.

In the case of experiments in presence of HIBA, the experiments were carried out in similar manner as for HA. Concentration of HIBA was $1.0 \times 10^{-3}$ M and $1.0 \times 10^{-5}$ M. The HIBA concentrations $1.0 \times 10^{-5}$ M and $1.0 \times 10^{-3}$ M will be hitherto represented as HIBA(I) and HIBA(II) respectively. Ternary system where HIBA was added before Cm are termed as Silica-HIBA-Cm and those with the reverse order of addition of Cm(III) and HIBA are referred to as Silica-Cm-HIBA. For binary silica-
Eu(III) and ternary silica-HIBA-Eu(III) systems, same methodology was followed and HIBA concentration was kept $2.5 \times 10^{-3}$ M.

4.2.3. Silica dissolution studies:

For the determination of dissolved silica, silica suspensions (10 g/L) of varying pH were equilibrated with Eu(III) ($5 \times 10^{-5}$ M) for 4 and 24 hours, respectively, on a mechanical shaker. The suspensions were centrifuged and the supernatant solutions were assayed for dissolved Si content by ICP-AES. The calibration of the instrument was carried out using 1000 mg/L standard Si solution (Merck) after suitable dilution.

4.2.4. Sorption of HIBA by silica:

In order to determine the sorption of HIBA by silica, the silica suspensions (10 g/L) of varying pH were contacted with HIBA ($2.5 \times 10^{-3}$ M) for 48 hours in a mechanical shaker. The suspensions were later centrifuged and the supernatant solutions were assayed for TOC.

4.2.5. TRFS measurements:

For the TRFS measurements 10 ml of silica suspensions (10 g/L) of varying pH (4.0-8.0) were contacted with Eu(III) solutions ($5.0 \times 10^{-5}$ M) for 24 hours. The suspensions were filtered using 0.1 micron membrane filter to remove any unsorbed Eu(III). Subsequently the solid samples were vacuum dried and mounted on glass plate for TRFS measurements. Similar exercise was carried out for preparation of sample in the case of ternary Eu(III)-silica-HIBA system.
4.3 Results and Discussion:

4.3.1 Characterization of Silica:

The surface area of silica was found to be 180 ± 5 m$^2$/g, which corresponds to particle size of 6.2 ± 0.2 nm. The point of zero charge (pH$_{PZC}$) of silica was obtained from zeta potential measurements and the value was found to be 2.4 (Kumar et al., 2006). The data of acid base titration of silica are shown in figure 4.1. These were analysed by FITEQL 4.0 to obtain the concentration of surface sites and log K for protonation (log K$_1$) and deprotonation (log K$_2$) of ≡ SiOH groups, which are given in Table 4.4. The log K$_2$ obtained in the present work is close to that reported by E.Osthols (1995) (log K$_2$ = -6.9) for Aerosil OX 200 silica.

![Figure 4.1](image_url)  
**Figure 4.1** Potentiometric titration of silica suspension (6 g/L) in 0.1 M NaClO$_4$.

4.3.2 Silica Dissolution Studies:

The results of the ICP-AES measurements of Si concentration in the supernatant solutions of Eu(III)-silica systems are given in Table 4.1. The amount of
dissolved Si is more for equilibration time of 4 hours than that of 24 hours, indicating the interaction of the dissolved silica with the solid surface.

Dissolution of silica can be characterized by the following equilibria ([Stumm and Morgen, 1996]):

\[
SiO_2(s, amorphous) + 2 H_2O \leftrightarrow Si(OH)_4 \quad (4.1)
\]

\[
Si(OH)_4 \leftrightarrow SiO(OH)_3^- + H^+ \quad (4.2)
\]

\[
SiO(OH)_3^- \leftrightarrow SiO(OH)_{2}^2^- + H^+ \quad (4.3)
\]

The dissolution of silica increases with pH. Furthermore, Eu(III) is known to promote the dissolution of silica by facilitating hydrolysis of Si-O-Si bonds ([Takahashi et al., 2006]). The concentration of silicic acid formed owing to the dissolution of silica in presence of Eu(III) is of the order of 10 mM, at which polysilicic acid is dominant ([Panak et al., 2005]). In absence of Eu(III), the concentration of silicic acid formed owing to the dissolution of silica is of the order of 2 mM ([Kar et al., 2012]). It is to be noted that in presence of Cm(III), the concentration of silicic acid has been assumed to be same as in case of bare silica owing to very low concentration of Cm(III) employed in the present work.

<table>
<thead>
<tr>
<th>pH</th>
<th>(4 hours)</th>
<th>(24 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.56</td>
<td>240</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
<td>310</td>
<td>240</td>
</tr>
<tr>
<td>7.86</td>
<td>510</td>
<td>260</td>
</tr>
</tbody>
</table>

**Table 4.1** Dissolved Si (ppm) in silica suspensions (10 g/L) in presence of Eu(III) (5.0 X 10^{-5} M) measured after different time of equilibration.

**4.3.3. Speciation Calculations:**

Speciation of Cm(III) in aqueous solution was calculated using the geochemical equilibrium speciation code MINTEQA2 ([Allison et al., 1991]) after
incorporating the stability constants of Cm$^{3+}$ complexes with OH$^-$ (Wimmer et al., 1992), HIBA (Shalinets, 1971) and silicic acid (Panak et al., 2005; Jensen and Choppin, 1996). The speciation of Cm(III) in presence of silicic acid was generated by considering the formation of CmOSi(OH)$_3^{2+}$ and Cm(OSi(OH)$_3$)$_2^{+}$. The stability constant for Cm(III) disilicate was not available in literature, thereby necessitating the use of stability constant value of Eu(III) disilicate (Jensen and Choppin, 1996).

Deprotonation constant of HIBA (Portanova et al., 2003) was also incorporated in MINTEQA2. Formation of Cm$^{3+}$ humate complexes was also considered by making use of the formation constant and site capacities as defined within MINTEQA2. The values of log $\beta$ for Cm-HA and site density of HA are 6.4 and 7.6 X 10$^{-3}$ eq.g$^{-1}$ respectively (Boily and Fein, 2000; Cornelis, 2005).

Speciation of Eu(III) was calculated after incorporating the log K for Eu(III)-HIBA (Jain et al., 2008), Eu(III) silicate complexes (Jensen and Choppin, 1996) and Eu(III) hydroxo complexes (Tetre et al., 2006). In view of the non-availability of the log K for interaction of europium and polysilicic acid, we studied the speciation of Eu(III) in presence of silicic acid considering the formation of EuOSi(OH)$_3^{2+}$ and Eu(OSi(OH)$_3$)$_2^{+}$. The log K for the Eu(III)-silicates were taken from Jensen and Choppin (1996). The log K of different complexes considered in the calculations are given in Table 4.2. The data was transformed to zero ionic strength before inserting as input in the code.

The carbonate concentration in the suspensions was assumed to be negligible as (i) millipore water was boiled before use, (ii) the sorption was carried out in air tight polypropylene tubes and (iii) the time period for closing the tubes after adjustment of pH was kept as short as possible.
### Table 4.2 Log $\beta$ used for calculating the aqueous speciation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm $^{3+}$ + H$_2$O $\rightarrow$ Cm(OH)$^{2+}$ + H$^+$</td>
<td>-7.2 $^a$</td>
</tr>
<tr>
<td>Cm $^{3+}$ + 2H$_2$O $\rightarrow$ Cm(OH)$_2$ $^{+}$ + 2 H$^+$</td>
<td>-15.1 $^a$</td>
</tr>
<tr>
<td>Cm $^{3+}$ + 3H$_2$O $\rightarrow$ Cm(OH)$_3$ + 3 H$^+$</td>
<td>-26.2 $^a$</td>
</tr>
<tr>
<td>(CH$_3$)$_2$COHCOO$^-$ + H$^+$ $\rightarrow$ (CH$_3$)$_2$COHCOOH</td>
<td>3.75 $^b$</td>
</tr>
<tr>
<td>Cm $^{3+}$ + (CH$_3$)$_2$COHCOO$^-$ $\rightarrow$ (CH$_3$)$_2$COHCOOCm$^{2+}$</td>
<td>2.96 $^c$</td>
</tr>
<tr>
<td>Cm $^{3+}$ + 2(CH$_3$)$_2$COHCOO$^-$ $\rightarrow$ ((CH$_3$)$_2$COHCOO)$_2$Cm$^+$</td>
<td>5.15 $^c$</td>
</tr>
<tr>
<td>Cm $^{3+}$ + 3(CH$_3$)$_2$COHCOO$^-$ $\rightarrow$ ((CH$_3$)$_2$COHCOO)$_3$Cm</td>
<td>6.36 $^c$</td>
</tr>
<tr>
<td>Cm $^{3+}$ + H$_4$SiO$_4$ $\rightarrow$ Cm(OSi(OH)$_3$)$^{2+}$ + H$^+$</td>
<td>-2.07 $^d$</td>
</tr>
<tr>
<td>Cm$^{3+}$+2H$_4$SiO$_4$ $\rightarrow$ Cm(OSi(OH)$_3$)$_2$$^+$+2 H$^+$</td>
<td>-6.87 $^e$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + H$_2$O $\rightarrow$ Eu(OH)$^{2+}$ + H$^+$</td>
<td>-7.8 $^f$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + 2H$_2$O $\rightarrow$ Eu(OH)$_2$$^{+}$+ 2 H$^+$</td>
<td>-16.4 $^f$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + 3H$_2$O $\rightarrow$ Eu(OH)$_3$ + 3 H$^+$</td>
<td>-25.2 $^f$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + 4H$_2$O $\rightarrow$ Eu(OH)$_4$$^+$+ 4 H$^+$</td>
<td>-35.3 $^f$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + (CH$_3$)$_2$COHCOO$^-$ $\rightarrow$ (CH$_3$)$_2$COHCOOEu$^{2+}$</td>
<td>3.32 $^g$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + 2(CH$_3$)$_2$COHCOO$^-$ $\rightarrow$ ((CH$_3$)$_2$COHCOO)$_2$Eu$^+$</td>
<td>5.50 $^g$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + 3(CH$_3$)$_2$COHCOO$^-$ $\rightarrow$ ((CH$_3$)$_2$COHCOO)$_3$Eu</td>
<td>6.62 $^g$</td>
</tr>
<tr>
<td>Eu $^{3+}$ + OSi(OH)$_3$ $\rightarrow$ Eu(OSi(OH)$_3$)$^{2+}$</td>
<td>7.26 $^g$</td>
</tr>
<tr>
<td>Eu$^{3+}$+2OSi(OH)$_3$$^-$ $\rightarrow$ Eu(OSi(OH)$_3$)$_2$$^+$</td>
<td>11.7 $^g$</td>
</tr>
</tbody>
</table>

(a: Wimmer et al., 1992; b: Portanova et al., 2003; c: Shalinets, 1971; d: Panak et al., 2005; e: Jenson and Choppin, 1996; f: Tetre et al., 2006; g: Kar et al., 2008)

The speciation diagrams in absence and presence of HA are shown in figures 4.2 (a) and 4.2 (b). It is worth mentioning that here the contribution of dissolved silicates is not included. During the interpretation of sorption data of addition order of Cm(III) and HA, it was realized that silica dissolution plays important role in deciding Cm(III) speciation. In absence of HA, hydrolyzed Cm(III) species dominate the
speciation above pH 6, while in presence of HA, the humate complex dominates the speciation in the pH range of 5-8, with the hydrolyzed species concentration increasing above pH 8. However, at higher pH (> 8) values carbonate complexation of Cm(III) cannot be ruled out.

Figure 4.2 Speciation of Cm(III) in (a) absence and (b) presence of (2 mg/L) HA.

\[ [\text{Cm(III)}] = 2.2 \times 10^{-10} \text{ M}, I = 0.1 \text{ M} \]

The speciation diagrams in absence and presence of HIBA are shown in figures 4.3 (a) and 4.3 (b and c) respectively. It can be seen that up to pH 7.0, Cm(OSi(OH)_{3})^{2+} is the dominant species above which Cm(OSi(OH)_{3})_{2}^{+} dominates. In the presence of 10^{-5} M HIBA (figure 4.3 (b)), curium silicate continues to dominate the speciation while in case of 10^{-3} M HIBA (figure 4.3 (c)), Cm(HIBA)^{2+} and Cm(HIBA)_{2}^{+} are also present up to pH 4.5 though the speciation is still dominated by silicate complexes.
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Figure 4.3 Curium speciation in absence (a) and presence (b and c) of HIBA.

\[ [\text{Cm(III)}] = 2.2 \times 10^{-10}; \ [\text{HIBA}] = 1 \times 10^{-5} \text{ M in (b) and } 1 \times 10^{-3} \text{ M (c). Ionic strength} = 0.1 \text{ M NaClO}_4. \]

\( \text{Cm}^{3+} \), \( \text{Cm(HIBA)}^{2+} \), \( \text{Cm(HIBA)}^{2+} \), \( [\text{Cm(OSi(OH)}_3]^{2+} \) (o) and \( [\text{Cm(OSi(OH)}_3]^{2+} \) (Δ).

Figures 4.4 (a) and 4.4 (b) show the speciation of Eu(III) in absence and presence of HIBA respectively. It can be seen that up to pH 7.0, Eu(OSi(OH)}_3]^{2+} \) is the dominant species above which Eu(OSi(OH)}_3]^{2+} \) dominates. In the presence of HIBA, Eu\(^{3+}\), Eu(HIBA\(^{2+}\) and Eu(HIBA\(^{2+}\) are also present up to pH 4.5 but the speciation continues to be dominated by silicate complexes.

Thus, silicates are major species in pH range of study for Cm(III) and Eu(III) irrespective of their concentration.
4.3.4. Kinetics study of sorption of Cm (III) by silica colloids:

Figure 4.5 shows the temporal profile of the sorption of Cm (III) by silica colloids at pH 6.5. The sorption reaches a equilibrium value in less than 24 hours. Ho. et al. (1998) did the comparison of various kinetic models and found that pseudo second order equation describes the sorption kinetics better than other models. The sorption kinetics in literature has been modeled by the pseudo second-order rate equation (Fan et al., 2008; Chen et al., 2007)

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{4.4}
\]
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$k$ (g mg$^{-1}$h$^{-1}$) is the pseudo second-order rate constant of adsorption, $q_e$ and $q_t$ are the amounts of metal ion sorbed (mg/g) at equilibrium and at time $t$ respectively.

![Graph showing sorption kinetics](image)

**Figure 4.5** Kinetics of sorption of Cm by silica. pH = 6.5, [Cm(III)] = $2.2 \times 10^{-10}$ M,
I = 0.1 M (NaClO$_4$), [Silica] = 5 g/l

Figure 4.6 shows the plot of $t/q_t$ vs $t$. The values of $q_e$ and $k$ calculated from slope and intercept are $9.88 \times 10^{-6}$ mg g$^{-1}$ and $1.35 \times 10^{-5}$ g mg$^{-1}$h$^{-1}$ respectively. The value of $q_e$ obtained from slope analysis was found close to $q_t$ at maximum contact time between curium and silica and low value of $k$ suggests that sorption equilibrium is attained slowly. The coefficient of regression for linear fitting is close to 1 which signifies that sorption kinetics can be described by pseudo second order rate equation. Similar trends have been observed in case of Th(IV) sorption on attapulgite (*Fan et al.*, 2008).
4.3.5. Sorption of Cm (III) by silica: Effect of HA:

The percentage sorption of curium by silica colloids increases with increasing pH and reaches a saturation value > 95 % at pH 6.5 above which it remains constant as shown in figure 4.7. This is understood in terms of positive charge on silica colloids at low pH (< 2.4) and increasingly negative charge above it. As the pH of the aqueous suspension increases above 2.4, the silica surface becomes more and more negatively charged thus resulting in the sorption of the positively charged Cm$^{3+}$ ions. The high percentage sorption at higher pH can be explained in terms of the surface complexation between Cm$^{3+}$ and $\equiv$SiO$^{-}$ surface sites of silica. The results are in agreement with the literature data for sorption of Am(III) by kaolinite (Samadfam et al., 2000) and that of Eu(III) by silica (Fairhurst et al., 1995 a).

In the presence of HA, the sorption of Cm(III) on silica is enhanced compared to the binary system of Cm(III)-silica system at lower pH values. The percentage sorption reaches a maximum at pH 6 and then falls to lower value in the pH range 6.5-
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8 above which it is found to increase again. The enhancement in the percentage sorption at low pH and reduction at high pH in presence of HA is also observed in the sorption studies with Eu (III) (Fairhurst et al., 1995a) and Am (III) (Sakuragi et al., 2004) and can be explained in terms of the sorption profile of HA on silica (Kumar et al., 2006). At low pH, the negatively charged HA molecules get sorbed on the positively charged silica surface (=Si-OH\(^+\)) by electrostatic interaction. With increase in pH the silica particles acquire negative charge due to the deprotonation of the =Si-OH surface sites, resulting in repulsion between the anionic HA molecules and the negatively charged silica particles and hence decrease in the sorption of HA by silica. The HA molecules present in the liquid phase, owing to their strong affinity for Cm(III) result in decreased sorption of Cm (III) onto the silica surface.

Figure 4.7 shows that in presence of HA, the decrease in the sorption at intermediate pH is much more in the case of silica-HA-Cm than that in case of silica-Cm-HA system. Further, the percentage sorption at varying length of time of equilibration 24-72 hours was found to be nearly same for the silica-Cm-HA system. The enhancement in the sorption of Cm(III) by silica at low pH is similar to that observed in the previous experiment Silica-HA-Cm. However, the decrease in the sorption of Cm(III) at intermediate pH values is not as high as was observed in the case of Silica-HA-Cm.

Various authors report the influence of addition sequence on metal ions distribution at solid liquid interface (Wang et al., 2000; Xu et al., 2006a; Reiller et al., 2005; Davis, 1984; Fan, 2009) while others rule out its effect on metal sorption (Xu et al., 2006b; Li et al., 2009; Liu et al., 2001; Wang et al., 2004). Wang et al. (2000) studied the effect of sequence of Yb(III) and FA addition to the alumina and found higher K\(_D\) values when FA addition preceded Yb(III) which was attributed to
different behavior of FA molecules sorbed on alumina and those in solution. Similar effect of addition order was observed in case of copper sorption on alumina (Davis, 1984). The EXAFS studies of Eu(III) sorbed by attapulgite, a hydrated Mg-Al-silicate, in presence of HA showed difference in the structure of the sorbed species when the order of addition of Eu(III) and HA was reversed (Fan, 2009). On the contrary, Wang et al. (2004) did not observe any effect of addition sequence of alumina and HA in the fluorescence spectra of Cm(III)-alumina-HA system. Thus the effect of the sequence of metal ion and HA addition to the solid sorbent influences the metal ion sorption, has to be investigated in detail.

Figure 4.7 Sorption of Cm by silica: Effect of addition order. [Cm(III)] = 2.2 \times 10^{-10} M, I = 0.1 M (NaClO₄), [Silica] = 5g/l, [HA] = 2 mg/L. The dash and dotted lines are the LAM fits of silica-HA-Cm(III) systems

In the present study of silica-Cm-HA, initially Cm(III) is sorbed quantitatively onto the silica surface. Addition of HA to this suspension results in complexation of
sorbed Cm(III) by HA. One of the explanations for the decreased desorption of Cm(III) in the Silica-Cm-HA at intermediate pH values, could be the incorporation of Cm(III) in silica matrix following dissolution of silica. The dissolution of silica increases with pH. Furthermore, Takahashi et al. (2006) found that presence of Eu(III) promotes the dissolution of silica by facilitating hydrolysis of Si-O-Si bonds. Chung et al. (1998) studied Cm(III) sorption on silica using TRLFS and obtained two lifetimes 220µs and 740µs. They assigned shorter lifetime component to ≡SiOCm²⁺ and larger lifetime component to co-precipitation of Cm and Si(OH)₄ formed as the result of silica dissolution.

4.3.5.1. LAM of ternary system:

With a view to understand the role of HA in influencing the sorption behaviour of Cm(III) by silica, LAM was carried out. This simple model, assumes that the sorption in the case of ternary Cm-silica-HA system can be explained in terms of the additive effect of the binary interactions between the individual components. According to this model, complexation of Cm(III) by mineral bound HA will enhance the sorption of Cm(III), while the HA present in solution will tend to decrease the sorption. The $K_D$ at any pH in the ternary system is given by the equation 2.19.

The $K_D^0$ for binary system as a function of pH was obtained from the measured sorption data. The fraction of HA bound to silica as a function of pH was obtained from the experimental data on sorption of Aldrich HA on silica measured by Fairhurst et al. (1995 a). For the stability constant of Cm(III)-HA, the data reported by Silva and Nitsche (1995), for Am(III)-HA as a function of pH was used. The percentage sorption of Cm(III) in the ternary system calculated from the $K_D$ values are shown as dotted and dashed lines in figure 4.7 for two conditions of $\beta_1$ and $\beta_2$, that is,
(i) $\beta_2 = \beta_1$ and (ii) $\beta_2 = 1.05 \beta_1$. The results show that the linear additive model can explain the observed trend of sorption data, that is, enhancement at lower pH and decrease at intermediate pH values qualitatively. Increasing the stability constant of Cm(III) complex with mineral bound HA by 5%, with respect to that in solution gives the results which are closer to the experimental data. However, the calculated sorption curves are far from the experimental data, indicating that the assumptions in the linear additive model that the $K_D$ values are additive may not be valid. This is plausible as the sorption of HA onto silica might modify the surface charge characteristics of the silica at lower pH. HA coated silica particles have been found to have more negative surface charge than bare silica particles (Ledin et al. 1994). The rise in percentage sorption at higher pH (> 8) is in agreement with that observed by Fairhurst et al. (1995 a) and could be due to the formation of carbonate complexes or incorporation of Cm in lattice (Panak et al., 1996; Takahashi et al., 2002). However, the exact mechanism of the rise is not clear. Speciation calculation of Cm(III) in aqueous system containing both HA and carbonate anions predicts the dominance of Cm(CO$_3$)$_2^-$ at pH above 9 while humate complexes dominate in the pH range of 7-9 (Takahashi et al., 2002). For a clear understanding of the effect of HA on the sorption of Cm(III) by silica, SCM of the ternary system is needed with input about the structure of the surface complexes from the spectroscopic techniques, such as EXAFS and TRLFS, which can provide direct signature of the metal ligand complex on the mineral oxides (Takahashi et al., 2002).

4.3.6. Sorption of Cm (III) by silica: Effect of ionic strength:

Figure 4.8 shows a plot of percentage sorption of curium by silica colloids as a function of ionic strength at pH 6.5. The percentage sorption remains nearly constant
indicating negligible effect of ionic strength on the sorption process. This suggests that the sorption follows inner sphere complex formation between Cm(III) and surface sites on silica. The small decrease in the percentage sorption with increasing ionic strength (I) up to I = 0.1 M may be due to the ionic strength dependence of the binding constant of Cm(III) with silica (Reed et al., 1999).

![Figure 4.8](image_url)  
**Figure 4.8** Effect of ionic strength on sorption of Cm by silica colloids. pH = 6.5, 

\[
[Cm(III)] = 2.2 \times 10^{-10} \text{ M}, [\text{Silica}] = 5 \text{ g/l}
\]

Figure 4.9 shows the speciation of Cm(III) as a function of ionic strength at pH 6.5 obtained using the geochemical code MINTEQA2. The concentration of Cm(OH)$_2^+$ decreases with increase in ionic strength up to I = 0.05 M which is attributed to a decrease in activity coefficient of Cm$^{3+}$ and Cm(OH)$_2^+$ with ionic strength. The decrease in activity coefficient of Cm$^{3+}$ is higher than that of Cm(OH)$_2^+$, hence Cm(OH)$_2^+$ concentration decreases initially. Above I = 0.05 M, the
concentration of both the species remains constant. The higher hydrolyzed species are not dominant at pH 6.5.

**Figure 4.9** Speciation of Cm(III) as a function of ionic strength at pH = 6.5.

In case of sorption reactions three factors are affected by ionic strength namely (i) Coulombic energy, (ii) dissociation constant of surface sites and (iii) activity coefficient of Cm$^{3+}$ in solution. The Coulombic energy and activity coefficient of Cm$^{3+}$ in solution decrease with ionic strength and dissociation constant of surface sites increases with ionic strength (Dzombak and Morel, 1990). Thus, the first two factors tend to decrease the sorption while third one favours the sorption with increasing ionic strength. The net effect is that there is a slight decrease in sorption initially with ionic strength. Thus, the negligible influence of ionic strength suggests the occurrence of inner sphere complexation between silica surface sites and curium.
4.3.7. Sorption of Cm (III) by silica: Effect of HA concentration:

The variation of the percentage sorption as a function of concentration of HA, at pH = 6.0, is plotted in Figure 4.10. Except for the lowest concentration of HA, the percentage sorption gradually decreases with increasing concentration of HA, which can be explained in terms of strong complexation of Cm(III) by HA in the intermediate pH range. Similar effect of HA concentration has been observed in case of Th(IV) sorption on hematite (Reiller et al., 2005).

![Figure 4.10 Sorption of Cm by silica as a function of [HA]. (pH = 6.0)](image)

4.3.8. Sorption of Cm (III) by silica: Effect of HIBA concentration:

The percentage sorption of curium by silica colloids in absence and presence of HIBA is shown in Figure 4.11. In the case of Silica-Cm-HIBA(I), the sorption data follow that of the binary system whereas the sorption edge is slightly shifted to higher pH for Silica-HIBA(I)-Cm system as compared to the binary Cm(III)-silica system as shown in figure 4.11. Similar trends are observed in Silica-Cm-HIBA(II) and Silica-
HIBA(II)-Cm systems (figure 4.11) but in case of Silica-HIBA(II)-Cm the shift of sorption edge is more pronounced as compared to Silica-HIBA(I)-Cm. This is attributed to higher HIBA concentration in these systems.

![Figure 4.11 Sorption of Cm(III) on silica in presence and absence of HIBA.](image)

**Figure 4.11** Sorption of Cm(III) on silica in presence and absence of HIBA. 

\[ [\text{Cm(III)}] = 2.2 \times 10^{-10} \text{ M}; \text{Silica} = 5 \text{ g/L}; [\text{HIBA(I)}] = 1 \times 10^{-5} \text{ M} ; [\text{HIBA(II)}] = 1 \times 10^{-3} \text{ M}; I = 0.1 \text{ M (NaClO}_{4})].

The effect of HIBA on the sorption of Eu(III) by silica can be understood considering the sorption of HIBA by silica. TOC values in the supernatant solutions were found to be close to that corresponding to the initial HIBA concentration indicating negligible sorption of HIBA by silica at all pH values. The low pK\(_{a}\) (3.78) of HIBA (Portanova et al., 2003) suggests that its anionic form dominates in the pH range of study in which the silica surface is negatively charged (PZC < 2.4) (Kumar et al., 2006), thereby resulting in negligible sorption of HIBA on silica. Thus, HIBA can be treated as a complexing anion present in silica suspension. For Silica-HIBA(I)-Cm
system, with the increase in pH of the suspension, the complexation of Cm(III) by HIBA results in decreased sorption of Cm(III) on silica surface. In the case of Silica-Cm(III)-HIBA(I) system, initially Cm(III) is sorbed quantitatively onto the silica surface. Introduction of HIBA to this suspension should result in complexation of sorbed Cm(III) by HIBA and thereby generation of sorption profile similar to Silica-HIBA(I)-Cm system. However, the decrease in the sorption of Cm(III) as observed in case of Silica-HIBA(I)-Cm is not seen in the case of Silica-Cm-HIBA(I). In most of the cases the effect of addition order of HA and metal ion on sorption to mineral oxides have been studied (Wang et al., 2000, 2004; Xu et al., 2006 a, 2006 b; Reiller et al., 2005; Davis, 1984; Fan, 2009; Li et al., 2009; Liu et al., 2001) but there is hardly any literature report dealing with addition order of small complexing anions and metal ions. One of the explanations for the decreased desorption of Cm(III) in the Silica-Cm-HIBA(I), could be the incorporation of Cm(III) in silica matrix following dissolution of silica. The log β for Cm-HA (Cornelis, 2005) is much more than that of Cm-HIBA which is responsible for the higher desorption capacity of HA as compared to HIBA.

4.3.9. SCM:

SCM was used to analyse the data of Cm(III) sorption on silica in absence and presence of HIBA to infer about the surface reactions governing the sorption process. In present studies DLM has been used which assumes the oxide-water interface to comprise of two charged layers, namely, surface layer and a diffuse layer of counter ions in solution. The Gouy-Chapman distribution of ions was assumed for the diffuse layer.
4.3.9.1. SCM of binary systems:

In Cm(III)-silica system, the most dominant species in the pH range of study are Cm$^{3+}$ and CmH$_3$SiO$_4^+$ as shown in figure 4.3(a). Thus, a model considering monodentate mononuclear curium surface complex $≡$SiOCm$^{2+}$ and monodentate mononuclear curium monosilicate surface complex $≡$SiOCmH$_3$SiO$_4^+$ was tried which successfully fit the sorption data for binary system. The corresponding surface complexation reactions are described in equations (4.5) and (4.6).

\begin{align}
≡ SiOH + Cm^{3+} & \Leftrightarrow ≡ SiOCm^{2+} + H^+ \quad (4.5) \\
≡ SiOH + CmH_3SiO_4^{2+} & \Leftrightarrow ≡ SiOCmH_3SiO_4^+ + H^+ \quad (4.6)
\end{align}

Although the above model fit the sorption data quite well, TRLFS of Cm(III) sorption on silica revealed the existence of two species with lifetimes 220 µs and 740 µs which correspond to 2 and 0 water molecules respectively (Chung et al., 1998), therefore the sorption data was fitted using monodentate mononuclear curium disilicate surface complex $≡$SiOCm(H$_3$SiO$_4$)$_2$ instead of monodentate mononuclear curium monosilicate surface complex $≡$SiOCmH$_3$SiO$_4^+$ as $≡$SiOCm(H$_3$SiO$_4$)$_2$ approximates more closely to the species containing no water molecules. The surface complexation reaction for $≡$SiOCm(H$_3$SiO$_4$)$_2$ is given below.

\begin{align}
≡ SiOH + 2CmH_3SiO_4^{2+} & \Leftrightarrow ≡ SiOCm(H_3SiO_4)_2 + 2H^+ \quad (4.7)
\end{align}

Thus, Cm(III) sorption on silica is described using monodentate mononuclear curium surface complex $≡$SiOCm$^{2+}$ and monodentate mononuclear curium disilicate surface complex $≡$SiOCm(H$_3$SiO$_4$)$_2$ as shown in figure 4.12.

4.3.9.2. SCM of ternary systems:

The sorption data for the ternary system of Cm(III)-silica-HIBA systems were modeled using similar analogy as that in case of binary system.
Figure 4.12 SCM of Cm(III) sorption by Silica in presence of HIBA (a) binary Silica-Cm system; (b) Silica-Cm-HIBA(I) system; (c) Silica-HIBA(I)-Cm system; 

\[ [\text{Cm(III)}] = 2.2 \times 10^{-10} \text{ M}; \text{Silica} = 5 \text{ g/L}; [\text{HIBA}] = 1 \times 10^{-5} \text{ M}. \]

4.3.9.2. (a) Silica-Cm-HIBA(I) system ([HIBA] = 10^{-5} M) :

In Silica-Cm-HIBA(I) system, the surface complex pertaining to Cm(III) and CmH_3SiO_4^+, the major species in aqueous phase in the pH range of study, were considered while modeling the sorption data of this ternary system. The sorption profile could be explained considering the surface complexes, namely, ≡SiOCm^2+ and ≡SiOCmH_3SiO_4^+. However, using the similar hypothesis, as in the case of binary system, that ≡SiOCm(H_3SiO_4)_2 approximates more closely to the species containing no water molecules, ≡SiOCm(H_3SiO_4)_2 and ≡SiOCm^2+ were considered as surface
complexes which gave the best fit as shown in figure 4.12 (b) and corresponding surface reactions are given by equations (4.5) and (4.7).

4.3.9.2. (b) Silica-HIBA(I)-Cm system ([HIBA] = 10^{-5} M):

The aqueous speciation is same in both Silica-HIBA(I)-Cm and Silica-Cm-HIBA(I) systems as it is independent of order of addition of HIBA and Cm(III). The surface complexes $≡$SiOCm$^{2+}$ and $≡$SiOCm(H$_3$SiO$_4$)$_2$ were evaluated to fit the sorption data but no convergence was obtained which in turn validated that order of addition of HIBA and Cm(III) does influence the surface species responsible for sorption. In case of Silica-HIBA(I)-Cm, when Cm(III) is added to silica suspension containing HIBA, Cm(III) can interact both with HIBA and silica. As the kinetics of complex formation (Cm-HIBA) is much faster than that of sorption, it can be concluded that Cm-HIBA complex is formed instantaneously and get sorbed on to silica surface, even though aqueous speciation calculations do not support their existence. Consideration of surface complexes, namely, $≡$SiOCm(iba)$^+$ and $≡$SiOCm(H$_3$SiO$_4$)$_2$ resulted in successful fitting of sorption data as shown in figure 4.12 (c). The surface complexation reactions for both the sorbates are given by equation (4.7) and (4.8).

$$≡SiOH + CmIBA^{2+} ⇔ ≡SiOCmIBA^+ + H^+ \quad (4.8)$$

4.3.9.2. (c) Silica-Cm-HIBA(II) system ([HIBA] = 10^{-3} M):

The speciation of Cm(III) is dominated by Cm$^{3+}$, Cm(iba)$^+$ and Cm(H$_3$SiO$_4$)$_{2^+}$ in the pH range of interest (figure 4.3(c)). As far as curium silicate species are concerned Cm(H$_3$SiO$_4$)$_{2^+}$ was considered as sorbate instead of CmH$_3$SiO$_4^{2+}$. All the permutations of the surface complexes involving the above
mentioned species were tried in order to fit the sorption profile but no convergence was obtained in any case. Therefore Cm(IBA)$_2^+$ complex, though formed in minute amount, was considered as a potential sorbate along with Cm(H$_3$SiO$_4$)$_2^+$. The two surface complexes comprising of these two species were found to fit the sorption data satisfactorily as shown in figure 4.13 (a). The corresponding surface complexation reactions are given by equations (4.7) and (4.9).

$$\equiv SiOH + (CmIBA)_2^+ \leftrightarrow \equiv SiO(CmIBA)_2 + H^+$$ (4.9)

4.3.9.2. (d) Silica-HIBA(II)-Cm system ([HIBA] = $10^{-3}$ M):

In Silica-HIBA(II)-Cm(III) system, the aqueous speciation is same as in Silica-Cm(III)-HIBA(II). The surface complexes pertaining to Cm(IBA)$_2^+$ and Cm(H$_3$SiO$_4$)$_2^+$ were evaluated for fitting the sorption data but satisfactory fit was not obtained as the 10-20 % sorption at low pH could not be explained by considering only these two surface complexes. In order to account for sorption at low pH, outer sphere surface complex $\equiv SiOH Cm(IBA)^+$ was tested along with the two surface complexes mentioned above which could successfully fit the sorption data as shown in figure 4.13 (b).

The need for an outer sphere complex can be attributed to sorption of HIBA on silica surface which was determined using TOC content in supernatant of the silica suspension after equilibration with HIBA. It is worth mentioning here that sorption of 2-3% HIBA on silica at low pH would not be manifested in the TOC measurement, though it would be sufficient to enhance the sorption of Cm(III) at low pH. The surface complexation reactions for all the three sorbates are given by equation (4.7), (4.9) and (4.10).

$$\equiv SiOH + CmIBA^{2+} \leftrightarrow \equiv SiOH CmIBA^{2+}$$ (4.10)
Figure 4.13 SCM of Cm(III) sorption by Silica in presence of HIBA (a) Silica-Cm-HIBA(II) system ; (b) Silica-HIBA(II)-Cm system; [Cm(III)] = 2.2 X 10^{-10} M; Silica = 5 g/L; [HIBA] = 1 X 10^{-3} M.

Thus, it appears that not only the aqueous speciation governs the various possibilities of surface complexes, but the addition order of HIBA and Cm(III) is also one of the important parameters influencing the type of surface complex formed at the solid solution interface. The stability constants of the surface complexes for all the systems are given in Table 4.3.
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Table 4.3 Optimized parameter values as obtained from FITEQL for Cm-silica and Cm-silica-HIBA systems

<table>
<thead>
<tr>
<th>System</th>
<th>Reaction</th>
<th>Log K</th>
<th>WSOS/ DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica-Cm(III)</td>
<td>≡SiOH + Cm$^{3+}$ + 2SiO(OH)$_3^-$ ↔ ≡SiOCm(OSi(OH)$_3$)$_2$ + H$^+$</td>
<td>-7.94</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>≡SiOH + Cm$^{3+}$ ↔ ≡SiOCm$^{2+}$ + H$^+$</td>
<td>-2.53</td>
<td></td>
</tr>
<tr>
<td>Silica-Cm(III)-HIBA(I)</td>
<td>≡SiOH + Cm$^{3+}$ + 2SiO(OH)$_3^-$ ↔ ≡SiOCm(OSi(OH)$_3$)$_2$ + H$^+$</td>
<td>-8.04</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>≡SiOH + Cm$^{3+}$ ↔ ≡SiOCm$^{2+}$ + H$^+$</td>
<td>-2.48</td>
<td></td>
</tr>
<tr>
<td>Silica-HIBA(I)-Cm(III)</td>
<td>≡SiOH + Cm$^{3+}$ + 2SiO(OH)$_3^-$ ↔ ≡SiOCm(OSi(OH)$_3$)$_2$ + H$^+$</td>
<td>-7.58</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>≡SiOH + Cm$^{3+}$ + HIBA ↔ ≡SiOCm(IBA)$^+$ + 2H$^+$</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>Silica-Cm(III)-HIBA(II)</td>
<td>≡SiOH + Cm$^{3+}$ + 2SiO(OH)$_3^-$ ↔ ≡SiOCm(OSi(OH)$_3$)$_2$ + H$^+$</td>
<td>-8.21</td>
<td>3.91</td>
</tr>
<tr>
<td></td>
<td>≡SiOH + Cm$^{3+}$ + 2HIBA ↔ ≡SiOCm(IBA)$_2$ + 3H$^+$</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>Silica-HIBA(II)-Cm(III)</td>
<td>≡SiOH + Cm$^{3+}$ + 2SiO(OH)$_3^-$ ↔ ≡SiOCm(OSi(OH)$_3$)$_2$ + H$^+$</td>
<td>-8.42</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>≡SiOH + Cm$^{3+}$ + HIBA ↔ ≡SiOCm(IBA)$_2$ + 3H$^+$</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>≡SiOH + Cm$^{3+}$ + HIBA ↔ ≡SOHcm(IBA)$_{2+}$ + H$^+$</td>
<td>5.19</td>
<td></td>
</tr>
</tbody>
</table>

4.3.10. Sorption of Eu(III) by silica: Effect of HIBA concentration:

Figure 4.14 shows the data on sorption of Eu(III) by silica both in absence and presence of HIBA. The sorption of Eu(III) by silica increases with the pH of the suspension approaching nearly 100% at pH 7.0. In the presence of HIBA, a significant
decrease in the sorption of Eu(III) by silica was observed in the pH range of 5.5 – 7.0. Similar observation was made by Pathak et al. (2007a) in the case of sorption of Eu(III) by silica in presence of citrate.

![Figure 4.14](image)

**Figure 4.14** Sorption of Eu(III) on silica in presence and absence of HIBA. [Eu(III)]

= 5.0 X 10^{-5} M; Silica = 10 g/L; [HIBA] = 2.5 X 10^{-3} M, I = 0.1 M (NaClO₄).

Sorption of HIBA by silica has been found to be negligible at all pH values, therefore HIBA can be treated as a complexing anion present in silica suspension. With the increase in pH of the suspension, the complexation of Eu(III) by HIBA results in decreased sorption of Eu(III) on silica surface. The similar decrease in the sorption of UO₂^{2+} on silica has been observed in presence of citric acid (Kar et al., 2012). At higher pH values, surface precipitation of Eu(OH)₃ is possible. Surface precipitation is likely to occur when metal concentration is more than 1/10 of the
solubility limit and surface coverage is greater than 1/3 of the total surface sites available for sorption (Dzombak and Morel, 1990).

In the present work, though, solubility limit is exceeded at pH 6.2, but even at 100% sorption only small fraction of the total surface sites will be occupied and hence surface precipitation is likely to be absent. Further, the TRFS measurements did not show any lifetime component (40±5 μs) (Plancque et al., 2003) corresponding to Eu(OH)₃ which confirms the absence of Eu(III) precipitation. Absence of surface precipitation was also reported by Rabung et al. (2000) in the metal ion concentration range 10⁻⁸ -10⁻⁴ M even at pH = 8. TRFS studies with 2 X 10⁻⁴ M Eu(III) on silica also showed that europium precipitation did not take place even at pH 7.5 (Takahashi et al., 2006). Fluorescence studies of Eu(III) (10⁻³ M) on silica revealed the existence of two surface complexes. However, no signature of Eu(OH)₃ precipitation was observed even at a concentration 20 times higher than that used in present work (Fouchard et al., 2004a).

4.3.10. 1. TRFS:

Figures 4.15 (a) and 4.15 (b) show the fluorescence emission spectra of Eu(III) sorbed on silica in absence and presence of HIBA respectively. The spectrum shows characteristic fluorescence emission due to the decay of the ⁵D₀ excited state of Eu³⁺ into ⁷Fₗ (j = 0-4) states. The spectra have been normalized with respect to the intensity at 592 nm, except for pH < 5.5, where no spectral features characteristic of Eu(III) were observed. The transition corresponding to 616 nm peak (⁵D₀ \rightarrow ⁷F₂) is hypersensitive owing to its electric dipole nature and its intensity is dependent on the symmetry around the metal ion. With the sorption of Eu(III) by silica, the chemical environment around the metal ion becomes more and more asymmetric leading to the
increase in the asymmetric ratio \( R = \frac{I_{616}}{I_{592}} \). This is evident from the increase in intensity of the 616 nm peak with respect to that of 592 nm peak as shown in figure 4.15 (a).

**Figure 4.15** Time resolved fluorescence emission spectra of Eu(III) sorbed on silica in absence (a) and presence (b) of HIBA. \([\text{Eu(III)}] = 5.0 \times 10^{-5} \text{M}; \text{Silica} = 10 \text{ g/L}; \text{[HIBA]} = 2.5 \times 10^{-3} \text{ M.}\)

Figure 4.16 shows the typical fluorescence decay curve for Eu(III) sorbed on silica at pH 8.06. The fluorescence decay data from 25 µs to 2.0 ms were fitted into multi-exponential functions to obtain the lifetime data. The best fit \( (\chi^2 \sim 1.4) \) was obtained with four lifetime components. The shortest lived component was found to be of the order of 1 µs which is due to instrumental artifact and does not vanish even
if the spectrum is recorded by giving an appropriate delay. The other short lived component is around 20 µs and did not show any signature of Eu(III) characteristic emission when the spectrum was gated with respect to this particular lifetime. Hence in further discussion two lifetime components, $\tau_1$ and $\tau_2$, having characteristic Eu(III) emission have been discussed. The emission spectrum of bare silica showed a broad band with maximum at 450 nm. It was found that silica exhibits a longer lived component (Figure 4.16 (b)) but its fraction is much smaller (4-5\%) than that observed (30-70\%) in case of europium sorbed on silica.

Figure 4.16 Comparison of the fluorescence decay curve of Eu(III) sorbed on silica at pH = 8.06 to that of bare silica.

Figure 4.17 shows the variation of $\tau_1$ and $\tau_2$ as a function of pH both in absence and presence of HIBA. The magnitude of the life times, 150 µs and 400 µs, remains nearly constant at all pH values. The error on the lifetime values is about 10\% which arises due to the instrumental drifts, temperature variation and sample
preparation. The magnitude of $\tau_1$ and $\tau_2$ is in agreement with the literature reports where in the $\tau_1$ and $\tau_2$ values of 130 $\mu$s and 350 $\mu$s (Fouchard et al., 2004a) and 137 $\mu$s and 335 $\mu$s (Tetre et al., 2006) have been observed.

![Fluorescence life time data of Eu(III) sorbed on silica in absence (a) and presence (b) of HIBA. [Eu(III)] = 5.0 X 10^{-5} M; Silica = 10 g/L; [HIBA] = 2.5 X 10^{-3} M.](image)

Figure 4.17 Fluorescence life time data of Eu(III) sorbed on silica in absence (a) and presence (b) of HIBA. [Eu(III)] = 5.0 X 10^{-5} M; Silica = 10 g/L; [HIBA] = 2.5 X 10^{-3} M.

The lifetime can be correlated to the number of water molecules by the relationship given in equation 3.2. Though this empirical correlation is applicable to Eu(III) complexes in solution, it can be used as a guide to predict the nature of sorbed Eu(III) species. The short lived component corresponds to 6-7 water molecules indicating that Eu(III) is sorbed onto silica through inner sphere complexation while the long lived component, corresponding to 1-2 water molecules, is attributed to sorbed Eu(III) silicate complexes. The lifetime data are similar in presence of HIBA.
indicating negligible effect of HIBA on the fluorescence characteristics of sorbed Eu(III). This further corroborates the negligible sorption of HIBA by silica.

![Figure 4.18](image.png)

**Figure 4.18** Lifetime data of Eu(III) sorbed on silica as function of equilibration time.

\[ [\text{Eu(III)}] = 5.0 \times 10^{-5} \text{ M; Silica} = 10 \text{ g/L}. \]

Takahashi et al. (1998) observed mono-exponential decay with the lifetime increasing with pH, while bi-exponential decay has been reported by many authors (Fouchard et al., 2004a; Tetre et al., 2006), though no comments were made about the nature of species. Similar observations were made by Chung et al. (1998) in the study of Cm(III) sorption on silica by TRFS. They assigned shorter lifetime component (220 µs) to \( \equiv \text{SiOCm}^{2+} \) and the longer lifetime component (740 µs) to co-precipitation of Cm and Si(OH)\(_4\) formed as a result of silica dissolution. Thus the
Chapter IV

TRFS studies clearly suggest the occurrence of two surface complexes having distinctly different chemical environments.

Figure 4.18 shows the fluorescence decay lifetime of Eu(III) sorbed on to silica as a function of aging time for two pH values (6 and 8). The constancy of the lifetimes over a period of 5 days suggests the absence of any aging effects which has been proposed as a mechanism of the incorporation of Eu(III) into the silica matrix (Takahashi et al., 2006).

4.3.10.2. SCM:

The information obtained from the TRFS measurements and the speciation calculation of Eu(III) in presence of silicic acid and HIBA have been used in the SCM of the binary and ternary systems using FITEQL 4.0. Based on the speciation diagram (figure 4.3), and the life time values, the two surface complexes can be attributed to sorption of Eu$^{3+}$ ($\tau_1$) and Eu(OSi(OH)$_3$)$_2^+$ ($\tau_2$) onto the silica surface. Though Eu(OSi(OH)$_3$)$_2^+$ is the dominant species in the pH range of study (figure 4.3), considering the inevitable formation of polysilicic acid, Eu(OSi(OH)$_3$)$_2^+$ has been considered, as a more realistic species, in SCM. Moreover, the two surface complexes owing to sorption of Eu$^{3+}$ and Eu(OSi(OH)$_3$)$_2^+$ onto the silica surface did not yield satisfactory fits which further corroborates the formation of polysilicic acid. The SCM predictions along with experimental data, considering Eu(OSi(OH)$_3$)$_2^+$, are shown as continuous curves in figure 4.19 (a) and 4.19 (b) for both binary and ternary systems respectively. The log K values for the surface complexes along with WSOS/DF are given in Table 4.4.
Table 4.4 Optimised parameter values as obtained from FITEQL for Eu-silica and Eu-silica-HIBA

<table>
<thead>
<tr>
<th>System</th>
<th>Reaction</th>
<th>log K</th>
<th>WSOS/DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiometric titration data fitting using DLM</td>
<td>SiOH + H⁺ ↔ ≡SiOH₂⁺</td>
<td>0.56</td>
<td>16.68</td>
</tr>
<tr>
<td></td>
<td>≡SiOH ↔ ≡SiO⁻ + H⁺</td>
<td>-6.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface sites ≡SiOH</td>
<td>-6.41</td>
<td>6.79</td>
</tr>
<tr>
<td></td>
<td>2(≡SiOH) + Eu³⁺ ↔ (≡SiO)₂Eu⁺⁻ + 2H⁺</td>
<td>-14.09</td>
<td></td>
</tr>
<tr>
<td>Eu-silica</td>
<td>2(≡SiOH) + Eu³⁺ ↔ (≡SiO)₂Eu⁺⁻ + 2SiO(OH)₃⁻</td>
<td>-6.78</td>
<td>21.09</td>
</tr>
<tr>
<td></td>
<td>2(≡SiOH) + Eu³⁺ ↔ (≡SiO)₂Eu⁺⁻ + 2SiO(OH)₃⁻</td>
<td>-14.93</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.19 shows that (≡SiO)₂Eu(OSi(OH)₃)₂⁻ dominates the sorption of Eu(III) by silica in the pH range of 6-8. This is further corroborated by the observation of dominating long lived component in the fluorescence decay data, indicating nearly 1-2 water molecules around the Eu³⁺ ion. The bidentate binding of Cm(III) to quartz surface has also been predicted by Stumpf et al. (2004). Since europium silicates are the dominant species in presence of HIBA (figure 4.3), the same surface complexes have been proposed for ternary system. Thus we find that, though presence of HIBA decreases the sorption of Eu(III) by silica in the intermediate pH range of 5.5 – 7.0, Eu-silicate complexes dominate the surface complexation with the un-complexed Eu(III) playing a minor role. The detail understanding of the sorption process would require the study of Eu(III) complexation with polysilicic acid.
Figure 4.19 SCM of Eu(III) sorption by Silica in absence (a) and presence of HIBA(b). \([\text{Eu(III)}] = 5.0 \times 10^{-5} \text{ M}; \text{Silica} = 10 \text{ g/L}; [\text{HIBA}] = 2.5 \times 10^{-3} \text{ M. L = OSi(OH)}_3^- \).

4.3.11. Comparison of Silica-Cm(III) and Silica-Eu(III) systems:

Sorption of Cm(III) and Eu(III) on silica, shown in figure 4.20 (a), follow the typical 'S' shaped curve with the sorption edge at pH 4 and pH 6 respectively. The observed difference in the sorption edge is a manifestation of five order of magnitude difference in concentration of Cm(III) (\(1 \times 10^{-10} \text{ M}\) and Eu(III) (\(5 \times 10^{-5} \text{ M}\)). In the case of Eu(III)-silica system, bidentate mononuclear europium surface complex \((\equiv \text{SO})_2 \text{Eu}^+\) and bidentate mononuclear europium disilicate surface complex \((\equiv \text{SO})_2 \text{Eu} (\text{H}_3\text{SiO}_4)_2^-\) were postulated to fit the sorption profile whereas for the Cm(III)-silica system, satisfactory fits were obtained with monodentate mononuclear curium surface complex \(=\text{SOCm}^{2+}\) and monodentate mononuclear curium disilicate.
surface complex =SO\text{Cm}(H_3\text{SiO}_4)_2. The different kind of binding in both the systems can be attributed to the different ratio of silica sites to metal ion involved, which is 50 for Eu(III)-silica system and about $10^7$ for Cm(III)-silica system.

![Graph showing sorption of Cm(III) and Eu(III) on silica in absence (a) and presence (b) of HIBA.](image)

**Figure 4.20** Sorption of Cm(III) and Eu(III) on silica in absence (a) and presence (b) of HIBA. For Silica-Cm(III) system: Silica = 5 g/L, [Cm(III)] = 2.2 X 10^{-10} \text{ M}, [HIBA] = 1 \times 10^{-3} \text{ M} and I= 0.1 \text{ M (NaClO}_4). For Silica-Eu(III) system: Silica = 10 g/L [Eu(III)] = 5 \times 10^{-5} \text{ M}, [HIBA] = 2.5 \times 10^{-3} \text{ M} and I=0.1 \text{ M (NaClO}_4) (Kar et al. 2011b).

The comparison of sorption data for ternary systems, namely, Silica-HIBA(II)-Cm with Silica-HIBA-Eu is shown in figure 4.20 (b) (Kar et al., 2011 b). Silica-
HIBA(II) -Cm system has been selected as concentration of HIBA and the order of addition of HIBA and metal ion are similar to Silica-HIBA-Eu system.

The shift of sorption edge to higher pH in case of Eu(III) is attributed to the higher concentration of Eu(III) than that of Cm(III). The bidentate mononuclear europium surface complex \((\equiv \mathrm{SO})_2 \text{Eu}^+\) and bidentate mononuclear europium disilicate surface complex \((\equiv \mathrm{SO})_2 \text{Eu}(\text{H}_3\text{SiO}_4)_2\) were able to fit the sorption profile in Silica – HIBA-Eu(III) system. Though presence of HIBA shifts the sorption edge to high pH, the speciation is still dominated by europium silicates in presence of HIBA. Therefore, the same surface complexes have been proposed for ternary system. In case of Silica-HIBA(II)-Cm, apart from the two inner sphere surface complexes \(\equiv \text{SiOCm(IBA)}_2\) and \(\equiv \text{SiOCm(H}_3\text{SiO}_4)_2\), which are different from that in Silica-Eu(III) system, an outer sphere complex \(\equiv \text{SiOHCM(IBA)}^{2+}\) is required to reproduce the sorption profile.

In case of Silica-HIBA(II)-Cm system, the surface complexes involving Cm(III)-HIBA also appear to participate in the sorption process in contrast to Silica-HIBA-Eu(III) owing to five order of magnitude higher value of \([\text{HIBA}]/[\text{M(III)}]\) in case of Cm(III) than that in case of Eu(III). Moreover, the concentration ratio of dissolved silica to HIBA is 2 in case of Silica-HIBA(II)-Cm system where as it is 4 for Silica-HIBA-Eu(III). Thus although stability constants for metal silicate complexes are very high as compared to metal HIBA complexes, due to the comparable concentration of HIBA and dissolved silica the contribution of Cm-HIBA complexes towards the surface speciation cannot be ruled out. However, in order to have detailed understanding about the role of HIBA, its concentration variation over a wide range need to be studied.
4.3.12. Comparison of Silica-HIBA(I)-Cm and Silica-HA-Cm systems:

HA is a natural organic matter with large heterogeneity. The high molecular weight with hydrocarbon networks leads to lipophilic interactions and functional groups like carboxylate and phenolate contribute to the lyophilic character of HA (Stevenson, 1982). HA is found to have significant influence on the migration of radio-nuclides in the aquatic environment (Choppin, 1999). The presence of carboxylic and hydroxyl groups, the major functional groups in HA, has attracted the attention of geochemists towards the adsorptive properties of low molecular weight organic acids which are considered building blocks of NOM. However, even if their influence on the adsorption of metal ions can be modeled accurately, the behaviour of these compounds may not be analogues to HA. With this in view, the data for sorption of Cm(III) by silica in presence of HIBA were compared with those in presence of HA. The data are shown in figure 4.21.

Unlike in the case of silica-HA-Cm, wherein strong influence of presence of HA was observed in the pH range 3-8, (enhancement at lower pH and decrease in sorption at higher pH), the effect of HIBA on sorption of Cm(III) by silica was found to be weak. This is partly due to the sorption of HA on silica at lower pH and negligible sorption at higher pH and partly due to the higher stability constant of Cm(III)-HA complexes than that of Cm(III)-HIBA. In the case of Silica-Cm-HIBA(I), the sorption data exhibits similar sorption profile as that observed for the binary Cm(III)-Silica system. This is again quite different from silica-Cm-HA system, wherein the Cm(III) sorption by silica is enhanced at low pH and decreased in the intermediate pH range, though not as much as in the case of silica-HA-Cm system.
Figure 4.21 Sorption of Cm(III) on silica in presence of HIBA and HA. Silica = 5 g/L; [Cm(III)] = 2.2 X 10^{-10} M; I = 0.1 M (NaClO₄); [HIBA] = 1 X 10^{-5} M and [HA] = 2 mg/L.

From the above observations, it is evident that the influence of HIBA on sorption of Cm(III) by silica is drastically different from that of HA, which can be attributed to polyfunctionality of HA. Thus, though small molecules can be studied in order to have fundamental understanding of the nature of binding between the different functional groups present in HA and metal ion, they cannot be used as analogues of HA.

4.4. Conclusions:

The present study has shown that the sorption of curium by silica is significantly influenced by the presence of HA in the entire pH range of 4-10. While the sorption is enhanced at lower pH (< 5) it is drastically decreased in the pH range of 6.5-8 in the presence of HA. The addition order of Cm(III) and HA was found to
affect the sorption data in the ternary silica-Cm-HA system. The incomplete desorption of Cm(III) in the case of ternary silica-Cm-HA system could be due to partial incorporation of Cm(III) in the silica matrix. The near independence of the sorption data on ionic strength indicates inner sphere complex formation between Cm$^{3+}$ ions and the silica surface sites.

In case of HIBA, Cm(III) sorption is dependent upon the addition order of Cm(III) and HIBA to the silica suspension. Cm(III) sorption by silica is decreased in presence of HIBA, if the HIBA is added before Cm(III), unlike in the case of silica-Cm(III)-HIBA, wherein the sorption follows binary Silica-Cm(III) profile. The observed discrepancies are attributed to partial incorporation of Cm(III) in the silica matrix in binary system and Silica-Cm-HIBA(I). Significant concentration of Si in the supernatant solutions of silica suspensions indicate the presence of dissolved silica that undergoes complexation with Cm(III) and dominates the speciation of Cm(III) even in the presence of HIBA. SCM using DLM showed the evolution of different surface complexes as a function of HIBA concentration as well as order of addition of HIBA and Cm(III).

TRFS of Eu(III) sorbed on silica provided evidence for the existence of two surface complexes which in turn validated the SCM hypothesis. The short lived component was attributed to $(\equiv$SiO)$_2$Eu$^+$, while the long lived component was attributed to $(\equiv$SiO)$_2$Eu(OSi(OH)$_3$)$_2^-$, with the latter dominating the sorption profile of Eu(III) in both in absence and presence of HIBA.

The comparison of effect of HIBA on sorption of Eu(III) and Cm(III) revealed effect of metal ion concentration on the sorption data. While the comparison of influence of HIBA and HA on Cm(III) sorption revealed that the behaviour of small organic molecules could not be considered as analogous to HA.