Hydration structure of Eu^{III} on aqueous ion-exchange resins using laser-induced fluorescence spectroscopy

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***Ca*. 2 and > 5 molecules of hydrated water are removed from the inner sphere of Eu^{III} on strongly and weakly acidic ion-exchange resins, respectively, showing the different mechanisms between ion-exchange reactions occurring on these two types of resins.**

Recently, the hydration structure of metal ions on strongly acidic cation-exchange resins (denoted as SCR) has been investigated by neutron diffraction.[1] However, descriptions on the structures of the exchanged ion have not been fully clarified, despite the wide applications of cation-exchange resins in chemistry and biology.[2] This is perhaps due to difficulties encountered in analysing the adsorbed metal species at a solid–water interface. The present study provides direct information on the hydration structures of Eu^{III} exchanged on SCR and weakly acidic cation-exchange resins (denoted as WCR) obtained through laser-induced fluorescence spectroscopy. This method has the advantages of having high sensitivity and good selectivity for Eu^{III}, and can be applied to the current resin system in the presence of an aqueous phase. Moreover, the method is able quantitatively to count the number of hydrated water molecules attached to Eu^{III}, unlike neutron diffraction.

The fluorescence lifetime of Eu^{III} ($^5D_0 \rightarrow {}^7F$ manifold) is related to N_{H_2O} (the number of H_2O molecules in the primary coordination sphere of the Eu^{III} ion) due to the energy transfer from the excited state of Eu^{III} to OH vibrations of the hydrated H_2O.[3] The method was therefore applied to measure N_{H_2O} values of Eu^{III} in both aqueous and solid phases.[3] In the present study, the method is, for the first time, applied to the study of the hydration structure of Eu^{III} at the solid–water interface.

AG 50WX8 (functional group: $-SO_3^-$; matrix: styrene divinylbenzonate; proton exchange capacity: 2.1 mequiv. g^{-1}) and Bio-Rex 70 (functional group: $-CO_2$; matrix: acrylate; proton exchange capacity: 3.5 mequiv. g^{-1}) purchased from Bio-Rad Lab., Inc. were used as the SCR and WCR samples, respectively. Linear poly(4-styrenesulfonic) acid (PSS) and linear polyacrylic acid (PAA) purchased from Aldrich were also employed. The concentrations of polyelectrolytes (SCR, WCR, PSS and PAA) and Eu^{III} are listed in Fig. 1. The pH and supporting electrolyte concentration (C_s) were adjusted by addition of small amounts of NaOH or $HClO_4$ and $NaClO_4$ respectively. An aqueous solution of Eu^{III} with no polyelectrolyte was also prepared (WP system). These solutions (or suspensions in the resin systems) were aged overnight prior to the subsequent procedures. The distribution of Eu^{III} between the aqueous and solid phases was measured using a ^{152}Eu tracer after centrifugation at 3000 rpm for 1 min. The solution or suspension contained in a quartz cell and magnetically stirred was exposed to light (395 nm) from a dye laser giving rise to the excitation of Eu^{III} ($^7F_0 \rightarrow {}^5L_6$). The decay curve for the emission at 615 nm was measured by a photomultiplier and recorded with a digital oscilloscope coupled with a personal computer.

The relation of N_{H_2O} with the lifetimes τ_{H_2O} and τ_{D_2O} measured in the H_2O and D_2O systems, respectively, is as follows:[3]

$$N_{H_2O} = 1.05\,(1/\tau_{H_2O} - 1/\tau_{D_2O})/\mathrm{ms}^{-1} \qquad (1)$$

For SCR, WCR, PSS and PAA systems, τ_{D_2O} values were 1.10, 1.98, 3.00 and 3.05 ms, respectively. These τ_{D_2O} values allow us to evaluate N_{H_2O} from the luminescence lifetime measurement data [eqn. (1)] and results are shown in Fig. 1 It is seen that N_{H_2O} of the europium(iii) aqua complex is 9.[3]

In the WP system, the N_{H_2O} decreases from the N_{H_2O} of Eu^{III} (aq) which indicates the formation of inorganic complexes of Eu^{III} such as $Eu(CO_3)^+$, $Eu(OH)^{2+}$ or $Eu(OH)_2^+$ between pH 6 and 7.5.[4] When pH > 7.5, the ^{152}Eu experiments shows that Eu^{III} formed inorganic colloids or precipitates.[4] Formation of such inorganic colloids or precipitates of Eu^{III} made its lifetime very short due to the non-radiative energy transfer among the neighbouring Eu^{III} in the colloids or precipitates.[5] In this pH region therefore, N_{H_2O} of Eu^{III} in the WP system apparently becomes much greater than 9. Such short lifetime values were not observed in the polyelectrolyte systems; therefore inorganic colloidal species were not formed, and all the Eu^{III} is completely complexed with the polyelectrolytes.

In the WCR system, Eu^{III} was shown from ^{152}Eu experiments to be adsorbed at pH > 4. N_{H_2O} decreased abruptly at pH *ca*. 3.5 due to the initiation of ion exchange. The N_{H_2O} value in the WCR system decreased gradually from 3.5 to 2.5 between pH 4 and 9, in a manner similar to the PAA system. This decrease suggests that more carboxylates are bound to Eu^{III} with increasing pH accompanied with an increasing degree of ionization of WCR or PAA.[6]

In the SCR system, Eu^{III} was adsorbed at pH > 0.5 at which N_{H_2O} of the adsorbed Eu^{III} on SCR was *ca*. 7.5. The exchanged Eu^{III} ion on WCR releases five to seven molecules of hydrated

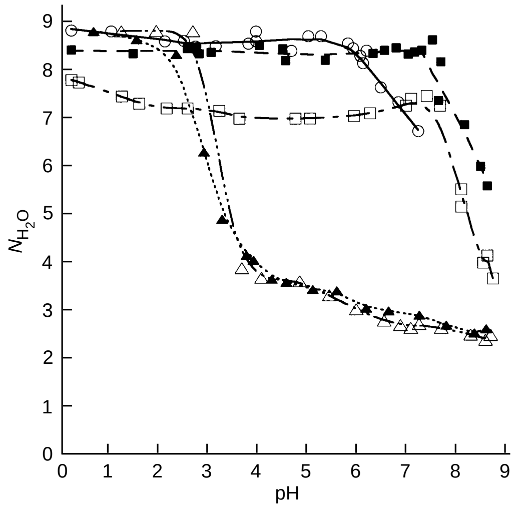

Fig. 1 pH dependence of N_{H_2O} in the SCR (□), WCR (△), PSS (■), PAA (▲) and WP (○) systems. Total concentration of Eu^{III} is 2×10^{-4} m. SCR and WCR systems: 4.0 g of AG 50WX8 and 10 g of Bio-Rex 70 suspended in 1 dm^3 water, respectively; PSS and PAA systems: aqueous solutions of polystyrenesulfonic acid (8.3 g dm^{-3}) and polyacrylic acid (3.0 g dm^{-3}), respectively; WP system: Eu^{III} in water without added polyelectrolyte.

water, while only one or two water molecules are released when adsorbed on SCR. This indicates that the hydration structure of Eu^{III} ion is much more affected by WCR than SCR. The present result suggests different mechanisms between the ion-exchange reactions in the SCR and WCR systems: the hydrated Eu^{III} ion interacts with SCR, whereas the dehydrated Eu^{III} ion interacts with WCR. Reports on the selectivities in the ion exchange of alkali, alkaline earth, and lanthanoid elements concludes that a metal ion with a larger ionic radius is more readily exchanged on SCR for metal ions having the same charge showing that hydrated ions interacts with SCR.[2] By contrast, WCR adsorbs a smaller ion more effectively, showing that the metal ion forms an inner-sphere complex with WCR.[2] The present results on the hydration structure of Eu^{III} have provided spectroscopic evidence for the different mechanisms of ion-exchange reactions on SCR and WCR, as has been suggested by thermodynamic data.[2]

In the PSS and SCR systems at higher pH region, N_{H_2O} begins to decrease at pH *ca*. 7.5. In contrast, in the absence of the polyelectrolytes (WP system), the decrease of N_{H_2O} was observed at pH > 6 due to the formation of inorganic complexes, as described earlier. This shows that the Eu^{III} ion was exchanged on PSS or SCR as a free hydrated ion accompanied by removal of the hydroxide or carbonate ligand at pH between 6 and 7.5. When pH > 7.5, the N_{H_2O} values in the PSS and SCR systems decreased with an increase in pH. This indicates that the complex ion of europium(III) hydroxide or carbonate [*e.g.*, $Eu(CO_3)^+$, $Eu(OH)^{2+}$ or $Eu(OH)_2{}^+$] is directly adsorbed on PSS and SCR at these pH values.

Although it is suggested that the hydrated ion interacts with SCR, the N_{H_2O} value of the adsorbed Eu^{III} on SCR was less than that of Eu^{3+} (aq). This shows that the SCR affects the hydration structure of Eu^{III} to some extent. On the other hand, the N_{H_2O} value of Eu^{III} complexed with PSS (linear polyelectrolyte analogue of SCR) was similar to that of the aqua complex. On comparing the N_{H_2O} values in the SCR and PSS systems, it is thought that the cross-linked structure of SCR may be responsible for its influence on the hydration structure of Eu^{III}. This is compatible with the result of neutron diffraction study[1] on the hydration structure of ion-exchanged Ni^{2+} and Li^+, showing that a sulfonate group penetrates into the primary hydration sphere of these ions.

As C_s (concentration of supporting electrolyte, $NaClO_4$) increases up to 1.0 M, N_{H_2O} values in the WCR and SCR systems remained almost constant (Fig. 2). This was also found to be the case for the WP system in the C_s region.[7] However, N_{H_2O} values in the PAA (linear polyelectrolyte of acrylate) system decreased. This is perhaps due to change in conformation, since the shape of PAA was folded as a result of shielding the repulsive forces between the dissociated carboxylate groups with the supporting cations.[8] This suggests that network structures of WCR and SCR resins are more rigid than the linear structure of PAA.

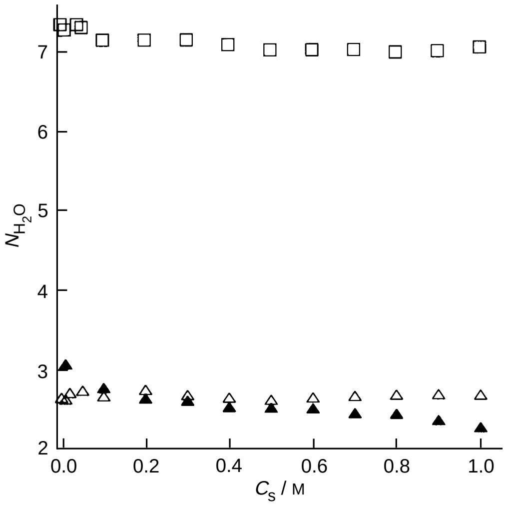

Fig. 2 Dependence of N_{H_2O} upon C_s in the SCR (□), WCR (△) and PAA (▲) systems. Experimental conditions were similar to those for Fig. 1.

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Footnotes

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