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Adsorption of Tetravalent Metal Ions to Chelating Resins Containing Iminodiacetic Acid Groups

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With respect to the selectivities, the compositions of species formed by the adsorption of tetravalent metal ions (M^{4+}) to chelating resins containing iminodiacetic acid groups ($-LH_2$) were estimated from the shapes of the adsorption curves and the infrared absorption spectra of the polymer complexes: $[-LM(OH)_2]$ for Zr^{4+} and Hf^{4+}, while $[(-LH)_4M]$, $[(-L)(-LH)_2M]$, and $[(-L)_2M]$ for Th^{4+}.

The adsorption of metal ions to chelating resins is expected to be much more selective than that to ion-exchange resins due to the complexation reactions. It has, however, been pointed out that the selectivity of a certain chelating ligand as a pendant group in the polymer phase is sometimes inferior to that of the corresponding monomeric ligand in solution. The reason for this discrepancy has been quantitatively explained with regard to the adsorption of divalent and trivalent metal ions to resins having iminodiacetic acid groups (IDA resin; $-LH_2$).[1,2] The adsorption of tetravalent metal ions, on the other hand, has been studied only from a practical point of view, such as a pretreatment for the determination of these metal ions.[3,4] In this paper, we estimate the compositions of the adsorption species for Zr^{4+}, Hf^{4+}, and Th^{4+}, the variation of which may modify the selectivities.

Under the condition that the total amount of metal ions is in excess against that of IDA groups ($TA_M > TA_L$), the adsorption of these metal ions to Amberlite IRC-718 (Na-form; IDA density of 2.10 $mmol\,g^{-1}$) was examined at varying acidities without considering the change in ionic strength. It took about one week for equilibration, at the longest. Precipitates were found on the chelating resin at $[H^+] < 0.2$ $mol\,dm^{-3}$ for Zr^{4+} and Hf^{4+}, and at $pH > 3.3$ for Th^{4+}. The equilibrium adsorption capacity (AC/$mmol\,g^{-1}$) is shown as a function of the medium acidity by the open symbols in Fig. 1. The curves for Zr^{4+} and Hf^{4+} steeply increased, reached respective maxima, and then sluggishly decreased along with an increase in $-\log[H^+]$. The maximum AC values observed were 1 $mmol\,g^{-1}$ for Zr^{4+} and 0.7 $mmol\,g^{-1}$ for Hf^{4+}. In contrast, the curve for Th^{4+} was spread over a much wider pH range; some preliminary equilibrium analyses, similar to those applied to the adsorption of group 3 metal ions,[2] indicated the presence of three species having metal-to-ligand ratios of 1 : 2, 1 : 3, and 1 : 4. The limiting adsorption capacities expected for these species (50, 33, and 25% occupation against the IDA groups) are shown as horizontal lines.

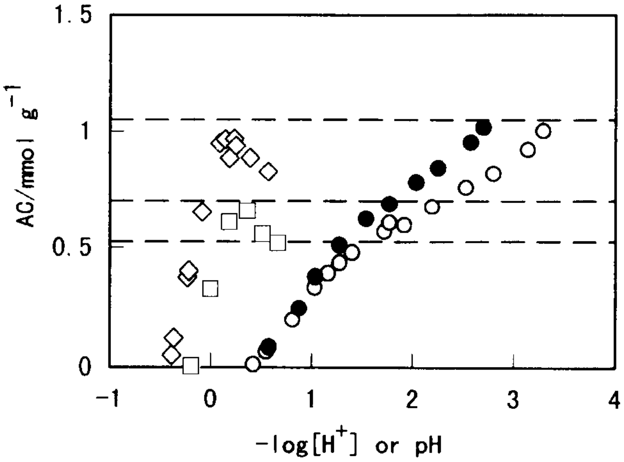

Fig. 1. Plot of adsorption capacity vs. $-\log[H^+]$ or pH for tetravalent metal ions under the condition $TA_M > TA_L$. Metal ions: Zr^{4+} (◇), Hf^{4+} (□), Th^{4+} (○, ●); supporting electrolyte: none (◇, □, ○), 1.0 $mol\,dm^{-3}$ KNO_3 (●). Aqueous solution: 100 cm^3 containing 0.1 mmol of metal ions; resin: Amberlite IRC-718; 0.025 g containing 0.05 mmol of IDA groups. Three horizontal lines indicate 50, 33, and 25% occupation of IDA groups, respectively.

The infrared spectra of the polymer complexes of Zr^{4+} and Th^{4+} with Amberlite IRC-718, obtained at various acidities, are shown in Fig. 2. The absorption at 1730 cm^{-1} characteristic of the H-type IDA-resin decreased and that at 1630 cm^{-1} increased with the loading of metal ions along with a decrease in acidity. The presence of an appreciable amount of a free IDA at Zr-loading of 1.0 $mmol\,g^{-1}$ (Fig. 2a, C), which corresponds to 48% occupation, indicated a stoichiometry of 1 : 1 for the reaction of Zr^{4+} with IDA. No strong absorption at 870—1020 cm^{-1} indicated the absence of a Zr=O bond. This was also the case at Hf-loading of 0.7 $mmol\,g^{-1}$. The polymer complex formed by the adsorption of Zr^{4+} or Hf^{4+} is thus expressed as $[-LM(OH)_2]$, where the coordinated water molecules are not considered. The extensive hydrolysis characteristics of these metal ions interfere with further adsorption and reduce the respective AC values above certain pH values. In the adsorption of Zr^{4+} to a polymer gel having IDA pendant groups (30 $\mu mol\,cm^{-3}$), Zr-loading up to 100% occupation was actually achieved, and even the hydrolysis of the resulting polymer complex was quantitatively characterized.[5]

In contrast, no absorption at around 1730 cm^{-1} for the Th-loading of 1.0 $mmol\,g^{-1}$ (Fig. 2b, C) indicated the absence of a free IDA group and the formation of $[(-L)_2Th]$. Only weak absorption at around 1730 cm^{-1} for the Th-loading of 0.45 $mmol\,g^{-1}$ (Fig. 2b, B) supported the formation of other higher species, like 1 : 3 and 1 : 4, although no absorption characteristics for such species were found. Taking into account the metal-to-ligand ratio of the complexes and the electro-neutrality of the resin phase, the compositions are es-

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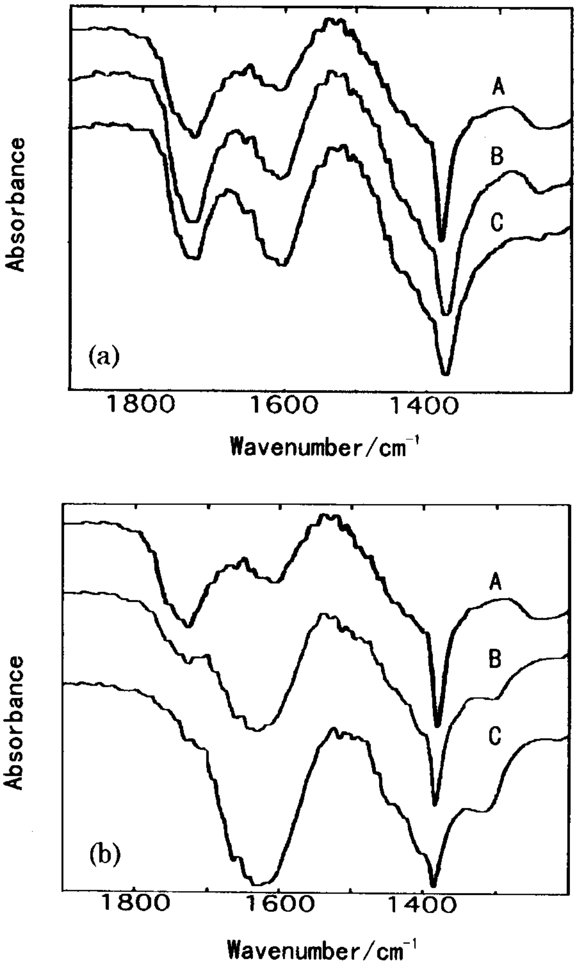

Fig. 2. Infrared absorption spectra of the polymer complexes of tetravalent metal ions with IDA resins. (a) metal ion: Zr^{4+}; $-\log[H^+]$: -0.23 (B), 0.15 (C); (b) metal ion: Th^{4+}; pH: 1.3 (B), 3.3 (C); (A) H-type amberlite IRC-718.

timated to be $[(-LH)_4Th]$ and $[(-L)(-LH)_2Th]$. Whether all of the IDA species, such as $(-L)^{2-}$ and $(-LH)^-$, are actually coordinated to Th^{4+}, or some of them simply lay close to Th^{4+} to neutralize the electric charge in these species including $[(-L)_2Th]$, could not be differentiated by IR spectroscopy.

The effects of the supporting electrolyte (1.0 mol dm^{-3} with KNO_3) on the adsorption curve of Th^{4+} to Amberlite IRC-718 under the condition $TA_M > TA_L$ are shown by the closed circles in Fig. 1. The adsorption was enhanced at pH > 1. This is just opposite to the general tendency in the complexation reaction of a metal with a polymer ligand,[6] and suggests the formation of a 1 : 1 species involving NO_3^- to neutralize the residual charge, as in the case of the In^{3+}–Br^- system.[2]

The adsorption curve of Th^{4+} under the reverse condition $TA_M < TA_L$ was also determined without considering the change in ionic strength; in contrast to the adsorption under the conditions of $TA_M > TA_L$, the shape of the adsorption curve was characteristic of the high charge of +4, and the half-adsorption pH was 0.8. Under such highly acidic conditions, $[(-LH)_4Th]$ is expected to be the main adsorption species. Although the possible formation of triply protonated species, $(-LH_3^+, X^-)$,[7] and the involvement of NO_3^- in the adsorption interfered with the rigorous equilibrium treatment, the adsorption curves under the conditions $TA_M < TA_L$ and $TA_M > TA_L$ could be roughly reproduced using the adsorption constant, $K_{44} = [(-LH)_4Th][H^+]^4/([-LH_2]^4[Th^{4+}])$, of 10^{-2}. The formation of species generally expressed as $[(-LH)_mM]^0$, which is advantageous for larger metal ions, like Mg^{2+}, Ca^{2+}, Y^{3+}, Sc^{3+}, and lanthanoids, enhances the adsorption of these metal ions, while varying or deteriorating the intrinsic selectivities of IDA.[1,2]

Experimental

Reagents. Stock solutions (10^{-2} mol dm^{-3}) of Zr^{4+} and Th^{4+} were prepared by dissolving $ZrO(NO_3)_2 \cdot 2H_2O$ in 2 mol dm^{-3} HNO_3 and $Th(NO_3)_4 \cdot 4H_2O$ in 10^{-2} mol dm^{-3} HNO_3, respectively. Hafnium tetrachloride was heated with concentrated HNO_3 to remove hydrochloric acid, and the mixture was carefully diluted to give a Hf^{4+} stock solution. The IDA resin, Amberlite IRC-718, was dried to a constant weight before use.

Measurement. In adsorption under the condition $TA_M > TA_L$, a solution containing 0.1 mmol of metal ion was added to 0.025 g of Amberlite IRC-718 (0.05 mmol of IDA groups), and the pH value was carefully adjusted by the addition of nitric acid or potassium hydroxide and then, in occasion, the ionic strength by the addition of KNO_3. After the total volume was adjusted to 100 cm^3, the resulting solution was left for equilibration at 25 °C. The supernatant was subjected to acidity and metal determination. The acidity was determined by acid-base titration based on a concentration scale in the cases of Zr^{4+} and Hf^{4+}, and with a pH meter calibrated on an activity scale in the case of Th^{4+}. The metal ions in solution were determined by complexometric titration. In the adsorption of Th^{4+} under the condition $TA_M < TA_L$, a solution containing 5 μmol of thorium ion was added to 0.25 g of the resin (0.5 mmol of IDA groups). After equilibration, free Th^{4+} in the supernatant was determined by spectrophotometry with xylenol orange. In both cases, the adsorption capacity, expressed in terms of mmol g^{-1}, was determined according to the difference from the total amount in the loading solution.

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