

Effect of alcohols on elution chromatography of trivalent actinides and lanthanides using tertiary pyridine resin with hydrochloric acid–alcohol mixed solvents

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Abstract

Elution chromatography with a tertiary pyridine resin has been used to separate the trivalent actinides (An^{3+}) from the lanthanides (Ln^{3+}) using an alcoholic hydrochloric acid solvent. Trivalent Am and Cm were separated from the Ln by employing a 1 cm(\varnothing) \times 10 cm resin column with the mixed solvent system composed of concentrated hydrochloric acid (HCl) and alcohols. The distribution coefficients (K_d) and the separation factors between An and Ln (α_{Ln}^{An}) increased as the alcohol content of the solvent mixture increased. On the other hand, the K_d and α_{Ln}^{An} decreased drastically upon the addition of water to the solvent mixture. Among the four alcohols investigated (methanol, ethanol, *n*-propanol and *n*-butanol), the ethanol–HCl mixed solvent system showed the largest K_d and α_{Ln}^{An} . The mechanism of adsorption for An and Ln cations on the pyridine resin is discussed in addition to the results presented herein.

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1. Introduction

The treatment of radioactive wastes is one of the most challenging problems associated with the present nuclear power generation system. Above all, high-level radioactive wastes (HLRWs), which are produced after reprocessing spent nuclear fuels, contain radioactive nuclides with extraordinarily long half-life. These wastes are extremely difficult to handle due to their high radioactivity.

Several methods for the treatment of HLRWs have been proposed and investigated. One of the most effective methods is the partitioning-transmutation (PT) method. In this method, nuclides with high radioactivity and long half-life are partitioned (separated) from low-level nuclides and

transmuted to other stable (or lower-level) nuclides using fast-breeder reactors (FBRs) or accelerators.

Although nuclear spent fuels contain a variety of radioactive nuclides, very few of them are regarded as targets of the PT method. Moreover, most of the targets are the actinides (An) [1]. Therefore, the separation of An from other nuclides in HLRWs is necessary prior to the transmutation process. However, the An separation poses one important obstacle: separation from the lanthanides (Ln). Spent fuels contain a considerable amount of Ln, produced as fission products of An. Unfortunately, the chemical properties of Ln are very similar to those of An, making them very difficult to separate. The Ln and the transplutonium elements form trivalent cations in solution and they have similar ionic radii [2]. These chemical similarities pose an additional challenge in separation process.

A number of researchers have concentrated their efforts on the trivalent An separation from the Ln. Muscatello et al.

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used neutral organophosphorus extractants in order to extract Am(III) and Eu(III) from thiocyanate solutions and obtained a high Am(III)–Eu(III) separation factor ($\alpha_{Sm}^{Am} = 10.8$) [3]. Weaver and Kappelmann reported that the Ln were completely separated from Am(III) in carboxylic solutions by using monoacidic phosphates [4]. Over the last several decades, a large number of studies have been focused on an extraction technique called trivalent actinide lanthanide separation by phosphorus reagent extraction from aqueous complexes (TALSPEAK) [5–7]. On the other hand, Some researchers have employed ion-exchange methods in order to separate these elements [8–10].

In addition, several recent studies have focused on the use of soft donor type extractants for the intergroup separation of An and Ln. These extractants interact with metals by soft donor ligands such as N- or S-donor ligand [11,12]. We have also employed pyridine ligands (N-donor ligands) for the chromatographic separation of trivalent An (Am and Cm) from Ln [13,14]. As compared with the earlier methods mentioned above, our method has two advantages: convenient reagents and simple procedures. We employ convenient solvents of hydrochloric acid (HCl) and alcohols as a mobile phase. Then, the mixture of HCl and alcohols acts both as the feed solutions and as the eluent. This means that only one solvent is necessary through the process and there is no need to change solvents during the operation. This makes the procedures simple and reduces liquid wastes from the process. Although we have obtained good separation results, further investigation is required in order to develop a suitable separation system and to understand the mechanism of separation.

In the present paper, elution chromatography using a tertiary pyridine resin with a mixed solvent system composed of HCl solution and alcohols is employed for the separation of trivalent An and Ln. The adsorption and separation behavior of trivalent An and Ln is also discussed as a function of the HCl and alcohol concentrations.

2. Experimental

2.1. Materials

A mixed trivalent An sample composed of ^{241}Am and ^{242}Cm was produced by irradiation of a $^{241}\text{AmO}_2$ shielded sample in the Japan Materials Testing Reactor (JMTR) and was chemically separated from the majority of the fission products. Radioactive Ln samples (^{141}Ce , ^{147}Nd , ^{168}Tm and ^{169}Yb) were produced by irradiation of their stable isotopes using electron linac at the Laboratory of Nuclear Science, Tohoku University. All solvents were reagent grade and supplied by Wako Japan.

2.2. Tertiary pyridine resin

The resin used in this study was a tertiary pyridine resin embedded in highly porous silica beads and contained

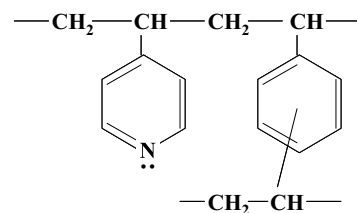


Fig. 1. Structure of tertiary pyridine resin.

0.8 mmol of tertiary pyridine functional sites per 1 cm^3 resin. The resin was synthesized in our laboratory. The chemical structure of the tertiary pyridine resin is shown in Fig. 1. The pyridine resin has a high resistance to radiation [15] and is thus fit for the use under high radiation dose conditions such as fuel reprocessing process. The silica beads were manufactured by Asahikasei Corp., Japan. The silica beads have a uniform particle size ($60\ \mu\text{m}$) and a large internal macro-porous structure (70% (v/v) of porosity), enabling the ions to readily diffuse into the resin, thus, chromatograms with sharp and well-defined peaks can be obtained.

2.3. Chromatography experiments

Samples for the chromatography experiments were prepared by dissolving a dried mixture of trivalent An (^{241}Am and ^{242}Cm) and Ln (^{141}Ce , ^{147}Nd , ^{168}Tm and ^{169}Yb) in the desired concentration of alcoholic hydrochloric acid solution. The compositions of the samples are shown in Table 1. A 0.5 cm^3 of sample was introduced into the plastic column, in which $1\text{ cm}(\text{Ø}) \times 10\text{ cm}$ of pyridine resin was packed as a stationary-phase. Then, a 0.5 mm height of liquid layer was retained onto the resin bed in the column during each experiment in order to avoid the inhalation of air into the resin bed. The sample was subsequently eluted using the same alcohol–hydrochloric acid solution used to prepare the sample. The experiments were performed at a constant flow rate of $100\text{ cm}^3/\text{h}$ at ambient temperature (about 293 K). The effluent from the column was collected in fractions. The ^{241}Am and ^{242}Cm in the collected fractions were detected using an α -ray spectrometer (IPC500-100-21EM, Eurisy Mesures or PG900-27AM, Canberra Industries) at 5.48 and 6.11 MeV for ^{241}Am and ^{242}Cm , respectively. The Ln in the fractions were detected using a coaxial n-type germanium detector (Eurisy Mesures, EGC 20-195-R) at 145.44, 91.11, 720.32 and 177.21 keV for ^{141}Ce , ^{147}Nd , ^{168}Tm and ^{169}Yb , respectively.

2.4. Distribution coefficients and separation factors

The distribution coefficients, which indicate the adsorbability of elements on the resin, were calculated from the obtained chromatograms. The distribution coefficient (K_d) is

Table 1
Compositions of feed samples for chromatography experiments

Sample number	Nuclide	Alcohol	Solvent composition: conc. HCl–water–alcohol (v/v)
1	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd		10:0:0
2	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd, ¹⁶⁸ Tm, ¹⁶⁹ Yb		8.5:0:1.5
3	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd, ¹⁶⁸ Tm, ¹⁶⁹ Yb		7:0:3
4	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd	Methanol	6:1:3
5	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd		6:0:4
6	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd		5:1:4
7	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd		5:0:5
8	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd	Ethanol	7:0:3
9	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd	<i>n</i> -Propanol	7:0:3
10	²⁴¹ Am, ²⁴² Cm, ¹⁴¹ Ce, ¹⁴⁷ Nd	<i>n</i> -Butanol	7:0:3

defined as:

$$K_d = \frac{V_M - V_S}{V_R} \quad (1)$$

where V_M is the volume of effluent at elution peak, V_S the dead volume of resin column and V_R the volume of resin. In a preliminary experiment, it has been observed that the silica beads themselves do not adsorb any metal cations in HCl–alcohols mixed solvents. This means that the adsorption observed in this study is caused by the pyridine resin of stationary-phase. Hence, V_R should be defined as the volume of the resin part of stationary-phase and thus was calculated from the mixing ratio of resin polymer and silica beads when synthesized. The V_S was calculated from the water content in the resin column. We have also confirmed in preliminary experiments that the elution curves in the present chromatography system correspond with Gaussian curves very well. Therefore, the elution curves obtained in this study were fitted with Gaussian curves. Then the V_M was calculated from the Gaussian curve fitted. The separation factors (α) were subsequently calculated from the distribution coefficients. The separation factor between A and B is defined as follows:

$$\alpha_B^A = \frac{K_d(A)}{K_d(B)} \quad (2)$$

3. Results and discussion

3.1. Concentrated hydrochloric acid–methanol mixed media

Fig. 2 shows the elution curves for trivalent An and Ln in a mixed media of concentrated HCl–methanol along with their Gaussian-fitted curves. In a concentrated HCl medium, the Ln were eluted immediately from the column, whereas the An slightly adsorbed on the resin, showing a relatively slow elution. As the volume fraction of methanol (X_{MeOH}) in the solvent increased, the elution curves broadened and the retention volume of each element increased. This means that adding methanol in the solvent promotes the adsorption of An and Ln cations on the resin. Furthermore, the elution

curves in Fig. 2, especially those of Am and Cm, show tailing profiles. This is probably due to the presence of the liquid layer on to the resin bed as mentioned in 2.3: the liquid layer encourages the diffusion of sample solutions out of the stationary-phase, broadening the tails of elution curves.

The distribution coefficients, K_d , of Am(III) and Ce(III) calculated from the elution curves are shown in Fig. 3. Although both the K_d of Am(III) and Ce(III) increased as X_{MeOH} increased, the K_d of Am(III) increased more drastically as compared with that of Ce(III). The separation factors between Am(III) and Ce(III) (α_{Ce}^{Am}) under different mixed solvent systems are shown in Fig. 4. The α_{Ce}^{Am} also increased as the X_{MeOH} increased. On the other hand, when a 10 vol.% of water was added to the mixed solvents, the K_d and α decreased as shown in Fig. 5 and Table 2. The K_d of Am (An) decreased more drastically than that of Ce (Ln) as the X_{water} increased. This indicates that the presence of excess water in the solvent prevents the adsorption of An and Ln to the resin. This effect appears more strongly on the adsorption of An than on that of Ln.

3.2. Other alcohols

In order to investigate the effect of different kinds of alcohols, chromatography experiments were performed using the mixed solvents systems composed of concentrated HCl

Table 2
Distribution coefficients (K_d) of Am(III) and Ce(III) and their separation factors (α_{Ce}^{Am}) in alcoholic hydrochloric acid solvents

	Solvent composition (conc. HCl–water–alcohol)	K_d (Am)	K_d (Ce)	α_{Ce}^{Am}
Methanol	10:0:0	42.3	8.4	5.0
	8.5:0:1.5	64.0	11.2	5.7
	7:0:3	99.0	14.5	5.9
	6:1:3	17.8	5.2	3.4
	6:0:4	99.8	13.5	7.4
	5:1:4	14.8	5.2	2.9
	5:0:5	113.7	14.1	8.1
Ethanol	7:0:3	150.7	20.1	7.5
<i>n</i> -Propanol	7:0:3	133.3	19.2	7.0
<i>n</i> -Butanol	7:0:3	98.7	14.9	6.6

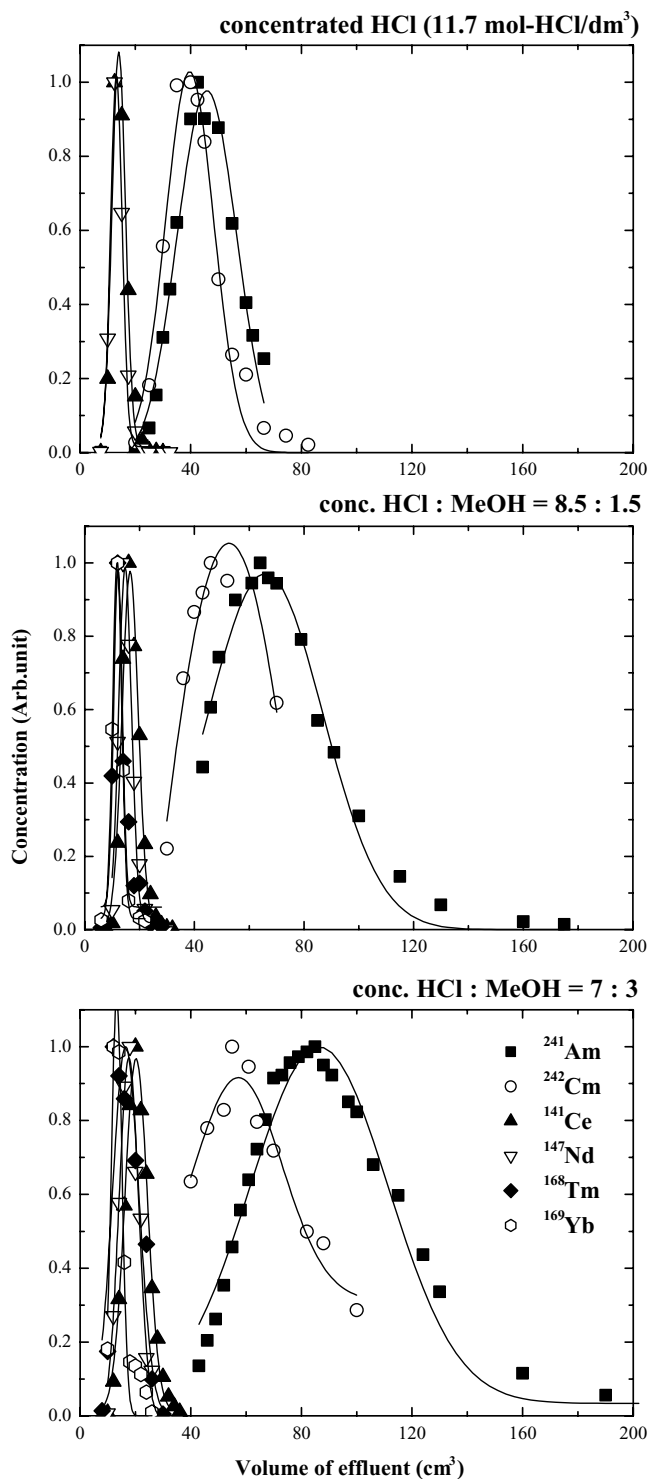


Fig. 2. Elution curves of trivalent An and Ln by using tertiary pyridine resin in conc. HCl–methanol mixed media.

and one of other three alcohols (ethanol, *n*-propanol and *n*-butanol). The mixing ratio of concentrated HCl to alcohol was 70–30 vol.%, respectively. Fig. 6 shows the variations of $K_d(\text{Am})$ and $\alpha_{\text{Ce}}^{\text{Am}}$ for the four alcoholic hydrochloric acid solvents. Convex-upward changes were observed with an increase in the carbon number of the alkyl group in the alco-

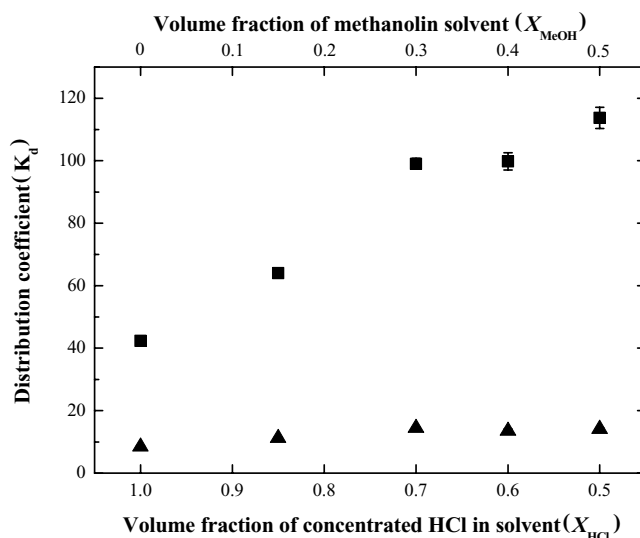


Fig. 3. Distribution coefficients of Am(III) and Ce(III) on tertiary pyridine resin in conc. HCl–methanol mixed media: (■) Am(III), (▲) Ce(III).

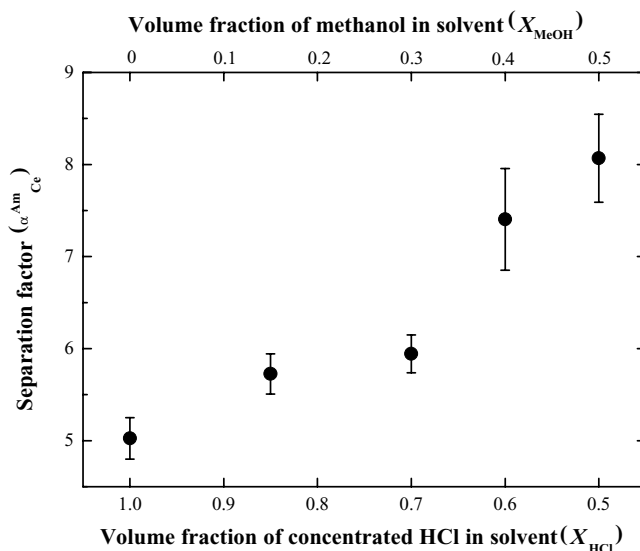


Fig. 4. Separation factors between Am(III) and Ce(III) in conc. HCl–methanol mixed media.

hol both in $K_d(\text{Am})$ and $\alpha_{\text{Ce}}^{\text{Am}}$: both $K_d(\text{Am})$ and $\alpha_{\text{Ce}}^{\text{Am}}$ were at a maximum in the ethanol mixed solvent and decreased as the carbon number increased above ethanol. Among the four alcoholic solvents, the methanol mixture gave the minimum $K_d(\text{Am})$ and $\alpha_{\text{Ce}}^{\text{Am}}$. Although the methanol mixed solvent had the minimum $\alpha_{\text{Ce}}^{\text{Am}}$, the chromatogram showed a sufficiently clear peak separation between the An and the Ln in this system. On the other hand, the elution curves for the ethanol mixture were rather broad and a greater amount of eluent was required in order to elute the whole components of the sample from the column. Therefore, the ethanol mixed solvent was not necessarily considered the best solvent for the separation of An from Ln. In order to determine the most practical solvent for the separation, the overall sep-

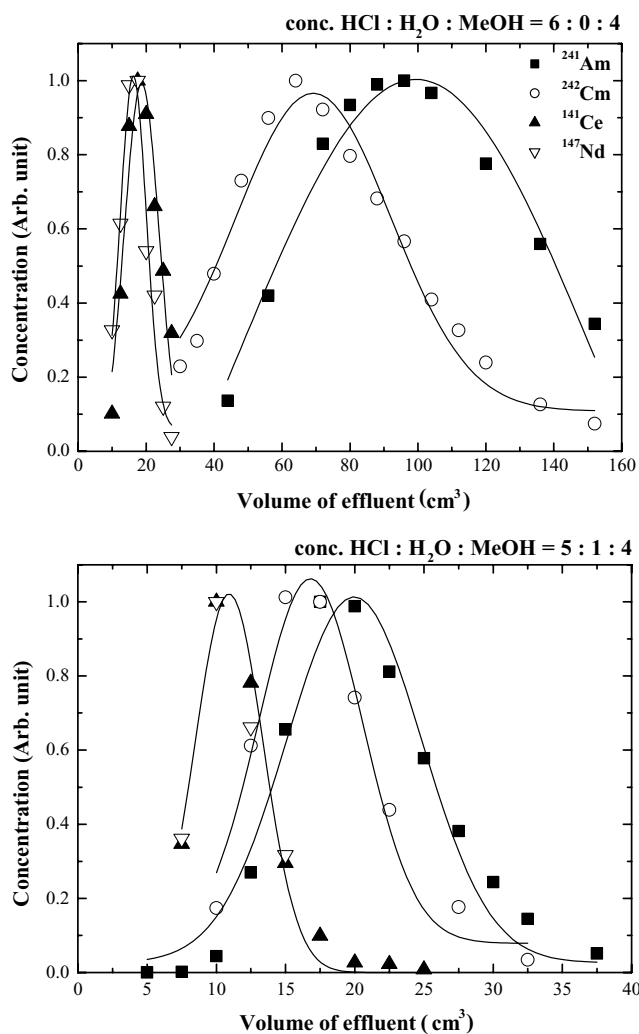


Fig. 5. Elution curves of trivalent An and Ln by using tertiary pyridine resin in HCl–methanol mixed media.

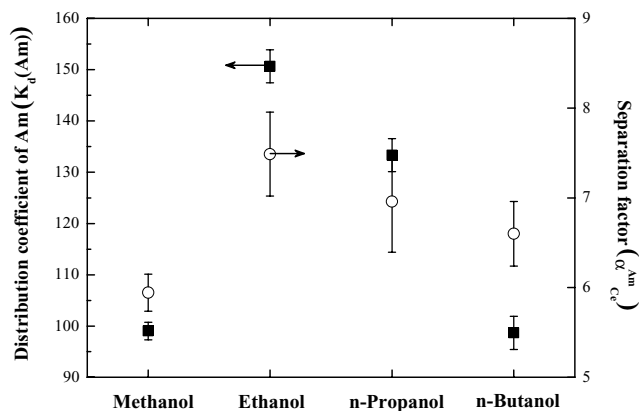


Fig. 6. Distribution coefficients of Am(III) and separation factors between Am(III) and Ce(III) in different alcoholic hydrochloric acid media. (Solvent: conc. HCl + alcohol, 70:30 (v/v)).

aration system should be taken into consideration, such as the size of resin column or the post-treatment required for the waste produced.

3.3. Adsorption mechanism

When discussing the effect of solvent on adsorption behavior, the adsorption mechanism in the system must be taken into consideration. The present system utilizes a tertiary pyridine resin, in which there are two possible mechanisms of adsorption between the pyridine groups and the metal cations: the adsorption caused by electrostatic interaction and that caused by covalent interaction. In the former mechanism, the pyridine groups are protonated by protons (H^+) using their lone pairs and thus carry a positive charge. The protonated pyridine groups attract anionic metal complexes, in which the metal cations are complexed with chloride ions (Cl^-), thus giving the metal complexes a negative charge. This mechanism is considered a sort of ion-exchange interaction [16]. In the latter mechanism, however, the pyridine groups are directly coordinated to the metal cations forming metal–pyridine complexes. This mechanism can be described as a liquid–solid extraction. As a matter of fact, a number of researchers have reported extraction studies of An and Ln using extractants containing pyridine [17–19].

In a previous report [14], the possibility of covalent interaction between the An and Ln cations and pyridine groups in the present system was suggested. If the adsorption was caused by electrostatic interaction, at least four Cl^- ions coordinate around one cation, forming anionic-Cl complexes. However, a number of studies [20–22] indicated that Cl^- hardly coordinated to the inner-spheres of An and Ln cations even at concentrations higher than $10 \text{ mol/dm}^3 Cl^-$. However, the cations could form outer-sphere Cl complexes. It is unlikely that the An and Ln cations are adsorbed to the pyridine resin as outer-sphere complexes, because the stability of outer-sphere complexes is far lower than that of inner-sphere ones. Therefore, the covalent interaction is thought to be reasonable for the cause of adsorption.

In the present system, the adsorbability of metal cations is primarily dominated by two factors: the protonation state of pyridine groups and the complexation state of metal cations. The protonation of pyridine groups prevents the interaction between pyridine and the metal cations. On the other hand, water molecules and Cl^- coordinate to the metal cations in solution, thereby preventing the interaction between the pyridine groups and the metal cations.

In a mixed solvent system of concentrated HCl and methanol, as X_{MeOH} increases and X_{HCl} decreases, the protonation of pyridine groups becomes weaker due to the decrease in proton activity (a_{H^+}). Increasing alcohol content of the solvent further suppresses the protonation of pyridine groups [23] and decreases the water activity (a_{H_2O}). Furthermore, the presence of alcohol in the solvent enhances the dehydration of metal cations in the resin phase [24]. Therefore, adding alcohol to the solvent may facilitate

the covalent interaction between the pyridine groups and the metal cations. As a result, it promotes the adsorption of metal cations on the resin. Contrastingly, adding water to the solvent increases the $a_{\text{H}_2\text{O}}$. A higher $a_{\text{H}_2\text{O}}$ facilitates the hydration of metal cations. These hydrated cations do not readily interact with pyridine groups. It is important to note that the K_d values for the four alcoholic hydrochloric acid solvents show the convex-shaped variations, although some physical properties of these alcohols such as dielectric constants or viscosity vary linearly with the carbon number of these alcohols [25]. This may indicate that alcohol affects the adsorption of metal cations in a number of ways, not one way. Further investigations are required in order to accurately interpret the effect of alcohols.

4. Conclusions

Trivalent Am and Cm were separated from the Ln by elution chromatography with a tertiary pyridine resin embedded in silica beads using a mixed solvent system composed of concentrated HCl and alcohol. The K_d of the An and Ln and the $\alpha_{\text{Ln}}^{\text{An}}$ were observed to increase as the alcohol content of the mixed solvent increased. Different alcohols show the different K_d and $\alpha_{\text{Ln}}^{\text{An}}$ values; among the four alcohols tested (methanol, ethanol, *n*-propanol and *n*-butanol), the ethanol mixed solvent was found to have the largest K_d and $\alpha_{\text{Ln}}^{\text{An}}$. The elution order for the trivalent An and the Ln in the present system was Tm–Yb–Nd–Ce–Cm–Am. The adsorption of metal cations on the pyridine resin is thought to involve the covalent interaction between the pyridine groups and the metal cations, not the electrostatic interaction like that in ion-exchange reactions.

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