Highly Efficient Europium(III) Uptake with an Extraction Chromatographic Resin Containing a Unique Multiple Diglycolamide Ligand with a Tetraaza-12-crown-4 Scaffold

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ABSTRACT: An extraction chromatographic resin was prepared by impregnating Chromosorb-W with a unique ligand consisting of four diglycolamide moieties functionalized to a tetraaza-12-crown-4 scaffold. This resin was evaluated for the uptake of Eu^{3+} , as a representative of trivalent lanthanides and actinides, from moderate acid solutions. The distribution coefficient of Eu^{3+} on the resin was very large ($>1 \times 10^4$) in the acid range 0.1–6 M HNO_3 , and its sorption followed the pseudo-second-order kinetic model. The sorption of Eu^{3+} proceeded via a chemisorption phenomenon with a sorption energy of 26 ± 2 kJ/mol. The Eu^{3+} sorption onto the resin was both enthalpy and entropy driven. FTIR and fluorescence measurements of the Eu^{3+} complex formed on the resin confirmed the chemical interaction between the Eu^{3+} and the ligand present on the solid support. The resin capacity was 14.4 ± 0.1 mg of Eu^{3+} per g of resin corresponding to the formation of a 1:1 metal/ligand complex. The sorbed Eu^{3+} from the resin could be efficiently desorbed with 0.1 M HEDTA (*N*-(2-hydroxyethyl)ethylenediamine triacetic acid). The column loading of Eu^{3+} was 83% of the equilibrium value with a narrow elution profile. The hydrolytic and leach stability of the impregnated resin was excellent, tested in five successive cycles of loading and elution.

1. INTRODUCTION

Although nuclear power is considered a major source of energy in the 21st century, its acceptance to the general public depends on various safety issues, including environmental contamination due to occasional accidents over the years. More recently, the Fukushima-Daiichi accident in Japan has near-field contamination, which needs to be efficiently monitored using matured technology.¹ The common radionuclides spewed in the environment include the long-lived actinides and important fission product nuclides such as ^{137}Cs , ^{90}Sr , etc. In actinide fractions, apart from large concentrations of U and various Pu isotopes, there are isotopes of minor actinides such as ^{237}Np ($t_{1/2}$: 2.1×10^6 y), ^{241}Am ($t_{1/2}$: 431 y), ^{243}Am ($t_{1/2}$: 7400 y), ^{243}Cm ($t_{1/2}$: 30 y), ^{244}Cm ($t_{1/2}$: 18.1 y), ^{245}Cm ($t_{1/2}$: 8532 y), etc. In addition to actinides, there are a few lanthanide fission product radionuclides like ^{152}Eu ($t_{1/2}$: 12.4 y) and ^{154}Eu ($t_{1/2}$: 8.5 y), which have significantly long half-lives and require monitoring in the environment. The contaminated soil needs to be digested in acid and subjected to separation methods such as precipitation,² solvent extraction,³ and ion exchange.⁴

Despite the existence of many efficient methods for the separation of radionuclides from acidic feeds,⁵ literature on the separation of trivalent actinides and lanthanides is still evolving. Out of the various separation methods, extraction

chromatography appears to be highly promising due to the use of a very small amount of organic solvents, generation of low amounts of secondary waste, and ease of technical operation when separations are carried out in a column.^{5–8} Use of selective organic extractants for trivalent lanthanides and actinides such as CMPO (carbamoylmethyl phosphine oxide),⁹ malonamide (*N,N'*-dimethyl-*N,N'*-dibutyl tetradecyl malonamide),¹⁰ and DGA (diglycolamide)^{11–13} in extraction chromatographic resins has shown good results for the separation of trivalent lanthanides and actinides. Out of these extractants, the DGA extractants such as TODGA (*N,N,N',N'*-tetraoctyl diglycolamide, Figure 1a) have given very impressive results in the separation of trivalent actinides from a variety of acidic feed solutions.¹³

In the recent decade, a variety of multiple DGA ligands with varying structural features have been synthesized with tripodal geometries (referred to as T-DGA, Figure 1b).^{14–17} These ligands have shown significantly high extraction efficiency for

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Figure 1. Structural formulas of the extractants investigated for trivalent actinides and lanthanides. (a) TODGA, (b) T-DGA, (c) C4DGA, (d) TAM-4-DGA.

trivalent actinides and lanthanides as compared to a normal DGA ligand like TODGA. These ligands have also shown better separation factors for Am(III) with respect to U(VI), Sr(II), and Cs(I). Further it was found that grafting of the DGA moieties onto macrocyclic scaffolds such as calix[4]arene (C4DGA, Figure 1c)¹⁸ and pillar[5]arene¹⁹ gave even better results with respect to preferential extraction of trivalent actinides and lanthanides over U(VI), Sr(II), and Cs(I). In this series, we synthesized a unique DGA ligand where four DGA moieties (containing terminal octyl groups) were tethered to a tetraaza-12-crown-4 scaffold (termed as TAM-4-DGA, Figure 1d).²⁰ Solvent extraction and complexation studies with TAM-4-DGA ligand gave the most encouraging results for the separation of trivalent lanthanides and actinides with all DGA extractants reported to date.²⁰ In view of this, it was of interest to prepare an extraction chromatographic resin containing TAM-4-DGA for the separation of trivalent lanthanides and actinides. The present paper deals with the preparation of extraction chromatographic resin by impregnating the TAM-4-DGA ligand onto Chromosorb-W. Studies pertaining to the characterization of resin and its behavior toward sorption of Eu^{3+} ions were investigated in detail. Eu^{3+} was the choice for the present work as a representative of lanthanides and also as a surrogate for trivalent actinides.

2. EXPERIMENTAL SECTION

2.1. Materials. TAM-4-DGA ligand, containing four diglycolamide moieties with a terminal octyl group, anchored to a tetraaza-12-crown-4 scaffold (Figure 1d), was synthesized as per the procedure reported elsewhere.²⁰ The purity of the ligand was checked by elemental analysis as well as NMR and HR-MS techniques and was found to be >95%. The diluents,

n-dodecane (Lancaster, UK) and isodecanol (>99%, SRL, Mumbai), were used as received. Chemicals such as *N*-(2-hydroxyethyl)ethylenediamine triacetic acid (HEDTA, Sigma-Aldrich), EDTA (Merck), and guanidine carbonate (99%, Sigma-Aldrich) were used without any further purification. Chromosorb-W (dimethyl dichlorosilane treated acid washed Celite diatomaceous silica, particle size: 175–250 μm) obtained from Johns Manville, USA was washed with distilled water, methanol, and acetone followed by air-drying before use. A known quantity of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) was dissolved in 0.01 M nitric acid to make standard $\text{Eu}(\text{NO}_3)_3$ solution followed by its volumetric titration with standard EDTA.²¹ Suprapur nitric acid (Merck, Germany) was used for the preparation of all dilute nitric acid solutions using Milli-Q water (Millipore, USA). All the other chemicals were of analytical reagent grade and were used as received. Radiotracer ^{152,154}Eu was procured from the Board of Radiation and Isotope Technology, Mumbai and used after confirming its radiochemical purity by an HPGe detector.

2.2. Instrumentation. Thermogravimetric analysis was performed using a Netzsch Thermobalance at a heating rate of 5 °C per minute in air atmosphere up to 1000 °C (Model: STA 409 PC Luxx). A stereoscan 100 Cambridge model SEM instrument was used for the surface morphology analysis. The analysis was performed at 15/25 kV with a magnification of 3000 $\times$ at a working distance of 15 mm at a tilt angle of 45°. Before the measurement, the sample was coated with gold (15 nm coating) with a Balzer's coating unit (model: CEA 30). Fluorescence emission spectra were recorded, and the fluorescence lifetime of Eu^{3+} was determined on a PTI QuantaMaster fluorometer (PTI QuantaMaster 400) adapted for time-resolved measurements. FTIR spectra of the solid

Table 1. Linearized Form of Different Sorption Isotherm Models

Isotherm	Linearized form ^a	Linear Plot	Parameters	ref
Langmuir	$\frac{C_e}{q_e} = \frac{[1]}{b \cdot q_{\max}} + \frac{C_e}{q_{\max}}$	$\frac{C_e}{q_e}$ vs C_e	$q_{\max} = 1/\text{slope}$, $b = \text{slope}/\text{intercept}$	25, 26
Freundlich	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$	$K_f = \text{intercept}$, $n = 1/\text{slope}$	27, 28
D-R	$\ln q_e = \ln q_{\max} - \beta \epsilon^2$	$\ln q_e$ vs ϵ^2	$q_{\max} = \text{intercept}$, $E = 1/2\beta^{0.5}$ (slope)	29, 30
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$	q_e vs $\ln C_e$	$B_T = \text{slope}$, $A_T = \text{intercept}/\text{slope}$	31

^a q_e = amount of Eu^{3+} sorbed per gram of resin at equilibrium; C_e = equilibrium concentration of Eu^{3+} in the aqueous phase; $q_{\max}$ = maximum mass of Eu^{3+} sorbed on the resin; K_f = maximum sorbed mass of Eu^{3+} .

samples were recorded on a Bruker Alpha II ATR-FTIR spectrometer. Quantification of Eu^{3+} in the analytical samples was done using $^{152,154}\text{Eu}$ tracer spiking, and the latter was analyzed by a well type NaI(Tl) scintillation counter (Para Electronics) interfaced with a multichannel analyzer (ECIL, India).

2.3. Preparation of the Extraction Chromatographic Resin. The extraction chromatographic resin was prepared by impregnating the TAM-4-DGA ligand on Chromosorb-W by following the method described earlier.²² The choice of Chromosorb-W as an inert solid support was due to its highly porous nature, and being a silica material, it has good radiation stability. A known weight of ligand (1 part) was dissolved in 3 parts of a 5% isodecanol/*n*-dodecane mixture in a stoppered conical flask to obtain a uniform solution. Since the ligand was insoluble in pure *n*-dodecane, 5% isodecanol/*n*-dodecane was used which gave a clear ligand solution.²⁰ To this solution, 5 parts of Chromosorb-W were added to give a ligand, solvent, and solid support weight ratio of 1:3:5. Finally, ca. 20 mL of acetone were added to the flask and the slurry was equilibrated for 24 h in a mechanical shaker at 100 agitations per minute. After equilibration, the solvent (acetone) was removed carefully by flushing nitrogen gas in the flask with gentle stirring to obtain a uniform ligand impregnated resin. The resultant resin was vacuum-dried at 60–80 °C until a constant weight was obtained to afford a free-flowing resin material for subsequent use. The ligand loading on the support (calculated from the initial weight of the support, ligand and the final weight of resin) was found to be 11.1% (w/w), which corresponded to 96.9 $\mu\text{mol/g}$ of resin.

2.4. Distribution Coefficient Measurements. The distribution coefficient of Eu^{3+} ion under different experimental conditions was measured by equilibrating about 10 mg of resin with 1 mL of aqueous solution. The equilibrations were performed in glass stoppered tubes in a thermostated water bath maintained at 25.0 ± 0.1 °C for about 1 h, which was found to be sufficient for reaching the equilibrium condition (*vide infra*). After equilibration, the tubes were centrifuged, and about 100 μL of aqueous supernatant phase were taken out and centrifuged a second time to remove any resin particles. Suitable aliquots from the aqueous phase were removed before and after equilibration for assaying $^{152,154}\text{Eu}$ radiometrically. The weight distribution ratio (K_d) value of Eu^{3+} on the resin was calculated as

$$K_d = \left[\frac{(C_o - C)}{C} \right] \cdot \frac{V}{W} \quad (\text{mL} \cdot \text{g}^{-1}) \quad (1)$$

where C and C_o are the concentrations of $^{152,154}\text{Eu}$ (in counts per unit time per unit volume) before and after equilibration. The terms V and W represent the volume of the aqueous phase (mL) and the weight of the resin (g) used, respectively. All the distribution measurements were carried out in triplicate, and the reported values are the mean values of the replicate measurements. The relative standard deviations (RSD) on the triplicate K_d values were less than 2% for the values in the range 1–1000. However, an RSD up to 7% was accepted where the K_d values were <1 or >1000.

2.5. Kinetic and Thermodynamic Studies. Kinetic experiments were performed at 0.1 M HNO_3 by equilibrating the aqueous phase, containing a $^{152,154}\text{Eu}$ tracer, with 10 mg of resin. The time of equilibrations was kept at 2–60 min, and the amounts of $^{152,154}\text{Eu}$ activity (in terms of counts) sorbed per g of resin were recorded as a function of time. The sorption data were subsequently fitted in Lagergren pseudo-first-order and pseudo-second-order rate equations given below.^{23,24}

$$\ln(q_e - q_t) = \ln q_{\max} - k_1 \cdot t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_{\max}^2} + \frac{t}{q_{\max}} \quad (3)$$

where k_1 = pseudo-first-order rate constant, k_2 = pseudo-second-order rate constant, q_e = amount of Eu^{3+} ions sorbed onto the resin at equilibrium, q_t = amount of Eu^{3+} ions sorbed onto the resin at time t , and $q_{\max}$ = maximum sorption value.

The kinetic data were also treated with the Elovich model (eq 4) and pore diffusion model given in eq 5.

$$q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln(t) \quad (4)$$

Here, the terms are α = initial sorption rate and β = desorption constant in the Elovich model.

$$q_t = k_{\text{id}} \cdot t^{0.5} + C \quad (5)$$

where k_{id} = interparticle constant. Here, C is a constant that provides information about the thickness of the aqueous film around the solid resin.

Thermodynamics studies were performed by measuring the K_d values of Eu^{3+} at 0.1 M HNO_3 at different temperatures in the range 15–55 °C. The equilibration time was maintained at 60 min to ensure that the system reached the equilibrium condition. Subsequently, the thermodynamic equilibrium constant, K_{eq} was calculated at different temperatures from the equilibrium reaction described later (*vide infra*).

2.6. Sorption Isotherm Studies. The Eu^{3+} sorption isotherm on the TAM-4-DGA resin was studied by measuring

its equilibrium sorption values from varying aqueous phase concentrations of $\text{Eu}(\text{NO}_3)_3$. The Eu^{3+} sorption data were treated by fitting in several sorption isotherm models such as the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R). The linear forms of these isotherm models are given in Table 1.

2.7. Column Studies. The column was prepared by packing about 0.4 g of resin in a 4 mm (dia) $\times$ 25 mm (height) glass column. Details about the preparation of column have been described in our earlier publication.³² The resin bed height in the column was 12.8 cm which corresponded to 1.61 cm^3 of bed volume and 0.25 g/cm^3 of bed density. The feed solution was 0.4 mg/mL $\text{Eu}(\text{NO}_3)_3$ at 3 M HNO_3 spiked with $^{152,154}\text{Eu}$ tracer. A constant flow rate of 0.3 mL/min was maintained during the Eu^{3+} loading, washing, and elution in the column. Preconditioning of the column was done by passing 10 mL of 3 M HNO_3 before loading the feed solution.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Resin Beads. The extraction chromatographic resin was obtained as free-flowing material with 11.1% (w/w) loading of the extractant. The presence of the ligand was confirmed from the FT-IR spectra which clearly show the carbonyl peak (in the region 1580–1690 cm^{-1} , Figure 2) of TAM-4-DGA (this peak was absent in

Figure 2. FT-IR spectra of the TAM-4-DGA coated Chromosorb-W resin.

the solid Chromosorb-W). The bands in the range 2850–2960 cm^{-1} are characteristic of the $-\text{CH}-$ groups of the alkyl chain. The absence of a broad band at $>3000\text{ cm}^{-1}$ suggests the absence of any moisture in the resin. Additionally, knowledge about the surface morphology can be obtained by SEM analysis which, in turn, would be of help to understand many of its physical and chemical properties.

Surface morphology information on the TAM-4-DGA resin was obtained from the SEM photographs at 700 $\times$ magnification. Figure 3a shows the SEM image of the pristine resin, while that of the resin after the uptake studies and regeneration after back extraction (*vide infra*) is presented in Figure 3b. The SEM photographs show large flakes of the Chromosorb-W

with honeycomb-like structures which may assist in the extractant loading as well as water intrusion into the pores resulting in a relatively fast mass transfer. The SEM photographs of both the resins are similar suggesting no degradation of the beads. The EDX spectra of the resins (Chromosorb-W, ligand loaded extraction chromatographic material, and resin loaded with Eu^{3+} ions) are presented in Figure 4 which indicate the presence of Eu^{3+} ions in the loaded resin.

3.2. Distribution Behavior of Eu^{3+} . The uptake of Eu^{3+} ions onto the extraction chromatographic resin was studied over a wide range of acidities. Figure 5a shows the K_d values of Eu^{3+} ions with TAM-4-DGA resin under varying feed acidities. The K_d value increased with increasing feed acidity from 0.01 to 4 M HNO_3 and remained very large ($>1 \times 10^5$) between 3 and 6 M HNO_3 . This is a typical solvation type extraction mechanism, generally observed with neutral ligands such as TODGA.³³ TAM-4-DGA, used in the present case, is similar to TODGA in metal ion binding, and hence, the uptake profiles appear analogous.

As evident from Figure 5a, the K_d value of Eu^{3+} on the TAM-4-DGA resin was very large (>200) even at 0.01 M HNO_3 , which means that the stripping of the sorbed Eu^{3+} from the resin may not be possible with dilute acid. It necessitated, therefore, the use of a complexing agent for efficient stripping of the loaded Eu^{3+} from the resin phase. Due to this, we used 0.1 M HEDTA (*N*-(2-hydroxyethyl)ethylenediamine triacetic acid) for back extraction of Eu^{3+} , where its K_d value was <10 . The advantage of using HEDTA is its large solubility even at high acid concentration (3 M HNO_3), unlike EDTA which is soluble only above pH 3.

To confirm the reusability and the stability of the TAM-4-DGA resin, Eu^{3+} (0.1 mg/mL at 3 M HNO_3) was sorbed on the resin and desorbed with 0.1 M HEDTA in five successive cycles. After desorption of Eu^{3+} , the resin was washed with water to remove the traces of HEDTA before starting the next cycle. As shown in Figure 5b, no change in the performance of the resin was observed in five successive cycles, confirming the excellent hydrolytic and leach stability of the resin.

The distribution coefficient values of actinide ions such as UO_2^{2+} , Pu^{4+} , and Am^{3+} , which are important from the radioactive waste management point of view, were also measured at 3 M HNO_3 and are listed in Table 2. Whereas the extraction of the trivalent and tetravalent actinides was very large, the hexavalent uranium was poorly extracted. This behavior was previously reported for DGA ligands where the presence of two axial O atoms in UO_2^{2+} gives rise to restrictions while coordinating with the bulky DGA ligand molecules.³⁵ The K_d values with the resins prepared by impregnating tripodal DGA ligand, T-DGA (Figure 1b), DGA-functionalized calix[4]arene, C4DGA (Figure 1c), and bare DGA ligand (TODGA, Figure 1a) are also included in Table 2 for comparison. The results indicate that the highest extraction efficiency for trivalent actinides and lanthanides can be achieved by the TAM-4-DGA ligand. This feature has also been shown in solvent extraction where the highest extraction of trivalent actinides was found with the TAM-4-DGA ligand.²⁷ These results indicated that the TAM-4-DGA ligand is a better candidate among various multiple DGA ligands for the recovery of trivalent actinide and lanthanide ions from acidic feed samples. Although the back extraction of trivalent actinides and lanthanides from the TAM-4-DGA resin phase seems to be nonviable with dilute acid (based on results shown

Figure 3. SEM images of (a) pristine Chromosorb-W and (b) Chromosorb-W loaded with the extractants (TAM-4-DGA) solution in 5% iso-decanol + 95% *n*-dodecane.

Figure 4. EDX spectra of (a) Chromosorb-W, (b) extraction chromatographic resin, and (c) Eu^{3+} loaded resin.

Figure 5. Uptake of Eu^{3+} onto the TAM-4-DGA resin. (a) Effect of feed acidity on the distribution coefficient (K_d) of Eu^{3+} ; (b) sorption and desorption of Eu^{3+} on the resin in five successive cycles to establish the stability of the resin.

Table 2. Distribution Coefficient (K_d) Values of Metal Ions with Resins Prepared by Different DGA Ligands^a

Metal ions	K_d at 3 M HNO_3			
	TAM-4-DGA ^b	T-DGA ^{34,c}	C4DGA ^{34,d}	TODGA ^{11,e}
Eu^{3+}	$(3.7 \pm 0.4) \times 10^5$	8335 ± 410	8330 ± 380	9018
Am^{3+}	$(4.3 \pm 0.4) \times 10^5$	9939 ± 340	6985 ± 253	7212
Pu^{4+}	$(2.9 \pm 0.3) \times 10^5$	4757 ± 138	5305 ± 168	5130
UO_2^{2+}	10.6 ± 2.1	9.8 ± 0.5	0.50 ± 0.31	110

^aAqueous phase: 3 M HNO_3 . Temperature: 25 °C ^bLigand loading: 11% (w/w), ^c10% (w/w), ^d10% (w/w), ^e47% (w/w).

Figure 6. (a) Variation of K_d value of Eu^{3+} with temperature and (b) variation of ΔG with temperature; Aqueous phase: 0.1 M HNO_3 .

Figure 7. (a) Sorption behavior of Eu^{3+} as a function of time on the TAM-4-DGA resin. Aqueous phase: 0.1 M HNO_3 . (b) Kinetic data fitted in pseudo-first-order rate kinetic and (c) pseudo-second-order rate kinetic.

in Figure 5a), use of complexing solution like HEDTA can be employed for this purpose.

3.3. Thermodynamics of Eu^{3+} Sorption. To obtain the various thermodynamics parameters such as ΔG , ΔH , and ΔS , it is desirable to have knowledge of the equilibrium reaction taking place between the ligand present on the resin and the Eu^{3+} ion in the aqueous phase. The equilibrium reaction for the distribution of Eu^{3+} on the resin can be described as

where the subscripts (aq) = aqueous phase and (s) = solid phase, and L = TAM-4-DGA ligand present on the solid support. Here, the term $[(\text{Eu}(\text{NO}_3)_3 \cdot \text{L}_x)_{(\text{s})}]$ is the metal ligand complex that is extracted or sorbed onto the resin. For simplicity, this term will be represented as $[\text{M} \cdot \text{L}]_{(\text{s})}$ in the subsequent text. The equilibrium constant, K_{ex} for the above equilibrium can be written as

$$K_{\text{ex}} = [\text{M} \cdot \text{L}]_{(\text{s})} / \{[\text{Eu}^{3+}]_{(\text{aq})} \cdot [\text{NO}_3^{-}]_{(\text{aq})}^3 \cdot [\text{L}]_{(\text{s})}^x\} \quad (7)$$

Since, $K_d = [\text{M} \cdot \text{L}]_{(\text{s})} / [\text{Eu}^{3+}]_{(\text{aq})}$, the eq 7 can be solved as

$$K_d = K_{\text{ex}} \cdot [\text{NO}_3^{-}]_{(\text{aq})}^3 \cdot [\text{L}]_{(\text{s})}^x \quad (8)$$

Converting the above equation into linear form, we obtain the following equation:

$$\log K_d = \log K_{\text{ex}} + 3 \log [\text{NO}_3^{-}]_{(\text{aq})} + x \log [\text{L}]_{(\text{s})} \quad (9)$$

For the calculation of the K_{ex} value, it is essential to have the activities of nitrate ions in the aqueous phase and that of the ligand on the solid. Although the concentration of ligand on the solid is known, its activity is not known. In such case, the K_{ex} shall be considered as the “conditional equilibrium constant” and its value was calculated from the known concentration of the ligand on solid phase and the nitrate ion concentration in the aqueous phase. In the equilibrium reaction 6, the value of x was taken as 2 based on the results obtained in slope analysis in solvent extraction as described in eq 9.²⁰ It is fairly good to assume a similar Eu^{3+} /ligand stoichiometry in extraction chromatography as observed in solvent extraction when the same solvent is used, for example ligand dissolved in 5% isodecanol/*n*-dodecane. Additionally, both studies were carried out with the tracer metal ion concentration, and a similar correlation for the extraction of metal ions by solvent extraction and extraction chromatography has been shown earlier.⁸ Therefore, the value of the conditional equilibrium constant (K_{ex}) for equilibrium reaction 6 was calculated by assuming the composition of the extracted complex as $[(\text{Eu}(\text{NO}_3)_3 \cdot \text{L}_2)_{(\text{s})}]$. From the calculated K_{ex} the value of the Gibb's free energy can be calculated using the standard relation ($\Delta G = -RT \ln K_{\text{ex}}$).

To understand the thermodynamics of Eu^{3+} sorption on the TAM-4-DGA resin, the temperature dependence of the K_d values of Eu^{3+} was measured. As indicated in Figure 6a, Eu^{3+} ion sorption onto the resin was exothermic in nature which was evident by an exponential decrease in the K_d values with

rising temperature. From the K_d values, the value of K_{ex} was calculated at different temperatures to gain ΔG values ($\Delta G = -RT \ln K_{ex}$). The values of ΔS and ΔH were obtained by plotting ΔG vs T ($\Delta G = \Delta H - T\Delta S$), which yielded the slope equal to ΔS and intercept equal to ΔH . From Figure 6b, values of ΔH and ΔS were calculated as -43.9 ± 1.3 kJ/mol and 146 ± 4 J/mol/K, respectively, indicating that the sorption of Eu^{3+} onto the TAM-4-DGA resin was both enthalpy and entropy driven. A large positive entropy change is an indication of dehydration of the metal ion primary hydration sphere where coordinated water molecules are replaced by the complexing ligand. On the other hand, the enthalpy change during dehydration of the metal ion and metal/ligand complexation reaction makes the overall process exothermic.

3.4. Sorption Kinetic of Eu^{3+} . To understand the kinetic model responsible for the sorption process, it was desirable to investigate the Eu^{3+} mass transfer from the aqueous phase to the resin phase with time. As shown in Figure 7a, the sorption kinetic was relatively fast and the equilibrium K_d values were obtained within 15 min of shaking time. The kinetic was relatively faster in the present work as compared to other analogous extraction chromatographic resins prepared from DGA-based ligands such as T-DGA and C4DGA, where equilibrium was reached in about 45 min.²² The sorption kinetic is dependent on the mass transfer rate, which is dependent on the complexation kinetic and the diffusion rate. If one assumes a similar complexation kinetic for TAM-4-DGA, T-DGA, and C4DGA ligands, then the overall sorption kinetic shall depend on the diffusion of the complex from the surface of the resin to the core. Since the diffusion of the complex is strongly influenced by the viscosity of the medium, the difference in the composition of the solvent of the resins (TAM-4-DGA resin and T-DGA/C4DGA resins) may show different kinetic patterns. While the previously reported resins have the solvent composition of 10% (w/w) ligand dissolved in 20% isodecanol/*n*-dodecane, the present solvent composition was 11.1% (w/w) ligand dissolved in 5% isodecanol/*n*-dodecane. This difference in the solvent composition might have favored the sorption kinetic in the present work. Nonetheless, a plateau region after 15 min of equilibration (Figure 7a) indicated that the Eu^{3+} ions sorbed on the resin were not desorbed even when the equilibration time was prolonged. In view of these observations, 30 min of shaking time were given for all the subsequent K_d measurements.

In order to investigate the type of kinetic followed, the sorption data were fitted in the pseudo-first-order and pseudo-second-order rate equations.^{23,24} As shown in Figure 7b, poor fitting of the data indicated the absence of a first-order rate kinetic in this case. Subsequently, when the data were fitted in the pseudo-second-order kinetic equation (eq 3), a straight line was obtained (Figure 7b). The value of k_2 was obtained as 6.33×10^{-7} g/cpm·min. As the fitting in the pseudo-second-order rate kinetic model was good, it was an indication that the interaction between the metal ion and the ligand on the resin was controlling the sorption process. This feature indicates that a monolayer of the Eu^{3+} ion is formed on the resin surface where it is chemically bonded with the ligands. To test this postulate, the Elovich model was used (eq 4) which states that, if a species is sorbed on the surface in a multilayer sorption process without its desorption, the rate of sorption will decrease with time due to an increase in the surface coverage.^{36,37} As evident from Figure 8a, a nonlinear plot of

the Elovich equation supports the absence of the multilayer sorption phenomenon.

Figure 8. (a) Elovich kinetic model plot and (b) diffusion kinetic for the sorption of Eu^{3+} on TAM-4-DGA resins. Aqueous phase: 0.1 M HNO_3 .

It is well understood that the metal ion sorption process onto extraction chromatographic resins involves a series of steps which can affect the sorption kinetic. It involves (i) diffusion of metal ions from the bulk aqueous phase to the surface of the solid sorbent, (ii) electrostatic interaction with the metal ion and the ligand at the boundary layer, and (iii) metal ligand complex diffusion from the surface of the resin bead into the pores of the solid matrix. In such processes, as the diffusion of a metal ion from the bulk solution to the boundary layer is rather fast, the rate-limiting step may be either the complexation (particularly for multiple DGA ligands) or the metal/ligand adduct diffusion into the pores of the solid matrix, commonly known as the pore diffusion process.³⁸ Assuming that the complexation is rather fast, in view of the involvement of only one DGA arm in metal ion binding,²⁰ the diffusion into the stationary phase pores is significant. To gain clarity on this phenomenon, the pore diffusion model (eq 5) was also tested. It is proposed³⁹ that if the plot of q_t vs $t^{0.5}$ in eq 5 gives a straight line, the sorption process is solely controlled by intraparticle diffusion. In contrast, if the linear fitting exhibits multilinear curves, two or more steps may be involved in the sorption process. In the present case (Figure 8b), the plot consists of two linear parts, which confirms that the sorption process proceeded at least by two sorption mechanisms: (i) the film diffusion and (ii) the intraparticle diffusion. The first part in Figure 8b with a positive slope is an indication that the boundary-layer diffusion (film diffusion) is probably limiting the sorption process. On the other hand, the second part of the curve with a zero slope indicates that the pore diffusion is perhaps limiting the sorption process. The value C (intercept of the Weber and Morris model) provides information about the thickness of the aqueous film around the solid resin.³¹ The positive C value in this work is an indication of an intraparticle diffusion process. One of the important conclusions that can be noted from Figure 8b is that the q_t vs $t^{0.5}$ plot does not pass through the origin. This feature indicates that the intraparticle diffusion is probably not a rate-controlling step for the sorption of Eu^{3+} . Thus one can conclude that the film and the intraparticle

diffusion are concurrently operating for Eu^{3+} ion sorption from bulk solution to the solid phase.

3.5. Sorption Isotherm for Eu^{3+} . To understand the interaction of the Eu^{3+} ion with the TAM-4-DGA ligand present on the surface of the solid, its sorption isotherm was investigated at 1 M HNO_3 . At equilibrium, the limiting sorption capacity of Eu^{3+} was 14.4 ± 0.1 mg per g of the resin that corresponds to $94.8 \mu\text{mole}$ of Eu/g resin. As mentioned above, $97 \mu\text{mol}$ of TAM-4-DGA were present per g of the impregnated resin suggesting the formation of a 1:1 metal/ligand complex. This contrasts with the results reported in solvent extraction studies where Eu^{3+} forms a 2:1 complex (ligand to metal).²⁰ However, the comparison of the present result may not be justified as the solvent extraction results are reported on tracer metal concentrations, while in the present work excess metal concentration (5 mg/mL) was used to saturate the ligand.

The sorption data of Eu^{3+} on the resin were fitted in several popular isotherm models such as Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) models given in Table 1. As shown in Figure 9a, the plot of C_e/q_e vs C_e was a

Figure 9. (a) Langmuir plot and (b) Freundlich plot for the sorption of Eu^{3+} on the TAM-4-DGA resin. Aqueous phase: 1 M HNO_3 .

straight line with a good fitting correlation coefficient. This behavior was an indication that the sorption followed the Langmuir monolayer sorption model. The value of q_{max} was 14.5 ± 0.1 mg of Eu/g resin, which is in excellent agreement with the value obtained experimentally in the batch experiment (14.4 ± 0.1 mg/g). The isotherm data were also treated for the multilayer sorption phenomenon in the Freundlich model (Table 1) which is based on multilayer coverage of the species on the surface of the extraction chromatographic resin. However, fitting data in the Freundlich model (Figure 9b) were poor, which gave an indication of the absence of the multilayer sorption phenomenon. To confirm this, the isotherm data were further fitted to the Temkin model (Table 1). The Temkin model considers that there are indirect interactions between the metal ions and the ligand present on the surface, and due to these indirect interactions, the sorption heat in different layers shall decrease linearly upon coverage. It means if the sorption data are fitting in the Temkin model, it would be an indication of the multilayer sorption process. However, poor fitting of the data in the Temkin isotherm equation (Figure 10a) further indicated the absence of multilayer sorption in this work.

Figure 10. (a) Temkin and (b) D–R plots for the sorption of Eu^{3+} on the TAM-4-DGA resin. Aqueous phase: 1 M HNO_3 .

In order to distinguish the sorption process in the present work as either physisorption or chemisorption, the sorption data were fitted in the D–R isotherm model (Table 1). The D–R model assumes that if the sorbent surface is heterogeneous where all the sites are energetically equivalent and the sorption is monolayer in nature, then the mean sorption energy quantity (β) is given as $E = 1/(-2\beta)^{1/2}$. Here, E = mean sorption energy which is the free energy needed for the transfer of 1 mol of metal ions from infinity to the surface of the sorbent.³⁰ The energy in the present work was obtained to be 26 ± 2 kJ/mol (Figure 10b). The value of E gives information about the type of sorption mechanism, chemisorption or physisorption.⁴⁰ A value of $E > 8$ kJ/mol signifies a chemisorption process, whereas a value < 8 kJ/mol points to a physical sorption process. Since the numerical value of E in the present work is > 8 kJ/mol (25.8 kJ/mol), it indicates that the sorption of Eu^{3+} ions on the resin takes place via a chemical interaction. The chemical interaction between the Eu^{3+} cation and the TAM-4-DGA ligand present on the resin was further confirmed by the spectroscopic measurements described below.

3.6. Interaction of Eu^{3+} with Resin. To further investigate the chemical reaction between the Eu^{3+} cation and the TAM-4-DGA ligand present on the solid support, FTIR and luminescence spectroscopy were applied. As shown in Figure 11, a peak in the region $1580\text{--}1690 \text{ cm}^{-1}$ in the FTIR spectra was an indication of the presence of the $>\text{C}=\text{O}$ group of the TAM-4-DGA ligand present in the impregnated resin (this peak was absent in the solid Chromosorb-W). Upon complexation with Eu^{3+} , a clear shift in the $>\text{C}=\text{O}$ vibrational frequency was observed confirming a chemical interaction between the ligand and the Eu^{3+} ion.

To obtain further elaboration on the Eu^{3+} /ligand complexation, emission spectra were recorded and the lifetime of Eu^{3+} was measured both in the aqueous phase and on the resin. As shown in Figure 12, the band features in the emission spectra originate from the electronic transitions of the $^5\text{D}_0$ state to the $^7\text{F}_1$ (589 nm) and $^7\text{F}_2$ (612 nm) states of the Eu^{3+} ion.⁴¹ The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ band (614 nm) is hypersensitive in nature, and its intensity increases upon complexation with the ligand due to replacement of water molecules from the coordination sphere of Eu^{3+} . On the other hand, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ band (590 nm) remains unaffected during the complexation. The ratio of the peak intensity (or band area) due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and

Figure 11. FTIR spectra of the blank solid support, ligand coated resin, and Eu^{3+} loaded resin.

$^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition bands is referred to as the *asymmetry factor* and is generally used to understand the symmetry in the complex.⁴² In the present work, the asymmetry factor for the Eu^{3+} /aquo complex in 1 M HNO_3 was found to be 1.34, which increased to 2.48 upon complexation with the ligand on the resin (Figure 12). In addition to this, splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ peak at 614 nm also indicates a symmetry change around the coordination sphere of the Eu^{3+} ion. The fluorescence decay lifetime of Eu^{3+} in 1 M HNO_3 and on the resin was calculated to be 0.121 and 1.34 ms, respectively (Figure 12). The number of water molecules in the first coordination sphere of the free Eu^{3+} ion was calculated from the lifetime data using the Barthelmy–Choppin equation:⁴³

$$N_{\text{H}_2\text{O}} = (1.05/\tau) - 0.7 \quad (10)$$

where τ is the lifetime in ms. 8.0 H_2O molecules were present in the inner coordination sphere of Eu^{3+} in the 1 M HNO_3 solution. These water molecules were successfully replaced by the ligands upon complexation, as indicated by the absence of

H_2O molecules in the complexed Eu^{3+} on the resin. This feature further confirms the chemical interaction between the Eu^{3+} ion and the ligand present on the resin during the sorption process.

3.7. Column Studies. After investigating the interaction of Eu^{3+} with the TAM-4-DGA resin, column studies were taken up to evaluate its application feasibility for separation of lanthanides. Figure 13 shows the loading, washing, and elution

Figure 13. Loading, washing, and elution curves for Eu^{3+} on the TAM-4-DGA resin column. Feed solution: 0.40 mg/mL Eu^{3+} at 3 M HNO_3 . Washing solution: 3 M HNO_3 . Eluent: (1) 1 M guanidine carbonate + 0.05 M EDTA, (2) 0.1 M HEDTA, (3) distilled water. Column dead volume: 1.0 mL. Flow rate: 0.3 mL/min.

profile of Eu^{3+} on the column. The breakthrough of Eu^{3+} was observed after passing 13 mL of the feed solution. After removing the dead volume of the column (1 mL), the amount of Eu^{3+} loaded on the column was found to be 12.0 mg/g of resin. Since the Eu^{3+} capacity by the resin obtained in batch static experiments was 14.4 mg/g, it indicates that the column capacity was about 83% of the resin capacity. It is worth mentioning that the column loading capacity is governed by several factors such as the column bed height, flow rate, and

Figure 12. (a) Emission spectra and (b) fluorescence decay curve of Eu^{3+} ion in the aqueous phase and (c) decay profile of Eu^{3+} ion loaded onto the resin. Excitation: 396 nm. Emission: 614 nm.

reaction kinetic between the metal ion and the ligand on the resin, and any variation in these factors may affect the column loading capacity significantly.

After loading the column to close to 100% of the breakthrough value, it was washed with 3 M HNO₃ to remove the physically sorbed or uncomplexed Eu³⁺ from the column followed by its elution. Elution of the loaded Eu³⁺ was carried out with three different solutions. Initially, distilled water was used as the eluent (curve 3 in Figure 13), which led to only about 40% elution in 10 mL. This feature indicates the inefficiency of water as the eluent for the back extraction of the sorbed Eu³⁺ from this column. Taking a clue from the literature,⁴⁴ we used a complexing buffer for elution, which comprised 1 M guanidine carbonate + 0.05 M EDTA dissolved in water. As shown by the elution curve 1, complete recovery of Eu³⁺ was possible in about 10 mL of this eluent. However, this buffer solution created bubbles in the column due to neutralization of the acid present in the column which led to the slowing down of the flow rate, gradually resulting in the choking of the column. It was decided, therefore, not to use this buffer mixture as eluent particularly when the column is loaded with acid. However, it can be used for a column where the loading is done at very low acidity, e.g. pH 3 solution.^{44,45} As an alternate eluent 0.1 M HEDTA was used as the complexing agent which yielded a similar elution curve (curve 2) to that of the guanidine carbonate, but without any physical problem of the column. The mass balance of the loaded Eu³⁺ and the eluted Eu³⁺ was within $\pm 4\%$. It is worth mentioning that HEDTA is a homologue of EDTA where one carboxylic acid group is replaced with a hydroxyl group which enhances its water solubility even at large concentrations of acid (>6 M HNO₃), unlike EDTA which precipitated below pH 3.

4. CONCLUSIONS

A diglycolamide-functionalized tetraaza-12-crown-4 (TAM-4-DGA) based extraction chromatographic resin was studied for its sorption behavior for Eu³⁺ ion. With only 11% (w/w) loading of the ligand on the solid support, the K_d value of Eu³⁺ was large enough in a wide acidity range (0.1–6 M HNO₃) suggesting its possible application for the separation of trivalent actinides and lanthanides from a wide range of feed acidity. The sorption kinetic was fast and required only about 15 min to attain equilibrium. The kinetic modeling of the data suggested a pseudo-second-order model. The sorption of Eu³⁺ followed the Langmuir monolayer model with a sorption energy of 26 ± 2 kJ/mol, which is an indication of chemisorption. The chemical interaction between the Eu³⁺ cation and the ligand on the resin was confirmed by FTIR and fluorescence spectroscopy. The sorption of Eu³⁺ on the resin was exothermic with a ΔH value of -43.9 ± 1.3 kJ/mol. The results suggest that the present extraction chromatographic resin material can be used for the separation of trivalent lanthanides as well as actinides from radioactive waste feeds as well as lean solutions such as environmental samples. However, the major shortcoming of this resin is the need for a complexing agent for eluting the loaded metal ions from the resin phase which necessitates the need for a suitable ligand which can give efficient extraction of metal ions and also efficient back extraction with mineral acids.

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Notes

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