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# Synthesis, characterization and ion exchange characteristics of a novel hybrid ion exchange material

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## ABSTRACT

In the present study, zirconium diethylene triamine pentamethylene phosphonate (ZrDETPMP), a hybrid ion exchanger of the class of tetravalent metal acid (TMA) salt, has been synthesized by soft chemistry route, sol-gel method. The material was characterized for elemental analysis (ICP-OES and CHN analyzer), thermal analysis (TGA), spectral analysis (FT-IR), X-ray diffraction and SEM. Chemical resistivity of the material was assessed in various media (acids, bases and organic solvents). Ion exchange capacity was determined and the effect of calcination on ion exchange capacity (IEC) was studied. The distribution behaviour ($K_d$) in different electrolyte media/concentrations, breakthrough capacity and elution behaviour of metal ions $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$ and $Th^{4+}$ were studied and discussed.

*Keywords*: Tetravalent metal acid salt; Metal phosphonate; Zirconium phosphonate; Hybrid ion exchanger

## 1. Introduction

Inorganic ion exchangers play a prominent role in water processing for the chemical and nuclear industries and are also used extensively for the removal and recovery of metal ions [1,2]. Amongst various processes developed for removal of metals from wastewater, it is observed that at low concentrations, the removal is more effective by ion exchange [1,2]. Different types of metal pollutants from chemical process industries, world wide, necessitates finding new ion exchangers [3] that have good ion exchange capacity, stability towards temperature, ionizing radiation and oxidizing solutions.

Tetravalent metal acid (TMA) salts have emerged as promising advanced materials owing to their high thermal and chemical stability, resistance towards ionizing radiations as well as their important applications as ion exchangers in separation science [4]. TMA salts are cation exchangers, possessing the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$, where M(IV) = Zr, Ti, Sn, Ce, Th, etc. and $X$ = P, W, As, Mo, Sb, etc. The protons present in the structural hydroxyl groups of these materials can be exchanged for several cations and thus they behave as cation exchangers. TMA salts with varying water content, composition and crystallinity can be obtained, depending on various factors viz. mole ratio of reactants $M : X$ ($M$ = tetravalent metal and $X$ = polyvalent anion), mode of mixing (tetravalent ion to polyvalent anion and vice versa), pH, temperature and rate of mixing. Variation in any of these parameters yields materials with different characteristics. The preparation procedure thus affects the structural hydroxyl groups, which is reflected in the variation of the ion exchange capacity (IEC) and hence its performance as an ion exchanger. Thus, the area of study

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of TMA salts is evergreen, newer materials with high IEC continuously being synthesized/investigated.

Recently, interest has been generated in the preparation of some organic based inorganic ion exchangers, such materials being termed as inorgano-organic hybrid ion exchangers that provide improved and tunable properties [5], mainly the ion exchange capacity and the promise of developing new materials with properties not seen in purely organic or purely inorganic solids. A major advantage of inorgano-organic hybrid materials is the rigid inorganic backbone and the flexibility of the organic groupings that creates opportunity to design compounds with specific properties.

Organic derivatives of inorganic ion exchangers of the class of TMA salts are of particular interest. Zirconium phosphate, an inorganic ion exchanger of the class of TMA salts, has been widely studied as an ion exchanger because of its excellent ion exchange behaviour and important applications in the field of ion exchange, besides exhibiting a number of advantages as an ideal host lattice [6] for the development of new ion exchangers. In the tetrahedral moiety of phosphoric acid, $PO(OH)_3$, if –H or –OH is replaced by –R (where R = alkyl/aryl possessing ionogenic groups such as –OH, $–SO_3H$, –COOH, etc.), phosphonic acids are obtained, which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce, etc. give rise to novel metal phosphonates [7–9]. Depending on the complexity of the phosphonic acid used, the material gives rise to two or three dimensional hybrid polymeric structures. These materials are interesting because of their potential utilization as ion exchangers [10].

Aminophosphonic acids possess effectiveness of donor groups in the binding of tetravalent metal ions, and have received considerable attention due to the diverse binding abilities [11,12]. Claw type phosphonic acid such as diethylene triamine pentamethylene phosphonic acid (Fig. 1), possessing ten structural hydroxyl groups, permits versatile control of the surface modification in terms of IEC, porosity and hydrophilic character, as well as the large number of exchange sites having the tendency to offer good affinity as well as selectivity for metal ions.

Sol-gel processing is one of the promising routes to inorgano–organic hybrids that can be formed using a soft chemistry, low temperature approach termed as “Chimie Douce” by the French. Metal phosphonates are obtained at low temperatures, often from aqueous solutions. Using the sol–gel route, it is possible to introduce a large variety of organic moieties into inorganic matrices, leading to the possibility of tailoring the physico-chemical properties. Zirconium hydroxy ethylidene diphosphonate (ZrHEDP) has been synthesized, characterized and ion exchange characteristics have been reported from our laboratory [13,14].

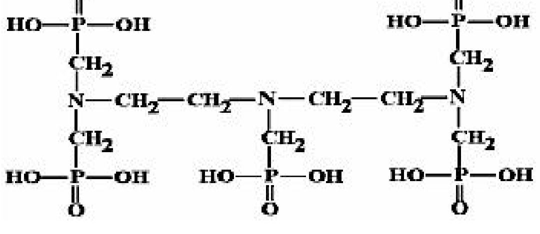

Fig. 1. Structure of DETPMP.

In the present study, zirconium diethylene triamine pentamethylene phosphonate (ZrDETPMP), a hybrid ion exchanger of the class of tetravalent metal acid (TMA) salt has been synthesized by soft chemistry route, sol-gel method. The material has been characterized for elemental analysis (ICP-OES and CHN analyzer), thermal analysis (TGA), spectral analysis (FT-IR), X-ray diffraction and SEM. Chemical resistivity of the material has been assessed in various media (acids, bases and organic solvents). Ion exchange capacity has been determined and effect of calcination on ion exchange capacity (IEC) studied. The distribution behaviour ($K_d$) in different electrolyte media/concentrations, breakthrough capacity and elution behaviour of metal ions $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$ and $Th^{4+}$ have been studied and discussed.

## 2. Experimental

### 2.1. Synthesis of ZrDETPMP

ZrDETPMP was prepared by mixing aqueous solutions of DETPMP (0.1M, 100 mL) and $ZrOCl_2$ (0.1 M, 100 mL) at room temperature, drop wise and with continuous stirring. A gelatinous precipitate was obtained, and solution along with precipitate further stirred for 1 h. The resulting gelatinous precipitate was allowed to age for 15 h, then filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature. The material was then broken down to the desired particle size [30–60 mesh (ASTM)] by grinding and sieving. This material was converted to the acid form by taking 5 g of the material and treating it with 50 mL of 1 M $HNO_3$ for 30 min with occasional shaking. The sample was then separated from acid by decantation and washed with conductivity water for removal of the adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. This material was used for all studies.

### 2.2. Ion exchange capacity (IEC)

The $Na^+$ ion exchange capacity (IEC) for ZrDETPMP was determined by the column method [15]. 0.5 g of ZrDETPMP ($H^+$ form) was packed in a glass column (45 × 1 cm) and washed with double distilled water to remove any excess of acid that remained on the particles. 250 mL of 0.5 M solution of sodium acetate was passed through the column maintaining the flow rate at 0.5 $mL \cdot min^{-1}$.

The effluent was collected and titrated against a standard NaOH solution to determine the total $H^+$ ions released. The ion exchange capacity (in meq·g$^{-1}$) was evaluated using formula

$$aV / w \quad (1)$$

where *a* is molarity and *V* is the volume of alkali used during titration, and *w* is the weight of the exchanger.

### 2.3. Calcination studies

The effect of heating on IEC was studied by heating several 1 g portions of the material for 2 h at different temperature from 100°C to 500°C with 100°C intervals in a muffle furnace and determining the $Na^+$ exchange capacity by the column method [15] at room temperature.

### 2.4. Chemical stability

The chemical stability of the material in various media — acids (HCl, $H_2SO_4$, $HNO_3$), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) — was studied by taking 0.5 g of the synthesized material in 50 mL of the particular medium and allowing to stand for 24 h. The change in colour, nature, weight as well as solubility was observed. Further, to confirm the stability/solubility of exchanger in particular media, supernatant liquid was checked qualitatively for respective elements of exchanger.

### 2.5. Instrumentation

The samples were analyzed for zirconium and phosphorus content using ICP-OES (Labtam, 8440 Plasmalab). X-ray diffractogram was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-K$\alpha$ X-ray source of wavelength 1.5418 Å and nickel filter. FTIR spectra was recorded using KBr powder on Shimadzu (Model 8400S). Thermal analysis (TGA) was carried out on a Shimadzu DT 30 thermal analyzer at a heating rate of 10°C·min$^{-1}$. SEM of the sample was scanned on Jeol JSM-5610-SLV scanning electron microscope.

### 2.6. Distribution studies

Distribution coefficient ($K_d$) is a measure of the fractional uptake of metal ions in a solution, competing for $H^+$ ions, in the case of a cation exchange material. Distribution coefficient ($K_d$) was evaluated using the expression [18]

$$K_d = \left[(I - F)/F\right] \times V / W \ (\mathrm{mL\,g^{-1}}) \quad (2)$$

where *I* = total amount of the metal ion in the solution initially; *F* = total amount of metal ions left in the solution after equilibrium; *V* = volume of the metal ion solution; *W* = weight of the exchanger. The distribution coefficient ($K_d$) for $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$ and $Th^{4+}$ was evaluated by batch method [16]. 0.1 g of ZrDETPMP in the $H^+$ form was equilibrated with 20 mL of 0.001 M metal solution for 24 h at room temperature. The metal ion concentration before and after exchange was determined by EDTA titration [17]. Distribution studies were carried out in aqueous as well as various electrolyte media like $NH_4NO_3$, $HNO_3$, $HClO_4$ and $CH_3COOH$ of 0.02 and 0.20 M concentration.

### 2.7. Breakthrough capacity (BTC)

5 mL (0.001 M) fractions of each of the metal ion [$La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Th^{4+}$] solution was passed through a column containing 0.5 g ZrDETPMP, maintaining flow rate of 6 BV/h. Each 5 mL fraction of the effluent was collected and concentration measured by EDTA titration. The process continued till the amount of metal ions was the same in the feed and the effluent. A breakthrough curve was obtained by plotting the ratio $C_e/C_o$ against the effluent volume, where $C_o$ and $C_e$ are the concentrations of the initial solution and effluent respectively. BTC is calculated using the formula[19,20]

$$\mathrm{BTC} = \left(C_o V_{(10\%)}\right) / W \quad (3)$$

where $C_o$ is the initial/feed metal ion concentration, mol L$^{-1}$, $V_{(10\%)}$ is the volume of metal ion solution passed through the column when exit concentration reaches 10% of the initial concentration, mL, and *W* is the weight of the exchanger, g.

### 2.8. Elution behaviour

10 mL (100 ppm) of metal ion solution was allowed to pass through the column containing 0.5 g of ZrDETPMP, maintaining a flow rate 0.5 mL·min$^{-1}$. It was eluted with reagents like $HNO_3$, $HClO_4$, $CH_3COOH$ and $NH_4NO_3$ of 0.2 M concentration. The amount of metal ions recovered was calculated as $(C_e/C_o) \times 100$ where $C_e$ is the concentration of the metal ions in the eluted solution and $C_o$ is the initial metal ion concentration.

## 3. Results and discussion

### 3.1. Material characterization

ZrDETPMP is obtained as white hard granules.

Based on ICP-OES data and CHN analysis, the mole ratio of zirconium to phosphorus is 1:2 (found Zr = 48.3 ppm, P = 27.1 ppm and % C = 7.6, % H = 4.0 and % N = 3.9).

The FTIR spectra (Fig. 2) of ZrDETPMP exhibit a broad band in the region ~3400 cm$^{-1}$ which is attributed to asymmetric and symmetric –OH stretches. A sharp medium band at ~1638 cm$^{-1}$ is attributed to aquo H–O–H bending. This indicates the presence of structural hydroxyl groups in these materials. A band at ~1450 cm$^{-1}$, indicates the presence of tertiary amine and band at ~1050 cm$^{-1}$ is attributed to P=O stretching.

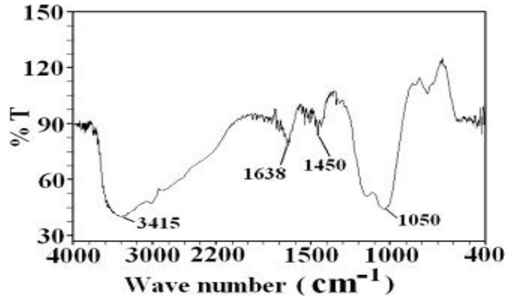

Fig. 2. FTIR of ZrDETPMP.

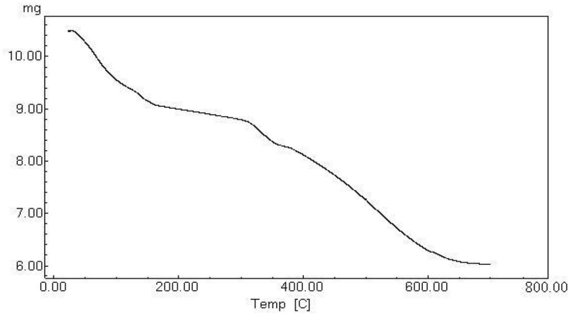

Fig. 3. TGA of ZrDETPMP.

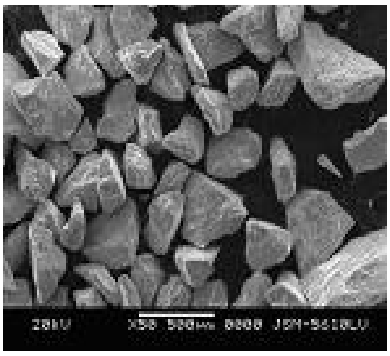

Fig. 4. SEM of ZrDETPMP.

TGA (Fig. 3) exhibits two regions of weight loss. The first weight loss ~7% up to 120°C is attributed to loss of moisture/hydrated water, while the second weight loss ~42% in the range of 200–700°C is attributed to the condensation of structural hydroxyl groups and decomposition of the organic moiety.

The absence of sharp peaks in X-ray diffractograms of ZrDETPMP indicates the amorphous nature of the material.

SEM (Fig. 4) of ZrDETPMP at room temperature, exhibits irregular particle size which indicates amorphous nature of the material.

The $Na^+$ IEC of ZrDETPMP was found to be 2.34 $meq \cdot g^{-1}$. The $Na^+$ IEC of the samples calcined at temperatures 100°C, 200°C, 300°C, 400°C and 500°C was found to be 2.39, 1.69, 3.25, 3.86 and 1.36 $meq \cdot g^{-1}$ respectively. The initial increase in the IEC value at 100°C could be attributed to loss of moisture adhered to it, thereby increasing the active exchanger content for same weight of material taken for IEC determination. Decrease in IEC at 200°C could be attributed to the condensation of structural hydroxyl groups. Increase in the IEC at 300°C and 400°C could be attributed to decomposition of organic moiety leading to the formation of active carbon. IEC decrease after 400°C is attributed to the loss of active carbon in the form of $CO_2$.

The results of chemical resistivity/stability study shows that ZrDETPMP is stable in acid medium, maximum tolerable limits being (18 N $H_2SO_4$, 16 N $HNO_3$, 11.3 N HCl) and in organic solvents (ethanol, benzene, acetone and acetic acid) but not so stable in base medium, maximum tolerable limits being (0.5 M NaOH and 0.5 M KOH).

### 3.2. Ion exchange studies

The smaller the size of the cation, greater is the tendency to be hydrated and greater the hydrated ionic radii. Larger ions being less hydrated exhibit higher affinity towards the exchange material. Less energy is utilized for dehydration of the metal ions to occupy a site on the exchanger, this plays a prominent role in determining the selectivity of metal ions [21]. In the present study, considering six coordinate aquated ions, the ionic radii (Å) [22] of metal ions [$La^{3+}$ (1.17), $Ce^{3+}$ (1.15), $Pr^{3+}$ (1.13), $Nd^{3+}$ (1.12), $Sm^{3+}$ (1.10) and $Th^{4+}$ (1.08)] being almost the same, it seems that other factors are responsible for selectivity. Selectivity order can be determined by $K_d$ values as well as by BTC for various metal ions.

$K_d$ values give an idea of metal ion affinity in aqueous as well as in various electrolyte media, about the possible binary metal ion separations as well as the eluants that can be used for metal ion separations. The distribution coefficients ($K_d$) evaluated for metal ions are presented in Table 1. Except $Th^{4+}$, all metal ions exhibit higher $K_d$ values in electrolyte media as compared to aqueous medium. This has also been observed earlier by other workers [23,24]. The most promising characteristic of the material is its high selectivity for $Th^{4+}$. In fact, complete exchange is observed in the case of 0.20 M $HNO_3$ and 0.20 M $HClO_4$.

BTC is the dynamic capacity or operating capacity of a known amount of ion exchange material in the column. The effective capacity is determined by means of breakthrough curves (Fig. 5). BTC depends on the flow rate of feed solution through the column, bed depth, selectivity co-efficient/size of the exchanging ion, particle size, temperature, etc.

The selectivity order of metal ions in aqueous medium with respect to $K_d$ values ($mL \cdot g^{-1}$) is $Th^{4+}$ (6723.05) > $Pr^{3+}$

Table 1
$K_d$ values of f-block metal ions

| Metal ion | Aqueous solution | 0.02 M $NH_4NO_3$ | 0.2 M $NH_4NO_3$ | 0.02 M $HNO_3$ | 0.2 M $HNO_3$ | 0.02 M HClO4 | 0.2 M $HClO_4$ | 0.02 M $CH_3COOH$ | 0.2 M $CH_3COOH$ |
|---|---|---|---|---|---|---|---|---|---|
| $La^{3+}$ | 94.03 | 64.71 | 2.82 | 83.67 | 22.86 | 97.50 | 140.78 | 32.10 | 73.68 |
| $Ce^{3+}$ | 180.00 | 367.69 | 6.06 | 200.00 | 220.69 | 28.57 | 14.17 | 55.48 | 40.00 |
| $Nd^{3+}$ | 170.68 | 48.73 | 340.74 | 116.00 | 191.43 | 2.57 | 271.79 | 122.22 | 154.30 |
| $Pr^{3+}$ | 220.00 | 408.00 | 976.00 | 77.35 | 31.49 | 77.96 | 52.30 | 626.00 | 380.00 |
| $Sm^{3+}$ | 5.71 | 20.34 | 26.67 | 11.24 | 72.22 | 73.68 | 91.18 | 41.03 | 186.70 |
| $Th^{4+}$ | 6723.05 | 874.44 | 6244.96 | 240.96 | CS | 229.87 | CS | 191.90 | 5786.00 |

*CS = complete sorption

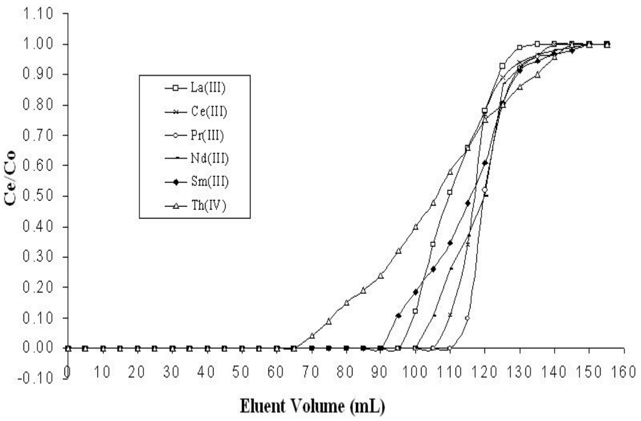

Fig. 5. Breakthrough curves of metal ions.

(220.00) > $Ce^{3+}$ (180.00) > $Nd^{3+}$ (170.68) > $La^{3+}$ (94.03) > $Sm^{3+}$ (5.71) and with respect to BTC (mmol·L$^{-1}$) is $Pr^{3+}$ (0.23) > $Ce^{3+}$ (0.22) > $Nd^{3+}$ (0.21) > $La^{3+}$ (0.20) > $Sm^{3+}$ (0.19) > $Th^{4+}$ (0.13). The same trend is observed for all the metal ions [$Pr^{3+}$, $Ce^{3+}$, $Nd^{3+}$, $La^{3+}$ and $Sm^{3+}$] except $Th^{4+}$. Discrepancy observed in the case of $Th^{4+}$ could be explained to be due to the fact that $K_d$ is determined by a batch process, where less amount of exchange material (0.2 g) and sufficient equilibrium time (24 h) is provided to ensure complete exchange. The complete exchange of a particular metal ion depends mainly on an equilibrium pattern, rate of exchange, contact time and other factors mentioned earlier in the text. Probably in the case of $Th^{4+}$, slow exchange rate seems to be the predominant factor.

Elution behaviour of metal ions is presented in Table 2. The study shows that 0.20 M $HNO_3$ is the best eluant for all metal ions. $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$ and $Th^{4+}$ exhibit 98.64 %, 97.74%, 96.55%, 95.98%, 97.14%, and 88.47% elution, respectively, using $HNO_3$.

Separation factor $\alpha$, the rate at which any two constituents separate on a column, is given by

Table 2
Elution behaviour of metal ions

| Eluent | | $La^{3+}$ | $Ce^{3+}$ | $Pr^{3+}$ | $Nd^{3+}$ | $Sm^{3+}$ | $Th^{4+}$ |
|---|---|---|---|---|---|---|---|
| 0.2 M $NH_4NO_3$ | $M_1$ | 2.2910 | 2.0608 | 2.2381 | 2.6439 | 2.0685 | 0.8793 |
| | $M_2$ | 2.1819 | 1.8284 | 2.0529 | 2.4616 | 1.9503 | 0.6931 |
| | % *E* | 95.24 | 88.72 | 91.72 | 93.10 | 94.29 | 78.82 |
| 0.2 M $HNO_3$ | $M_1$ | 2.2910 | 2.0608 | 2.2381 | 2.6439 | 2.0685 | 0.8793 |
| | $M_2$ | 2.2598 | 2.0144 | 2.1609 | 2.5376 | 2.0094 | 0.7779 |
| | % *E* | 98.64 | 97.74 | 96.55 | 95.98 | 97.14 | 88.47 |
| 0.2 M $HClO_4$ | $M_1$ | 2.2910 | 2.0608 | 2.2381 | 2.6439 | 2.0685 | 0.8793 |
| | $M_2$ | 2.2131 | 1.9214 | 2.0374 | 2.3248 | 1.9208 | 0.7035 |
| | % *E* | 96.60 | 93.23 | 91.03 | 87.93 | 92.86 | 80.00 |
| 0.2 M $CH_3COOH$ | $M_1$ | 2.2910 | 2.0608 | 2.2381 | 2.6439 | 2.0685 | 0.8793 |
| | $M_2$ | 2.1351 | 1.8904 | 2.0220 | 2.3856 | 1.9208 | 0.7448 |
| | % *E* | 93.20 | 91.73 | 90.34 | 90.23 | 92.86 | 84.71 |

$M_1$ = metal loaded (mg), $M_2$ = metal eluted (mg), %*E* = percentage elution

Table 3
Proposed metal ion pairs for separation

| Metal ion pairs | Separation factor ($\alpha$) |
|---|---|
| $La^{3+} – Sm^{3+}$ | 16.47 |
| $Ce^{3+} – Sm^{3+}$ | 31.52 |
| $Nd^{3+} – Sm^{3+}$ | 29.89 |
| $Pr^{3+} – Sm^{3+}$ | 38.52 |
| $Th^{4+} – La^{3+}$ | 71.49 |
| $Th^{4+} – Ce^{3+}$ | 37.35 |
| $Th^{4+} – Nd^{3+}$ | 39.54 |
| $Th^{4+} – Pr^{3+}$ | 30.55 |
| $Th^{4+} – Sm^{3+}$ | 1174.80 |

$$\alpha = K_{d1} / K_{d2} \tag{4}$$

where $K_{d1}$ and $K_{d2}$ are the distribution coefficients of the two constituents being separated. The separation factor was calculated and possible metal ion pairs for a few separations proposed (Table 3).

The proposed separation of metal ion pairs is in progress in our laboratory.

## 4. Conclusion

ZrDETPMP, synthesized in the present endeavour, exhibits good ion exchange characteristics — good IEC, thermal stability, chemical resistivity and very good affinity for $Th^{4+}$. High separation factor values also indicate good separation for the metal ion pairs suggested. ZrDETPMP exhibits the characteristics of a promising ion exchange material in the area of separation science.

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