

## Adsorption of some hazardous radionuclides on cerium(IV) antimonate

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Cerium(IV) antimonate was prepared by dropwise addition of 0.6M antimony pentachloride and 0.6M cerium ammonium nitrate solutions by a molar ratio of Ce/Sb 0.75. Exchange isotherms for  $H^+/Co^{2+}$ ,  $H^+/Cs^+$ ,  $H^+/Zn^{2+}$ ,  $H^+/Sr^{2+}$  and  $H^+/Eu^{3+}$  were determined at 25, 40 and 60 °C. Besides, it was proved that europium is physically adsorbed, while zinc, strontium, cobalt and cesium are chemically adsorbed. Moreover, the heat of adsorption of zinc, strontium, cobalt and cesium on cerium(IV) antimonate was calculated and indicated that cerium(IV) antimonate is of endothermic behavior towards these ions. Also the distribution coefficients of these ions were determined and it was found that the selectivity is in the order:  $Eu^{3+} > Sr^{2+} > Cs^+ > Na^+$ .

### Introduction

In the last decade a good deal of interest has grown in synthetic inorganic ion exchangers.<sup>1</sup> This is mainly because of their greater power to withstand higher radiation doses and temperatures than the commonly-used organic-based resins. In addition to this, they sometimes exhibit highly specific properties which might permit improved separations under ordinary conditions. A large number of insoluble salts formed from multivalent metals and polybasic acids have been investigated as inorganic ion exchangers. Although most of the work deals with studies on zirconium phosphate, other phosphates, arsenates, antimonates, tungstates, molybdates and hydrous oxides have also been studied as potential ion exchangers. Amongst the antimonates of quadrivalent elements which form an equally promising series, zirconium<sup>2,3</sup> and tin(IV) antimonates<sup>4,5</sup> have already been investigated earlier. In continuation of the previous studies cerium(IV) antimonate was explored for its ion-exchange properties.

The aim of the present work is to investigate the ion-exchange properties of cerium(IV) antimonate, CeSb, as well as to explore the usefulness of the sorbent for the separation and preconcentration of some fission products from nitrate media of variable composition at different temperatures of the equilibrating solution.

### Experimental

All chemicals used were of A.R. grade and used without further purification.

#### Preparation of cerium(IV) antimonate

Cerium(IV) antimonate was prepared by the dropwise addition of 0.6M antimony pentachloride

solution to 0.6M ceric ammonium nitrate solution with a molar ratio of Ce/Sb 0.75 in a water bath at 60 °C with constant stirring. After an overnight standing, the precipitate was filtered, washed with bidistilled water and dried at 50 °C. The product was ground and sieved (0.12–0.44 mm) and finally air dried at room temperature.

The water content of cerium(IV) antimonate in the  $Zn^{2+}$ ,  $Sr^{2+}$ ,  $Co^{2+}$  and  $Eu^{3+}$  forms were determined by calcination of 1 g of CeSb sample in the metal ion form at 850 °C, and the water loss were found to be 11.87%, 12.23%, 11.98% and 10.94% (w/w) for  $Zn^{2+}$ ,  $Sr^{2+}$ ,  $Co^{2+}$  and  $Eu^{3+}$ , respectively.

The exchange capacities were determined by repeated batch equilibration of the samples with salt chloride solutions in a shaker thermostat at  $25 \pm 1$  °C, until saturation was attained. The capacities were found to be 0.97, 0.93, 0.86 and 0.89 meq/g for  $Zn^{2+}$ ,  $Sr^{2+}$ ,  $Co^{2+}$  and  $Eu^{3+}$  ions, respectively.

#### Distribution coefficients

Distribution coefficients ( $k_d$ ) values of the individual cations  $Na^+$ ,  $Cs^+$ ,  $Sr^{2+}$  and  $Eu^{3+}$  labeled with  $^{22}Na$ ,  $^{134}Cs$ ,  $^{85}Sr$  and  $^{60}Co$ , respectively, in  $HNO_3$  solutions on cerium(IV) antimonate were determined by batch experiments (Table 1). Mixtures of 0.1 g of the dry exchanger ( $m$ ) and 10 cm<sup>3</sup> acid solution of the respective tracer element were equilibrated in a shaker thermostat adjusted to  $25 \pm 1$  °C. In all cases, shaking was maintained overnight to attain equilibrium. The corresponding  $k_d$  values (cm<sup>3</sup>·g<sup>-1</sup>) were determined from the counting rates in solution before adding the exchanger ( $A_0$ ) and after equilibration ( $A_e$ ) using the following equation:

$$k_d = \frac{A_0 - A_e}{A_e} \cdot \frac{V}{m} \text{ cm}^3 \cdot \text{g}^{-1} \quad (1)$$

Table 1.  $K_d$  values and separation factors ( $\alpha$ ) of  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  in  $\text{HNO}_3$  media on CeSb

$\text{HNO}_3$	$K_d, \text{ ml}\cdot\text{g}^{-1}$			
	$\text{Na}^+$	$\text{Cs}^+$	$\text{Sr}^{2+}$	$\text{Eu}^{3+}$
0.1	53	265 (5)	10100 (190) (38)	V.H
0.25	23.8	115 (4.8)	1339 (56) (11.7)	V.H
0.5	12	63 (5)	451 (37.6) (7.5)	7000 (58) (11.6) (1.5)
1.0	6	35 (5.8)	110 (18.3) (3.2)	820 (136.6) (23.6) (7.4)
2.0	3.3	17.5 (5.3)	25 (7.6) (1.4)	115 (34.8) (6.6) (4.7)
3.0	2.4	12 (5)	12 (5) (1)	48 (20) (4) (4)
4.0	1.4	4.8 (6.5)	7 (4.7) (0.7)	13 (8.7) (1.3) (1.9)
6.0	1.2	6.5 (5.4)	3.4 (2.8) (0.5)	3.6 (3) (0.6) (1.1)

*Sorption isotherms*

Sorption isotherms for  $\text{Eu}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cs}^+$  were determined over the concentration range of  $5 \cdot 10^{-4}$ – $10^{-2}$  at 1M  $\text{HNO}_3$  and a constant  $V/m$  value of  $100 \text{ cm}^3 \cdot \text{g}^{-1}$ .

Experiments were carried out in a shaker thermostat at 25, 40 and 60 °C. After equilibrium, the mixture was filtered and the filtrate and CeSb sample were counted.

*Radiometric assay*

The counting rates of  $^{22}\text{Na}$ ,  $^{134}\text{Cs}$ ,  $^{85}\text{Sr}$  and  $^{60}\text{Co}$  were counted using a NaI scintillation detector connected with an ST6 scalar timer (Nuclear Enterprises). The counting rates were at least 10 times as that of the background. Each result was recorded and tabulated or graphed as a mean value of three readings obtained under the same geometrical conditions, calculated after corrections for background. Generally, the net counting rates has a standard deviations less than  $\pm 3\%$ .

**Results and discussion**

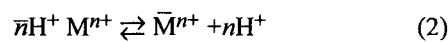
The results of solubility measurements showed that cerium(IV) antimonate is stable in water,  $\text{HNO}_3$  up to 6M, while in HCl solutions, the CeSb sample is physically quite stable up to 5M HCl.

The X-ray diffraction patterns of cerium(IV)antimonate revealed that the investigated solid is amorphous. Nevertheless, the crystallinity of the material slightly increased with the increase in heating temperatures from 50–600 °C.

Differential thermal analysis (DTA) and thermal gravimetry (TG) for cerium(IV) antimonate support the fact that cerium(IV) antimonate has a good thermal stability. From the above results, we can conclude that, the prepared material was very stable in water,  $\text{HNO}_3$  and HCl and has a good thermal stability and this material is suitable for use in nuclear technology.

*Equilibrium and distribution coefficient*

The cation exchange process between  $\text{H}^+$  and  $\text{M}^{n+}$  in solution is represented as follows:



The selectivity coefficient can be defined by the following equation:<sup>6</sup>

$$K_H^M = \frac{[\bar{\text{M}}^{n+}][\text{H}^+]^n}{[\bar{\text{H}}^+]^n[\text{M}^{n+}]} \quad (3)$$

where  $[\bar{\text{M}}^{n+}]$  and  $[\bar{\text{H}}^+]$  denote to the concentrations of  $\text{M}^{n+}$  and  $\text{H}^+$  ions in the cation exchanger, and  $[\text{H}^+]$  and  $[\text{M}^{n+}]$  their concentrations in the solution. As  $k_d$  is given by

$$k_d = \frac{[\bar{\text{M}}^{n+}]}{[\text{M}^{n+}]} \quad (4)$$

So Eq. (4) can be written as:

$$K_H^M = k_d \frac{[\text{H}^+]^n}{[\bar{\text{H}}^+]^n}$$

or  $\log k_d = \log K_H^M [\bar{\text{H}}^+]^n - n \log [\text{H}^+]$  (5)

when  $[\bar{\text{H}}^{n+}] \ll [\bar{\text{H}}^+]$  and  $[\text{M}^{n+}] \ll [\text{H}^+ \cdot \bar{\text{H}}^+]$   $K_H^M$  can be considered as a constant, Eq. (5) can be reduced to

$$\log k_d = C - n \log [\text{H}^+]$$

When  $\log k_d$  values of  $n+$  valent metal ions are plotted against  $\log [\text{H}^+]$  a straight line having a slope  $-n$ , should be obtained.

Figure 1 shows the nitric acid concentration-dependency of  $k_d$  values for  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  for  $10^{-4}\text{M}$  concentration of these cations in the solutions.

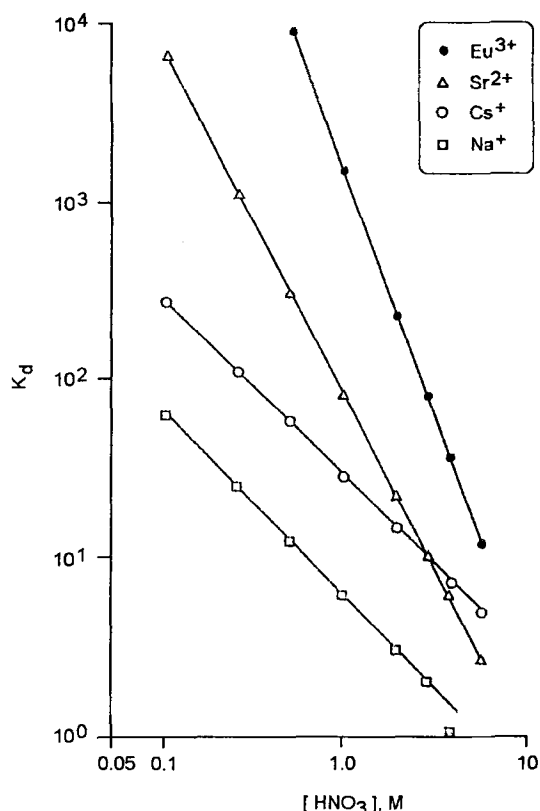


Fig. 1. Log  $K_d$  of  $\text{Eu}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cs}^+$  and  $\text{Na}^+$  as a function of nitric acid concentration on cerium(IV) antimonate at 25 °C

A linear relation between  $\log k_d$  and the nitric acid concentrations was observed. Straight lines were obtained with slopes to the valency of the ion sorbed. This figure also indicates that the order of selectivity is:  $\text{Eu}^{3+} > \text{Sr}^{2+} > \text{Cs}^+ > \text{Na}^+$ . This may be due to the generally stronger electrostatic interaction of multivalent cations compared to monovalent ones.<sup>7</sup>

#### Sorption isotherm

The sorption isotherms of europium, zinc, strontium, cobalt and cesium are presented in Figs 2–6. As the concentration in solution of europium increases,

the amount held on the sorbent increases. The maximum capacity achieved for europium is 0.095 mmol/g at equilibrium concentration of  $5 \cdot 10^{-4} \text{M}$  as shown in Fig. 2, which also indicates that europium is physically adsorbed on cerium(IV) antimonate. While in case of adsorption of zinc, strontium, cobalt and cesium, the results fit quite well the linear form of the Langmuir adsorption isotherm over the entire range of element concentration investigated ( $10^{-2}$ – $5 \cdot 10^{-4} \text{M}$  in 1M  $\text{HNO}_3$  at 25, 40 and 60 °C). When the adsorption obeys the Langmuir isotherm, the following equation can be applied in the case of adsorption of solutions:<sup>8,9</sup>

$$\frac{C}{W} = \frac{C}{M} + \frac{1}{aM} \quad (6)$$

where  $C$  is the equilibrium concentration,  $W$  is the amount of ion sorbed per gram of sorbent,  $M$  is the saturation capacity of the sorbent and  $a$  is a constant related to the heat of adsorption. From the slopes of the linear plots of  $C/W$  vs.  $C$  (Figs 3–6) the values of  $M$ , the saturation capacity of cerium(IV) antimonate for Zn(II), Sr(II), Co(II) and Cs(I) at the investigated temperatures and 1M  $\text{HNO}_3$  can be obtained and are found to be 0.76, 0.73 and 0.58 meq/g for Zn(II); 1.6, 1.43 and 1.0 meq/g for Sr(II); 0.57, 0.485 and 0.48 meq/g for Co(II) and 1.19, 0.9 and 0.84 meq/g for Cs(I).

The value of  $a$  in Eq. (6) is related to the heat of adsorption,  $\Delta H$  as follows:<sup>10</sup>

$$a = \bar{a} e^{-\Delta H/RT} \quad (7)$$

Figure 7 is a plot of  $\ln a$  vs.  $1/T$ . Accordingly the values of  $\Delta H$ , the heat of adsorption at saturation for Zn(II), Sr(II), Co(II) and Cs(I) on cerium(IV) antimonate can be calculated and were found to be  $-8.314$ ,  $-4.99$ ,  $-4.16$  and  $-2.99$  kJ/mol, respectively. These values of  $\Delta H$  indicate the endothermic behavior of cerium(IV) antimonate. Also these values are low compared with the heat of absorption for cobalt on  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and montmorillonite which are  $-62.37$ ,  $-59.85$ ,  $-66.97$  and  $-26.37$  kJ/mol.<sup>11,12</sup> This may be attributed to two reasons: (1) the hydroxyl groups of the synthetic cerium(IV) antimonate may be easily ionized which might facilitate the surface reaction, and (2) the decrease in the surface charge suggests the weaker electrostatic interaction of Co(II) and cerium(IV) antimonate, leading to a lower heat of adsorption.

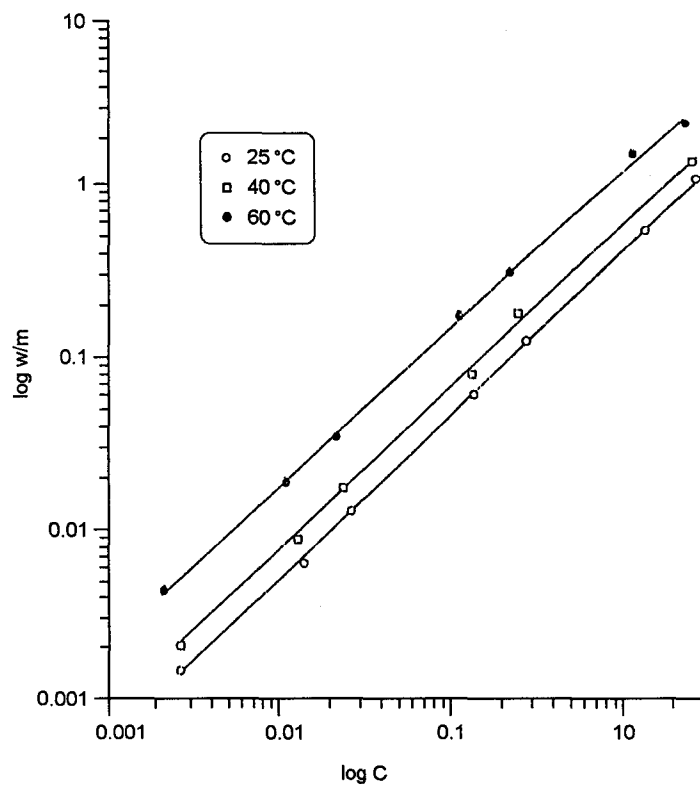


Fig. 2. Freundlich adsorption isotherm for the adsorption of  $\text{Eu}^{3+}$  ion on cerium(IV) antimonate at different reaction temperatures

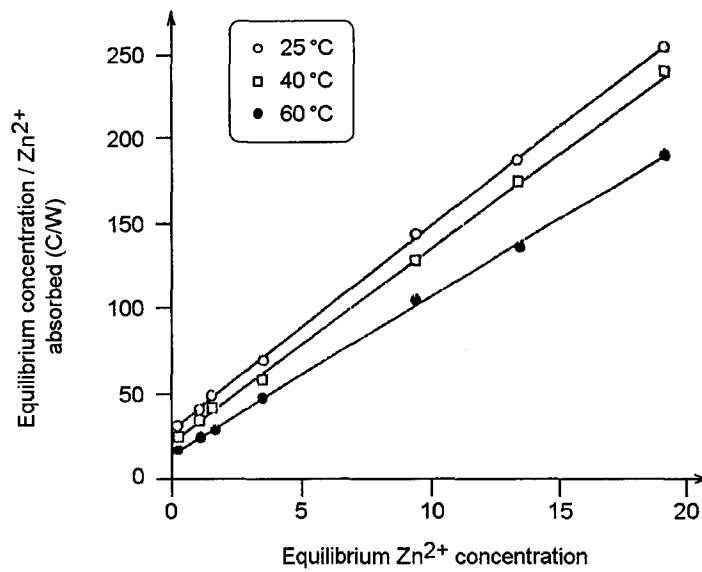


Fig. 3. Langmuir adsorption isotherm for adsorption of  $\text{Zn}^{2+}$  ion on cerium(IV) antimonate at different reaction temperatures

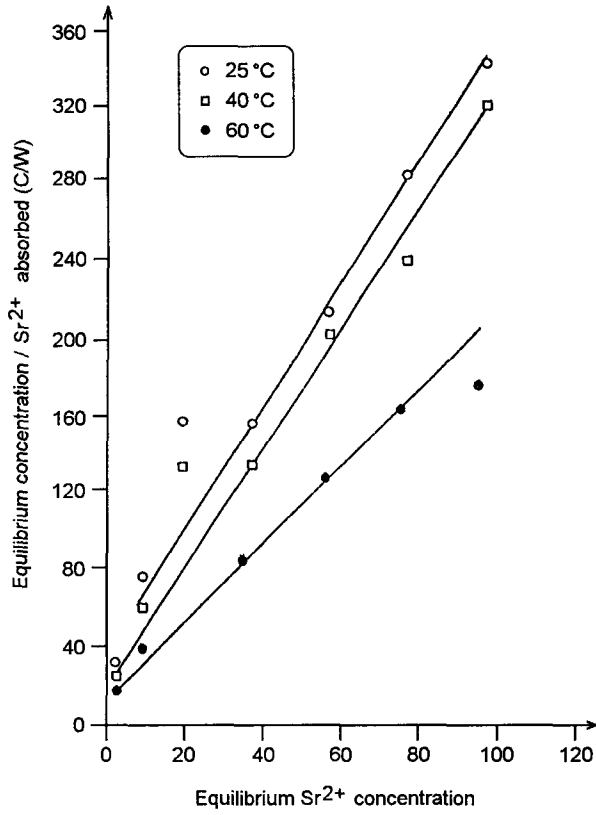


Fig. 4. Langmuir adsorption isotherm for adsorption of Sr<sup>2+</sup> ion on cerium(IV) antimonate at different reaction temperatures

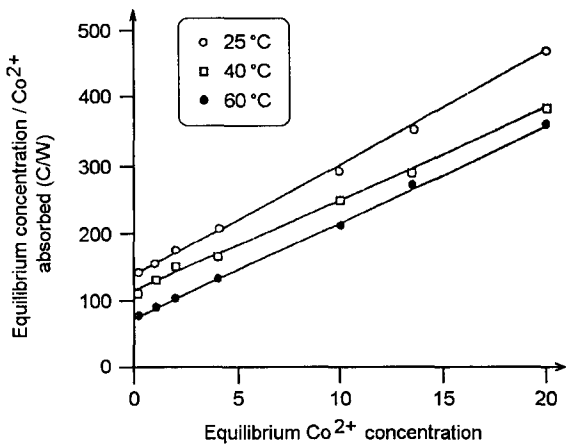


Fig. 5. Langmuir adsorption isotherm for adsorption of Co<sup>2+</sup> ion on cerium(IV) antimonate at different reaction temperatures

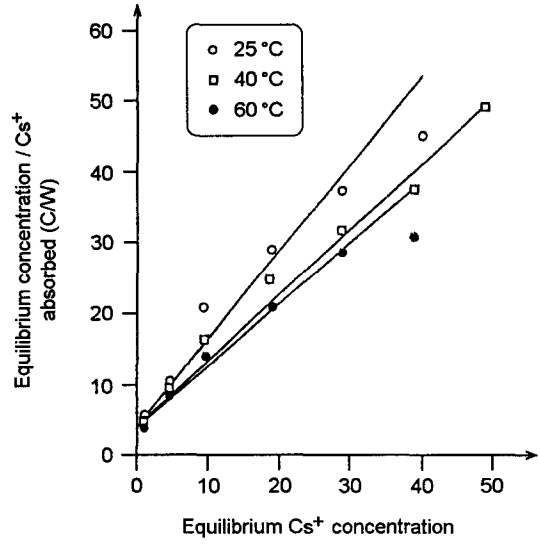


Fig. 6. Langmuir adsorption isotherm for adsorption of Cs<sup>+</sup> ion on cerium(IV) antimonate

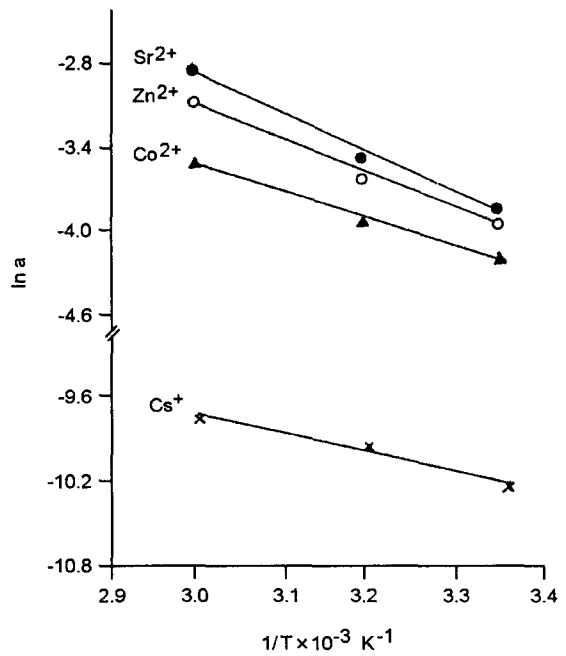


Fig. 7. Plot of ln a against 1/T for adsorption of Zn<sup>2+</sup>, Sr<sup>2+</sup>, Co<sup>2+</sup> and Cs<sup>+</sup> on cerium(IV) antimonate

### Conclusions

From the above mentioned data and discussion, it is clear that the chemical composition and behavior of cerium(IV) antimonate ion exchanger have important advantages in the field of nuclear waste processing. Promising results could be achieved even from nitrate solutions of high acidity (e.g., 1M HNO<sub>3</sub>) and it can also be concluded that europium is physically adsorbed on cerium(IV) antimonate while zinc, strontium, cobalt and cesium are chemically adsorbed on cerium(IV) antimonate cation exchanger.

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