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Adsorption of Some Hazardous Radionuclides on Cerium(IV) Antimonate

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ABSTRACT

Cerium(IV) antimonate had been prepared by the dropwise addition of 0.6 M antimony pentachloride and 0.6 M cerium ammonium nitrate solutions by a molar ratio of Ce/Sb 0.75. Exhcange isotherms for H^+/Co^{2+}, H^+/Cs^+, H^+/Zn^{2+}, H^+/Sr^{2+} and H^+/Eu^{3+} have been determined at 25, 40 and 60°C. Besides it was proved that europium is physically adsorped while zinc, strontium, cobalt and cesium are chemically adsorbed. Moreover, the heat of adsorption of zinc, strontium, cobalt and cesium on cerium(IV) antimonate had been calculated and indicated that cerium(IV) antimonate is of endothermic behaviour towards these ions. Also the distribution coefficients of these ions were determined and it was found that the selectivity 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 [1]. 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 some-times 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 [2,3] and tin(IV) antimonates [4,5] have already been investigated by earlier workers. 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 if 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 0.6 M antimony pentachloride solution to 0.6 M 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 ions form at 850°C, and the water loss values 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±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, K_d:

Distribution coefficients (k_d) values of the individual cations Na^+, Cs^+, Sr^{2+} and Eu^{3+}, in HNO_3 solutions on cerium(IV) antimonate were determined by batch experiments. Mixture of 0.1 g of the dry exchanger (m) and 10 cm^3 acid solution (V) of the respective tracer element were equilibrated in a shaker thermostat adjused at 25±1°C. In all cases, shaking was maintained overnight to attain equilibrium. The corresponding k_d values ($cm^3\ g^{-1}$) were determined from the counting rates in solution before adding the exchanger (A_o) and after equilibration (A_e) using the following equation

$$k_d = \frac{A_o - A_e}{Ae} \cdot \frac{V}{m}\ cm^3\ g^{-1} \qquad (1)$$

Sorption Isotherm:

Sorption isotherms for Eu^{3+}, Zn^{2+}, Sr^{2+}, Co^{2+} and Cs^+ were determined over the concentration range $5x10^{-4}$ - 10^{-2} at 1 M HNO_3 and a constant V/m value of 100 ml g^{-1}.

Experiments were carried out in a shaker thermostat at 25, 40 and 60°C. After equilibrium, the mixture was filtered and analysed for Eu^{3+}, Zn^{2+}, Sr^{2+}, Co^{2+} and Cs^+.

The counting rates were measured using of a NaI (Tl) scintillation counter.

RESULTS AND DISCUSSION

The results of solubility showed that cerium(IV) antimonate is stable in water, HNO_3 up to 6 M. While in HCl solutions, the CeSb sample is physically quite stable up to 5 M HCl.

The X-ray diffraction patterns of cerium(IV)antimonate sample revealed that the investigated solid is amorphous. Nevertheless, the crystallinity of the material is 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 have a good thermal stability. From the above results, we can conclude that, the prepared material was very stable in water, HNO_3 and HCl and have a good thermal stability and this material is suitable for use in nuclear technology purposes.

Equilibriuun and Distribution Coefficient:

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

$$\bar{n}H^{+} \; M^{n+} \; \text{=====} \; \bar{M}^{n+} + nH^{+} \qquad (2)$$

The selectivity coefficient can be defined by the following equation [6] :

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

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

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

So equation (4) can be written as:

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

or

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

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

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

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

Figure (1) shows the nitric acid concentration-dependency of k_d values for Na^{+}, Cs^{+}, Sr^{2+} and Eu^{3+} for 10^{-4}M concentration of these cations in the solutions. The linear relation between log k_d and the nitric acid concentrations was observed. The slopes of the straight lines equal to the valency of the ion sorbed were obtained. This figures also indicates that the order of the selectivity is $Eu^{3+} > Sr^{2+} > Cs^{+} > Na^{+}$. This may be due to the generally stronger electrostatic interaction of the multivalent cations compared to the monovalent one [7].

Sorption Isotherm:

The sorption isotherms of europium, zince, strontium, cobalt and cesium are presented in Figs. 2-6 it show that as the concentration in solutions of europium increases the amount held on the sorbent increases. The maximum capacity achieved for europium is 0.095 m mol/g at equilibrium concentration of $5x10^{-4}$M as shown in Fig.(4), which also indicates that europium is physically adsorped on cerium(IV) antimonate. While in case of adsorption of zinc, strontium, cobalt and cesium, the results fit quite well the linear form of Langmuir adsorption isotherm over the entire range of each element concentration investigated (10^{-2} - $5x10^{-4}$M in 1 M HNO_3 at 25, 40 and 60°C). When the adsorption obey Langmuir isotherm, the following equation can be applied in case of adsorption of solutions [8,9]

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

where C is the equilibrium concentration, W is the amount of ions 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. Figures (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 1 M HNO_3 can be obtained and are found to be 0.76, 0.73 and 0.58 meq/g for Zn(II) and 1.6, 1.43 and 1.0 meq/g for Sr(II) and 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 equation (6) is related to the heat of adsorption, ΔH as follows [10].

$$a = \bar{a}\, e^{-\Delta H/RT}$$

Figure (7) is a plot of ln a vs. 1/T, accordingly the values of ΔH, heats of adsorption at saturation for each of Zn(II), Sr(II), Co(II) and Cs(I) on cerium(IV) antimonate can be calculated and are found to be -8.314, -4.99, -4.16 and -2.99 kJ/mol,respectively. These values of ΔH indicate the endothermic behaviour of cerium(IV) antimonate also these values are low compared with the heat of absorption for cobalt on Al_2O_3, MnO_2, Fe_2O_3 and montmorillonite which are -62.37, -59.85, -66.97 and -26.37 kJ/mol.[11,12]. Which may be attributed to two reasons firstly the hydroxyl groups of the synthetic cerium(IV) antimonate might be easily ionized which might facilitate the surface reaction and second the decrease in the surface change suggests the weaker electrostatic interaction of Co(II) and cerium(IV) antimonate which leads to lower heat of adsorption.

CONCLUSION

From the above mentioned data and discussion, it is clear that the chemical composition 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 1 M HNO_3) and also it can be concluded that europium is physically adsorped on cerium(IV) antimonate while zinc, strontium, cobalt and cesium are chemically adsorbed on cerium(IV) antimonate cation exchanger.

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Table (1): K_d values and separation factors (α) of Na^+, Cs^+, Sr^{2+} and Eu^{3+} in HNO_3 media on CeSb

HNO_3	K_d(ml g^{-1})			
	Na^+	Cs^+	Sr^{2+}	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)

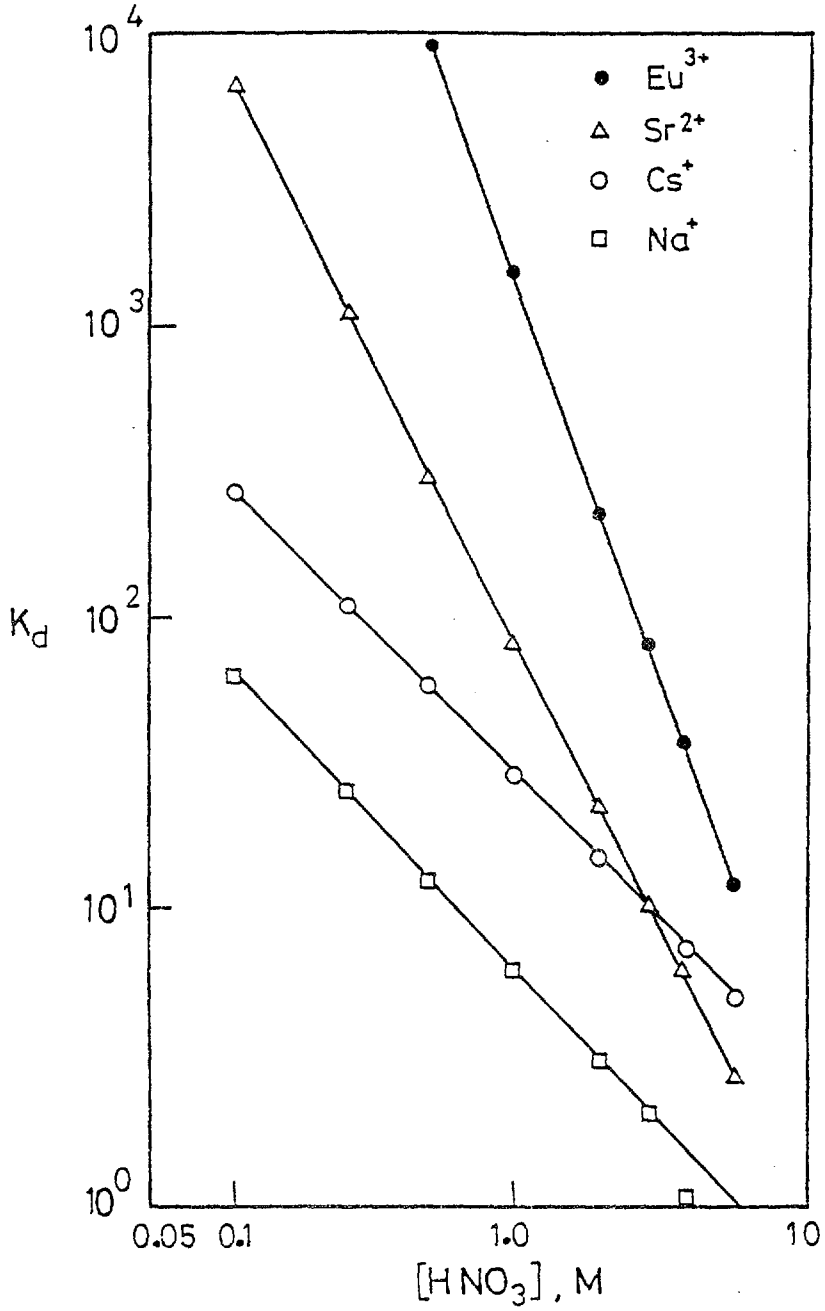

Fig. 1 : Log K_d of Eu^{3+}, Sr^{2+}, Cs^+ and Na^+ as a function of nitric acid concentration on cerium (IV) antimonate at 25 °C.

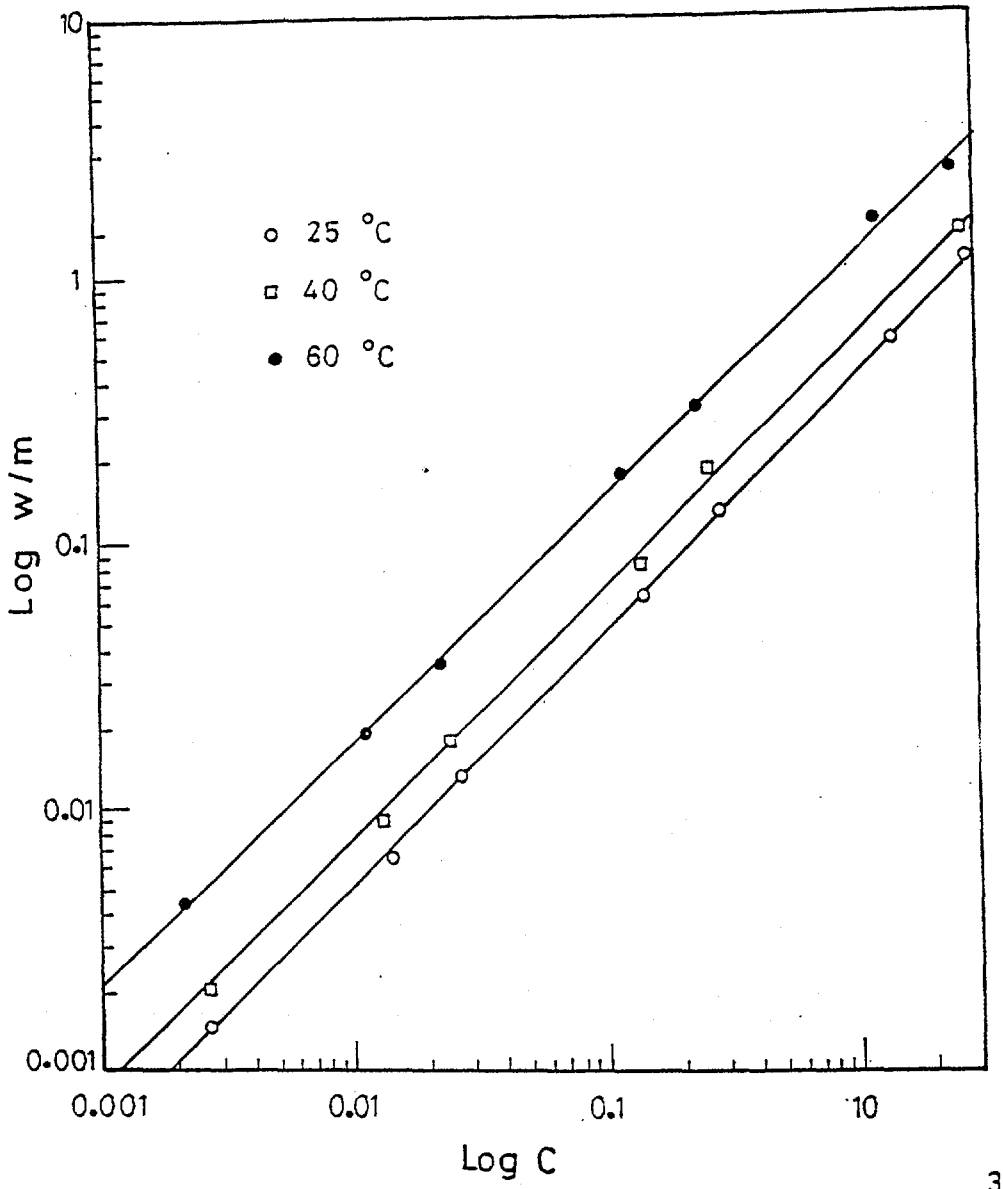

Fig.2 : Freundlich adsorption isotherm for the adsorption of Eu^{3+} ion on cerium (IV) antimonate at different reaction temperatures.

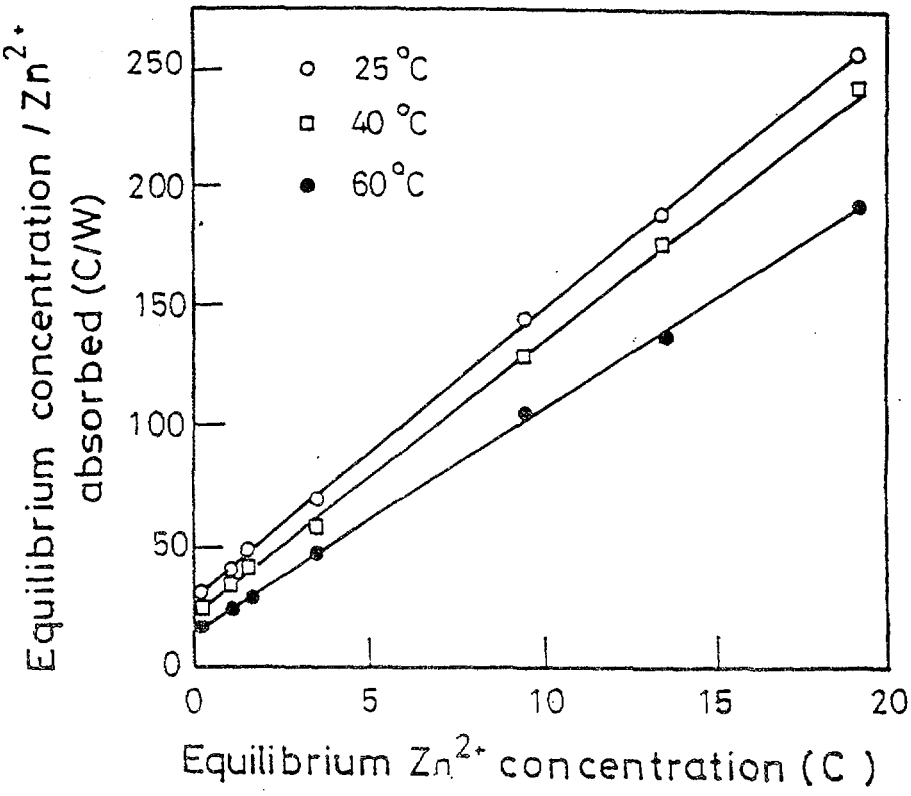

Fig. 3 : Longmuir adsorption isotherum for adsorption of Zn^{2+} ion on cerium (IV) antimonate at different reaction temperatures.

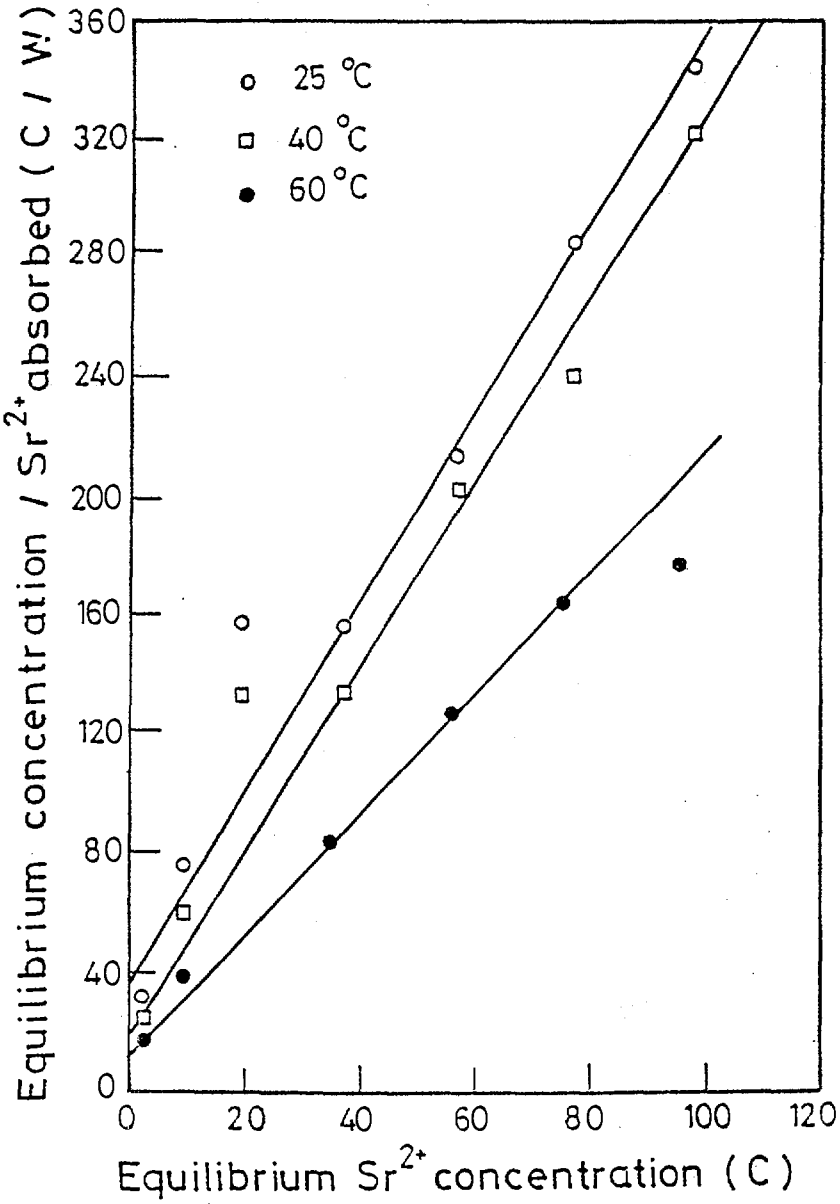

Fig. 4 :Longmuir adsorption isotherum for adsosorption of Sr^{2+} ion on cerium (IV) antimonate at different reaction temperatures.

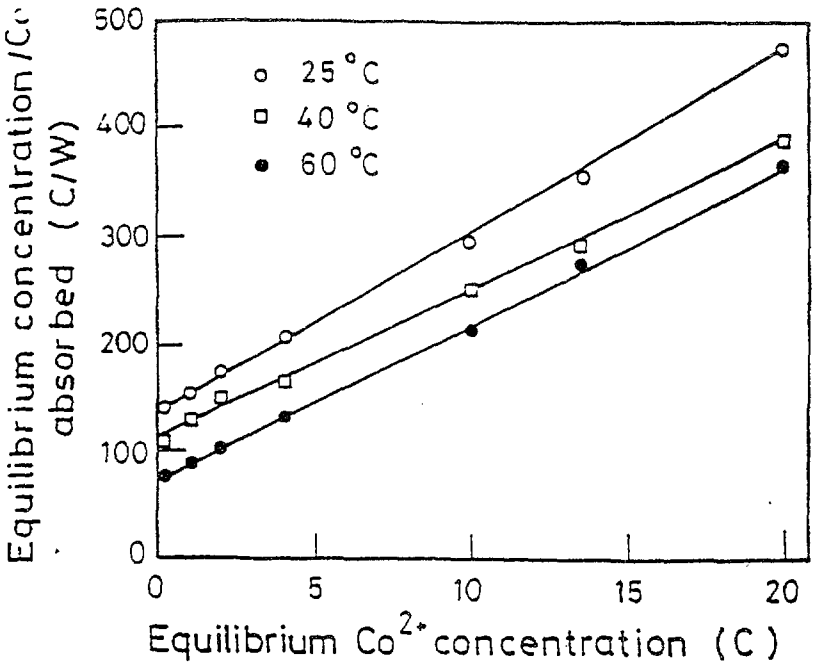

Fig. 5 . Longmuir adsorption isotherum for adsorption of Co^{2+} ion on cerium (IV) antimonate at different reaction temperatures .

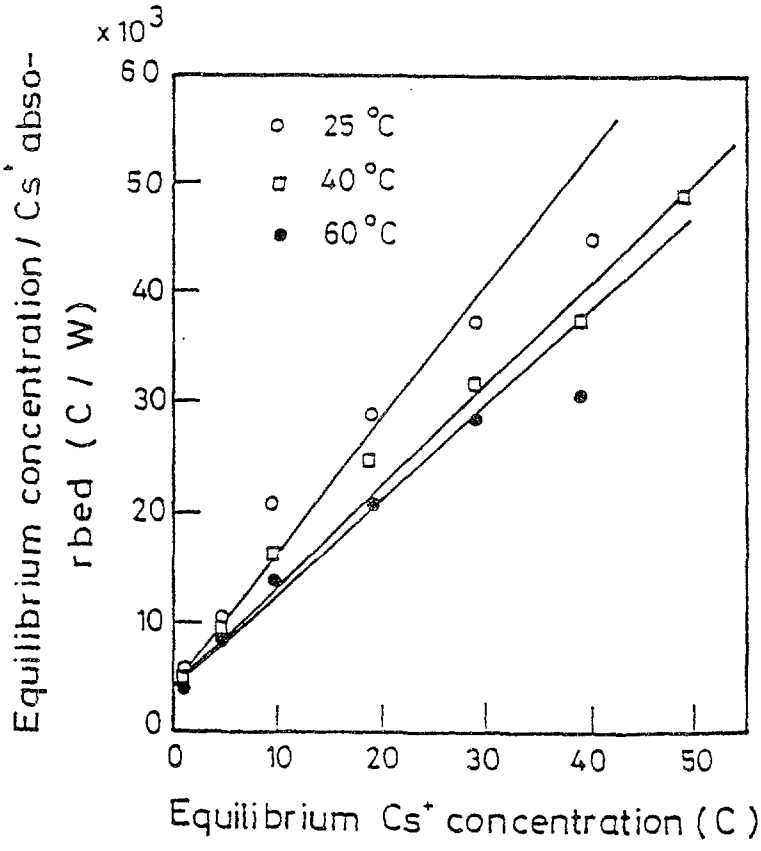

Fig. 6 : Longmuir adsorption isotherum for adsorption of Cs^{+} ion on cerium (IV) antimonate

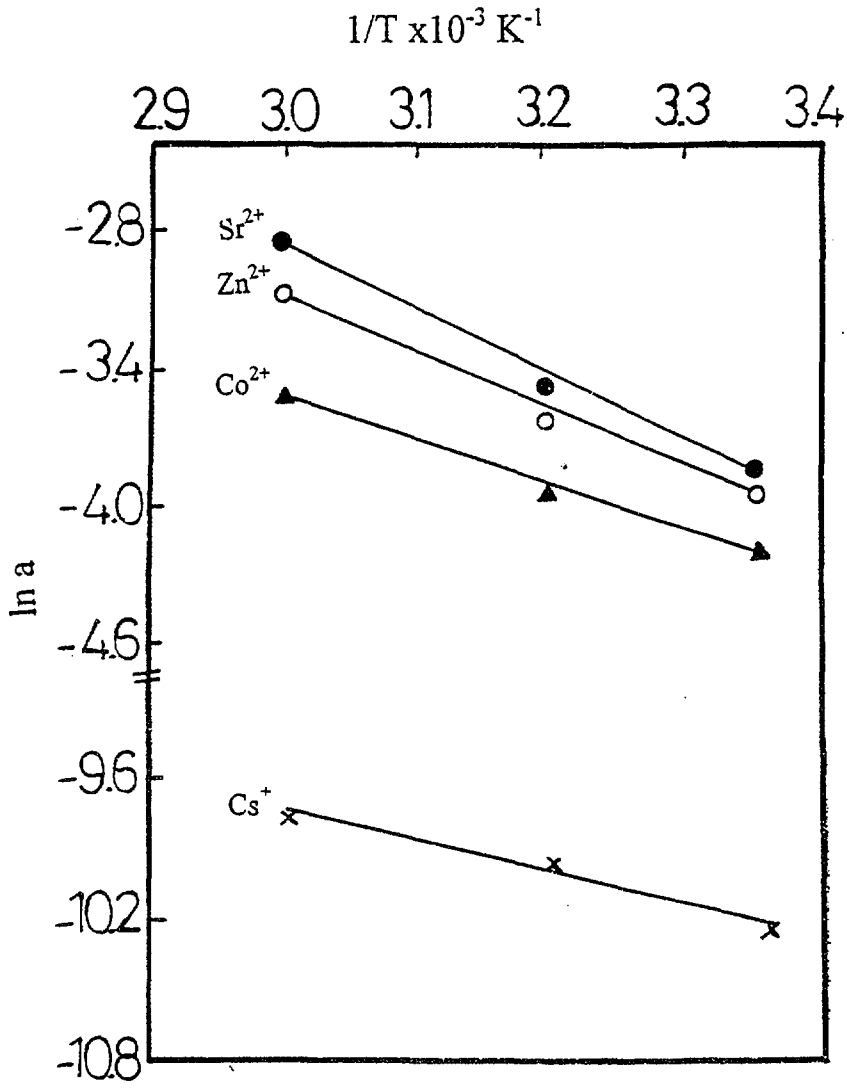

Fig.(7): Plot of Ln a against 1/T for adsorption of Zn^{2+}, Sr^{2+}, Co^{2+} and Cs^{+} on cerium(IV) antimonate.