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On the Sorption Behaviour of Some Cations on Cobalt Hexacyanoferrate(III) Exchanger. Binary Separations of Rb^+ and Cs^+ on Columns

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Synopsis. Sorption behaviour of Ag, Cs, Rb, Co(II), Zn(II), and Fe(III) ions at low concentration (0.2 mmol) is studied in different concentrations of nitric acid and ammonium nitrate on cobalt hexacyanoferrate(III) exchanger. log K_d *vs.* log concentration plots show that the sorption of these ions is not followed through ion exchange mechanism, only. In case of Rb^+ and Cs^+, a very low K_d is observed at high concentration of nitric acid (>5 mol dm^{-3}) thereby showing the possibility of their elution on columns. For various other ions, such as Ba, Sr, Mn, Hg(II), Mg, Cd, Ca, Pb, Ni, La, and Th, the K_d values are almost zero. Thus the binary separation of Rb^+ and Cs^+ from a number of ions on the columns of this exchanger has been carried out.

During the last two decades a number of inorganic sorbents[1–6] have been prepared and their ion exchange behaviour studied. Although a number of hexacyanoferrates(III)[7–9] are insoluble, they have been little studied, with regard to their sorption behaviour. Recently we have reported on the sorption properties of chromium hexacyanoferrate(III).[10] This sorbent was found to be chemically more stable and showed better selectivity in sorption behaviour as compared to corresponding chromium hexacyanoferrate(II).[11] In view of better stability and selectivity of this hexacyanoferrate(III) exchanger, we have thought it desirable to investigate the exchange properties of other metal hexacyanoferrates(III). In a recent preliminary communication,[12] we have reported on the use of cobalt hexacyanoferrate(III)(CoFic) as Cu(II) selective exchanger. This exchanger is highly stable in salt solution and mineral acids and possesses potentiality for important separations. Further, sorption studies on this exchanger have now been undertaken.

Experimental

Cobalt(II) chloride (B. D. H.) and potassium hexacyanoferrate(III) (Sarabhai merck) both analytical reagent grade were used in the preparation of the exchanger without further purification. All other salts and acids were also of analytical grade. Radioisotopes of ^{134}Cs, ^{86}Rb, ^{110m}Ag, ^{85}Sr+^{89}Sr, ^{133}Ba, ^{54}Mn, ^{58}Co, ^{65}Zn, ^{203}Hg, and ^{55}Fe+^{59}Fe were obtained from Bhabha Atomic Research Centre, Bombay.

Apparatus. pH measurements were made with ELICO pH meter model LI 10. Bausch and Lomb spectronic 20 was used for spectrophotometric determination of ions. Gamma counting of ^{110m}Ag, ^{134}Cs, ^{86}Rb, $^{85+89}$Sr, ^{54}Mn, ^{58}Co, ^{65}Zn, ^{203}Hg, and ^{55}Fe+^{59}Fe was done on a Scintillation counter (ECIL, Hyderabad) employing a well type NaI (Tl) crystal.

Preparation of Exchanger. Cobalt(II) potassium hexacyanoferrate(III) ($KCoFe(CN)_6 \cdot 5H_2O$) as reported earlier,[12] was obtained by the gradual addition of cobalt(II) chloride (0.12 mol dm^{-3}) to potassium hexacyanoferrate(III) (0.06 mol dm^{-3}) in a thermostat at 80 °C. The precipitate thus obtained was digested for ≈35 h and finally was washed with distilled water by centrifugation and dried in an oven at 80 °C. The precipitate was equilibrated with 1 mol dm^{-3} HNO_3 for 48 h, the acid being intermittently replaced. All further studies were carried out with exchanger pretreated with HNO_3.

Determination of Ions. Mg, Ca, Ni, Cu(II), Pb, Cd, Al, and Bi were determined by EDTA titrations and radiometric method was used for the determination of radio isotopes.

Determination of Distribution Coefficient. The distribution coefficients were determined by the batch equilibration method by shaking the exchanger (0.1 gm) with 10 cm^3 of 2×10^{-4} mol dm^{-3} metal ion solution in different concentrations of nitric acid or ammonium nitrate.

Determination of Sorption Capacity for Cs^+ and Rb^+ and Column Operation. Studies on the maximum uptake of Cs^+ and Rb^+ on cobalt hexacyanoferrate(III) were carried out by shaking 50 mg of the exchanger with 20 cm^3 solution of Rb^+ or Cs^+ (10^{-6} to 10^{-1} mol dm^{-3}). For column operations, a column of i.d. 0.5 cm containing 0.5 g exchanger was used. Column capacity was determined from breakthrough experiment using Rb^+ or Cs^+ solution (0.1 mol dm^{-3}) at 4 drops (≈0.2 cm^3) per minute and found to be 0.4 mequiv. g^{-1} both for Cs^+ and Rb^+. For separation studies, the column was loaded with a mixture of the metal ions pair to be separated and the elution was started after 15 min at a flow rate of 4 drops (≈0.2 cm^3) per minute.

Results and Discussion

The extent of static sorption of Rb^+ and Cs^+ at different concentrations is given in Table 1. It is seen that in dilute solutions (10^{-4}—10^{-6} mol dm^{-3}) the sorption of Rb^+ and Cs^+ is almost cent percent and it attains. a constant value at concentration of 10^{-1} mol dm^{-3} The maximum sorption capacity is found to be 1.68 mequiv. g^{-1} for Cs^+ and 3.4 mequiv. g^{-1} for Rb^+ ions. This high sorption capacity indicates that K^+ is substituted by Rb^+ or Cs^+, the theoretical exchange capacity on the basis of K^+ being liberated is 2.5 mequiv. g^{-1}. The release of K^+ was detected experimentally. The excess sorption capacity of Rb^+ ions may be due to molecular adsorption of Rb^+.

Sorption behaviour of Rb^+, Cs^+, Ag^+, Co^{2+}, Zn^{2+}, and Fe^{3+} For the efficient use of this exchanger in the separation and isolation, it is necessary to have information about their sorption behaviour in presence of acids and salt solutions. Therefore, in order to work out the conditions for the elution of these ions from the column, the variation of their K_d values at 2×10^{-4} mol dm^{-3} concentration was investigated as a function of NH_4NO_3 and HNO_3 concentration. As usual these results in terms of log K_d *vs.* log concentration of NH_4NO_3 and HNO_3 are shown in Figs. 1 and 2, respectively. Perusal of

Table 1. Sorption of Cs^+ and Rb^+ ions on cobalt hexacyanoferrate(III) as a function of $CsNO_3$ or RbCl concentration

Concentration of $CsNO_3$ or RbCl / mol dm^{-3}	mequiv. of Cs sorbed g^{-1} of the exchanger	mequiv. of Rb sorbed g^{-1} of the exchanger
5×10^{-1}	1.68	3.4
3×10^{-1}	1.68	3.4
1×10^{-1}	1.68	3.4
1×10^{-2}	0.76	1.66
8×10^{-3}	0.62	1.48
5×10^{-3}	0.50	1.41
2×10^{-3}	0.32	0.68
1×10^{-3}	0.31	0.38
1×10^{-4}	0.04	0.04
1×10^{-5}	0.004	0.004
1×10^{-6}	0.0004	0.0004

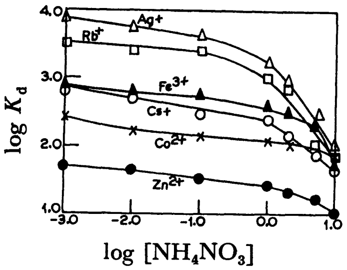

Fig. 1. Variation of log K_d of Cs^+, Rb^+, Ag^+, Co^{2+}, Zn^{2+}, and Fe^{3+} ions with log NH_4NO_3 concentration.

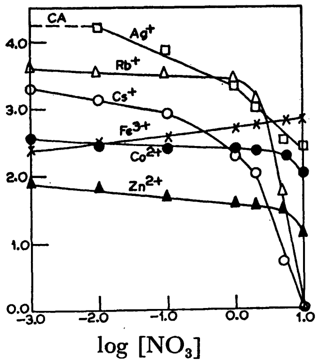

Fig. 2. Variation of log K_d of Cs^+, Rb^+, Ag^+, Co^{2+}, Zn^{2+}, and Fe^{3+} ions with log HNO_3 concentration.

these plots (Fig. 1) shows that the sorption of Ag^+, Rb^+, and Cs^+ ions is little affected upto NH_4NO_3 concentration of 1 mol dm^{-3} and the slope of the plots (-1.3; -1.0, -0.7 for Ag^+, Rb^+, and Cs^+) in the range 1 mol dm^{-3} to 10 mol dm^{-3} approximate to -1 indicating that sorption of these ions may be proceeding through ion exchange mechanism. In the lower concentration range, 10^{-3} to 1 mol dm^{-3}, the exchanger does not get saturated with the NH_4^+ ions and the slope of ≈ -1.0 is not thus obtained. The effect of HNO_3 on K_d (Fig. 2) is different in that the K_d of Cs^+ and Rb^+ falls approximately to zero value at 10 mol dm^{-3} HNO_3 and slope of -1 is obtained only for Ag^+ in higher concentration range.

The effect of HNO_3 or NH_4NO_3 concentration on Co^{2+}, Zn^{2+}, and Fe^{3+} is significantly different from that of Cs^+, Rb^+, and Ag^+. The K_d values of these ions remains almost unchanged even in higher concentration of the acid and salt. These ions thus appear to be irreversibly sorbed on the exchanger. This irreversible sorption may be due to the formation of a mixed phase involving the substitution of potassium and cobalt(II) ions. The K_d values of Fe^{3+} surprisingly increases at higher acidity, which possibly indicates the formation of more stable new phase. Similar behaviour was observed for the adsorption of number of bivalent ions on zinc hexacyanoferrate(II) and hexacyanoferrate(III).[7)]

Separations of Cs^+ and Rb^+. It is seen from K_d values (Table 2) that the exchanger can be used to separate Cs^+ and Rb^+ from a number of metal ions. 10 mol dm^{-3} HNO_3 was used to elute Cs^+ or Rb^+ from the columns as the K_d of these ions is decreased to appeoximately zero value (Fig. 2) in higher acid concentration. Although, the exchanger has high affinity for Ag^+, but it cannot be used for its recovery because its elution from the columns is very difficult. Further Cs^+ and Rb^+ can also not be separated from Co^{2+}, Zn^{2+}, and Fe^{3+} as they can not be eluted even at high HNO_3 or NH_4NO_3 concentration. The low K_d values (≈ 0 to 43) of the metal ions, such as Ba(II), Sr(II), Mn(II), Hg(II), Cd(II), Ca(II), Pb(II), Ni(II), Al(III), La(III), Bi(III), and Th(IV), were obtained in their 0.002 mol dm^{-3} solution in 0.01 mol dm^{-3} corresponding acid. Thus the separation of Cs^+ and Rb^+ from these metal ions, which can be eluted with 0.01 mol dm^{-3} HNO_3 is possible and a number of binary separations (Table 2) of analytical importance have been carried out. The recovery of other ions is sharp and quantitative whereas more than 90 percent of Rb^+ and Cs^+ could be eluted with 18 cm^3 of 10 mol dm^{-3} HNO_3. With larger amounts of HNO_3, almost complete recovery of Cs^+ and Rb^+ is possible. Few typical separations are shown in Fig. 3.

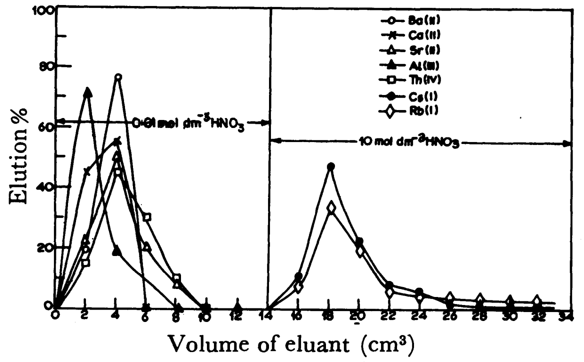

Fig. 3. Separation of Cs^+ or Rb^+ from other cations on cobalt hexacyanoferarte(III)

TABLE 2. BINARY SEPARATIONS OF Cs^+ (K_d=200) AND Rb^+ (K_d=2401) FROM VARIOUS CATIONS ON COBALT HEXACYANOFERRATE(III) COLUMNS

Sample No.	Other cation	Amount taken/μg				Recovery of Cs^+	Recovery of Rb^+
		K_d[a)] / cm^3 g^{-1}	Cs^+	Rb^+	Other cations	%	%
1	Ba(II)	1	531.64	342	549.44	96.0	90.5
2	Sr(II)	12	531.64	342	350.54	96.2	90.5
3	Mn(II)	4	531.64	342	219.76	95.0	91.0
4	Hg(II)	1	531.64	342	802.44	95.9	91.0
5	Mg(II)	0	531.64	342	97.28	96.0	90.8
6	Cd(II)	0	531.64	342	449.64	95.8	90.6
7	Ca(II)	0	531.64	342	160.32	96.0	90.6
8	Pb(II)	5	531.64	342	828.84	95.2	90.6
9	Ni(II)	0	531.64	342	234.84	95.9	90.5
10	Al(III)	11	531.64	342	107.92	96.0	90.7
11	La(III)	0	531.64	342	555.68	96.0	90.9
12	Bi(III)	43	531.64	342	836.00	95.2	90.2
13	Th(IV)	0	531.64	342	928.40	96.0	90.6

Recovery of all other cations is almost 100%. a) K_d values of Cs^+, Rb^+, and other metal ions are determined at 0.002 mol dm^{-3} concentration of the metal salt solution in 0.01 mol dm^{-3} corresponding acid.

Thus this exchanger is useful for many important separation of Cs^+ and Rb^+ from large number of metal ions and is superior to nickel and cobalt hexacyanoferrate(II)[13)] exchangers where the elution of Cs^+ from the column is difficult.

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