

## ION EXCHANGE PROPERTIES OF VANADIUM FERROCYANIDE EXPERIMENTS UNDER STATIC CONDITIONS

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Inorganic ion exchangers have found a wide range of application in radiochemistry and radiochemical technology, owing to their high selectivity and radiation stability. A number of sorbents have been proposed and tested in practice, e.g. zirconium phosphate, silica gel, insoluble oxides, ammonium salts of heteropolyacids, also recently insoluble ferro- and ferricyanides. Some papers describe the sorption properties of various ferrocyanides<sup>1,2</sup> in static<sup>2</sup> as well as in dynamic<sup>3</sup> conditions for the isolation and concentration of heavy alkali metals, namely <sup>137</sup>Cs.

The exchange properties of insoluble ferrocyanides of bivalent metals are the ones that have been studied most frequently; for instance zinc and nickel ferrocyanides of the limiting type  $\text{Me}^{\text{II}}_2[\text{Fe}(\text{CN})_6]$ , which show good properties for sorption of various ions. The exchange of, for instance, cesium and other alkali metals may then be explained by the formation of a double salt of the type  $\text{Cs}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ . It has been found that the sorption of heavy alkali metals is reversible, and that the ions sorbed may be eluted with acid or ammonium salt<sup>4,5</sup>.

A slightly different type of sorbent is formed by the reaction of ferrocyanide ions with metals which form hydrolytic products, or isopolyacids. So far only molybdenum<sup>6,7</sup> and tungsten<sup>8,9</sup> ferrocyanides have been described in the literature. We may, in general, take them to be inorganic polymers containing -OH groups with hydrogen atoms of varying degrees of acidity, which are exchangeable for different ions.

In this paper the sorption properties of vanadium ferrocyanide which have not previously been studied are described; the ferrocyanide is formed by the reaction of  $\text{VO}_3^-$  and  $\text{VO}^{2+}$  ions with ferrocyanic acid.

A description of the preparation and formation of vanadium ferrocyanide precipitates by the reaction of potassium ferrocyanide with vanadyl salts is given in the literature. The composition varies depending on which component is present in excess<sup>10</sup>. In studying this system, WYROUBOFF<sup>11</sup> found that the precipitate formed may contain alkali metal. This is supported by RIVENQ<sup>12</sup>, who found by potentiometric measurements that vanadium ferrocyanide cannot be ascribed a single formula, since the composition of the precipitate depends on the ratio of reacting components. A detailed study of the system  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ ,  $(\text{VO})\text{SO}_4$  has been reported by GLUSHKOVA AND SEIFER<sup>13</sup>.

They found by means of electroconductivity studies, pH measurements and solubility determinations, that with a molar ratio of  $\text{Fe}(\text{CN})_6^{4-}/\text{VO}^{2+} < 0.5$  a normal vanadium ferrocyanide salt is formed, peptisation of the precipitate occurs when the ratio is greater than 0.5 and less than 1, and with a molar ratio greater than 1 a

precipitate of variable composition, containing sodium in the molecule, is formed. In our case the sorption properties of the normal vanadium ferrocyanide were studied.

## EXPERIMENTAL

### *Sorbent preparation*

Two types of the sorbent were prepared; either sodium vanadate was precipitated by ferrocyanic acid or ferrocyanic acid was precipitated by vanadyl chloride. Ferrocyanic acid, prepared from  $K_4Fe(CN)_6$  by passing through a column of Dowex 50 in the  $H^+$  form, was mixed in the first case with a  $NaVO_3$  solution (initial molar ratio  $V:Fe = 3:1$ ) and the final acidity was adjusted with hydrochloric acid to a concentration of 1 to 2  $M$ . The black precipitate was separated by suction, dried at  $80^\circ$ , carefully washed with a 0.5  $M$   $HNO_3$  and dried again.

After decomposing the precipitate with concentrated  $H_2SO_4$ , iron and vanadium were determined potentiometrically. The analyses show a resulting ratio of  $V:Fe = 3.86:1$  (sorbent No. 1).

The second sorbent was prepared as follows: ferrocyanic acid was precipitated by a three-fold molar excess of vanadyl chloride, which had been prepared by reducing  $NaVO_3$  with an excess of sodium sulphite (the excess of  $SO_2$  was removed by boiling). The final acidity of the solution after precipitation was adjusted to 1 to 2.5  $M$  with  $HCl$ . The light-green precipitate was separated by suction, dried at  $80^\circ$ , and after carefully washing with 0.5  $M$   $HNO_3$ , the precipitate was dried and used for the experiments. The results of analyses (potentiometric determination of iron and vanadium after decomposition of the precipitates with concentrated  $H_2SO_4$ ) show a ratio of  $Fe:V = 1:0.93$  (sorbent No. 2).

The sorption of fission products was studied on both sorbents under static conditions. The following experimental arrangement was used: 0.1 g sorbent was shaken with 6 ml of a solution containing a microamount of a radioisotope and different concentrations of nitric acid, ammonium nitrate, sodium nitrate or their mixtures. For labelling the following radioactive indicators were used: nitrates of  $^{137}Cs$ ,  $^{90}Sr$ - $^{90}Y$ ,  $^{144}Ce$ - $^{144}Pr$ ;  $^{95}Zr$ - $^{95}Nb$  nitrates in 10  $M$   $HNO_3$ ,  $^{106}RuNO(NO_3)_3$  in 6  $M$   $NH_4NO_3$ . After shaking the samples until equilibrium had been reached (experiments have shown that equilibrium is achieved after 20 h) both phases were separated by centrifugation and the distribution of the activity between the precipitate and solution was determined radiometrically. The distribution coefficients defined as:

$$K_d = \frac{\text{activity of the radioisotope in 1 g of the sorbent}}{\text{activity of the radioisotope in 1 ml of the solution at equilibrium}}$$

were calculated.

All reagents used were of reagent-grade purity.

## RESULTS AND DISCUSSION

### *Rb and Cs sorption*

The sorption of  $^{137}Cs$  and  $^{86}Rb$  was studied in more detail. By analogy of this sorbent with molybdenum and tungsten ferrocyanides we may assume an increased selectivity of heavy alkali metals for vanadium ferrocyanide.

The dependence of the distribution coefficient  $K_d$  for Cs and Rb on the concentration of  $\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3$  for both sorbents is shown in Figs. 1 and 2. The relationship between  $K_d$  and acid concentration was found to be linear except for Cs sorption on both sorbents at higher acid concentration ( $> 2 M$ ). This decrease in the sorptive properties at the acidity values mentioned may be caused either by the oxidative effect of the nitric acid or by influence of the acid on the dissociation of the acid hydrogen atoms of the sorbent. Parallel experiments with sorbent No. 1,

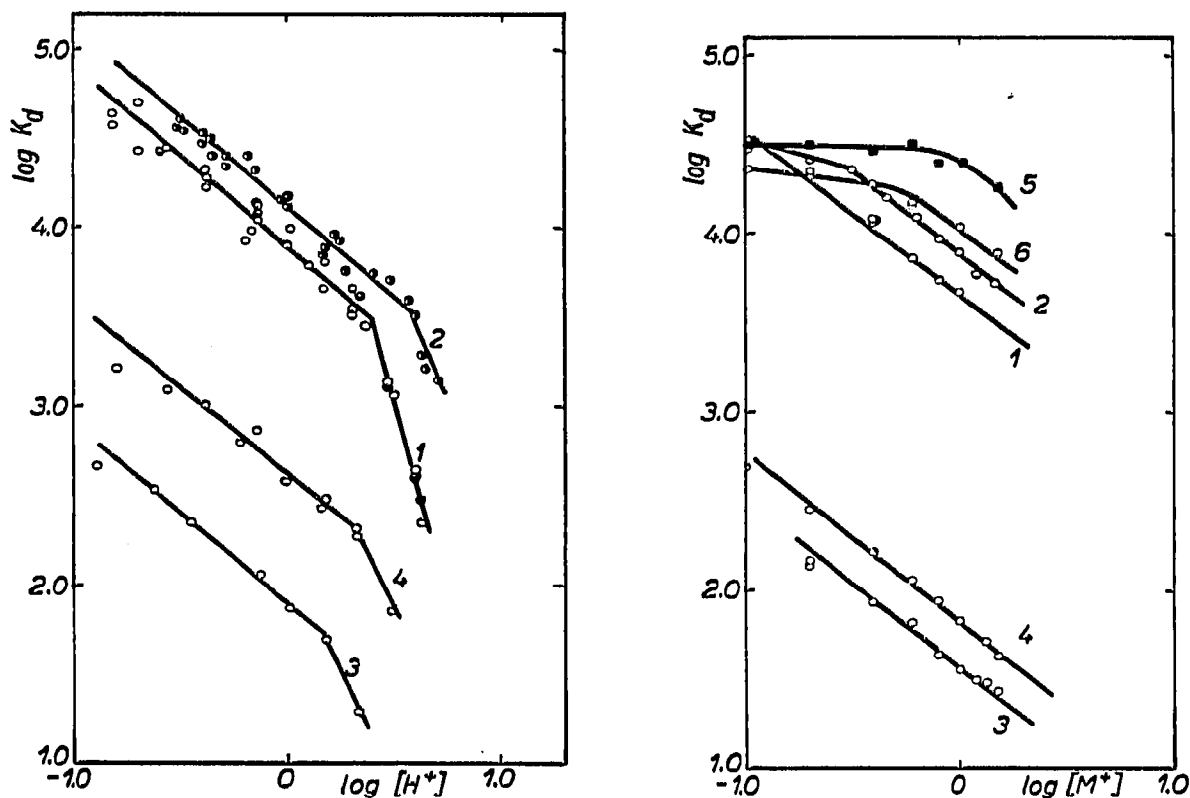


Fig. 1. Dependence of the distribution coefficients of Cs and Rb on nitric acid concentration. (1)  $K_d(\text{Cs}) = f([\text{H}^+])$ , sorbent No. 1 ( $\bullet \dots$  denotes experiments with HCl); (2)  $K_d(\text{Cs}) = f([\text{H}^+])$ , sorbent No. 2; (3)  $K_d(\text{Rb}) = f([\text{H}^+])$ , sorbent No. 1; (4)  $K_d(\text{Rb}) = f([\text{H}^+])$ , sorbent No. 2.  $K_d$  = distribution coefficient ( $\text{ml} \cdot \text{g}^{-1}$ );  $[\text{H}^+]$  = molarity of  $\text{HNO}_3$  (HCl).

Fig. 2. Dependence of the distribution coefficients of Cs and Rb on the concentration of ammonium, sodium and potassium nitrate. (1)  $K_d(\text{Cs}) = f([\text{NH}_4^+])$ , sorbent No. 1; (2)  $K_d(\text{Cs}) = f([\text{NH}_4^+])$ , sorbent No. 2; (3)  $K_d(\text{Rb}) = f([\text{NH}_4^+])$ , sorbent No. 1; (4)  $K_d(\text{Rb}) = f([\text{NH}_4^+])$ , sorbent No. 2; (5)  $K_d(\text{Cs}) = f([\text{Na}^+])$ , sorbent No. 2; (6)  $K_d(\text{Cs}) = f([\text{K}^+])$ , sorbent No. 2. Concentration of  $\text{HNO}_3$  in all experiments 0.12 M.  $K_d$  = distribution coefficient ( $\text{ml} \cdot \text{g}^{-1}$ );  $[\text{Me}^+]$  = molarity of  $\text{NH}_4\text{NO}_3$  ( $\text{NaNO}_3$ ,  $\text{KNO}_3$ ).

using hydrochloric acid in the concentration range of 0.12 to 0.4 M have eliminated the first assumption. It may be thus assumed, that probably the influence of the hydrogen ions is the only effect. From the above results several conclusions may be drawn.

First of all, the capacity for Cs sorption in the range of acid concentrations studied is very high, and the sorbent may be therefore successfully used for the isolation of cesium from such acid media. The sorption of  $^{86}\text{Rb}$  is much lower than that of  $^{137}\text{Cs}$ . These differences should permit a good separation of  $^{86}\text{Rb}$  from  $^{137}\text{Cs}$ .

The behaviour of microamounts of  $^{137}\text{Cs}$  in the presence of ammonium salts is somewhat unusual. In the case of tungsten<sup>8</sup> and molybdenum<sup>14</sup> ferrocyanide ammonium salts decreased substantially the sorption of cesium (rubidium) due to their mutual exchange. The use of ammonium salts, possibly in mixtures with a mineral acid, would therefore be useful for the elution of the sorbed cesium (rubidium) and for regeneration of the sorbent. On the other hand, the sorbent could not be used for the sorption of heavy alkali metals from solutions containing ammonium salts. The experimental results for vanadium ferrocyanide show that ammonium salts have little influence on the sorption of cesium, whereas in the case of rubidium the effect of ammonium salts is far greater. The reasons for this surprising effect of the ammonium salts on cesium sorption may be based either on the steric arrangement or on the quite different bond strength, which in the case of  $^{137}\text{Cs}$  is evidently exceptional. On comparison of these results with the results of coprecipitation of alkali metals with the ferrocyanides of various metals, it is observed that cesium often has an exceptional position among the alkali metals and the ammonium group; only cesium is coprecipitated, for instance in the case of lead ferrocyanide<sup>15</sup>. It is thus concluded that Cs and Rb are sorbed by means of the ion exchange mechanism.

The ion exchange of monovalent ions may be expressed by the following equations:



where R = skeleton of the sorbent.

In equilibrium, and after modification, we obtain

$$\log \frac{KQ}{F} = \log K_d + \log [\text{H}^+]_L \quad (2)$$

where

$[\text{Me}]_s/[\text{Me}]_L = K_d$  = the distribution coefficient for the microcomponent

$[\text{H}]_L$  = the concentration of the macrocomponent

$F = \gamma^{\pm}_{\text{H}}/\gamma^{\pm}_{\text{Me}}$  = the ratio of the activity coefficients in the aqueous phase

$Q$  = the total capacity of the sorbent.

For the calculation of the selectivity coefficients it is necessary to determine the maximum capacity of the sorbent. The total capacity has been determined from the maximum cesium uptake. The dependence of cesium uptake on its concentration in the solution is given for both sorbents in Fig. 3.

The observed capacity is 2.28 mmoles/g for sorbent No. 1 (concentration of  $\text{HNO}_3 = 0.24 M$ ), and 2.36 mmoles/g for sorbent No. 2 (concentration of  $\text{HNO}_3 = 0.12 M$ ).

The calculated values of the selectivity coefficients for exchange of Rb and Cs are given in Table I.

The values of the selectivity coefficients show that both sorbents may be used for the sorption of cesium from strongly acid solutions with a 100% uptake. The selectivity coefficient for the exchange of hydrogen ions for cesium ions is, for cesium, comparable with the value of the selectivity coefficient of the exchange of cesium for ammonium. The separation factor values (rubidium and cesium, mainly when

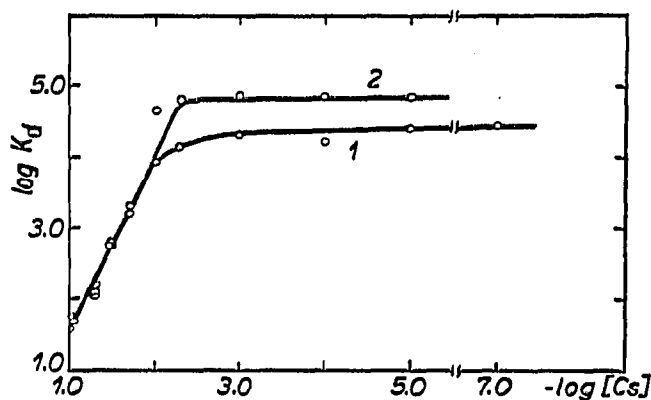


Fig. 3. Dependence of the  $K_d$  of Cs on the initial Cs concentration. (1)  $[\text{HNO}_3] = 0.24 \text{ M}$ , sorbent No. 1; (2)  $[\text{HNO}_3] = 0.12 \text{ M}$ , sorbent No. 2.  $K_d = \text{distribution coefficient (ml}\cdot\text{g}^{-1})$ ;  $[\text{Cs}] = \text{molarity of cesium}$ .

using ammonium salts) are far greater than the values usually given for conventional organic cation exchangers, and are for instance greater than the values for separation factors measured for ammonium salts of heteropolyacids<sup>15</sup>.

Assuming that the exchange of Rb and Cs on vanadium ferrocyanide follows equation (1), then the relation  $\log K_d$  vs.  $\log [\text{H}^+]$  should be linear, with a slope of  $-1$  (see equation (2)). The results obtained for Cs as well as Rb fully satisfy this condition. Thus the results fully confirm the assumption that Rb and Cs are sorbed on vanadium ferrocyanide by means of an ion exchange mechanism.

TABLE I

SELECTIVITY COEFFICIENTS FOR Cs AND Rb EXCHANGE ON VANADIUM FERROCYANIDE

Reaction	Sorbent No. 1	Sorbent No. 2	$[\text{HNO}_3]$
$K_{\text{Cs}/\text{H}}$	$3.2 \cdot 10^3$	$5.4 \cdot 10^3$	
$K_{\text{Cs}/\text{NH}_4}$	$2.0 \cdot 10^3$	$3.1 \cdot 10^3$	$0.121 \text{ M}$
$K_{\text{Rb}/\text{H}}$	$3.5 \cdot 10^1$	$1.7 \cdot 10^2$	
$K_{\text{Rb}/\text{NH}_4}$	$1.7 \cdot 10^1$	$2.7 \cdot 10^1$	$0.121 \text{ M}$
$K_{\text{Cs}/\text{Rb}} \text{ H}$	$9.3 \cdot 10^1$	$3.2 \cdot 10^1$	
$K_{\text{Cs}/\text{Rb}} \text{ NH}_4$	$1.0 \cdot 10^2$	$1.1 \cdot 10^2$	

The influence of potassium and sodium salts on cesium sorption is negligible, and appears only at higher concentrations than  $1 \text{ M}$  (Fig. 1, curves 5 and 6).

Comparing the mechanical properties of the two sorbents we have found that sorbent No. 2 is mechanically more stable than sorbent No. 1.

#### Sorption of the other fission products on vanadium ferrocyanide

For a possible utilisation of vanadium ferrocyanide for the isolation of  $^{137}\text{Cs}$  from a solution of fission products it is necessary to know the behaviour of the other fission products, and to find the conditions of their minimum adsorption.

Among the other long-lived fission products, the sorption of  $^{90}\text{Sr}$ ,  $^{144}\text{Ce}$  on both sorbents, and the sorption of  $^{95}\text{Zr}$  and  $^{106}\text{RuNO}$  on sorbent No. 2 only was studied.

The dependence of sorption values of  $^{90}\text{Sr}$  and  $^{144}\text{Ce}$  on acidity and the con-

centration of Na and  $\text{NH}_4$  salts is shown in Fig. 4 and Table II. From the results in Fig. 4 it can be seen that Sr and Ce are sorbed far less than cesium at the same acidity value. We may therefore conclude that vanadium ferrocyanide will not appreciably sorb fission products such as  $^{90}\text{Sr}$  and  $^{144}\text{Ce}$  but that this sorbent will easily separate elements of the rare earth group and alkaline earths from heavy alkali metals (mainly Rb and Cs).

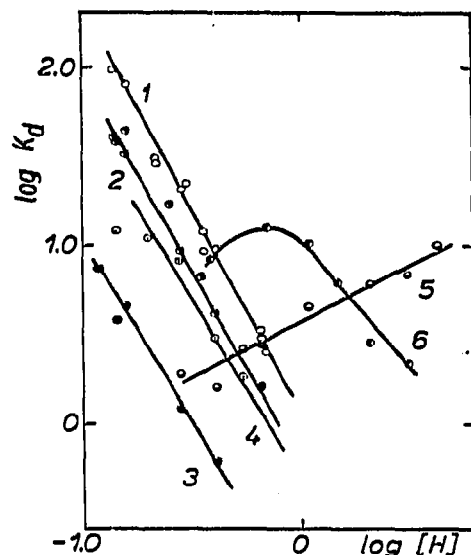


Fig. 4. Dependence of  $K_d$  of Sr, Ce, Ru and Zr on the nitric acid concentration. (1)  $K_d(\text{Sr}) = f([\text{H}^+])$ , sorbent No. 1; (2)  $K_d(\text{Sr}) = f([\text{H}^+])$ , sorbent No. 2; (3)  $K_d(\text{Ce}) = f([\text{H}^+])$ , sorbent No. 1; (4)  $K_d(\text{Ce}) = f([\text{H}^+])$ , sorbent No. 2; (5)  $K_d(\text{Ru}) = f([\text{H}^+])$ , sorbent No. 2; (6)  $K_d(\text{Zr}) = f([\text{H}^+])$ , sorbent No. 2.  $K_d$  = distribution coefficient ( $\text{ml} \cdot \text{g}^{-1}$ );  $[\text{H}^+]$  = molarity of  $\text{HNO}_3$ .

The behaviour of cerium is notable. The slope of the relation  $\log K_d$  vs.  $\log [\text{H}^+]$  is approximately equal to 2, as opposed to the expected 3. This phenomenon can only be explained by the fact that  $\text{Ce}^{3+}$  is only bound to the sorbent by two of its valencies, the third being taken up by an anion.

The presence of foreign ions ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ) decreases strontium and cerium uptake. This could be of practical importance, since this would allow solutions of sodium

TABLE II

INFLUENCE OF AMMONIUM AND SODIUM SALTS ON THE SORPTION OF  $^{144}\text{Ce}$  AND  $^{90}\text{Sr}$  ON VANADIUM FERROCYANIDE

$M_e M$	% sorption of			
	$^{144}\text{Ce}$		$^{90}\text{Sr}$	
	Na	$\text{NH}_4$	Na	$\text{NH}_4$
0.1	24.5	22.2	7.0	7.3
0.2	21.5	12.2	4.5	7.3
0.4	4.0	4.5	3.0	6.0
0.6	3.0	—	—	6.0
0.8	2.0	0.5	—	—

$[\text{HNO}_3] = 0.12 M$ , sorbent No. 2.

or ammonium salts (or their mixtures with an acid) to be used for the elution of  $^{90}\text{Sr}$  or  $^{144}\text{Ce}$ , and for their separation from heavy alkali metals. Generally, we may say that  $^{90}\text{Sr}$  and  $^{144}\text{Ce}$  are sorbed on both sorbents by an ion exchange mechanism. This is illustrated by the curve of  $\log K_d$  vs.  $\log [\text{H}^+]$  and by the influence of sodium and ammonium ions on their sorption.

In addition, the sorption of  $^{95}\text{Zr}$  and  $^{106}\text{RuNO}^{3+}$  was studied on sorbent No. 2. The results are given in Fig. 4, curves 4 and 5. In the case of ruthenium the sorption increases with the acidity, and the variation of  $\log K_d$  with  $\log [\text{H}^+]$  is linear. The increased sorption at higher acidity values may very probably be explained as due to a salting-out effect.

From the shape of the relation  $\log K_d$  vs.  $\log [\text{H}^+]$  for  $^{95}\text{Zr}$  in the  $\text{NH}_4\text{OH}$  concentration range (4.25–1.0 M) it may be deduced that ion exchange takes place. At lower acidities, a number of other effects evidently have an influence. From the dynamic experiments conditions may be deduced by which  $^{106}\text{RuNO}$  and  $^{95}\text{Zr}$  are practically unabsorbed.

## CONCLUSIONS

Vanadium ferrocyanides are sorbents with a high degree of selectivity for the alkali metals. Cesium and rubidium are sorbed even from highly acid solutions, with a 100 % uptake, whereas other fission products,  $^{90}\text{Sr}$ ,  $^{144}\text{Ce}$ ,  $^{95}\text{Zr}$ ,  $^{106}\text{Ru}$ , are practically unabsorbed under these conditions.

## SUMMARY

The ion exchange properties of vanadium ferrocyanide have been investigated. The behaviour of Rb and Cs on this sorbent, and the sorption of other fission products (Sr, Ce, Ru, Zr) have been studied in detail from the point of view of the application of vanadium ferrocyanide to the isolation or separation of fission products. The influence of acidity and of Na and  $\text{NH}_4$  salts on the sorption of Cs, Rb, Sr, Ce, Ru and Zr was studied, and selectivity coefficients for the exchange have been determined for some ion pairs.

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