Ion Exchange of Cesium on Potassium Nickel Hexacyanoferrate(II)s

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The ion exchange of Cs^+ on a nonstoichiometric compound $\text{K}_{0.87}\text{Ni}_{0.57}[\text{NiFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ (KNiFC) was examined by batch methods. The distribution coefficient of Cs^+ , $K_{d,\text{Cs}}$, was independent of Na^+ concentration up to 5 M ($=\text{mol/dm}^3$), while it decreased with increasing concentrations of both K^+ and NH_4^+ . The separation factor for Cs/Rb, $\alpha_{\text{Cs/Rb}}$, was 4.7×10^2 in the presence of 5 M Na^+ . The decreasing order of $K_{d,\text{Cs}}$ in the coexisting cations was found to be $\text{NH}_4^+ > \text{K}^+$, $\text{H}^+ > \text{Na}^+$, Ca^{2+} . The uptake of Cs^+ on KNiFC followed a Langmuir-type isotherm and the maximum amount of Cs^+ taken up was estimated to be 2.57 ± 0.074 mmol/g. The free energy of $\text{K}^+ \rightleftharpoons \text{Cs}^+$ ion exchange was calculated to be -15.4 ± 1.4 kJ/mol by Kielland plot.

KEYWORDS: ion exchange, cesium, cesium ions, potassium nickel hexacyanoferrates, distribution coefficient, separation factors, Langmuir isotherm, thermodynamic equilibrium constant, free energy, Kielland plot, ion-exchange selectivity, concentration dependence, distribution functions

I. INTRODUCTION

Much attention has been focused on the selective removal of ^{137}Cs from radioactive waste solutions⁽¹⁾⁽²⁾. A number of studies have been carried out on the separation of Cs^+ using ion exchange with various inorganic ion exchangers. Among them insoluble hexacyanoferrates have shown the highest selectivity for Cs^+ and have been employed for Cs^+ removal in the decontamination of radioactive wastes⁽³⁾⁻⁽⁷⁾. One of the most promising cesium-selective hexacyanoferrates is potassium nickel hexacyanoferrate (KNiFC)⁽⁶⁾ and its preparation methods have been developed by Kourim⁽⁸⁾⁽⁹⁾ and Vol'khin^{(10) et al.}

The composition and structure of KNiFC have been studied. It was found to have a face centered cubic (FCC) structure with iron and nickel ions located at the corners of the elementary cubes, cyano groups on the edges and exchangeable potassium cations at the body center⁽¹¹⁾⁽¹²⁾. The lattice parameter of the unit cell was estimated to be $1.012 \text{ nm}^{(12)}$ and the FCC structure consists of narrow channel system, which gives the lattice an ion-sieving ability to larger hydrated cations. As for the adsorption properties, the distribution of Cs^+ at tracer

level has been examined by Kourim⁽⁸⁾. However, little is known about the ion-exchange selectivity in connection with the selective removal of Cs^+ from radioactive waste solutions and especially about the influence of coexisting macro ions.

The present study deals with ion exchange selectivity and the uptake behavior of Cs^+ in the presence of other cations.

II. EXPERIMENTAL

1. Preparation of KNiFC

Nonstoichiometric potassium nickel hexacyanoferrate (II) was prepared by slowly adding 150 cm^3 of 0.5 M ($=\text{mol/dm}^3$) $\text{K}_4[\text{Fe}(\text{CN})_6]$ to 200 cm^3 of 0.5 M $\text{Ni}(\text{NO}_3)_2$ at a molar ratio of $\text{Ni/Fe}=1.33$. The composition of the product was found to be $\text{K}_{0.87}\text{Ni}_{0.57}[\text{NiFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ (abbreviated as KNiFC). The theoretical ion-exchange capacity was estimated to be 5.92 meq./g (2.58 meq. K and 3.34 meq. Ni). This value was calculated by using the dry weight of the exchanger. The water content was calculated from the weight loss after heating the sample at 180°C for 1 d, and it was found to be 15.8%, corresponding to 3.5 moles of water per mole of the compound. The product was ground and sieved to give a particle size of 20-50 mesh (0.295-0.833 mm), 50-100 mesh (0.147-0.295 mm) and less than 100 mesh (under 0.147 mm). For the determination of the ion-exchange isotherm, the product was treated with 1 M

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KCl solution in order to convert it completely into K^+ -form ($K_2[NiFe(CN)_6] \cdot nH_2O$, abbreviated as K^+ -form KNiFC).

2. Ion Exchange Experiments

(1) Determination of Distribution Coefficients

The distribution coefficient of Cs^+ was determined by a batch method. A 7 cm^3 portion of aqueous solution containing 10 ppm ($7.5 \times 10^{-5}\text{ M}$) Cs^+ labeled with ^{134}Cs was shaken with 0.070 g of the KNiFC sample in a centrifugal precipitation tube at 20°C for 5 d. After equilibration, the aqueous phase was centrifuged at 3×10^4 rpm for 15 min, and then the γ -activity of the supernatant was measured with a well-type NaI(Tl) scintillation counter (Wallac 1280 Ultragamma counter). The percentage of Cs^+ removed from the solution, R (%), and the distribution coefficient of Cs^+ , $K_{d,Cs}$ (cm^3/g), were determined as

$$R = \frac{A_i - A_t}{A_i} \times 100 \quad (\%), \quad (1)$$

$$K_d = \frac{A_i - A_f}{A_f} \times V/m \quad (\text{cm}^3/\text{g}), \quad (2)$$

where A_i , A_t and A_f (cpm/ cm^3) are the counting rates at the start, at time t , and at equilibrium, respectively; m (g) the dry weight of the KNiFC sample; V (cm^3) the volume of the aqueous phase.

The effect of following parameters on the $K_{d,Cs}$ were studied by using the KNiFC sample:

- Equilibrium time using different grain sizes,
- Concentration of coexisting ions Na^+ , K^+ , NH_4^+ and Ca^{2+} in the range of 10^{-4} –5 M; in addition the K_d of trace Rb as a function of Na^+ was determined,
- Equilibrium pH, adjusted with 0.1 M (H, Na) NO_3 ,
- Cs^+ concentration in the range of 0.015–0.1 M.

(2) Determination of Cs/K Ion-Exchange Isotherm

The ion-exchange selectivity of K^+ -form KNiFC for Cs^+ was examined by determining the isotherm of ion exchange for K^+ - Cs^+ equilibrium⁽¹³⁾⁽¹⁴⁾. The isotherm presents the equivalent ionic fraction of Cs^+ in the exchanger phase as a function of that in the solution. Samples (0.070 g) of K^+ -form KNiFC were equilibrated for 5 d with 7 cm^3 of 0.1 M (Cs, K) Cl solutions spiked with ^{134}Cs . The solid was then separated by centrifugation and ^{134}Cs activity of the solution was determined. Measuring changes in ^{134}Cs activity in the solution, the concentrations of the exchanging ion in the solution and the exchanger were calculated. The temperature in these experiments was 25°C and the pH 8.21–8.49.

III. RESULTS AND DISCUSSION

1. Uptake Behavior

The uptake behavior of Cs^+ on KNiFC was examined by determining the distribution coefficient, $K_{d,Cs}$. The distribution coefficient is often a proper quantity to express the distribution of an ion between the exchanger

and solution phase. This is especially true when the exchanging ion is present in trace concentration, since the ionic composition of the exchanger does not practically change at macro level in trace ion exchange. Distribution coefficients are mainly used for the following purposes:

- Assessing the behavior of ions for ion chromatography and other separation processes. Separation factor, $\alpha_{A/B} = K_{d,A}/K_{d,B}$, which is the ratio of the distribution coefficients for the ions A and B determined at identical experimental condition, is a measure of the separation of these ions,
- To study the effect of various parameters, such as coexisting macro ions and pH, on the ion exchange processes,
- To study the mechanism of ion uptake processes.

(1) Ion Exchange Rate of Cs^+

Figure 1 shows the effect of equilibration time on the uptake percentage of Cs^+ on KNiFC. The uptake rate increased with decreasing particle size of the sample, suggesting that the rate determining step of the adsorption of Cs^+ would be governed by an intergranular diffusion through the tunnel in the FCC structure of KNiFC.

(2) Effect of Na^+ concentration on $K_{d,Cs}$

The effect of the concentration of coexisting Na^+ on the $K_{d,Cs}$ is illustrated in Fig. 2. Here the K_d of Cs^+ is compared with that of Rb^+ . The $K_{d,Cs}$ value was almost constant in a fairly wide range of Na^+ concentration from 10^{-4} to 5 M, and no difference in $K_{d,Cs}$ values between NaCl and $NaNO_3$ solutions was observed. Even at high Na^+ concentration such as 5 M, the $K_{d,Cs}$ value was above $10^5\text{ cm}^3/\text{g}$, suggesting high selectivity for Cs^+ . On the other hand, the $K_{d,Rb}$ value decreased markedly with Na^+ concentrations above 1 M. The KNiFC exchanger consists of very narrow tunnel structure⁽¹³⁾, and the selectivity of monovalent cations has been reported to be $Cs^+ > Rb^+ > NH_4^+ \gg K^+ > Na^+$ ⁽⁸⁾⁽¹⁵⁾, which agrees with the order of the size of hydrated cations⁽¹⁶⁾. At higher concentrations of Na^+ , the distribution of Rb^+ is

Fig. 1 Rate of Cs^+ uptake by KNiFC with different particle sizes

Fig. 2 Effects of Na^+ concentration on $K_{d,\text{Cs}}$ and $K_{d,\text{Rb}}$

thus affected by Na^+ concentration, compared to that of Cs^+ .

The separation factor ($\alpha_{\text{Cs/Rb}} = K_{d,\text{Cs}}/K_{d,\text{Rb}}$) for the ion pair Cs/Rb in the presence of 5 M Na^+ was calculated to be 4.7×10^2 from the K_d values of Cs^+ and Rb^+ . This is considerably greater than that for ferrierite, a Cs-selective zeolite, which gave an $\alpha_{\text{Cs/Rb}}$ value of 1.7 in the presence of 5 M Na^+ .

(3) Effects of K^+ , NH_4^+ and Ca^{2+} concentrations on $K_{d,\text{Cs}}$

Figures 3 and 4 show the effect of K^+ and NH_4^+ concentrations on $K_{d,\text{Cs}}$. The $K_{d,\text{Cs}}$ tended to decrease with increasing concentration of either K^+ or NH_4^+ . The $K_{d,\text{Cs}}$ values at lower concentration of NH_4^+ below 0.1 M were, within experimental error, the same as those in the presence of other cations, because the error of $K_{d,\text{Cs}}$ in the range of 10^5 to $10^6 \text{ cm}^3/\text{g}$ was estimated to be about 50%. The error decreased markedly with decreasing the K_d value. The $K_{d,\text{Cs}}$ was influenced considerably by the NH_4^+ concentration; with NH_4^+ concentrations above 0.1 M, $K_{d,\text{Cs}}$ decreased linearly with a slope of approximately -1 , suggesting that the uptake of Cs^+ on KNiFC is substantially governed by a cation-exchange reaction⁽¹⁷⁾⁽¹⁸⁾. The $K_{d,\text{Cs}}$ values for the original sample containing both K^+ and Ni^{2+} as exchangeable cations, were similar to those for the K^+ converted form, and both samples showed a slope of about -1 , suggesting that the Cs^+ is exchanged only with K^+ in the original sample. In the presence of Ca^{2+} , the $K_{d,\text{Cs}}$ value was almost constant in a fairly wide range of Ca^{2+} concentration from 10^{-4} to 2 M and high $K_{d,\text{Cs}}$ values of $>10^5 \text{ cm}^3/\text{g}$ were obtained; the distribution of Cs^+ is practically independent of Ca^{2+} concentration (**Fig. 5**).

Fig. 3 Effect of K^+ concentration on $K_{d,\text{Cs}}$

Fig. 4 Effect of NH_4^+ concentration on $K_{d,\text{Cs}}$

(4) Effect of Equilibrium pH on $K_{d,\text{Cs}}$

The effect of equilibrium pH on the $K_{d,\text{Cs}}$ is shown in **Fig. 6**. Here the ionic strength (μ) was 0.1 and the pH was adjusted by 0.1 M (H, Na)Cl. The $K_{d,\text{Cs}}$ slightly increased with pH, though relatively large $K_{d,\text{Cs}}$ values were obtained in a wide range of pH from 1 to 9.

Based on Figs. 2-6, we can conclude that the order of $K_{d,\text{Cs}}$ in the presence of coexisting cations was found to be $\text{NH}_4^+ > \text{K}^+$, $\text{H}^+ > \text{Na}^+$, Ca^{2+} , which closely resembles the order of the size of the hydrated cations⁽¹⁶⁾.

(5) Langmuir-Type Treatment of Cs Uptake with KNiFC

The isotherm of Cs^+ uptake by KNiFC is shown in **Fig. 7(a)**. The amount of Cs^+ taken up by KNiFC approached a constant value at solution concentrations

Fig. 5 Effect of Ca^{2+} concentration on $K_{d,\text{Cs}}$

Fig. 6 Effect of equilibrium pH on $K_{d,\text{Cs}}$

of Cs^+ above about 20 mmol/dm^3 . The profile of the isotherm suggests that the uptake of Cs^+ follows a Langmuir adsorption equation⁽¹⁹⁾. The Langmuir equation is given by

$$Q_{\text{eq}} = \frac{KQ_{\text{max}}C_{\text{eq}}}{1 + KC_{\text{eq}}} \quad (\text{mol/g}), \quad (3)$$

where C_{eq} (mol/dm^3) and Q_{eq} (mol/g) are the equilibrium concentrations of Cs^+ in the aqueous and solid phases, respectively; Q_{max} (mol/g) is the maximum amount of Cs^+ taken up; K (dm^3/mol) is the Langmuir constant. The equation can be rewritten as follows:

$$\frac{C_{\text{eq}}}{Q_{\text{eq}}} = \frac{1}{KQ_{\text{max}}} + \frac{1}{Q_{\text{max}}}C_{\text{eq}} \quad (\text{g/dm}^3). \quad (4)$$

(a) Uptake isotherm

(b) Langmuir plot

$\text{pH}_{\text{eq}} 7.49-9.32$; Equilibration: 25°C , 5 d

Fig. 7 Isotherm for Cs^+ uptake by KNiFC

A fairly linear relation was obtained from the Langmuir-plot as seen in Fig. 7(b). The values of Q_{max} (mmol/g) and K (dm^3/mol) were calculated to be 2.57 ± 0.074 and $6.0 \times 10^2 \pm 1.5 \times 10^2$ from the slope and intercept, respectively, by the least-squares method. The maximum amount of Cs^+ taken up was close to the content of K^+ (2.58 meq./g) in the non-stoichiometric product, suggesting that Cs^+ was exchanged only with K^+ .

(6) Uniformity of Distribution of Cs^+ in K^+ -form KNiFC

In order to check the uniformity of the Cs^+ distribution in a K^+ -form KNiFC granule, a sample saturated with Cs^+ was submitted to electron probe micro analysis (EPMA, Hitachi X-650S). Photograph 1 shows the SEM image of the granule cross section, and the resulting line analysis of Cs-L α . Figure 8 shows an energy dispersive spectrum (EDS) for the position "A" in Photo. 1. The Cs concentration in the granule was almost constant in the granule and Cs^+ was found to be uniformly dispersed throughout the particle. EDS shows that Cs-saturated sample still contains the exchangeable K^+ ions; about 40% of the exchangeable K^+ ions in K^+ -form sample were exchanged with Cs^+ .

2. Equilibrium of K for Cs Exchange in K^+ -form KNiFC

To obtain data to compare with other Cs-selective

20–50 mesh granule; treated with 1,000 ppm Cs⁺ for 5 d

Photo. 1 SEM photograph of cross section of K⁺-form KNiFC granule treated with Cs⁺ and line analysis of CsL_α

Fig. 8 EDS of K⁺-form KNiFC granule treated with Cs⁺

exchangers, the corrected selectivity coefficient and thermodynamic equilibrium constant for exchange of Cs⁺ for K⁺ in K⁺-form KNiFC were calculated in the chloride media of 0.1 M (Cs, K) Cl. The method developed by Gaines and Thomas⁽²⁰⁾ was applied to the experimental results obtained in the determination of the ion-exchange isotherm.

The thermodynamic equilibrium constant for exchange of Cs⁺ for K⁺ is expressed as follows:

$$K = \frac{\bar{X}_{Cs} X_K}{X_{Cs} \bar{X}_K} \times \frac{\bar{f}_{Cs} f_K}{f_{Cs} \bar{f}_K}, \quad (5)$$

where $\bar{X}_{Cs}$ and $\bar{X}_K$ are the equivalent ionic fractions of the corresponding ions in the exchanger phase, and X_{Cs} and X_K are those in the solution. Since most probably only K ions participated in the exchange process, the isotherm was normalized so that the maximum uptake of 2.57 mmol/g was considered as $\bar{X}_{Cs}=1$ and all

the other isotherm $\bar{X}_{Cs}$ values were normalized to this value. $\bar{f}_{Cs}$ and $\bar{f}_K$ are the activity coefficients of the ions in the exchanger and f_{Cs} and f_K those in the solution. The activity of the ions in the exchanger cannot be determined directly, and therefore the corrected selectivity coefficient, K' , which is corrected by taking into account only the activity coefficients in the solution, is calculated as follows:

$$K' = \frac{\bar{X}_{Cs} X_K}{X_{Cs} \bar{X}_K} \times \frac{f_K}{f_{Cs}}. \quad (6)$$

The ratio of the individual ions f_K/f_{Cs} is equal to the ratio f_{KCl}^2/f_{CsCl}^2 , where f_{KCl} and f_{CsCl} are the mean molar activity coefficients of KCl and CsCl, respectively. f_{KCl} and f_{CsCl} for the mixed 0.1 M KCl-CsCl solution were calculated by the method of Glueckauf⁽²¹⁾ using f_{KCl} and f_{CsCl} of the pure solutions obtained from the literature⁽²²⁾. The ratio f_{KCl}^2/f_{CsCl}^2 was found to be 1.038 over the entire composition range of the solution.

Figures 9(a) and **(b)** show the normalized Cs⁺/K⁺ exchange isotherm and the corrected selectivity coefficient

(a) Normalized Cs⁺/K⁺ exchange isotherm

(b) Corrected selectivity coefficient, K' , for Cs⁺/K⁺ exchange as a function of degree of exchange ($\bar{X}_{Cs}$)

pH 8.21–8.49; 0.1 M (Cs, K)Cl solution;
Equilibration: 25 °C, 5 d

Fig. 9 Ion exchange isotherm and selectivity coefficient for Cs⁺/K⁺ exchange in K⁺-form KNiFC

cient, K' , for Cs^+ to K^+ exchange in K^+ -form KNiFC as a function of the degree of exchange ($\bar{X}_{\text{Cs}}$). The selectivity plot K' vs. $\bar{X}_{\text{Cs}}$ (Kjelland plot)⁽¹³⁾⁽²³⁾ is the most important "working function" of the ion exchanger. When accurately determined, the selectivity plot can give valuable information on the nature of exchanging sites and gives possibilities of modeling the behavior of selectivity in the exchanger. The high corrected selectivity coefficient values indicate very favorable selectivity of K^+ -form KNiFC for Cs^+ . Log K' decreases almost linearly as a function of Cs^+ uptake. The thermodynamic equilibrium constant can be obtained by integrating the K' curve from $\bar{X}_{\text{Cs}}=0$ to $\bar{X}_{\text{Cs}}=1$. In this case, since log K' is a linear function of $\bar{X}_{\text{Cs}}$, we can apply an approximation by interpolating the value of log K' at $\bar{X}_{\text{Cs}}=0.5$ ⁽²³⁾,

$$\log K = \int_0^1 \log K' d\bar{X}_{\text{Cs}} = [\log K']_{\bar{X}_{\text{Cs}}=0.5}. \quad (7)$$

The value of K attained to 489, and hence a Gibbs standard free-energy, ΔG° , was found to be -15.4 ± 1.4 kJ/mol, which is considerably lower than those of Cs-selective zeolites such as ferrierite ($\Delta G^\circ = -10.7$ kJ/mol)⁽²⁴⁾.

IV. CONCLUSIONS

A nonstoichiometric compound $\text{K}_{2-x}\text{Ni}_{x/2}[\text{NiFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ (KNiFC) was found to have high distribution coefficient of Cs^+ , $K_{d,\text{Cs}}$. The value was above $10^5 \text{ cm}^3/\text{g}$ in the presence of Na^+ , while it decreased with increasing K^+ or NH_4^+ concentration. The separation factor for Cs/Rb was estimated to be 4.7×10^2 in the presence of 5 M NaCl. The uptake of Cs^+ followed a Langmuir isotherm and the maximum amount of Cs^+ was estimated to be $2.57 \pm 0.074 \text{ mmol/g}$. This corresponds to the amount of K^+ in the exchanger. The free energy for the ion exchange of $\text{K}^+ \rightleftharpoons \text{Cs}^+$ was found to have the rather low value of $-15.4 \pm 1.4 \text{ kJ/mol}$, suggesting high ion-exchange selectivity of Cs^+ for K^+ -form KNiFC.

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—REFERENCES—

- (1) IAEA Technical Rep. Ser. No.356, (1993).
- (2) Kubota, M., et al.: "High Level Radioactive Waste and Spent Fuel Management" (Proc. Joint Int. Waste Management Conf. (1989)), Vol.2, Am. Soc. Mechanical Eng., New York, 537 (1989).
- (3) Veselý, V., Pekárek, V.: *Talanta*, **19**, 1248-1253 (1972).
- (4) Loos-Neskovíc, C., et al.: *Talanta*, **31**, 1133-1147 (1984).
- (5) Hendrickson, W.F., Riel, G.K.: *Health Phys.*, **28**, 17 (1975).
- (6) Faubel, W., Ali, A.: *Radiochim. Acta*, **40**, 49 (1986).
- (7) Harjula, R., Lehto, J., Tusa, E.H., Paavola, A.: *Nucl. Technol.*, **107**, 272 (1994).
- (8) Kourim, V., Rais, J., Million, B.: *J. Inorg. Nucl. Chem.*, **26**, 1111 (1964).
- (9) Kourim, V., Rais, J., Stejskal, J.: *J. Inorg. Nucl. Chem.*, **26**, 1761 (1964).
- (10) Vol'khin, V.V., Kolesova, S.A.: *Zh. Prikl. Khim.*, **40**, 342 (1967).
- (11) Kuznetsov, V.G., Popova, Z.V., Seifer, G.B.: *Russ. J. Inorg. Chem.*, **15**, 956 (1970).
- (12) Vol'khin, V.V., Shil'ga, E.A., Zil'berman, M.V.: *Inorg. Mater.*, **7**, 69 (1971).
- (13) Čeranić, T.S., Adamović, R.: *Z. Naturforsch.*, **34b**, 1275 (1979).
- (14) Čeranić, T.S.: *J. Chem. Soc., Faraday Trans.*, **80**, 823 (1984).
- (15) Dolezal, J., Kourim, V.: *Radiochem. Radioanal. Lett.*, **1**, 295 (1969).
- (16) Laitinen, H.A., Harris, W.E.: "Chemical Analysis", McGraw-Hill, p.14 (1975).
- (17) Lehto, J., Paarjanen, A., Harjula, R.: *J. Radioanal. Nucl. Chem., Lett.*, **164**, 39 (1992).
- (18) Amphlett, C.B.: "Inorganic Ion Exchangers", Elsevier Publ., Amsterdam, (1964).
- (19) Takeuchi, Y.: "Kagaku Kogaku", Baifukan, p.190 (1982).
- (20) Gains, G.L., Thomas, H.C.: *J. Chem. Phys.*, **21**, 714 (1953).
- (21) Glueckauf, E.: *Nature (London)*, **163**, 414 (1949).
- (22) Robert, C.W.: "Handbook of Chemistry and Physics", D-169, CRC Press, (1980).
- (23) Breck, D.W.: "Zeolite Molecular Sieves", Robert E. Krieger Publ., Florida, p.529-536 (1974).
- (24) Mimura, H., Tachibana, F., Akiba, K.: *J. Nucl. Sci. Technol.*, **29**[2], 184 (1992).