Mechanism of Caesium Ion Exchange on Potassium Cobalt Hexacyanoferrates(II)

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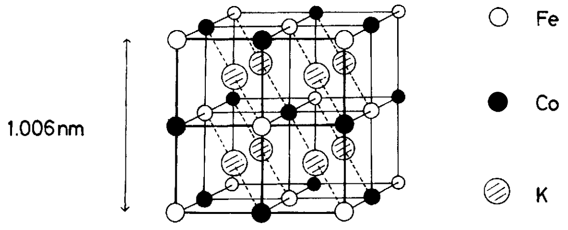
The caesium uptakes by $K_2[CoFe(CN)_6]$ and non-stoicheiometric compounds $K_{2-x}Co_{x/2}[CoFe(CN)_6]$ were found to correlate directly with the specific surface areas of the products with $x < 1$. The exchange process is assumed to involve only the outermost surface layer of their crystals, which have a cubic lattice, *i.e.* only potassium (or cobalt) ions inside the elementary cubes closest to the surface of the crystals are exchanged for caesium ions. Compounds with $x > 1$ are mixtures of cubic potassium cobalt hexacyanoferrate(II) and tetragonal $Co_2Fe(CN)_6$. The thermodynamic equilibrium constant of the caesium exchange on $K_2[CoFe(CN)_6]$ was found to have a high value of 125.

A great number of insoluble hexacyanoferrates(II) of transition and alkali metals have shown high selectivities for caesium.[1-3] In most cases the purpose of studying these compounds has been their prospective use in the selective separation of radioactive ^{137}Cs from nuclear waste solutions.[4,5]

One of the most promising caesium-selective hexacyanoferrates is potassium cobalt hexacyanoferrate(II),[6] which has a face-centred cubic structure. The unit cell[7] $K_8[CoFe(CN)_6]_4$ is shown below. Cobalt and iron are located at the corners of the elementary cubes and the exchangeable potassium ions are at the body centre. Cyanide groups are placed between the iron and cobalt atoms. The *a* parameter of the unit cell is 1.006 nm. The salt $Cs_2[CoFe(CN)_6]{\cdot}yH_2O$ is isostructural, the *a* parameter being only slightly greater at 1.030 nm.[8] Therefore, exchange of K^+ for Cs^+ does not require any drastic rearrangement of the lattice.



Depending on the method of preparation, the product is either $K_2[CoFe(CN)_6]{\cdot}yH_2O$ or a non-stoicheiometric compound $K_{2-x}Co_{x/2}[CoFe(CN)_6]{\cdot}yH_2O$ with *x* variable. Within the square are the ions forming the cubic framework and those outside are the exchangeable ions. The theoretical ion-exchange capacity of $K_2[CoFe(CN)_6]$, *i.e.* the amount of potassium, is 5.73 mequiv. g^{-1}, but none of the products reported so far has absorbed caesium to this extent: the effective capacities have been 0.24—1.24 mequiv. g^{-1}.[6,9-13]

Recently Lehto *et al.*[14] showed a correlation between a caesium uptake of 0.35 mequiv g^{-1} and a specific surface area of 62 m^2 g^{-1} for a non-stoicheiometric potassium cobalt hexacyanoferrate. It was concluded that caesium ions are only absorbed in the outermost layer of the crystals, *i.e.* only potassium (or cobalt) ions inside the elementary cubes closest to the surface of the crystals participate in the exchange process. The present paper probes this problem in more detail by studying several products of different compositions. In addition, the thermodynamic equilibrium constant for the caesium exchange on $K_2[CoFe(CN)_6]$ was determined.

Experimental

Practically pure $K_2[CoFe(CN)_6]$ was prepared by slowly adding 0.5 mol dm^{-3} $Co(NO_3)_2$ (200 cm^3) to 0.5 mol dm^{-3} $K_4[Fe(CN)_6]$ (200 cm^3). Non-stoicheiometric potassium cobalt hexacyanoferrates were prepared using the reverse order of mixing. The experimental conditions for these preparations are summarized in Table 1.

The compositions of the products were determined by first dissolving samples of them in boiling concentrated H_2SO_4. The acid solutions were then evaporated to dryness and the residues dissolved in concentrated HCl. The contents of iron, cobalt, and potassium were determined by atomic absorption spectrophotometry (a.a.s.) using a Perkin-Elmer Zeeman 5000 instrument. The water contents were calculated from the weight losses after drying at 180 °C, which temperature is, according to thermoanalysis, sufficiently high to remove all the water.

The *X*-ray diffraction patterns of powder samples of the hexacyanoferrates were determined with a Siemens Kristalloflex 4 diffractometer using monochromatized Cu-K_α radiation.

The specific surface areas of the products were determined by the nitrogen absorption method and the BET (Brunauer, Emmett, and Teller) equation using a Carlo Erba Sorptomatic 1800 apparatus.

The crystal sizes of the hexacyanoferrates were calculated from micrographs taken with a JEOL 100 CX transmission electron microscope using magnifications of 10^4—1.6×10^5.

The solubilities of the hexacyanoferrates were determined by shaking samples (0.2 g) with deionized water (20 cm^3) for 24 h. The solid was then separated by centrifugation and the amount of iron in the solution was determined by a.a.s.

The ion exchange of caesium on the hexacyanoferrates was studied by determining isotherms for exchange of Cs^+ for K^+ and Co^{2+}. The isotherms present the equivalent ionic fraction of caesium in the exchanger phase as a function of that in the solution. Samples (0.2 g) of the exchangers were equilibrated for 3 d with different volumes of 0.01 mol dm^3 CsCl containing ^{134}Cs tracer. The solid was then separated by centrifugation and the ^{134}Cs activity of the solution was determined with a Wallac 1280 Ultrogamma counter. From the changes in ^{134}Cs activity in the solution, the concentrations of the exchanging ions in the solution and the exchanger were calculated. The temperature in these experiments was 20 °C and the pH 7—9.

Results and Discussion

Compositions of Hexacyanoferrates.—The compositions of the hexacyanoferrates are shown in Table 2. They were

Table 1. Experimental conditions used in the preparation of potassium cobalt hexacyanoferrates

Product	0.5 mol dm^{-3} $K_4[Fe(CN)_6]$ V/cm^3	$Co(NO_3)_2$ C/mol dm^{-3}	V/cm^3	Molar ratio Co/Fe in starting material
(1)	200	0.5	200	1.0
(2)	200	0.5	20	0.1
(3)	200	0.5	100	0.5
(4)	140	0.5	200	1.43
(5)	50	0.5	200	4.0
(6)	60	0.1	1 000	3.33
(7)	60	0.05	2 000	3.33
(8)	10	0.1	250	5.0
(9)	75	3.0	600	48
(10)	60	3.0	1 000	100

Table 2. Compositions of potassium cobalt hexacyanoferrates

Product	Composition	Water content (%)
(1)	$K_2[CoFe(CN)_6]$	6.9
(2)	$K_{1.96}Co_{1.02}Fe(CN)_6$	7.5
(3)	$K_{1.92}Co_{1.04}Fe(CN)_6$	8.0
(4)	$K_{1.76}Co_{1.12}Fe(CN)_6$	7.0
(5)	$K_{1.64}Co_{1.18}Fe(CN)_6$	7.9
(6)	$K_{1.34}Co_{1.33}Fe(CN)_6$	11.6
(7)	$K_{1.20}Co_{1.40}Fe(CN)_6$	12.3
(8)	$K_{0.78}Co_{1.61}Fe(CN)_6$	14.4
(9)	$K_{0.64}Co_{1.68}Fe(CN)_6$	14.2
(10)	$K_{0.58}Co_{1.71}Fe(CN)_6$	17.3

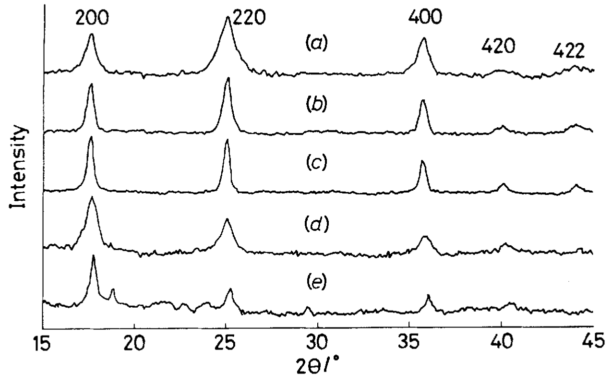


Figure 1. X-Ray diffraction patterns of $K_2[CoFe(CN)_6]$ (*a*), $K_{1.64}Co_{1.18}Fe(CN)_6$ (*b*), $K_{1.20}Co_{1.40}Fe(CN)_6$ (*c*), $K_{0.78}Co_{1.61}Fe(CN)_6$ (*d*), and $K_{0.58}Co_{1.71}Fe(CN)_6$ (*e*)

calculated by taking the amount of iron as unity and normalizing the cobalt amount to this value. The proportion of potassium was then calculated on the basis of the iron and cobalt values and taking into account electrical neutrality. The overall procedure is assumed to introduce an error of 5—10% into the results.

Structures of Hexacyanoferrates.—Figure 1 shows the X-ray diffraction patterns for $K_2[CoFe(CN)_6]$ and for some non-stoicheiometric products. The rather large widths of the reflections seem to indicate small crystal sizes of the products; low crystallinity can't be ruled out either. The pattern for $K_2[CoFe(CN)_6]$ [product **(1)**] indicates a face-centered cubic structure.[7] Products **(2)**—**(6)** have almost identical patterns to that of **(1)**, the most intense reflection being 220. Also $K_{1.20}Co_{1.40}Fe(CN)_6$ has a cubic structure, with a similar pattern to those of products **(1)**—**(6)**, but the intensity of the reflection 200 is now as high as that of 220. In the patterns of products **(8**—**(9)** the reflection 200 is the most intense. In addition to this cubic component the non-stoicheiometric product with the highest cobalt content, $K_{0.58}Co_{1.71}Fe(CN)_6$, showed a minor phase having a tetragonal structure, $Co_2Fe(CN)_6$ (a = 1.022, c = 1.266 nm).[7] The most intense reflection of this tetragonal pattern at 18.8° (2θ) can also be seen in the patterns of products **(8)** and **(9)**. Not only the intensities but also the positions of reflections 200 and 220 altered when the cobalt content increased. In the patterns of products **(1)**—**(7)** these reflections occurred at practically identical positions; 200 at 17.5—17.6 (2θ) and 220 at 24.9—25.0° (2θ). In the patterns of products **(8)**—**(10)** the corresponding values were somewhat higher: 200 at 17.6—17.7 (2θ) and 220 at 25.0—25.2° (2θ), which may indicate a slight distortion of the structure.

The X-ray diffraction results allow us to conclude that when cobalt ions replace potassium ions in $K_2[CoFe(CN)_6]$ the exchanged products have cubic lattices practically identical with that of the original compound. Potassium ions and the excess of cobalt ions are located inside the elementary cubes. Increasing cobalt content finally results in the appearance of two phases with a potassium content of less than 1.20 mol per mol. In the original $K_2[CoFe(CN)_6]$ there is one potassium ion in each elementary cube. Because of the difference in valences the replacement of K^+ by Co^{2+} leaves one elementary cube unoccupied. The products with increasing cobalt content accommodate more water to fill the space left unoccupied by potassium ions (see Table 2).

In our previous paper[14] it was shown that in a non-stoicheiometric product $K_{1.76}Co_{1.12}Fe(CN)_6$ the potassium and cobalt are exchanged for caesium in the same ratio as they are present in the exchanger. When 0.346 mequiv. g^{-1} of caesium was absorbed, 0.301 mequiv. g^{-1} of potassium and 0.040 mequiv. g^{-1} of cobalt were released. Taking also this into account, it is concluded that potassium cobalt hexacyanoferrates with a potassium content of 2.0—1.20 mol per mol have a cubic lattice with the exchangeable potassium and cobalt ions randomly distributed in the channels of the lattice.

The widths of the reflections in the X-ray diffraction patterns indicate that the crystal size of the cubic component was considerably smaller when the potassium content was 2.0—1.92 [products **(1)**—**(3)**] than when the content was 1.76—1.20 [products **(4)**—**(7)**] and again smaller when the potassium content was 0.78—0.58 mol per mol [products **(8)**—**(10)**]. Diameters, calculated from the f.w.h.m. (full width at half-maximum) of the 400 reflections, were approximately 20 nm for products **(1)**—**(3)**, 25—30 nm for **(4)**—**(7)**, and 20—25 nm for **(8)**—**(10)**.

Ion-exchange Mechanism.—The ion-exchange isotherms for three hexacyanoferrates are shown in Figure 2. The theoreti-

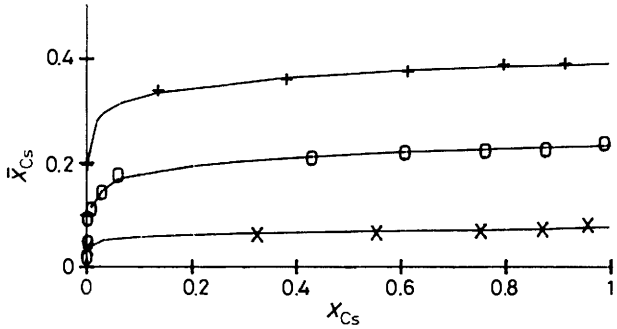


Figure 2. Caesium ion-exchange isotherms for potassium cobalt hexacyanoferrates: (+) $K_{0.64}Co_{1.68}Fe(CN)_6$, (0) $K_2[CoFe(CN)_6]$, and (X) $K_{1.76}Co_{1.12}Fe(CN)_6$. $\bar{X}_{Cs}$ = Equivalent ionic fraction of caesium in the exchanger, X_{Cs} = equivalent ionic fraction of caesium in the solution. Concentration of the CsCl solution was 0.01 mol dm^{-3}

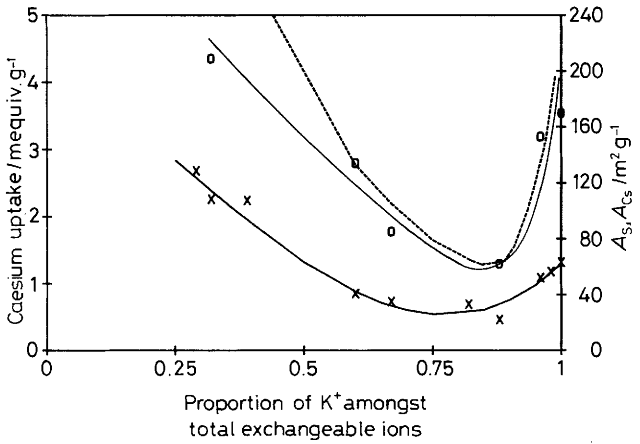


Figure 3. Caesium uptake (x), specific surface area, A_s (o), and calculated area occupied by caesium ions assuming that each ion absorbed covers an area of 0.25 nm^2 A_{Cs} (- - -), as a function of the equivalent fraction of potassium ions amongst the total exchangeable ions

cal ion-exchange capacities used in the calculations differed according to the compositions of the products. That used for the potassium cobalt hexacyanoferrate was 5.73 mequiv. g^{-1}, while that for the non-stoicheiometric product $K_{1.76}Co_{1.12}Fe(CN)_6$ was 5.77 mequiv. g^{-1} (5.02 mequiv. K and 0.75 mequiv. Co) and that for $K_{0.64}Co_{1.68}Fe(CN)_6$ 5.95 mequiv. g^{-1} (1.90 mequiv. K and 4.05 mequiv. Co). All the values were calculated on the basis of the dry weights of the exchangers.

The shapes of the isotherms are more or less similar. However, the maximum uptake by the different products varied widely; it was only about 7% of the theoretical capacity for $K_{1.76}Co_{1.12}Fe(CN)_6$, 23% for $K_2[CoFe(CN)_6]$, and 39% for $K_{0.64}Co_{1.68}Fe(CN)_6$. Figure 3 shows the caesium uptake of different products plotted against the equivalent fraction of potassium ions amongst the total exchangeable ions. A minimum in the caesium uptake was found at a potassium fraction of 0.75—0.80. This minimum corresponds well with the maximum in crystallinity of the products observed in the X-ray diffraction determinations.

In our previous paper[14] it was assumed that caesium exchange only takes place in the outermost surface layer and each caesium ion absorbed occupies an area of 0.25 nm^2 (length of the elementary cube 0.5 nm). A good correlation was found between a caesium uptake of 0.35 mequiv. g^{-1} and a specific surface area of 62 m^2 g^{-1} (0.35 mequiv. g^{-1} = 0.35×10^{-3} mol g^{-1} $\times 6.023 \times 10^{23}$ Cs^+ mol^{-1} = 2.1×10^{20} Cs^+ g^{-1}; 0.25×10^{-18} m^2 per Cs^+ $\times 2.1 \times 10^{20}$ Cs^+ g^{-1} = 52 m^2 g^{-1}). Corresponding results for the hexacyanoferrates in this study are shown in Figure 3. The correlation was very good for products (**1**)—(**7**) and shows that the surface-layer exchange mechanism is valid for all potassium cobalt hexacyanoferrates with the cubic structure. For products with the additional tetragonal phase of $Co_2Fe(CN)_6$ the specific surface area [209 m^2 g^{-1} for $K_{0.64}Co_{1.68}Fe(CN)_6$] was considerably lower than the calculated area (350 m^2 g^{-1}). In $Co_2Fe(CN)_6$ the cobalt ions are probably exchangeable not only in the surface layer, but throughout the tetragonal lattice with the ion-exchange capacity being 6.06 mequiv. g^{-1}.

Caesium uptakes by potassium cobalt hexacyanoferrates reported by other authors match well the results in Figure 3. Ceranic[9] reported an uptake of 1.24 mequiv. g^{-1} for $K_2[CoFe(CN)_6]$, Lee and Streat[12] 0.58 mequiv. g^{-1} for $K_{1.87}Co_{1.08}Fe(CN)_6$, Dubrovin *et al.*[13] 0.35 mequiv. g^{-1} for $K_{1.75}Co_{1.13}Fe(CN)_6$, and Prout *et al.*[6] 0.3—0.5 mequiv. g^{-1} for $K_{1.60}Co_{1.40}Fe(CN)_6$.

Crystal Sizes of Hexacyanoferrates.—The transmission electron micrographs obtained revealed the crystals of $K_2[CoFe(CN)_6]$ and the non-stoicheiometric products to be identically ellipsoidal/spherical in shape (Figure 4). Diameters were only 10—40 nm. The resolution of the micrographs is, however, so low that on their basis only approximate values can be given. These very small sizes are consistent with the hypothesis of the surface-layer exchange process. For example, $K_{1.20}Co_{1.40}Fe(CN)_6$ had a caesium uptake of 0.85 mequiv. g^{-1} (14.5% of the theoretical capacity). If the crystals are taken as spheres with a radius of r nm, the volume of a crystal is $4/3\ \pi r^3$. Since 14.5% of the volume is occupied by caesium ions in the surface layer of thickness 0.5 nm, the rest, 85.5%, has a volume of $4/3\pi(r - 0.5)^3$. Solving the equation $0.855(4/3\pi r^3) = 4/3\pi(r - 0.5)^3$ for r gives a value of 10 nm (diameter 20 nm). The diameter calculated from the f.w.h.m. of the reflection 400 in the X-ray diffraction pattern gave a value of 28 nm for the same product.

The micrograph of the mixed phase $K_{0.58}Co_{1.71}Fe(CN)_6$ shows the large $Co_2Fe(CN)_6$ crystals among the small potassium cobalt hexacyanoferrate crystals (Figure 4), in good agreement with the X-ray diffraction results. The large crystals of $Co_2Fe(CN)_6$ were found also in the micrographs of $K_{0.64}Co_{1.68}Fe(CN)_6$ and $K_{0.78}Co_{1.61}Fe(CN)_6$ indicating that these products are mixtures of two phases, too.

Solubilities of Hexacyanoferrates.—Solubilities of potassium cobalt hexacyanoferrates decreased when the proportion of cobalt increased amongst the exchangeable ions. The solubility of $K_2[CoFe(CN)_6]$ was high, 12%. The value for $K_{1.92}Co_{1.04}Fe(CN)_6$ was 2.0%, that for $K_{1.76}Co_{1.12}Fe(CN)_6$ 0.29%, and those for products (**5**)—(**10**) were 0.12—0.17%.

Thermodynamic Equilibrium Constant for Exchange of Cs^+ *for* K^+ *in* $K_2[CoFe(CN)_6]$.—To obtain better understanding of the ion-exchange equilibrium, the thermodynamic equilibrium constant for exchange of Cs^+ for K^+ in $K_2[CoFe(CN)_6]$ was calculated. The method developed by Gaines and Thomas[15] was applied to the experimental results obtained in the determination of the isotherm.

The thermodynamic equilibrium constant for exchange of Cs^+ for K^+ is expressed as in equation (1) where $\bar{X}_{Cs}$ and $\bar{X}_K$ are

$$K = \frac{\bar{X}_{Cs}X_K}{X_{Cs}\bar{X}_K} \cdot \frac{\bar{f}_{Cs}f_K}{f_{Cs}\bar{f}_K} \quad (1)$$

the equivalent ionic fractions of the corresponding ions in the exchanger phase and X_{Cs} and X_K those in the solution. Since only a part of the exchanger (23%) participates in the exchange process, the isotherm was first normalized so that the maximum

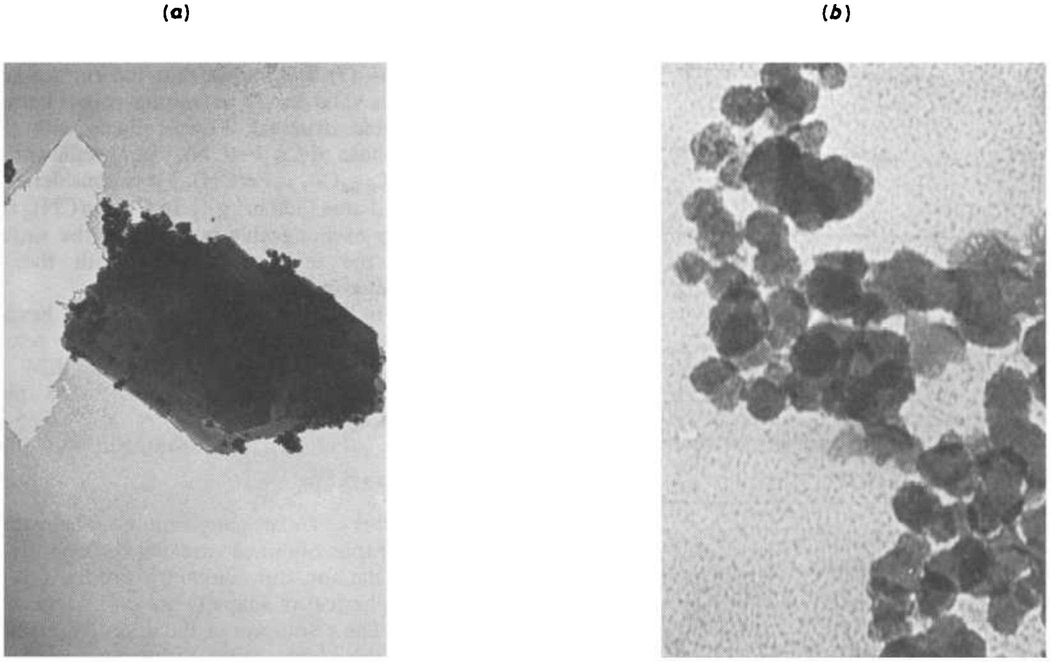


Figure 4. Transmission electron micrographs of $K_{0.58}Co_{1.71}Fe(CN)_6$ (magnification 1.3×10^4) (*a*) and $K_{1.92}Co_{1.04}Fe(CN)_6$ (magnification 1.6×10^5) (*b*)

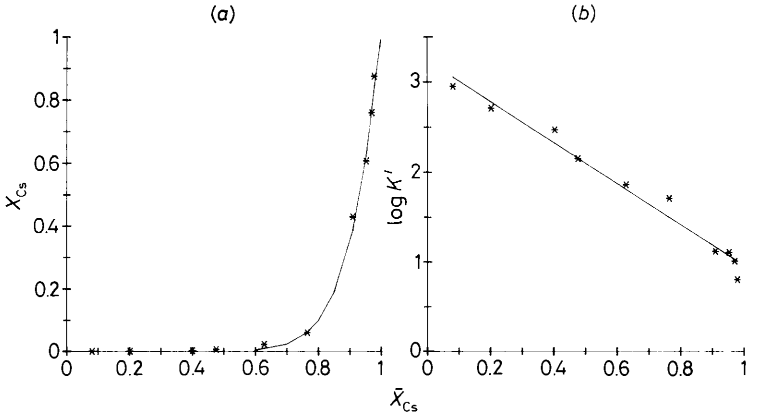


Figure 5. Normalized Cs^+/K^+ exchange isotherm (*a*) and corrected selectivity coefficient, *K'*, for Cs^+ to K^+ exchange in $K_2[CoFe(CN)_6]$ as a function of the degree of exchange ($\bar{X}_{Cs}$) (*b*). Concentration of the CsCl solution 0.01 mol dm^{-3}

uptake of 23% 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 coefficients of the ions in the exchanger cannot be determined directly, and therefore the corrected selectivity coefficient, '*K'* which takes into account only the activity coefficients in the solution, is calculated first [equation (2)]. The ratio of the individual ions f_K/f_{Cs} is equal to

$$K' = \frac{\bar{X}_{Cs} X_K}{X_{Cs} \bar{X}_K} \cdot \frac{f_K}{f_{Cs}} \qquad (2)$$

the ratio f^2_{KCl}/f^2_{CsCl}, where f_{KCl} and f_{CsCl} are the mean molal activity coefficients of KCl and CsCl, respectively; f_{KCl} and f_{CsCl} for the mixed 0.01 mol dm^{-3} KCl—CsCl solution were calculated by the method of Glueckauf.[16] The ratio f^2_{KCl}/f^2_{CsCl} was found to be 1.004 over the entire composition range of the solution.

When the corrected selectivity coefficient is now presented as a function of the degree of exchange ($\bar{X}_{Cs}$) (Figure 5), the thermodynamic equilibrium constant can be obtained by integrating the *K'* curve from $\bar{X}_{Cs} = 0$ to $\bar{X}_{Cs} = 1$. The integration of the *K'* curve in Figure 5 gives a high value of 125, indicating a strong preference for caesium over potassium. The shape of the curve indicates that there is only one type of exchange site in the exchanger.

Our value of the thermodynamic equilibrium constant is somewhat lower than that (166) presented by Ceranic.[9] In both studies log *K'* decreases linearly with increasing $\bar{X}_{Cs}$.

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