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Uptake of Silver by Potassium Cobalt Hexacyanoferrate(II)

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Uptake of Ag^+ ions by potassium cobalt hexacyanoferrate(II), $K_2CoFe(CN)_6 \cdot 1.4H_2O$, was found to occur in a stepwise manner. The maximum uptake value was 4.9 moles per mole of $K_2CoFe(CN)_6$. The solid products formed at the maximum uptake were AgCN, $Ag_4Fe(CN)_6$, $Fe_4[Fe(CN)_6]_3$, and $Fe(OH)_3$, the first one being the dominant product. In addition, the distribution coefficient (K_D) of trace silver (^{110m}Ag) on potassium cobalt hexacyanoferrate(II) was determined as a function of pH and potassium ion concentration. © 1991 Academic Press, Inc.

1. Introduction

Silver metal and different silver compounds are used in many applications. Silver nitrate is extensively used in photography. Silver is a traditional coinage metal and is used in many alloys. Because of the toxicity and price of silver, its recovery from photoprocessing and other industrial waste solutions has environmental and economic aspects. Silver is also present in trace concentration in nuclear waste solutions as ^{108m}Ag and ^{110m}Ag, the removal of which facilitates aging and discharge of these solutions. The methods presently available for recovery of silver are electrolysis, ion exchange, sulfide precipitation, and metallic replacement.

Transition metal hexacyanoferrate(II)s have shown to be effective agents for the separation of silver ions from solutions (*1–4*). These studies claim that the framework of hexacyanoferrate(II)s is decomposed by the uptake of silver ions and a new, less soluble, phase of $Ag_4Fe(CN)_6$ is formed. The possible presence of AgCN in the resulting solid product has been reported as well (*1*). This paper concentrates on the mechanism of the silver uptake process on potassium cobalt hexacyanoferrate(II). This inorganic ion exchanger has shown high selectivity for cesium and is being studied for the separation of ^{137}Cs from nuclear waste solution (*5–9*).

2. Experimental

$K_2CoFe(CN)_6$ was prepared by slowly adding 200 ml of 0.5 *M* $Co(NO_3)_2$ to 200 ml of 0.5 *M* $K_4Fe(CN)_6$ (*8*). The composition (Co, Fe, K) of the product was determined after dissolving a sample in boiling concentrated H_2SO_4 using atomic absorption spectrophotometry (AAS) with a Perkin–Elmer Zeeman 5000. The water content was calculated from the weight loss after drying at 180°C, a sufficient temperature determined

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by thermoanalysis *(10)*. The composition was found to be $K_{1.90}Co_{1.05}Fe(CN)_6 \cdot 1.4H_2O$, which given in the range of experimental error can be considered as pure $K_2CoFe(CN)_6$.

Uptake of silver by $K_2CoFe(CN)_6$ was studied using the following batch technique: 0.08 g samples of $K_2CoFe(CN)_6$ were shaken for 60 hr with 8 ml of 0.01–0.4 *M* $AgNO_3$ solution with ^{110m}Ag tracer ($T_{1/2}$ = 253 days). The solid and the solution were separated by centrifugation using a *G*-value of 25,000, and the pH of the supernatant was measured immediately following the separation. The concentration of silver in the solution was determined by measuring the ^{110m}Ag tracer activity with a NaI crystal and a single channel analyzer. The amounts of potassium, cobalt, and iron ions released into the solution were determined by AAS. The uptake values, as well as the concentrations of the ions in solution, were calculated as moles per mole of dry $K_2CoFe(CN)_6$. All the experiments were performed in polypropylene centrifuge tubes in the dark. The chemicals used were of analytical grade.

Crystal phases of the solid products were identified by the X-ray diffraction patterns of powder samples using a Siemens Kristalloflex 4 diffractometer with monochromatized Cu*Kα* radiation. The samples were washed twice with deionized water and dried at 80°C prior to measurement.

The distribution coefficient (K_D) of trace silver (^{110m}Ag) in deionized water on $K_2CoFe(CN)_6$ was determined as a function of pH, which was adjusted by HNO_3, and as a function of potassium ion concentration in the range of 10^{-5} to 1.0 *M*. The experimental procedure was as described above except for a shaking time of 18 hr. The distribution coefficient is defined as

$$K_D = \left(\frac{A_0}{A} - 1\right) \cdot \frac{V}{m} (\mathrm{ml/g}), \qquad (1)$$

where A_0 and A are the activities of ^{110m}Ag in the solution before and after the uptake reaction, respectively, V is the volume of the solution, and m is the dry mass of the exchanger.

The kinetics of silver uptake by $K_2CoFe(CN)_6$ was also studied using the same batch technique and varying the shaking time between 10 min and 93 h. The $AgNO_3$ solution of 0.2 *M* was used.

3. Results and Discussion

3.1. Silver Uptake by Potassium Cobalt Hexacyanoferrate(II)

As the silver concentration of the batch solution was increased, it was all retained in the solid phase until an uptake level of approximately 4.5 mole per mole of dry $K_2CoFe(CN)_6$ was reached (Fig. 1).

After the first appearance of silver in the supernatant, silver uptake still increased until a value of 4.9 mole/mole at which point no more silver was retained. In some studies the uptake of silver on hexacyanoferrate(II)s has been described as a total conversion to $Ag_4Fe(CN)_6$, which would correspond to an uptake value of 4.0 mole/mole for $K_2CoFe(CN)_6$ *(4)*. To explain the observed "excess" in silver uptake, the concentrations of all the components of the hexacyanoferrate (K, Co, Fe) and the pH were measured along with the increasing uptake level of silver. Several parallel processes were found.

In the first step, up to the uptake value of about 0.38 mole/mole, only potassium ions were observed in the solution. The amount of potassium ions in the solution corresponded closely to the amount of silver taken up. Therefore, this step could be considered as an ion exchange process represented by the following equation:

$$K_2CoFe(CN)_6 + xAg^+ \rightleftarrows K_{2-x}Ag_xCoFe(CN)_6 + xK^+ \qquad (2)$$

The uptake value of 0.38 mole/mole cor-

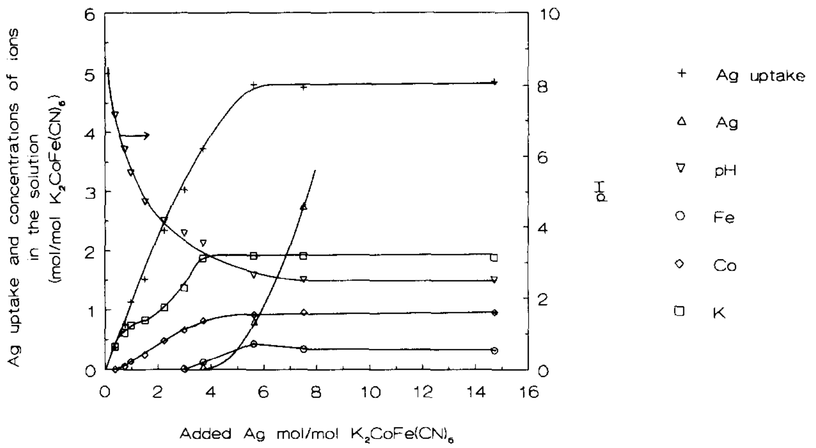

FIG. 1. Silver uptake and concentrations of silver, potassium, cobalt, iron, and hydrogen ions in the solution as a function of Ag^+ amount added to the solution (8 ml) containing a constant amount (0.075 g) of $K_2CoFe(CN)_6$.

responding to the Ag^+/K^+ exchange is identical to the uptake of cesium ions by the same $K_2CoFe(CN)_6$ product. In our previous paper (*8*) it was shown that Cs^+ is exchanged in the surface layer of the hexacyanoferrate(II) crystals. Therefore, it would be reasonable to presume that the Ag^+ ions in the first step are exchanged in the same manner.

The X-ray diffraction pattern (Fig. 2, pattern b) at silver uptake level of 0.38 mole/mole shows that in addition to $K_2CoFe(CN)_6$ (*11*) a new phase has appeared. The most intensive reflections of this phase are at 29.7° and about 24° (a shoulder at the 25.0° reflection of $K_2CoFe(CN)_6$). These reflections fit the patterns of AgCN and $Ag_4Fe(CN)_6$ (*12*). If the uptake of silver at this range is due to the formation of either of these compounds the ion exchange presented in Eq. (2) is questionable.

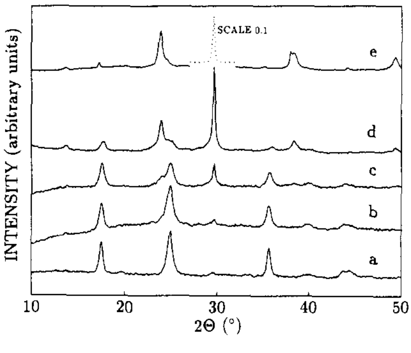

FIG. 2. X-ray powder diffraction patterns of the solid products at increasing uptake of silver on potassium cobalt hexacyanoferrate(II). *a*, original $K_2CoFe(CN)_6$; b, silver uptake 0.38 mol/mol; c, silver uptake 0.73 mol/mol; d, silver uptake 3.0 mol/mol; e, silver uptake 4.9 mol/mol.

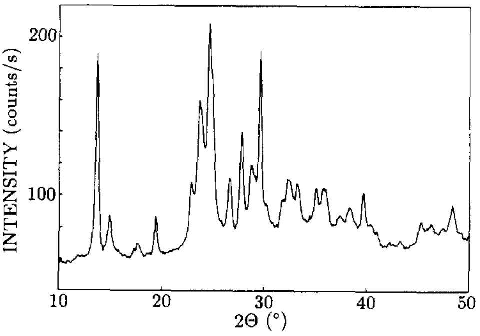

FIG. 3. X-ray powder diffraction pattern of $Ag_4Fe(CN)_6$.

The powder diffraction data for $Ag_4Fe(CN)_6$ is rather limited and therefore we prepared this compound and determined its powder diffraction pattern (Fig. 3). Ag_4

$Fe(CN)_6$ was prepared by the addition of 100 ml of 0.025 *M* $Na_4Fe(CN)_6$ to 100 ml of 0.1 *M* $AgNO_3$. The solution was filtered and the solid was dried at 80°C for 1½ hr. The Ag to Fe ratio in the product was found to be 4 : 1.

It is not clear whether the additional phase in the first step is $Ag_4Fe(CN)_6$ or AgCN, because the two most intensive reflections of both patterns are approximately at the same position. The weak and diffuse reflections at about 14° and 28° in pattern b may indicate that the additional phase is $Ag_4 Fe(CN)_6$. As already mentioned, no cobalt or iron was found in the solution at this silver uptake range. The pH was so high, above seven, that if any $Ag_4Fe(CN)_6$ or AgCN was formed the free cobalt and iron thus formed would have been precipitated as hydroxides.

Taking into account both the concentrations of the ions in the solution and the X-ray diffraction patterns of the solid products, a reasonable conclusion for the first step of silver uptake (up to 0.38 mole/mole) is that the main process is the ion exchange between silver and potassium ions and the major products at this uptake level are $K_{2-x}Ag_x CoFe(CN)_6$ and $K_2CoFe(CN)_6$. At the same time the original hexacyanoferrate structure begins to decompose, resulting in the formation of the minor products of $Ag_4 Fe(CN)_6$ and $Co(OH)_2$.

The contradictions between the concentration measurements and the X-ray diffraction patterns may be due to the effects of washing and drying of the solid products prior to measurement. These procedures may change the nature of the solid products.

In the second step, up to a silver uptake about 4.2 mole/mole, the original compound $K_2CoFe(CN)_6$ is totally decomposed. The concentrations of potassium and cobalt in the solution leveled off at the identical values as they are present in $K_2CoFe(CN)_6$, which also eliminate $KAg(CN)_2$ and $KAg_3 Fe(CN)_6$ as possible candidates for solid products of the uptake reaction. At this uptake range free cobalt is not precipitated as $Co(OH)_2$ because the pH is below seven. The X-ray diffraction patterns also indicate total decomposition of $K_2CoFe(CN)_6$: in pattern d (representing silver uptake of 3.0 mole/mole the reflections of $K_2CoFe(CN)_6$ can still be seen, but in pattern e (representing silver uptake of 4.9 mole/mole) they are absent.

Above a silver uptake of about 2.8 mole/mole, iron was also found in the solution; its concentration leveled off at 0.35 mole/mole at a silver uptake of 4.9 mole/mole. It is improbable that free hexacyanoferrate ions would be present in the solution, and therefore it is assumed that a part of hexacyanoferrate(II) ions are decomposed: silver strips CN ligands from iron and forms AgCN. According to X-ray diffraction patterns, the formation of AgCN begins before the first appearance of iron ions in the solution. The 29.8° reflection is the strongest in pattern d, a feature that is characteristic of AgCN. It is probable that AgCN is formed also below the silver uptake value of 2.8 mole/mole, but the forming free iron is precipitated as hydroxide.

The presence of $Ag_4Fe(CN)_6$ is rather difficult to judge, because its most intensive reflections (24.6° and 29.6°) overlap with those of AgCN and $K_2CoFe(CN)_6$. In all the patterns b to e its presence looks probable though, because of a weak and diffuse reflection at about 13.8° (best seen in pattern d). In pattern e there is also a shoulder at 24.6° in the 24.1° reflection of AgCN.

As a conclusion from the second step of silver uptake, we can say that the original $K_2CoFe(CN)_6$ decomposes totally and the solid products formed are AgCN, $Ag_4 Fe(CN)_6$, and $Fe(OH)_3$, the proportion of AgCN increasing along with the increasing uptake level of silver.

In the third step free silver is present in the solution when the silver uptake is above 4.5 mole/mole and no more uptake occurs above 4.9 mole/mole. Above this maximum uptake value the concentrations of iron, cobalt, and potassium, as well as the pH, have constant values. According to the X-ray diffraction patterns AgCN dominates among the solid products. In addition to the solid products already mentioned, AgCN, $Ag_4Fe(CN)_6$, and $Fe(OH)_3$, $Fe_4[Fe(CN)_6]_3$ was also detected. Its most intensive reflections can be seen at 17.5° and 35.2°.

The valence of iron in the solution is assumed to be +3 because the pH of the solution was 2.5. Hydrolyzation of Fe^{3+} to $Fe(OH)^{2+}$ brings H^+ ions into solution. The stability constant for the reaction $Fe^{3+} + H_2O \leftrightharpoons Fe(OH)^{2+} + H^+$ is 6.7×10^{-3}. For simplification it was assumed that $[Fe(OH)^{2+}] = [H^+]$. For a solution with an iron concentration of 0.0092 mol/liter (corresponding to the iron plateau value in Fig. 1), the pH would be 2.3. This is very close to the observed value. The observed pH being somewhat higher than that required for $Fe(OH)_3$ to precipitate, the solid was analyzed for the presence of iron in that form. A solid product sample from the plateau range was leached with 0.1 *M* HNO_3 and the leachant was measured for iron and silver by AAS. The product was prepared by contacting 25 ml of 0.2 *M* $AgNO_3$ solution with 0.234 g of $K_2CoFe(CN)_6$. Silver uptake in this case was 4.8 mole/mole and the iron concentration in the solution was 0.34 mole/mole. The solid weighed 0.461 g after drying at 80°C. This sample was shaken for 16 hr with 46 ml of 0.1 *M* HNO_3 and then separated by centrifugation. No silver was found in the leachant, indicating that iron in the leachant did not originate from $Ag_4Fe(CN)_6$. The amount of iron in the leachant was 0.0333 mmole, which is assumed to originate from $Fe(OH)_3$. As a conclusion from these analyzes, we can say that after contacting a mole of $K_2CoFe(CN)_6$ with $AgNO_3$, in amounts sufficient to reach the plateau values in Fig. 1, 0.34 mole of iron can be found in the solution, 0.05 mole in the solid phase as $Fe(OH)_3$, and the rest, 0.61 mole, in the solid phase as $Ag_4Fe(CN)_6$ and $Fe[Fe(CN)_6]_3$. These values are meant to give only approximate proportions of the above-mentioned products.

The pH of deionized water contacted with potassium cobalt hexacyanoferrate in the solution volume to exchanger weight ratio of 100 rises from 6.0 to 9.1, which is due to the hydrolyzation of the exchanger [Eq. (3)]. Calculation from the pH difference shows that only a very minor part, 0.02%, of the exchanger is converted to the hydrolyzed form, $H_2CoFe(CN)_6$. Ignorance of the hydrolyzation does not introduce any significant error to our conclusions and calculations. The pH of the $AgNO_3$ solutions was between 6.0 (0.01 *M*) and 5.2 (0.4 *M*). In these solutions the hydrolyzation is obviously even lower than in the case of deionized water.

Before reaching the plateau value of 2.5, pH decreases slowly from 9 (Fig. 1). Before the appearance of iron in the solution, this decrease in pH is most probably caused by the precipitation of $Fe(OH)_3$ and the lower hydrolyzibilities of $Ag_4Fe(CN)_6$, AgCN, and $Fe_4[Fe(CN)_6]_3$ compared to $K_2CoFe(CN)_6$.

The oxidation of iron to the +3 state would suggest a respective reduction of silver to metal. If, however, all the Fe^{+3} ions formed caused the formation of a corresponding amount of Ag, 9 mg of silver would have been deposited in each 8-ml trial. This would have been seen as a clearly visible mirror on the vial walls, which was not observed. A minor part of the silver may have been deposited as metallic silver though the experiments were performed in the dark. In the X-ray diffraction patterns only in pattern e were reflections of silver seen at 38.1° and 44.3°. What caused the iron to oxidize is not known.

Wald *et al.* (*4*) concluded from their silver uptake value of 4.0 mole/mole on a nonstoichiometric potassium cobalt hexacyanoferrate(II) product with an approximate formula of $K_{1.5}Co_{1.25}Fe(CN)_6$ (calculated by us), that all the hexacyanoferrate had turned into $Ag_4Fe(CN)_6$. The reaction time in their experiments was only 1 hr, which may have not been long enough for the formation of AgCN. However, as can be seen from our kinetic studies (see 3.2) the formation of $Ag_4Fe(CN)_6$ and its transformation into AgCN occur in parallel. Therefore, a part of the silver taken up in the experiment of Wald *et al.* may have been in the form of AgCN, but no phase analysis was performed. As a whole, their results are in good agreement with ours.

Tananaev and Levina (*3*) found that cobalt ions start to release first from $K_4Co_{10}[Fe(CN)_6]_6$. In our experiments the reverse was found: potassium ions were released first. Their product, $K_{0.67}Co_{1.67}Fe(CN)_6$, was probably a mixture of two phases: cubic $K_{2-x}Co_{x/2}[CoFe(CN)_6]$ and tetragonal $Co_2Fe(CN)_6$ (*8*). Most probably the latter product is more readily transformable to a silver compound. Tananaev and Levina also reported that from another product $K_{12}Co_8[Fe(CN)_6]_7$ (which can be represented also as the following formula $K_{1.71}Co_{1.14}Fe(CN)_6$), where the potassium to cobalt ratio is much higher, "cobalt is displaced by silver with greater difficulty" than from $K_{0.67}Co_{1.67}Fe(CN)_6$. This product should be a single phase nonstoichiometric compound with a cubic lattice (*8*). From this product the release of cobalt and potassium ions from the crystal surfaces occurs equally.

A study with very similar results to ours was reported by Loos-Neskovic and Federoff (*1*). They studied the uptake of silver on several hexacyanoferrate(II)s, one of which, $Na_{2x}Ni_{2-x}Fe(CN)_6 \cdot xH_2O$, is a compound very similar to our product. They also reported on the excess of silver uptake compared to the sole formation of $Ag_4Fe(CN)_6$ and assumed this to be caused by the formation of AgCN. No relative proportions of the two compounds were given.

3.2. Kinetics of Silver Uptake on Potassium Cobalt Hexacyanoferrate(II)

The kinetics of silver uptake is rather fast in its first step (Fig. 4). This step requires only less than 10 min to occur. The following steps, formation of $Ag_4Fe(CN)_6$, AgCN, and $Fe_4[Fe(CN)_6]_3$, are much slower. Total destruction of $K_2CoFe(CN)_6$ requires more than 20 hr. The uptake experiments described in 3.1. were carried out using 60 hr equilibration time. As seen from Fig. 2, at 93 hr the uptake

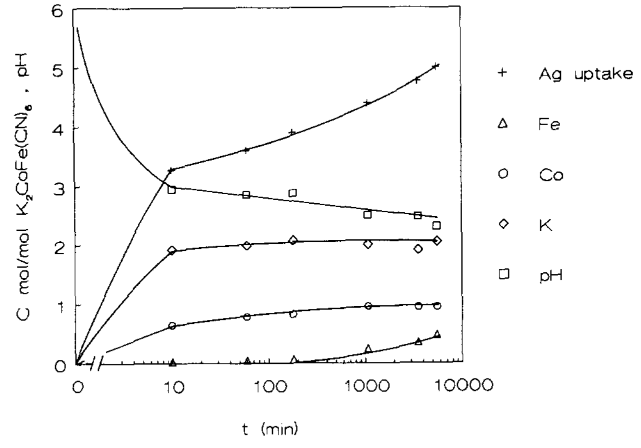

FIG. 4. Uptake of silver on potassium cobalt hexacyanoferrate(II) and concentrations of potassium, iron, cobalt, and hydrogen ions in the solution as a function of time. Initial concentration of silver in the solution, 0.2 *M*.

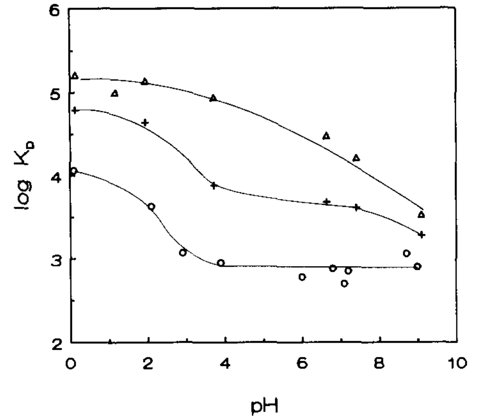

FIG. 5. Distribution coefficient (K_D) of ^{110m}Ag on potassium cobalt hexacyanoferrate(II) as a function of pH. Centrifugal forces (*G*-values) and centrifugation times used for the separation of the exchanger from the solution: △, 63,000 G, 1 hr; +, 25,000 G, 1 hr; ○, 11,000 G, 0.5 hr. Solution volume 8 ml, exchanger weight 0.08 g.

has still increased (5.0 mole/mole), pH has decreased to 2.3, and the iron concentration increased to 0.47 mole/mole. This means that a larger amount of AgCN has formed. The low pH of 2.3 prevents iron from precipitating as $Fe(OH)_3$. It is probable that still longer reaction times give AgCN as the only solid product (corresponding to the silver uptake of 6 mole/mole).

Loos-Neskovic and Fedoroff treated the kinetics of silver uptake by $Na_{2x}Ni_{2-x}Fe(CN)_6$ in terms of ion exchange (*1*). None of the theoretical models experimented fitted the observed results. This is obvious because, if ion exchange of silver for potassium is responsible for the uptake process, it is limited only to very low uptake levels.

3.3. Distribution Coefficient of ^{110m}Ag on Potassium Cobalt Hexacyanoferrate(II) as a Function of pH

$K_2CoFe(CN)_6$ is a possible candidate for the separation of silver from solutions. As said earlier, ion exchange of silver for potassium is a possible mechanism for silver uptake at low levels. Therefore, uptake of trace silver (^{110m}Ag) on $K_2CoFe(CN)_6$ is treated below in terms of ion exchange.

The distribution coefficient (K_D) of trace silver (^{110m}Ag) on potassium cobalt hexacyanoferrate is rather high, about 10^5, in the acidic region, and goes slowly down below 10^4 in the alkaline region (Fig. 5). The value of the K_D was highly dependent on the centrifugal force used for the separation of the exchanger from the solution. At lower centrifugal forces the K_D value was lower by 1–2 orders of magnitude. This indicates that the exchanger is partly peptized.

3.4. Distribution Coefficient of ^{110m}Ag on Potassium Cobalt Hexacyanoferrate(II) as a Function of Potassium Ion Concentration

The distribution coefficient (K_D) of ^{110}Ag on potassium cobalt hexacyanoferrate is constant, about 4000, in the potassium ion concentration region of 10^{-5}–10^{-2} mol/liter (Fig. 6). At higher concentrations the K_D

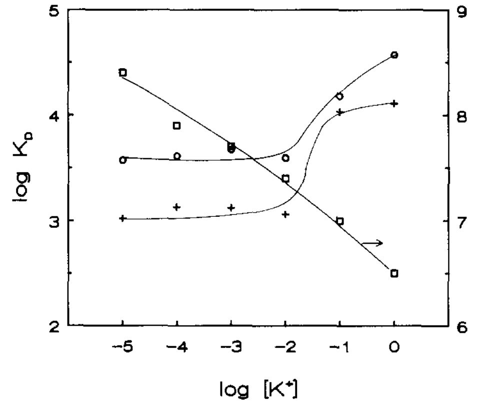

FIG. 6. Distribution coefficient (K_D) of ^{110m}Ag on potassium cobalt hexacyanoferrate(II) as a function of potassium ion concentration. Centrifugal forces (*G*-values) and centrifugation times used for the separation of the exchanger from the solution: ○, 25,000 G, 1 hr; +, 11,000 G, 0.5 hr; □, pH. Solution volume 8 ml, exchanger weight 0.08 g.

increases by a factor of about 10, which is in contradiction if ion exchange is the mechanism responsible for the uptake process. The probable explanation for this contradictory phenomenon is decreasing solubility and/or peptization of the exchanger along with increasing potassium ion concentration. At lower centrifugal forces used for the separation of the exchanger from the solution the value of the K_D was considerably lower. This phenomenon indicates that the exchanger is rather readily peptizable. At higher centrifugal forces the peptized exchanger can be removed from the solution. Higher potassium concentration (> 0.01 mol/liter) partly prevents the peptization. When increasing the potassium concentration in the solution the pH of the solution decreases from 8.4 to 6.5. This is as expected because higher potassium concentrations prevent the hydrolyzation of the exchanger as shown in Eq. (3),

$$K_2CoFe(CN)_6 + 2H_2O \rightleftarrows H_2CoFe(CN)_6 + 2OH^- + 2K^+ \quad (3)$$

The limited solubility of potassium nitrate did not enable experiments at still higher potassium concentrations. It looks obvious that the K_D begins to decrease at a certain potassium concentration above 1.0 mol/liter because increasing the potassium concentration should force the equilibrium to left side in Eq. (4):

$$K_2CoFe(CN)_6 + 2Ag^+ \rightleftarrows Ag_2CoFe(CN)_6 + 2K^+ \quad (4)$$

This is of course valid only if a real ion exchange reaction takes place.

Acknowledgments

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