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Preparation and Ion-exchange Behavior of Potassium Zinc Ferrocyanide

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Since the early work of Miller[1] in 1896, a number of compounds containing potassium, zinc and ferrocyanide have been prepared and their compositions investigated mainly for the study of volumetric determination of zinc ion or of ferrocyanide ion.[2-7] During the past few years, considerable interest has been shown in the ion-exchange property of zinc ferrocyanide.[8-12]

In an attempt to elucidate this property of the ferrocyanides, the authors tried to prepare zinc ferrocyanide $Zn_2Fe(CN)_6$, according to the procedure described by Kohn.[13] The resulting product was found to be potassium zinc ferrocyanide $K_2Zn_3[Fe(CN)_6]_2$, but not zinc ferrocyanide. This paper describes some ion-exchange properties and X-ray diffraction data concerning potassium zinc ferrocyanide and zinc ferrocyanide.

Experimental

Preparation by the Kohn Method.[13] Into 300 m*l* of 0.1 M $K_3Fe(CN)_6$, 630 m*l* of 0.1 M $ZnSO_4$, 180 m*l* of 15% sodium acetate and 300 m*l* of 3% hydrogen peroxide were added little by little in this order. On continuous stirring, the slurry was heated on a boiling water bath until its color changed from yellow to white. It was then poured into cold water, tenfold in volume of the slurry, allowed to stand for 24 hr, filtered, washed thoroughly and dried at 60°C for 24 hr.

Zinc Ferrocyanide.[10,11] Zinc ferrocyanide was prepared by mixing 300 m*l* of 0.1 M $Na_4Fe(CN)_6$, and 900 m*l* of 0.1 M $Zn(NO_3)_2$. The white slurry was obtained by dropping the solutions little by little simultaneously into a beaker for 30 min under stirring. It was heated with stirring on a boiling water bath for 2 hr, allowed to stand for 24 hr, filtered, washed thoroughly and dried at 60°C for 24 hr. The ferrocyanides thus prepared were compressed into pills under a pressure of about 300 kg/cm^2, allowed to break down in water for several days, air dried, and sieved into 200—300 mesh.

Analyses. The ferrocyanides were dissolved with a minimum amount of 0.1 M EDTA-ammonium solution, followed by dilution with water to a given volume, to be subjected to the determination of potassium, zinc and ferrocyanide. Zinc and ferrocyanide were determined by volumetric analysis, and potassium by atomic absorption spectroscopy.

Distribution Coefficient. Distribution coefficients (m*l*/g) for cesium were determined by equilibrating 0.1 g of the ferrocyanides with 5 m*l* of NH_4NO_3 solutions (3×10^{-2}—3.5 M) containing 5×10^{-2} mmol of $CsNO_3$ tagged with ^{137}Cs, followed by centrifugation at 1000 g for 15 min. The radioactivity of the supernatant was measured by a well type scintillation counter.

Results and Discussion

The product prepared by the Kohn method[13] was analyzed, the result of which is shown in Table 1. The stoichiometrical composition is best represented by $K_2Zn_3[Fe(CN)_6]_2$. The same compound can be prepared by adding 0.1 M potassium ferrocyanide to 0.1 M zinc nitrate in the mole proportion of 1 : 1.5, followed by the same treatment as with zinc ferrocyanide. Adsorption rates of cesium ion on potassium zinc ferrocyanide and zinc ferrocyanide[10,11] were determined. Figure 1

TABLE 1. ANALYTICAL RESULTS OF THE PRODUCT OBTAINED BY THE KOHN METHOD

Percent			Ratio			Composition
K	Zn	$Fe(CN)_6$	K	Zn	$Fe(CN)_6$	
8.5	21.5	46.4	2.0	3.0	2	$K_2Zn_3[Fe(CN)_6]_2$

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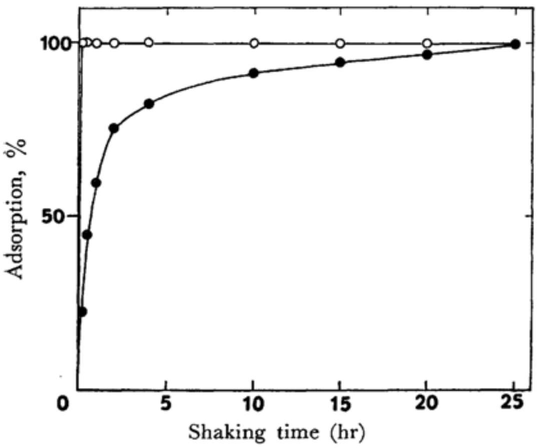

Fig. 1. Relative adsorption rate for Cs on $K_2Zn_3[Fe(CN)_6]_2$ and $Zn_2Fe(CN)_6$.
-○- $K_2Zn_3[Fe(CN)_6]_2$ -●- $Zn_2Fe(CN)_6$
Adsorbed percent was determined by shaking 0.1 g of adsorbents with 5 m*l* of 0.01 M $CsNO_3$ tagged with ^{137}Cs.

TABLE 2. X-RAY DIFFRACTION DATA

Potassium zinc ferrocyanide		Zinc ferrocyanide	
d(Å)	I/I_0	*d*(Å)	I/I_0
6.49	0.10		
6.33	0.09		
5.45	0.79		
4.52	0.43	4.33	0.85
4.09	1.00		
3.79	0.08	3.80	1.00
3.69	0.22		
3.63	0.40		
3.43	0.13	3.29	0.19
3.14	0.09	3.16	0.08
3.10	0.31		
2.99	0.13	2.86	0.33
2.71	0.15		
2.68	0.09	2.64	0.21
2.54	0.12		
2.52	0.14	2.29	0.41

X-ray powder patterns were taken on an apparatus from Rigaku Denki Co., Ltd., Tokyo, Japan, using filtered CuK_α radiation (1.5418Å).

shows that the adsorption rate of potassium zinc ferrocyanide is significantly higher than that of zinc ferrocyanide.

Comparison of these ferrocyanides was made by means of X-ray diffraction. Table 2 shows that the X-ray diffraction patterns of potassium zinc ferrocyanide are quite different from those of zinc ferrocyanide. The discrepancy of X-ray data, *viz.*, the difference in crystal structure, may be comparable to the difference of the adsorption rate.

Ion-exchange behaviors of both ferrocyanides were studied in ammonium nitrate solutions. The relations of the log K_d *versus* log$[NH_4]$ showed a straight line of slope -1. Further experiments showed that, in the batch equilibration in the concentration <0.01 M Cs, potassium ions in the potassium zinc ferrocyanide are equivalently replaced by the adsorption of cesium ion in the external solution and zinc ions in the zinc ferrocyanide by the adsorption of cesium ion in the external solution. Therefore, the precipitation mechanism reported by Veseleý and Pekárek[14] was not observed in either ferrocyanide.

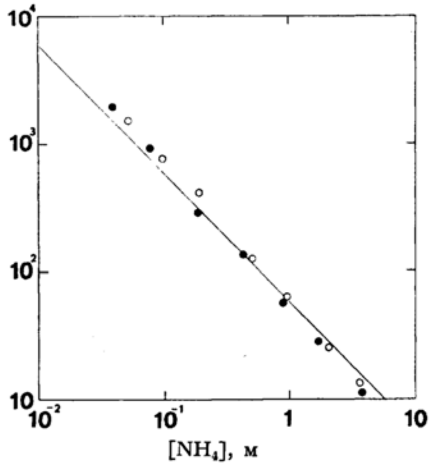

Fig. 2. Relationship between distribution coefficient for Cs and ammonium ion concentration.
-●- $Zn_2Fe(CN)_6$ -○- $Na_2Zn_3[Fe(CN)_6]_2$

These results indicate that the reaction is an ion-exchange ruled by the mass action law. The ferrocyanides were unfavorable for column work, since both were relatively fine powder and broken down slightly in aqueous suspension. However, the powdery characters were suitable as an adsorbent in thin layer chromatography. Potassium zinc ferrocyanide could advantageously be applied to a rapid separation of sodium, potassium, rubidium and cesium by thin layer chromatography.[12] This might be attributed to its rapid adsorption rate.