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Some Observations on Ion Exchange Properties of Crystalline Zirconium Phosphate

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Many synthetic inorganic ion exchangers have been studied because of the fact that they are more stable than organic exchangers under certain conditions, *e.g.* high temperature or the presence of ionizing radiation.[1] Most attentions have been given to zirconium phosphates, gelatious and crystalline, and relation between the structure of the crystalline zirconium phosphate and the mechanism of ion exchange also has been discussed. However, the observations differed among investigators.[2-7] Present study was initiated in order to prepare crystalline zirconium phosphate (c-ZP) which has a constant chemical composition and gives reproducible results of ion exchange experiments, and to apply the product to the separation of alkali metals. Distribution coefficients and pH-titration curves of c-ZP for alkali metal ions were measured and it was found that ion exchange on c-ZP for rubidium and cesium was not ideal when the concentration of metal ions was 1×10^{-3} N.

Experimental

Reagents and Preparation of Crystalline Zirconium Phosphate. The preparation method of c-ZP reported by Clearfield and Stynes[3] has been modified in some points. All reagents used were of reagent grade and not purified further. Details of the preparation procedure are as follows: 100 m*l* of 18 v/v% phosphoric acid and 10 v/v% sulfuric acid solution was added slowly to 100 m*l* of well-stirred 10 v/v sulfuric acid solution of zirconyl chloride octahydrate at 70°C. After standing for two days, the gelatinous suspension was centrifuged and the resulting solid was washed several times with 2% phosphoric acid until free from sulfate ions and then with distilled water. It was dried in air at 110°C. The dried product was suspended in 6.7 M phosphoric acid and refluxed for 120 hr. After refluxing, the solution was stood for another 24 hr, then the precipitate was filtered and washed with 2% phosphoric acid and then with distilled water until free from phosphate ions. It was dried in air at 50°C and microcrystalline zirconium phosphate (c-ZP) was obtained. The dried micro-crystals were made into tablets under pressure of 400 kg/cm² and sieved to grain size of 100—200 mesh. This final product was used for further experiments. X-Ray powder patterns and optical microscopic observation showed that the solids obtained have a good crystallinity. The powder patterns were obtained with nickel filtered copper X-Ray using a Geigerflex (Rigaku Denki Co., Ltd.).

Distribution Coefficients. Batch distribution coefficients were measured at 25°C by equilibrating

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[1] C. B. Amphlett, "Inorganic Ion Exchangers," Elsevier, Amsterdam (1964).

[2] C. B. Amphlett, L. A. McDonald and M. J. Redman, *J. Inorg. Nucl. Chem.*, **6**, 220 (1958).

[3] A. Clearfield and J. A. Stynes, *ibid.*, **26**, 117 (1964).

[4] G. H. Nancollas and V. Pekárek, *ibid.*, **27**, 1409 (1965).

[5] J. Albertsson, *Acta Chem. Scand.*, **20**, 1679 (1966).

[6] A. Clearfield and G. D. Smith, *J. Colloid Interfac. Sci.*, **28**, 325 (1968).

[7] A. Clearfield, R. H. Blessing and J. A. Stynes, *J. Inorg. Nucl. Chem.*, **30**, 2249 (1968).

weighed amounts of c-ZP with a known volume of suitable solutions, followed by analysis of the supernatant. The ratio of solution to solid was usually 100 m*l*/g.

For all alkali metal concentrations studied, the exchange reaction attained to equilibrium within 6 hr. Determination of the batch equilibrium coefficients has been made after reaction mixtures were shaken for at least 24 hr.

Analytical methods employed included the use of radioisotopes such as ^{22}Na, ^{86}Rb and ^{137}Cs as tracers. Measurement of radioactivity was taken on a well-type NaI(Tl) scintillation counter. Flame photometry was used for the determination of potassium.

pH-Titration Curves. 0.5 g of c-ZP was equilibrated with 50 m*l* of a solution containing the appropriate metal chloride and metal hydroxide, the total metal concentration being 0.1 N. pH of the sample solution was measured on a HM-5A pH-meter (Toa Electronics Ltd.). Throughout the measurement the sample was maintained at 25°C in a thermostat and bubbled with nitrogen gas to remove CO_2 gas.

Results and Discussion

X-Ray diffraction powder patterns are given in Table 1. The d values agreed with those reported by Clearfield and Stynes.,[3] though details differ from them. If the c-ZP was dried over P_2O_5 for two months it changed crystalline to amorphous. Hence the drying conditions, temperature and desiccants have to be selected carefully. Distribution coefficients K_d (mequiv/g of exchanger ÷ mequiv/m*l* solution at equilibrium) for alkali metal ions in neutral solutions on the hydrogen form of c-ZP are shown in Table 2. The K_d values for c-ZP are lower than those for gelatinous zirconium phosphate,[2] but the affinity series is identical *i.e.*, $Na^+ < K^+ < Rb^+ < Cs^+$.

When values of Kd for alkali metal ions as a funtion of acidity are plotted in the form log K_d

Table 1. X-Ray powder patterns of crystalline zirconium phosphate

d	I/I_0	*d*	I/I_0
7.69	57	2.00	
4.51	34	1.89	5
4.47	18	1.88	
4.08		1.87	
3.59	100	1.83	
3.56	50	1.79	5
3.31		1.77	5
3.23	6	1.73	
3.09		1.72	
2.65	23	1.70	
2.64	22	1.66	5
2.49		1.65	5
2.42	9	1.64	
2.36		1.61	
2.20		1.60	
2.19		1.54	
2.16		1.53	
2.12		1.51	
2.05	9	1.47	
2.02			

I/I_0 values not given in the table indicate that they are less than 5%.

Table 2. Distribution coefficients (K_d values)

$[M^+]$	Na^+	K^+	Rb^+	Cs^+
1×10^{-3}	9 200	— —	170 —	260 8000
1×10^{-2}	1 36	3 84	11 182	12 200
1×10^{-1}	0 6	— —	— —	0 12

In each concentration row, upper values are Kd's for c-ZP and lower ones for gelatinous ZP.[2]

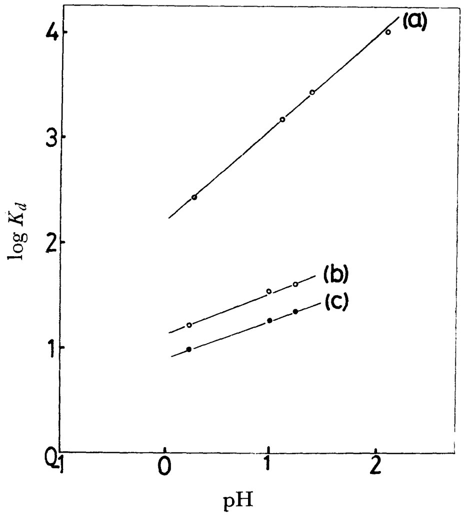

Fig. 1. log K_d *vs.* pH plots.
(a) Cs^+ 1×10^{-5} N
(b) Cs^+ 1×10^{-3} N
(c) Rb 1×10^{-3} N

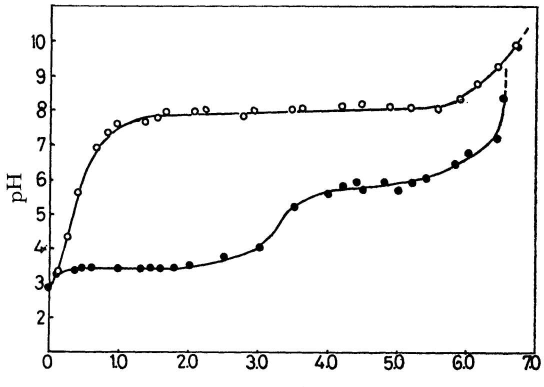

Fig. 2. pH titration curves.
○ Cs^+ ● Na^+

vs. pH, straight lines were obtained (Fig. 1). If ion exchange takes place ideally according to the reaction,

$$H^+\cdot X^- + M^+ \rightleftharpoons M^+\cdot X^- + H^+,$$

they must show the slope of unity since only univalent cations are involved in ion exchange. The slopes of lines observed were 0.47 for Rb^+ and Cs^+ when $[M^+]=10^{-3}$ N, and 0.94 for Cs^+ when $[M^+]=10^{-5}$ N, respectively. It is apparent that ion exchange on c-ZP is not ideal when $[M^+]$ is 1×10^{-3} N, though it has been reported that ion exchange on gelatinous zirconium phosphate is ideal.[2] The reason why c-ZP and gelatinous zirconium phosphate exhibit the different behaviour may be substantially the structural change of c-ZP during ion exchange. As sodium ion is not exchanged in acid solution, the pH-Kd plot and the ideality of ion exchange can not be discussed for this ion. The pH-titration curves of c-ZP showed that, for sodium ion, hydrogen atoms in c-ZP matrix behave bifunctionally, whereas, for cesium, they appear to behave monofunctionally. The results agreed with those of Albertsson.[5]

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