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Temperature dependence of distribution coefficients of some cations on a crystalline zirconium phosphate over the range 25 to 80 °C

Many synthetic inorganic ion exchangers have been studied because they show greater resistance to heat and ionizing radiation and higher selectivities for alkali metal ions than organic ion exchangers, and most attention has been given to zirconium phosphate.

Recently, crystalline zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZP), was prepared and its ion-exchange characteristics were investigated. This ion exchanger is considered to be useful as it has a known and reproducible composition and less tendency towards hydrolysis compared with amorphous zirconium phosphate.

Distribution coefficients, K_d, for several cations were determined at 20° by ALBERTSSON[1] and at 25° by HASEGAWA AND TOMITA[2,3]. The values depend upon the load of the exchanger and therefore upon the concentrations of cations in the contacted solution.

Another factor that contributes to the values of distribution coefficients in practice seems to be temperature. As experimental results on this aspect are very scarce, an attempt was made to determine the temperature dependence of distribution coefficients on α-ZP over the range 25 to 80°.

Experimental

Crystalline zirconium phosphate was prepared and treated as reported previously[2,3], and identified by means of X-ray powder diffraction.

Distribution coefficients, K_d. Mass distribution coefficients were measured for Na^+, K^+, Cs^+, Ca^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+} and Ce^{3+} by a batch method at 35, 50, 65 and 80°. Weighed amounts (m) of α-ZP were equilibrated with metal chloride solutions of known volume (v), v/m being 100 ml/g. The initial concentrations of metal ions were chosen to be $1 \cdot 10^{-3}$ N in all instances. No acid or base was added to each solution to adjust the hydrogen ion concentration. For all ions studied, the exchange reaction attained equilibrium within 24 h. Determinations were therefore made after the reaction mixtures had been shaken for about 24 h in a thermostat regulated at the desired temperature.

After shaking, the mixture was centrifuged and the resulting supernatant was analyzed for metal ions. Most analyses included the use of radioisotopes such as ^{22}Na, ^{137}Cs, ^{133}Ba, ^{65}Zn, ^{60}Co and ^{144}Ce as tracers. Radioactivities were measured with a well-type NaI(Tl) scintillation counter. Flame photometry was used for the determination of potassium and atomic-absorption spectrometry for calcium.

Usually, three runs were carried out for an ion at a particular temperature. The agreement of obtained K_d values was reasonable and mean values were taken.

Results and discussion

The temperature dependences of K_d values for various cations are shown in Figs. 1, 2 and 3, numerical values of K_d being given in Table I.

TABLE I

DISTRIBUTION COEFFICIENTS, K_d (ml/g), AT VARIOUS TEMPERATURES

Ion	*Temperature (°C)*				
	25[a]	*35*	*50*	*65*	*80*
Na^+	9	10.3	6.4	3.5	2.2
K^+	94	82	83	64	62
Cs^+	260	324	301	317	233
Ca^{2+}	190	305	326	281	251
Ba^{2+}	280	320	361	266	253 (71°)
Co^{2+}	230	263	311	314	369
Zn^{2+}	340	368	406	359	370
Ce^{3+}	$3.6\cdot10^4$	$5.5\cdot10^4$	$6.1\cdot10^4$	$3.0\cdot10^5$	$3.4\cdot10^5$

[a] Results given by HASEGAWA AND TOMITA[2,3].

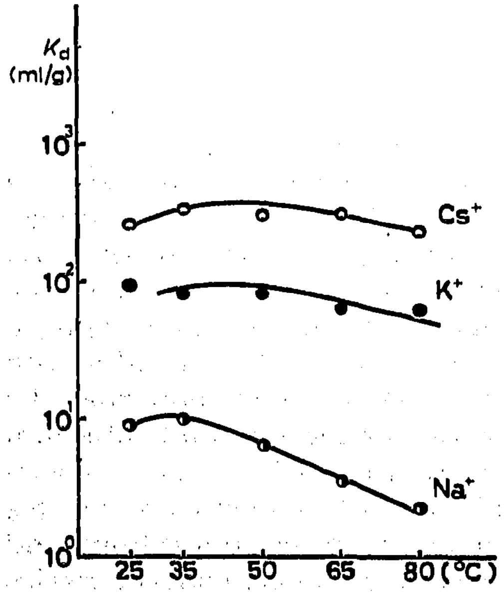

Fig. 1. Temperature dependence of K_d values for alkali metal ions.

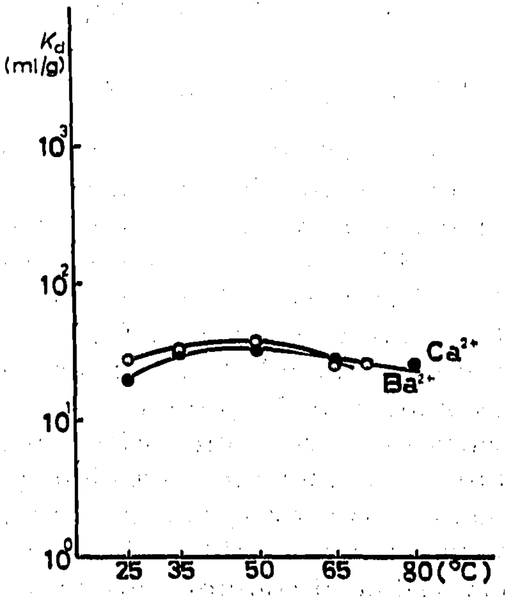

Fig. 2. Temperature dependence of K_d values for alkaline earth metal ions.

The behaviour of sodium, potassium and caesium ions is similar to each other, *i.e.*, the K_d values decrease gradually with increasing temperature (Fig. 1). Values at 25° were taken from refs. 2 and 3, in which an α-ZP preparation of a different batch had been used*.

For calcium and barium, the K_d values become closer to each other as the temperature increases, although it is not clear whether selectivity reversal takes place within the temperature range studied (Fig. 2). One of the salient features of the K_d *vs.* temperature curves for these cations is the existence of a maximum at about 50°

With cobaltous ions, there seems to be a slight increase in the K_d values with increasing temperature (Fig. 3). Zinc ions behave similarly, but in this case the K_d

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* There are small differences in K_d values between crystalline ion exchangers of differen batches owing to differences in the degree of crystallinity.

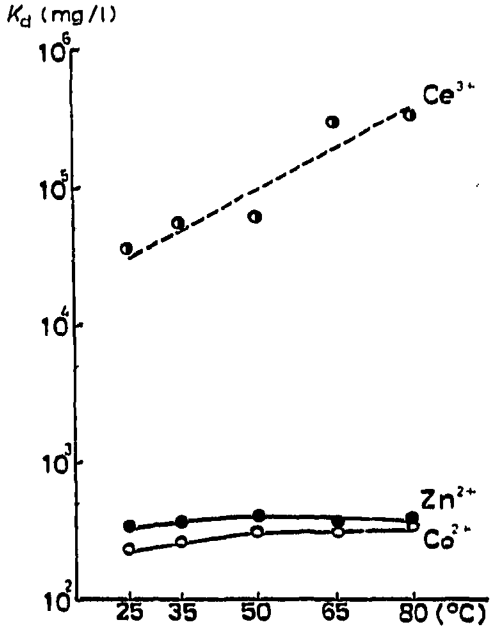

Fig. 3. Temperature dependence of K_d values for some transition metal ions.

values remain almost constant over the range 50 to 80°. However, zinc ions show a higher affinity for the exchanger than cobalt ions over the whole temperature range.

The affinity of cerous ions apparently increases with increasing temperature. For "semi-crystalline" zirconium phosphate, BAETSLÉ[4] has pointed out that the temperature coefficient for the rare earth ion exchanges is of the opposite sign to those for the alkali metals and alkaline earths. This is verified for the crystalline ion exchanger in the present study. On the other hand, BAETSLÉ's results show that the variation of K_d values with temperature is very important for caesium and rubidium but is small for rare earth ions (tracer concentrations were used in BAETSLÉ's experiments). However, the present results show that influence of temperature on K_d values is remarkable only for cerium. The basic difference between amorphous and crystalline zirconium phosphate is that the latter possesses ion-sieving characteristics towards caesium and rubidium ions. Hence the sorption of these ions on α-ZP decreases drastically with increasing concentrations. Furthermore, it is conceivable for the ion exchanger with poor crystallinity that hydrolysis proceeds to a greater extent at higher temperatures. The extent of hydrolysis must affect the adsorption properties. The combination of these factors may contribute to the ion-exchange behaviour on these two exchangers in a different way.

From Figs. 1, 2 and 3, the affinity series are found to be as follows:
over the range 25 to 65°:

$$Ce^{3+} > Zn^{2+} > Cs^{+} > Co^{2+} > K^{+} > Ba^{2+} > Ca^{2+} > Na^{+};$$

over the range 65 to 80°:

$$Ce^{3+} > Zn^{2+} > Co^{2+} > Cs^{+} > K^{+} > Ca^{2+}, Ba^{2+} > Na^{+}.$$

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