EFFECT OF THE DRYING TEMPERATURE ON THE ION-EXCHANGE PROPERTIES OF ZIRCONIUM PHOSPHATE

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A considerable amount of study has been carried out recently on the ion-exchange properties of synthetic inorganic materials such as zirconium phosphate, titanium phosphate, zirconium oxide, thorium oxide, etc.[1-11]. The chief interest of such exchangers lies in the fact that they are more highly resistant to strong doses of ionizing radiations and to high temperatures than organic resins, which makes them particularly suitable for tackling problems of ion separation arising in reactor operation.

In two earlier papers we reported on certain preliminary experiments regarding the possibility of improving the separation of Sr^{2+} and Cs^+ on zirconium phosphate dried at various temperatures. The separation can be considerably improved either by first applying ion adsorption at room temperature and afterwards drying the exchanger at 180°,[12] or by drying the exchanger first at temperatures ranging from 180° to 260° and adsorbing and eluting the ions afterwards[13].

In this paper the effect of the drying temperatures on the ion-exchange properties of zirconium phosphate (ZP) are studied.

EXPERIMENTAL

The ZP was prepared as indicated by GAL AND GAL[10]. 200 ml 4 N HCl containing 30 g $ZrOCl_2 \cdot 8H_2O$ were poured slowly into 500 ml of a 4 N HCl solution containing 64 g H_3PO_4. The high PO_4/Zr ratio (7:1) in the reagents is necessary in order to have an exchanger with many acid phosphate groups. The product thus obtained is dried at 50° for 24 h and finely ground and sieved. In the experiments described here, the fraction corresponding to a particle size of 0.1–0.2 mm was used. To heat the sample a furnace thermoregulated within ± 1° was used.

The ions Na^+, K^+ and Li^+ were determined by flame photometry. The ions Cs^+, Rb^+, Tl^+, Ba^{2+}, Sr^{2+} were determined radiometrically, using the radioactive isotopes ^{137}Cs, ^{86}Rb, [204]Tl, [140]Ba and ^{89}Sr as tracers.

Effect of drying temperature

(a) *Weight loss.* When the ZP prepared as described above is heated, it can be observed that as the drying temperature increases the weight decreases rapidly at

first (up to temperatures of about 250°) and more slowly from 250° to 800°. From 800° to 1,000° there is no further appreciable dehydration. Fig. 1 shows the weight loss of ZP, measured on a Stanton thermobalance, as a function of the temperature. For drying temperatures above 150° the dehydration was also observed to be partly irreversible.
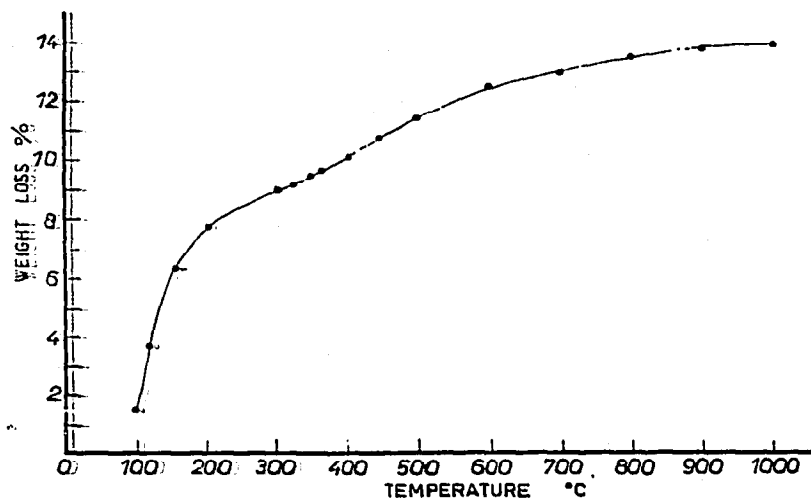

Fig. 1. Weight loss of ZP as a function of drying temperature. Heating rate: 4°/min.

(b) Exchange capacity. For drying temperatures in the 50–110° range, the specific exchange capacity of the ZP (mequiv./g ZP) increases, at a given pH, in proportion to the loss in weight of the exchanger. For drying temperatures in the 110–300° range, as AMPHLETT has pointed out[6], there are changes in properties as compared with the undried ZP, which depend on the pH value at which the determinations are carried out. The values are now no longer the same, even with the exchange capacity value corrected for weight loss of the exchanger.

Fig. 2 shows the exchange capacity of the ZP dried at 50° for 24 h and at 260° for 1 h 15 min as a function of the pH. As the drying temperature increases, the exchange capacity of the ZP decreases for pH values between 8 and 11, while for pH values below 7 the exchange capacity remains the same, or increases slightly.
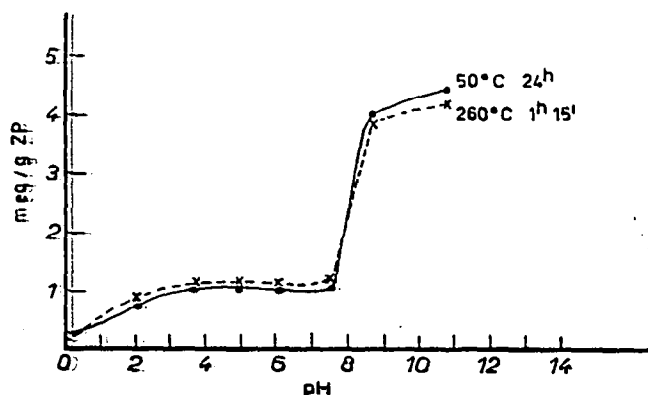

Fig. 2. Cation exchange capacity for K^+ ion of ZP dried at 50° for 24 h and at 260° for 1 h 15 min.

Table I shows the exchange capacity values obtained for certain ions in a solution at pH 2 on ZP dried at 50° for 24 h and at 260° for 1 h 15 min. It can be seen that the exchange capacity values also depend on the ion under consideration, and that

TABLE I

EXCHANGE CAPACITY AT pH 2 OF ZP DRIED AT DIFFERENT TEMPERATURES
(mequiv./g ZP referred to original weight)

Drying temperature	Li+	K+	Cs+	Sr²+
50° (24 h)	0.184	0.75	0.9	0.6
260° (1 h 15 min)	0.113	0.92	0.976	0.538
500° (8 h)	—	0.405	—	—

the ZP does not lose its exchange capacity, even after prolonged drying at high temperatures (500° for 8 h).

At this point we must mention that the exchange capacity of the ZP also depends on the PO_4/Zr ratio in the reagents[6].

(c) *Titration curves*. The ZP titration curves also depend on the drying temperature. Fig. 3 gives curves for ZP dried at 50° for 24 h and at 260° for 1 h 15 min.

(d) *Mass distribution coefficients*. Table II gives the mass distribution coefficients (mequiv./g exchanger per mequiv./ml solution) at equilibrium for alkali metal ions and Tl+, Sr²+, Ba²+, Th⁴+ and UO_2^{2+} ions as obtained at different pH values on ZP dried at 50° for 24 h and at 260° for 1 h 15 min. The values were determined by equilibrating weight amounts of exchanger (0.5 g) with known volumes of suitable solutions (30 ml 0.008 N solution of the ion under investigation).

When equilibrium is reached the ZP is separated by centrifugation. The pH of the solution and the concentration of the ion in question are then measured. As can be seen from the values given in Table II, the temperature at which the ZP is dried has a considerable influence on the mass distribution coefficients. This influence is due only in small part to the loss in weight of the exchanger (14 %).
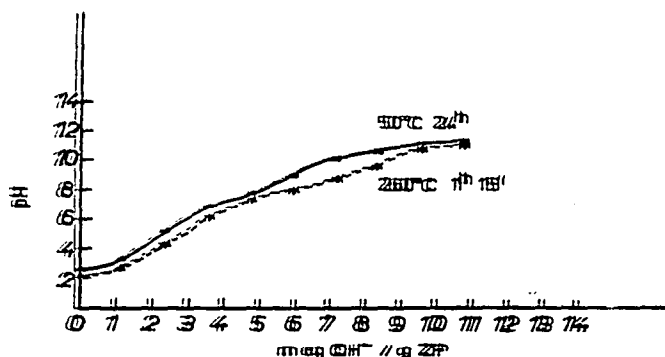

Fig. 3. Titration curve for ZP dried at 50° for 24 h and at 260° for 1 h 15 min. Mole ratio of phosphate to zirconium in reagents: $PO_4/Zr = 7:1$.

TABLE II

MASS DISTRIBUTION COEFFICIENTS ON ZP (mequiv./g ZP per mequiv./ml soln.)

A: ZP dried at 50° for 24 h. B: ZP dried at 260° for 1 h 15 min.

	Li^+ A	Li^+ B	Na^+ A	Na^+ B	K^+ A	K^+ B	Rb^+ A	Rb^+ B	Cs^+ A	Cs^+ B	Tl^+ A	Tl^+ B	Sr^{2+} A	Sr^{2+} B	Ba^{2+} A	Ba^{2+} B	Th^{4+} A	Th^{4+} B	UO_2^{2+} A	UO_2^{2+} B
HCl 4 N							<1	15	6	35										
HCl 2 N					<1	9	<1	21	7	45										
HCl 1 N			<1	<1	<1	11	7	39	18	70	<1	3⁰ (HClO₄, 1 N)	<1	<1	<1	<1	703	625		
HCl 0.1 N					18	140			60	480										
pH 1.6							38	222	1501	>10⁶ (carrier free)										
pH 2	<1	<1		44		220	7.5	370					116	120		171				
pH 2.4	<1					240				2670									230	9
pH 2.5	9	7																		
pH 2.6			40	68	91															
pH 2.7									322											
pH 3															59				>5000	468
pH 3.2			44																	

It is interesting to note that the increase in the mass distribution coefficients obtained by heating the ZP is not constant for all the ions studied. Thus, while there are considerable differences between the mass distribution coefficients for K^+, Rb^+ and Cs^+ obtained on ZP dried at 50° for 24 h and at 260° for 1 h 15 min, the differences obtained with Li^+ and Sr^{2+} are negligible.

For the monovalent and bivalent ions studied, the effect of the temperature on the mass distribution coefficients decrease in the following order: $Tl^+ > K^+ \geqslant Rb^+ \geqslant Cs^+ \gg Na^+ \gg Li^+$ and $Ba^{2+} > Sr^{2+}$. The separation coefficients between any two ions obtained on ZP dried at high temperature will therefore be different from those obtained on ZP dried at a temperature of 50°. This may be of considerable practical interest in view of the possibility of improving a number of separations on ZP dried at temperatures above 150°.

The measurements that were made further demonstrated that between 100° and 260° the value of the mass distribution coefficient increases with the rise in the drying temperature. For drying temperatures above 300° this value decreases progressively (Table III).

TABLE III

MASS DISTRIBUTION COEFFICIENT ON ZP DRIED AT DIFFERENT TEMPERATURES

(Exchanger in hydrogen form equilibrated with 0.25 mequiv. Cs^+ in 30 ml 2 N HCl)

Drying temperature	$K_D \left(\dfrac{mequiv./g\ ZP}{mequiv./ml\ soln.} \right)$
50° (24 h)	7
180° (1 h 30 min)	11
260° (1 h 15 min)	45
260° (15 h)	45
500° (8 h)	1
850° (8 h)	< 1

(e) *Rates of exchange.* Determinations of the exchange rate on ZP dried at different temperatures have shown that the rate decreases as the drying temperature increases, a fact which is very noticeable in the case of ions with larger radii, such as complex ions. Fig. 4 shows the variation in the mass distribution coefficient as a function of time for the zinc–ammonia complex (0.5 mequiv. Zn^{2+} in 30 ml 1 N NH_4OH) on ZP dried at 50° for 24 h and at 260° for 1 h 15 min.

(f) *Column elutions and separations.* For elution experiments small glass columns (diam. 0.6 cm) filled with 0.5 g ZP dried at a given temperature were used[12,13]. 0.025 mequiv. of a given ion was then adsorbed on each column. Elution was carried out with HCl of different concentrations. For each ion a series of elution curves is thus obtained (several examples are given in Figs. 5, 6, 7) from which it can be seen that K^+, Rb^+ and Cs^+ ions have a greater resistance to elution the higher the temperature at which the ZP is dried. In the case of other ions, e.g. Na^+ and Ba^{2+}, the increase in resistance is very small, while the process is negligible and even reversed slightly for Li^+ and Sr^{2+}. The mass distribution coefficient values are thus confirmed. It was expected that a number of separations would be easier if ZP dried
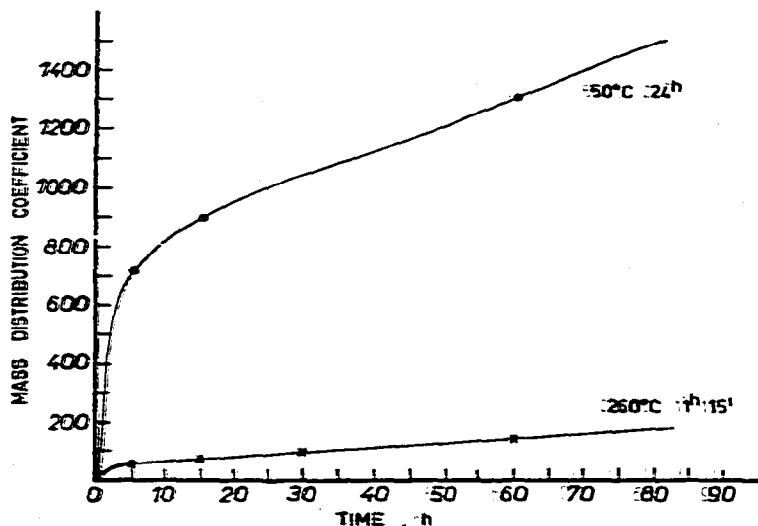
Fig. 4. Initial variations in the mass distribution coefficient (K_D) of zinc-ammonia complex on ZP dried at 50° for 24 h and at 260° for 1 h 15 min. Conditions: 0.5 mequiv. Zn^{2+} in 30 ml 1 N NH₄OH on 0.5 g ZP.
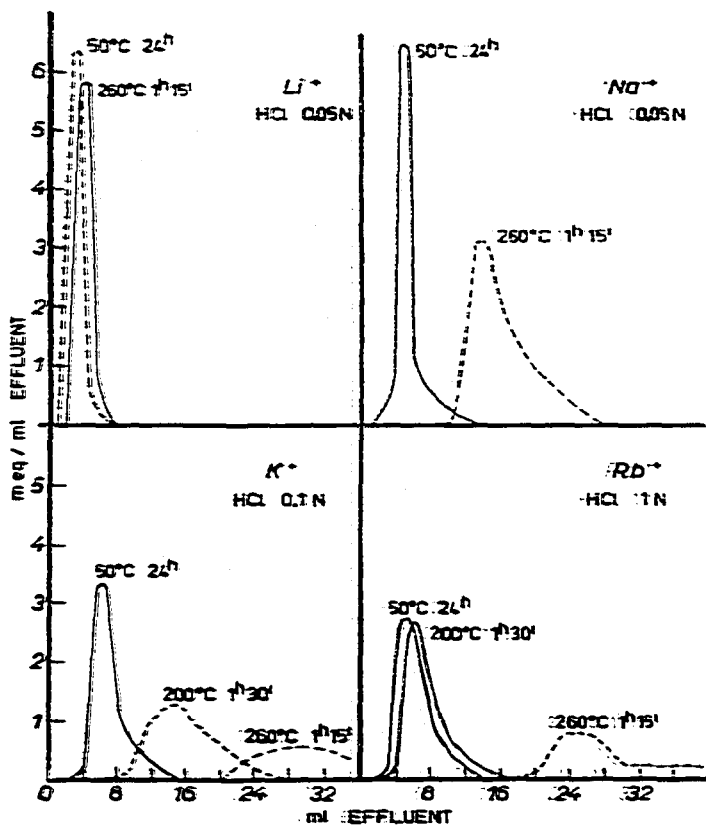

Fig. 5. Elution curves for Li^+, Na^+, K^+, Rb^+ ions, with various concentrations of HCl, on ZP dried at different temperatures. Conditions: 0.0125 mequiv. of each ion are adsorbed on 0.5 g ZP. Flow rate: 0.8 cm/min.
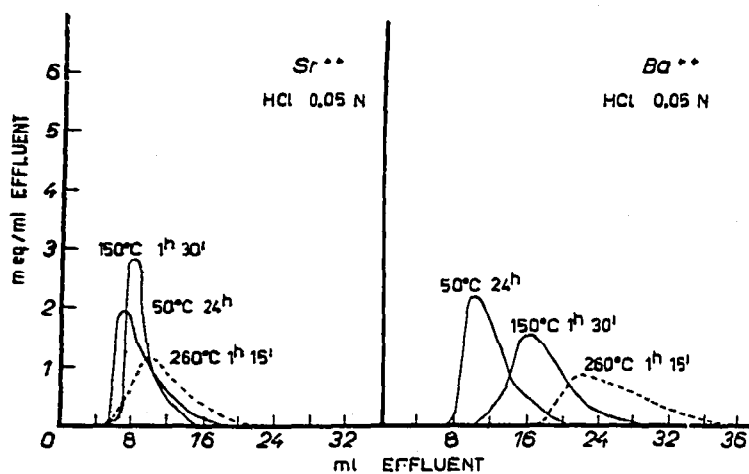
Fig. 6. Elution curves for Sr²⁺ and Ba²⁺ ions, with various concentrations of HCl, on ZP dried at different temperatures. Conditions: 0.01 mequiv. of each ion are adsorbed on 0.5 g ZP. Flow rate: 0.8 cm/min.
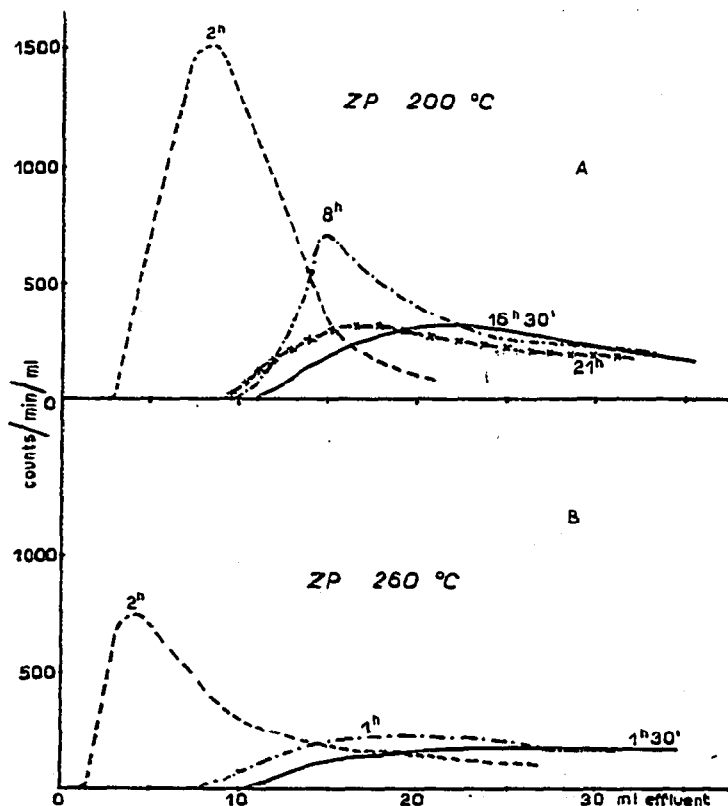
Fig. 7. Elution curves with 2 *N* HCl of 0.025 mequiv. Cs⁺ adsorbed on 0.5 g ZP dried at 200° (A) and at 260° (B) for varying drying times. Flow rate: 0.8 cm/min.

at temperatures in the 150–300° range was used; this was in fact subsequently confirmed. In Figs. 8 and 9 separations are shown of 0.0025 mequiv. Cs^+ from 0.025 mequiv. Sr^{2+} and of 0.0125 mequiv. Li^+ from 0.00125 mequiv. Na^+ on ZP dried at both high and low temperatures.
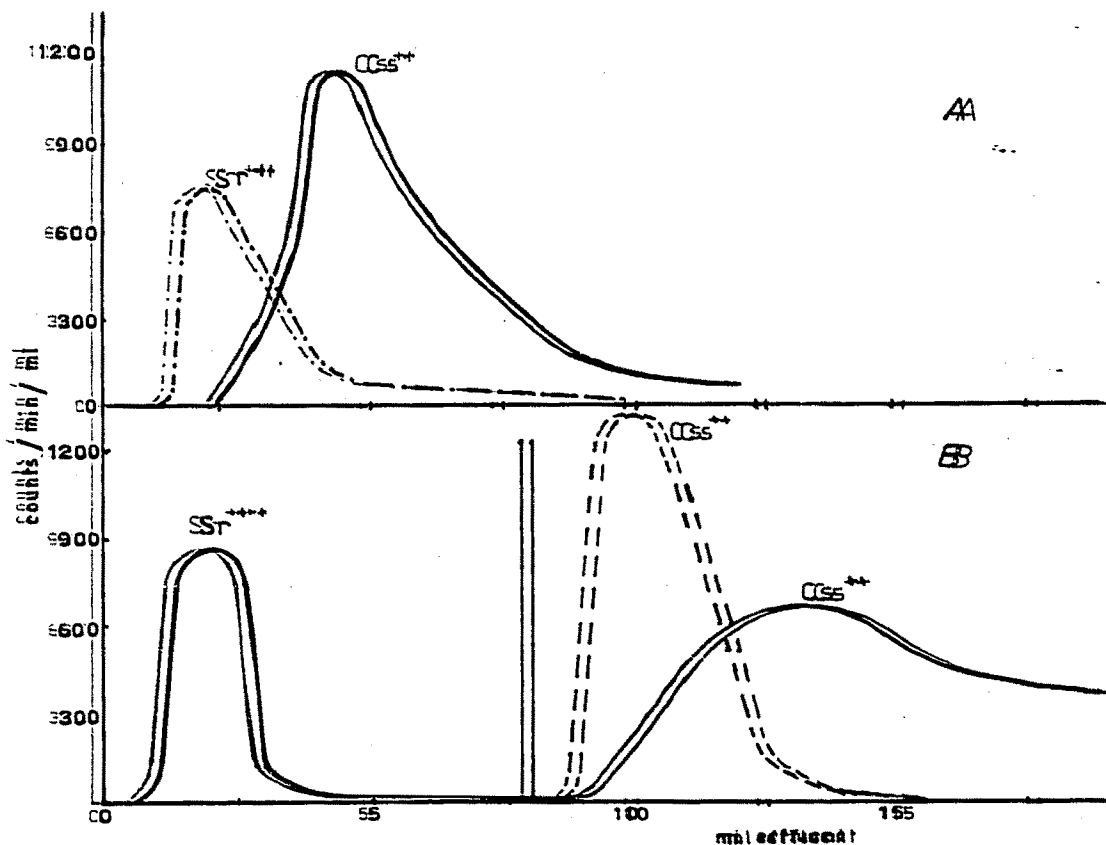

Fig. 8. Separation of 0.025 mequiv. Sr^{2+} from 0.0025 mequiv. Cs^+: (A) on 0.55 g ZP dried at room temperature; (B) on 0.55 g ZP dried at 260° for 1 h 55 min. ———— elution with 2 N HCl. – – – – elution with 5 N $NH_4Cl + 1$ N HCl. Flowrate: 0.88 cm/min.
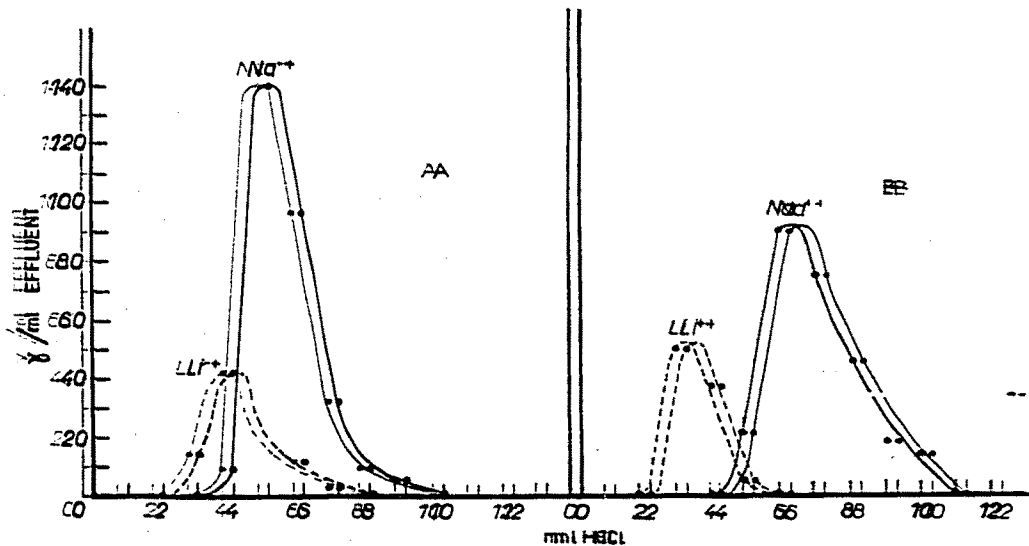

Fig. 9. Separation of 0.0125 mequiv. Li^+ from 0.00125 mequiv. Na^+: (A) on 0.55 g ZP dried at 50° for 24 h; (B) on 0.55 g ZP dried at 260° for 1 h 55 min. Elution with 0.05 N HCl.

DISCUSSION

These experiments show that as the drying temperature of ZP, precipitated in excess phosphoric acid, is raised, a considerable alteration in its ion-exchange properties occurs in addition to an irreversible dehydration.

The most important variations are those found for the mass distribution coefficients of the various ions. From Table II it can be seen that for monovalent ions the ratios of the mass distribution coefficients obtained on ZP dried at 260° and 50°, decrease in the following order:

$$Tl^+ > K^+ \geqslant Rb^+ \geqslant Cs^+ > Na^+ > Li^+$$

This order is the same as that obtained by ARGERSINGER, DAVIDSON AND BONNER[14] for organic resins with high and low degrees of cross-linking. In our case it was further observed that on ZP dried at high temperature the exchange rate decreases, especially in the case of ions with larger radii, e.g. complex ammonia ions. As is known[15,16], the same decrease takes place with resins with high degrees of cross-linking. Analogies between the ion-exchange properties of ZP dried at high temperature and such properties of organic resins with high degrees of cross-linking could then be easily explained by the assumption that an increase in the drying temperature causes a greater condensation in the structure of the ZP. This is corroborated by the irreversible loss of water, a fact which led AMPHLETT et al.[6] to propose the hypothesis that at high temperature "the process taking place may involve condensation of acid phosphate groups to form condensed P–O–P structures and further cross-linking". The phenomena observed with ZP dried at different temperatures would then be analogous to those studied by several authors with resins of varying degrees of cross-linking[17–19].

The structure and chemical composition of ZP precipitated in excess phosphoric acid and dried at both high and low temperatures are being investigated in order to obtain further confirmation of the above hypothesis.

SUMMARY

The ion-exchange properties of zirconium phosphate, dried at temperatures ranging from 150° to 850°, are compared with those of zirconium phosphate dried at 50°. In addition to partially irreversible dehydration, permanent changes in certain properties of zirconium phosphate dried at temperatures above 150° could be observed. Variations in selectivity for certain ions of ZP dried at high temperature can be employed to improve the separation of these ions from each other. All phenomena observed can be explained by the assumption that an increase in drying temperature causes a greater condensation in the structure of the exchanger.

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