ION EXCHANGE IN FUSED SALTS

III. PREPARATION, THERMAL STABILITY AND ION EXCHANGE PROPERTIES OF AMORPHOUS ZIRCONIUM PHOSPHATE COMPLETELY CONVERTED TO THE SALT FORM[*]

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(Received July 21st, 1967)

When amorphous zirconium phosphate in the hydrogen form (ZPH is heated at temperatures higher than $160-180°$ a gradual condensation of the $=HPO_4$ groups to P—O—P groups takes place and its ion exchange capacity is correspondingly decreased[1]. This condensation can be avoided by converting ZPH to a salt form. However, a complete conversion cannot be obtained in aqueous solutions since, as shown by titration curves[2], higher and higher pH values are required as the conversion proceeds and the last hydrogens of ZPH can only be exchanged at high pH values (> 10) where this exchanger is strongly hydrolysed[2]. For this reason, in a previous paper of this series[3], ZP samples not completely converted to the salt form were employed and the experiments were limited to temperatures below $180°$ to avoid condensation due to the presence of hydrogen in the exchanger. In this paper the preparation of fully converted zirconium phosphate, which permits ion exchange experiments to be performed at relatively high temperature, is described. Owing to the impossibility of achieving this in aqueous solution, conversion was studied in fused salts systems. The thermal stability of the salt form of ZP and the selectivity coefficients of some metal ions dissolved in fused salts are also reported and discussed.

EXPERIMENTAL

Chemicals

All reagents (Erba RP products) were vacuum dried at $110°$ for 24 h, mixed in the proportions shown in Table II and then vacuum dried again at $110°$. ZPH was ZP-1 of Bio Rad Laboratories (grain size $\geqslant 100$ mesh U.S. standard screen; $PO_4/Zr = 2$).

Preparation of the lithium–potassium form of ZP

A sample of ZPH was partially converted to the sodium form (5.9 mequiv. Na^+/g of anhydrous ZPH) according to the procedure described in a previous paper[4] and then dried at $160°$ for 48 h. Weighed amounts of this sample and $(Li–K)NO_3$ eutectic were mixed (1:100 in weight) in a Pyrex cylinder with a sintered glass disc G-4 sealed

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in at the bottom. After equilibration, ZP was separated from the (Li–K)NO$_3$ melt by vacuum filtration (see Fig. 1). In order to exchange the last hydrogens of the exchanger the melt was made alkaline either by gradual addition, while stirring, of weighed amounts of an alkali oxide (or hydroxide) or by an electrolytic method. In the latter procedure O^{2-} ions are produced by cathodic reduction of nitrate ions[5].

Since some NO$_2$ is produced at the anode[3], the cathodic and anodic compartments must be separated to avoid mixing. For this reason a platinum electrode (cathode) was dipped directly in the cylinder containing the exchanger while another platinum electrode (anode) was dipped into a separate small cylinder with a sintered glass disc G-1 sealed in at the bottom (see Fig. 1).
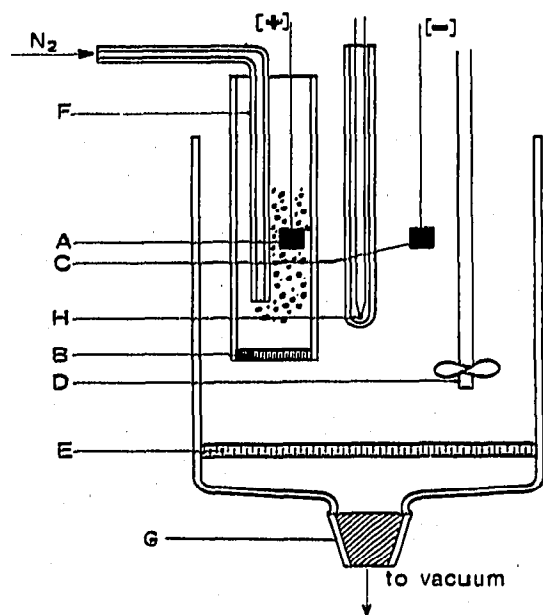

Fig. 1. Apparatus for electrolytic conversion of zirconium phosphate to the complete salt form. A = Anode; B = sintered disc G-1; C = cathode; D = stirrer; E = sintered disc G-4; F = gas inlet; G = glass joint; H = thermocouple.

An adequate electric field was applied to obtain an electric current of a few mA. The alkalinity of the melt was determined, from time to time, by dissolving about 1 g of eutectic in 10 ml of distilled water and then measuring the pH value of the solution. When a pH value of 7.5–7.8 was obtained, the electric current was decreased to about 1 mA and then stopped when a pH of 8 to 8.1 was reached. The alkalinity of the melt was controlled to remain constant at least 48 h. If the pH value was found to decrease with time, the electric current was passed again. Finally the melt was vacuum filtered and the exchanger was washed two times with molten (Li–K)NO$_3$.

Analytical procedures

400–500 mg of exchanger were dissolved in 20 ml of 1 *M* HF and distilled water was added to 100 ml. The alkali metal ions were determined with an E.E.L. flame photometer. Since some melt was found to adhere to the surface of the exchanger, proper corrections must be made (see ref. 3) to obtain the amount of alkali metal ions present as counter-ions. In this paper nitrate ions were determined as nitron nitrate[6]

and chloride ions by the Mohr titration[6]. Orthophosphate and zirconium were determined in the HF solution as described elsewhere[4]. Pb and Ni were determined gravimetrically in the (Li–K)NO$_3$ filtrate as chromate[6] and as the dimethylglyoxine complex[6], respectively. To determine the distribution and selectivity coefficients, 1 g of exchanger was allowed to equilibrate in 50 g of melt, with mechanical stirring, for three days under nitrogen atmosphere.

RESULTS AND DISCUSSION

Conversion of ZP to the salt forms

The mequiv. of alkali metal ions per g of anhydrous ZPH after conversion by the procedures described, are shown in Table I. Assuming the formula Zr(HPO$_4$)$_2$ for amorphous anhydrous ZPH with a PO$_4$/Zr ratio = 2, the theoretical ion exchange capacity would be 7.06 mequiv./g. Thus, as shown in Table I, the complete conversion

TABLE I

CONVERSION OF AMORPHOUS ZP TO THE Li–K FORM
Solvent: (Li–K)NO$_3$ eutectic at 160°

Method		mequiv. M$^+$/g of amorphous ZPH
Electrolysis		7.0
KOH addition[a]	1	7.2
	10	8.5
	100	14.8

[a] mequiv. OH$^-$ per gram of ZP (in partial Na$^+$ form) in 100 g of melt.

of ZPH in fused salts can be achieved either by electrolysis or by adding small amounts of an alkali oxide (or hydroxide) to the melt. Furthermore the experimental ion exchange capacity was found to be even higher than the theoretical value when a greater amount of alkali oxide was added. Since neither phosphate nor zirconium were found in the filtrate, the latter phenomenon could be easily explained assuming that, in fused salts, ZP is partially hydrolyzed by a high O^{2-} (or OH$^-$) concentration and the hydrolyzed phosphates are precipitated as Li$_3$PO$_4$*. Thus, since this precipitate is separated together with the partially hydrolyzed salt form of the exchanger, more than one mequiv. of alkali metal per mmole of phosphate will be found. For this reason too high O^{2-} (or OH$^-$) concentrations in the melts must be carefully avoided. Furthermore the temperature must be kept $\leqslant$ 180° to prevent condensation during the conversion process. To overcome this difficulty the (Li–K)NO$_3$ eutectic was chosen as solvent (m.p. 132°) and the mixed lithium–potassium form of ZP (ZP(Li–K)) was thus obtained.

Owing to the high thermal stability of ZP(Li–K), a pure alkali metal form can

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* The low solubility of Li$_3$PO$_4$ in our experimental conditions, was shown by adding small amounts of an alkali phosphate to a (Li–K)NO$_3$ eutectic at 160°, followed by the analysis of the precipitate formed.

be obtained by percolating through the ZP(Li–K) the corresponding fused alkali nitrate. By percolating fused $NaNO_3$ through it at 350° the pure sodium form with theoretical values was obtained. With $LiNO_3$ at 300° the pure lithium form with 9.2 mequiv. of Li^+ per g of exchanger was found, indicating that some Li_3PO_4 was precipitated. Only 3 mequiv. of K^+/g were found with KNO_3; thus a full conversion of ZP into the potassium form and very likely to the rubidium or cesium form cannot be obtained by the procedure described.

Stability of ZP salt forms in melts at high temperatures

Table II shows that a completely converted ZP form exhibits good thermal stability up to 400–500°. At higher temperatures zirconium and phosphate ions are found in the melts. This partial dissolution of ZP in ionic melts is the principal obstacle to using ZP as an ion exchanger at very high temperatures. However, many fused systems exist up to 500° and therefore completely converted ZP is a very suitable material for studying ion exchange at high temperatures.

TABLE II

SELECTIVITY COEFFICIENTS OF Li^+ AND K^+ IONS ON ZP AT VARIOUS TEMPERATURES

Solvent composition (mole %)		$t(°C)$	$K_{K^+}^{Li^+}$
$LiNO_3$	43	160	12
KNO_3	57		
$LiNO_3$	43	300	8
KNO_3	57		
LiCl	59	450	9
KCl	41		
NaCl	50	700	solubilisation
KCl	50		
Li_2SO_4	72	700	solubilisation
K_2SO_4	28		

Selectivity and distribution coefficients of some inorganic ions on ZP

In Table II some ion exchange data of fully converted ZP in various melts at relatively high temperatures are shown. In (Li–K)Cl the selectivity coefficient is very close to that found in the (Li–K)NO₃ eutectic, thus confirming the high selectivity of ZP for the Li^+ ion.

The differences in lithium–potassium selectivity, the incomplete conversion of ZP into the K^+-form and the fact that Cs^+ is not exchanged by ZP in fused salts[3] may be explained by taking into account the peculiar structure of amorphous ZP.

As discussed in a previous paper[7] amorphous ZP can be considered as an ion exchanger with a wide range of channel and cavity sizes (of zeolytic type); thus species with high ionic sizes may be mechanically excluded from some internal parts of the exchanger.

In fused salts steric effects are still more important than in aqueous solutions

owing to the dehydration which further lowers channels and cavities sizes. Under these conditions only Li^+ and Na^+ ions fit well with the exchange sites, K^+ ions can be exchanged only partially, while Cs^+ ions are almost completely excluded.

To test the selectivity of ZP for ions other than alkali metal ions the distribution coefficients of Ni(II) and Pb(II) dissolved in $(Li–K)NO_3$ eutectic at 160° were determined (see Table III). To avoid oxide formation NH_4NO_3 was added to the $(Li–K)NO_3$ eutectic (10 % by weight). The low distribution coefficients are in agreement with chromatographic experiments performed on glass-fiber paper impregnated with ZP[8], thus confirming that a given metal ion dissolved in trace amounts in a molten salt cannot be exchanged to any great extent by an ion exchanger since the ions of the solvent will compete for the exchangeable sites. However, higher distribution coefficient values would be expected if the ions of the molten solvent cannot enter (or enter only partially into the exchanger. In agreement with this view Table III shows that the distribution coefficient of lithium ion is very high in molten KNO_3. Thus determination of the distribution coefficients on ZPLi or ZPNa of various metal ions dissolved in trace concentrations in molten $RbNO_3$ or $CsNO_3$ could be very interesting.

TABLE III

DISTRIBUTION COEFFICIENTS OF Li(I), Pb(II), Ni(II) ON ZP IN FUSED NITRATES

Ion	Solvent	$t(°C)$	mequiv. M^+ per g of melt (final compos.)	$K_d^{M^+}$
Pb(II)	$(Li–K)NO_3$ + 10 % NH_4NO_3	160	$2 \cdot 10^{-2}$	3
Ni(II)	$(Li–K)NO_3$ + 10 % NH_4NO_3	160	$2 \cdot 10^{-2}$	2
Li(I)	KNO_3	450	$2 \cdot 10^{-2}$	200

SUMMARY

Amorphous zirconium phosphate was first converted to a lithium–potassium form in molten nitrates at 160° and then to the pure sodium or lithium form by percolating sodium or lithium nitrate through it.

The fully converted salt form of zirconium phosphate ($\simeq$ 7 mequiv./g) was found to exhibit a good thermal stability in molten salts up to 400–500°.

Distribution and selectivity coefficients of some inorganic ions on the completely converted salt form of zirconium phosphate are also reported and discussed.

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