

ION EXCHANGE IN FUSED SALTS

II. DISTRIBUTION COEFFICIENTS OF SOME ALKALI METAL IONS ON ZIRCONIUM PHOSPHATE IN FUSED NITRATES

GIULIO ALBERTI, SERGIO ALLULLI AND ARMINIO CONTE

Laboratorio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N., Istituto di Chimica Generale ed Inorganica, Università di Roma, Rome (Italy)

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In a previous paper¹ the chromatographic behaviour of various metal cations dissolved in fused salts, on glass fiber paper impregnated with synthetic inorganic ion exchange materials, has been reported.

These preliminary results, in spite of their qualitative nature, showed that there is a marked analogy between the adsorption of a given metal ion and its solubility in fused salts; and that metal ions are adsorbed by ion exchange, although other mechanisms such as oxide precipitation on the exchanger materials, are possible.

To extend the knowledge on ion exchange in fused salts and to confirm the differences predicted¹ between the properties of ion exchangers in aqueous solutions and in ionic melts more quantitative data were required.

In the present communication the distribution coefficients of lithium, sodium, potassium and cesium ions, on zirconium phosphate (ZP), in fused nitrates, are reported and discussed.

Owing to the well known high solubility of alkali metal oxides in fused nitrates, the distribution coefficients of these metal cations should not be affected by oxide precipitation on the ion exchanger.

The lack of knowledge on the behaviour of ZP in ionic fused media, also made it necessary to determine the rate of ion exchange, the extent of ZP hydrolysis and the degree of condensation of $=\text{HPO}_4$ to $\text{P}-\text{O}-\text{P}$ groups, under the operating conditions.

EXPERIMENTAL

Preparation of the solvents

LiNO_3 , NaNO_3 , and KNO_3 (Erba RP) vacuum dried at 100° for 24 h, were weighed and mixed in the proportions shown in Table I, then vacuum dried again at 110° .

ZP salt forms

ZP in the sodium form (ZPNa) and in the potassium form (ZPK) were prepared from the H^+ form of ZP (ZP-1, Bio Rad Laboratories, grain size >100 mesh) according to a procedure described elsewhere². After dehydration at 110° materials containing 5.2 mequiv. Na^+/g ZPNa (corresponding to 5.9 mequiv. Na^+/g anhydrous ZPH) and 4.7 mequiv. K^+/g ZPK (corresponding to 5.8 mequiv. K^+/g anhydrous ZPH) were obtained.

TABLE I

DISTRIBUTION COEFFICIENTS FOR LITHIUM, SODIUM AND POTASSIUM IONS ON ZPK AND ZPNa IN FUSED NITRATES, AT 160°

Exchanger	Initial molar composition of melts (%)		Mequiv. Me ⁺ per g of melt (final composition)		Mequiv. Me ⁺ per g of anhydrous ZPH		K_d^a		Selectivity coefficients			
ZPK	LiNO ₃	43	Li ⁺	4.8	Li ⁺	4.1	K_d^{Li}	0.85	K_{K}^{Li}	3.7		
	KNO ₃	57	K ⁺	6.6	K ⁺	1.5	K_d^{K}	0.23				
ZPNa	LiNO ₃	43	Li ⁺	4.8	Li ⁺	5.1	K_d^{Li}	1.06	K_{K}^{Li}	15		
	KNO ₃	57	Na ⁺	0.11	Na ⁺	0.15	K_d^{Na}	0.069				
ZPK	LiNO ₃	30	Li ⁺	3.3	Li ⁺	3.0	K_d^{Li}	0.91	K_{K}^{Li}	3.6		
	NaNO ₃	23	Na ⁺	2.6	Na ⁺	1.2	K_d^{Na}	0.46			K_{Na}^{Li}	2.2
	KNO ₃	47	K ⁺	5.4	K ⁺	1.4	K_d^{K}	0.26				
ZPNa	LiNO ₃	30	Li ⁺	3.3	Li ⁺	3.7	K_d^{Li}	1.12	K_{K}^{Li}	15		
	NaNO ₃	23	Na ⁺	2.7	Na ⁺	1.6	K_d^{Na}	0.59			K_{K}^{Na}	7.9
	KNO ₃	47	K ⁺	5.3	K ⁺	0.40	K_d^{K}	0.075				

^a K_d = mequiv. Me⁺ per g of anhydrous ZPH/mequiv. Me⁺ per g of melt.

ZP in the cesium form (ZPCs) was prepared by equilibrating ZP-1 with a Cs⁺ solution, labelled with ¹³⁷Cs, at about pH 8. The pH value was kept roughly constant by operating in the presence of anion exchangers in OH⁻ form (Dowex 1, 20–50 mesh). After 4 days, ZPCs was mechanically separated from the anionic resin and analyzed for the Cs⁺ content (~ 4 mequiv. Cs⁺ per g ZPCs weighed after dehydration at 110°).

Determination of distribution coefficients

The experiments were performed at 160 ± 2°, in a dry nitrogen atmosphere, in an oven (Bicasa) provided with an internal mechanical stirrer. 1.130 g of ZPNa or 1.234 g of ZPK (weighed after drying at 110° and corresponding to 1 g of anhydrous ZPH*) was left for 48 h at the operating temperature (160°), then added to 50 g of alkali nitrates melt, contained in a pyrex cylinder, provided with a sintered glass disk (G4) at the bottom to separate ZP from the melt after equilibration by vacuum filtration. After filtering and cooling, known amounts of 2 N HCl solution were passed through ZP until complete elution of all alkali cations was achieved.

Analytical procedures

The concentrations of lithium, sodium and potassium ions were determined by an E.E.L. flame photometer. Potassium concentrations were also determined gravimetrically by precipitating with tetraphenylboron³.

Cesium was determined radiometrically.

Nitrate ion concentration was determined by VOGEL's⁴ method, after reducing NO₃⁻ to ammonia with Devarda's alloy.

ZP hydrolysis and P—O—P formation were determined according to the techniques described elsewhere⁵.

* For this equivalence, see ref. 2.

RESULTS AND DISCUSSION

ZP hydrolysis

It is well known that zirconium phosphate hydrolyzes in aqueous solutions⁶. Under our experimental conditions, it was found that hydrolysis occurs only to a very small extent (< 1 %) in fused alkali nitrates.

Pyrophosphate formation

On heating ZP-1 above 160–180° a gradual condensation of =HPO₄ to P—O—P groups takes place and the ion exchange rate correspondingly decreases considerably⁵. Since ZP in salt form, prepared as described above, contain a high percentage of the hydrogen form, all the experiments were performed at 160°. After 70 h at this temperature in a fused LiNO₃–KNO₃ eutectic, formation of P—O—P groups was found to be negligible (< 1 %).

Rate of ion exchange

Fig. 1 shows the equivalent ionic fractions of potassium and lithium found in 1 g of ZPK, left in contact with 50 g of LiNO₃–KNO₃ eutectic, plotted *vs.* time of equilibration. The experiments were performed with and without stirring. It can be seen that stirring does not appreciably influence the rate of ion exchange. Owing to the high ionic concentration of fused salts, the rate-determining step is probably controlled by particle diffusion, therefore it does not depend on stirring. All the following experiments were therefore performed without stirring. Fig. 1 also shows that, when considering the exchange between potassium and lithium, the equilibrium is achieved in about 10–12 h.

Since a decrease in the rate of exchange between potassium and ions with greater ionic radii is to be expected, the time for all the ion exchange experiments was not less than 70 h. It must be pointed out that the presence of lithium in all the ionic media employed facilitates ion exchange, even when it should be very slow or hindered, considering a two-way traffic mechanism⁷.

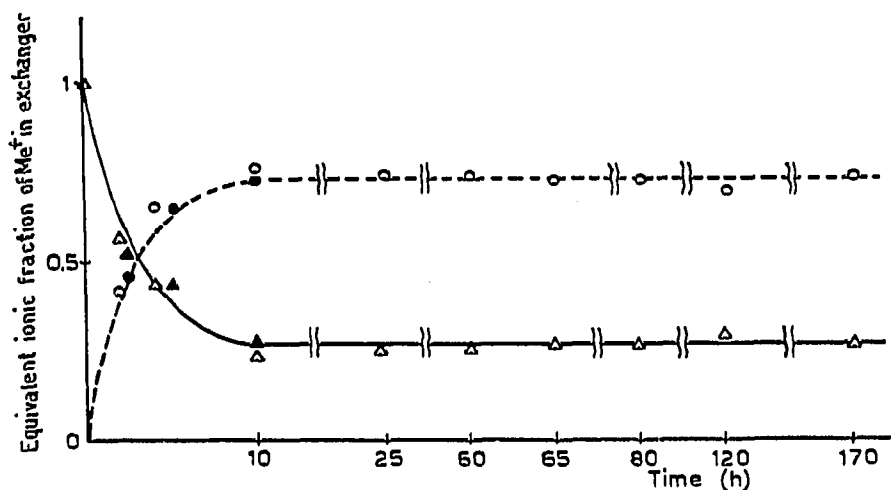


Fig. 1. Equivalent ionic fraction of K⁺ (solid line) and Li⁺ (dashed line) in zirconium phosphate (initially in potassium form) as a function of time of equilibration. (●▲) stirred solution; (○△) unstirred solution.

Distribution coefficients

Many difficulties arise when the distribution coefficients of alkali metal ions on ZP are determined. As pointed out above, the salt forms of ZP contain a remarkable number of P-OH groups which condense to P-O-P groups at temperatures higher than 160°, and thus decrease the ion exchange rate. Therefore it was not possible to study fused systems, such as LiNO₃-NaNO₃ or NaNO₃-KNO₃, owing to their relatively high melting points.

Furthermore, some of the melt, even after careful filtration, is found to adhere to the walls of the pyrex container and to the surface of the exchanger. For this reason alkali metal ions of the melt are mixed, during the elution, with the exchangeable ions of the exchanger. Since the alkali ions of the melt are present as nitrates and the melt molar composition is known (see Table I), the proper corrections can be made by determining the nitrate concentration in the eluate.

It was also observed that the distribution coefficients of alkali metal ions depend greatly on the initial salt form of the exchanger.

Table I shows that, after 90 h of equilibration, 1.5 and 0.45 mequiv. K⁺ per g of anhydrous ZPH are found using ZPK and ZPNa, respectively. Such a difference could be due to incomplete equilibrium, but, since the amount of K⁺ present in the exchanger does not decrease much from 12 to 100 h of equilibration (see Fig. 1), it was concluded that about 1 mequiv. of K⁺ ion is exchanged at a very low rate or even encaged in the exchanger.

Therefore, when ZPK is used, the values of the distribution and selectivity coefficients are invalidated by the excess of potassium remaining in the exchanger even after 90 h of equilibration.

Increase of the ionic crystal radius of the initial exchangeable ion increases this effect and could be connected with the shrinking of the exchanger produced by dehydration at 160°. It was found *e.g.*, that by adding 4 g of ZPCs to 40 g of a melt composed by 38.4 g of LiNO₃-KNO₃ eutectic and 1.6 g CsNO₃, less than 0.1 mequiv. Cs⁺/g ZPCs was exchanged, while addition of 4 g of ZPK to 40 g of a melt composed by 35.3 g of LiNO₃-KNO₃ eutectic and 4.7 g CsNO₃, resulted in less than 0.1 mequiv. K⁺/g ZPK being exchanged by Cs⁺ ions (after 100 h of equilibration). In this case, owing to the large difference between the results obtained with ZPCs and ZPK, it is not possible to draw any conclusion on the selectivity of ZP for Cs⁺ ion dissolved in molten alkali nitrates.

On the other hand, Table I shows that when ZPNa is left in contact with LiNO₃-KNO₃ eutectic, only 0.15 mequiv. Na⁺ per g of anhydrous ZPH are found in the exchanger, part of this being due to the distribution of Na⁺ between the exchanger and the melt. Therefore when ZPNa is employed, the small amount of Na⁺ ion eventually not exchanged (<0.15 mequiv. Na⁺ per g of anhydrous ZPH) will not affect appreciably the distribution of alkali metal ions on zirconium phosphate.*

It should be pointed out that the K_{Na}^{Li} value obtained using ZPK is in good agreement with that determined on ZPNa. Therefore the distribution coefficients of Li⁺ and Na⁺ ions are altered by the amount of K⁺ ion not exchanged whilst the coefficient K_{Na}^{Li} is not.

* It should be expected that an even smaller amount of unexchanged Li⁺ will remain in the exchanger initially in the lithium form, but it was not possible to test this point since the conversion of ZPH to ZPLi, by the method previously reported², appears to be unsatisfactory, owing to the poor solubility of lithium phosphate in water.

From the values of the selectivity coefficients found when the exchanger was initially in the sodium form, the following order of selectivity in molten alkali nitrates is derived: $\text{Li} > \text{Na} \gg \text{K}$.

By comparing the ion exchange behavior of ZP in nitrate melts and in aqueous solution, the most striking feature is that on decreasing the crystal radii of alkali metal ion, the selectivity of the ZP increases in fused media while it decreases in aqueous solutions. This confirms what was already found in a previous paper¹ from a qualitative point of view, and is also in good agreement with the results obtained by LIQUORNIK AND MARCUS⁸ with a Linde Molecular Sieve 4 A in fused nitrates.

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SUMMARY

Some experiments on the ion exchange properties of zirconium phosphate in fused alkali nitrates, at 160°, are reported. The results obtained show that the ion exchange equilibrium is reached after about 10–12 hours and that condensation and hydrolysis of the exchanger are negligible. Values of distribution coefficients for some alkali metal ions are reported. The selectivity decreases with increasing the ionic crystal radius in fused media and this is found to be reversed relative to aqueous solutions.

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