CHROM. 4361

ION EXCHANGE IN FUSED SALTS

IV. ION-EXCHANGE PROPERTIES OF CRYSTALLINE ZIRCONIUM PHOSPHATE IN MOLTEN NaNO₃–KNO₃ AT 450°

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(Received September 9th, 1969)

SUMMARY

The chemical stability of crystalline zirconium phosphate in molten KNO_3 and $NaNO_3$ has been determined. It was found that ion-exchange experiments can be carried out, without appreciable decomposition of the material, up to 350° or 500° with the H form or the salt form of the exchanger, respectively. Forward and reverse ion-exchange isotherms for Na/K exchange in molten $NaNO_3$–KNO_3 mixtures at 450° show that contrary to what is found in aqueous solution, no appreciable hysteresis occurs. The isotherm curves show two well-defined vertical portions, each being related to the coexistence of two immiscible phases, one transforming into the other. The shape of the isotherm curves also indicates that Na^+ is always preferred to K^+ over the whole range of the solvent composition.

INTRODUCTION

In previous papers[1-3] ion exchange of alkali metal ions in molten nitrates has been investigated by using amorphous zirconium phosphate as exchanger. Crystalline zirconium phosphate seems a more suitable exchanger to obtain better insight into the ion-exchange phenomena occurring in molten salt media. In fact, with this material instead of the amorphous, it is possible to follow structural changes occurring during the ion-exchange process by X-ray analysis[4-6]. On the other hand, ion-exchange experiments on molten salt media at high temperature also seem to be useful to obtain additional information on the ion-exchange mechanism of crystalline zirconium phosphate. Since crystalline zirconium phosphate has never been employed for ion-exchange studies in fused salts, preliminary research on its stability in molten sodium and potassium nitrates at various temperatures has been performed. Also the forward and reverse Na^+–K^+ exchange in molten $NaNO_3$–KNO_3 mixtures at 450° has been investigated over the whole range of the ionic composition of the solvent.

EXPERIMENTAL

Chemicals

All reagents (ERBA RP products) were dried at 110° for 24 h, mixed in proper proportions and then dried again at 110°. Dimethylsulphone (DMS) was supplied by K & K Laboratories; crystalline zirconium phosphate in the sodium form (ZPNa) was obtained by titrating the hydrogen form (ZPH) prepared according to a procedure described in a previous paper[5]; ZPK was obtained from ZPNa as reported by TORRAC-CA[6]. The anhydrous sodium and potassium forms of the exchanger were obtained by vacuum drying at 160° and 110°, respectively.

Apparatus and procedures

The experiments were performed in an electrical furnace, the temperature of which was controlled by a Ni–Cr thermocouple and SAE 136 thermoregulator at ± 5°.

Several ZPNa (or ZPK) samples (1 g) were added to 50 g of $NaNO_3$–KNO_3 mixtures, at various compositions, contained in a Pyrex cylinder provided with a sintered-glass disk (G 4) at the bottom. Each sample was left for a given time at the operating temperature, vacuum filtered at 450°, cooled and then washed several times with fused DMS at 160° to eliminate the small amount of nitrates adhering to the surface of the exchanger even after careful filtration*. Finally the excess of DMS was removed by washing with acetone at room temperature.

Isotherm curves were obtained by determining the ionic equivalent fraction of potassium ($\overline{X}_K$) in the exchanger at the various melt compositions. The equivalent fraction of potassium in the melt (X_K) before and after the equilibrium was assumed to remain constant, since the number of mequiv. of alkali counter-ions in 1 g of exchanger is negligible with respect to the number of mequiv. contained in 50 g of fused solvent.

Analytical procedures

400–500 mg of the exchanger were dissolved in 20 ml of 1 M hydrofluoric acid, and distilled water was added to 100 ml. The alkali metal ions were determined with an E.E.L. flame photometer. Orthophosphate and zirconium ions were determined as reported in ref. 7.

X-ray diffraction patterns were obtained with copper radiation (Cu Kα, λ = 1.542 Å).

RESULTS AND DISCUSSION

Stability of crystalline ZP in fused alkali nitrates

Crystalline ZPH exhibits a good thermal stability, condensation of its acid groups to pyrophosphate starting at about 320°–350° and reaching to completeness only at about 600°[4].

Some preliminary experiments in $NaNO_3$ at 350° showed that the hydrogen of the exchanger can be easily substituted by Na^+. During the exchange, nitrogen

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* During the washing with DMS ion-exchange reactions seem to be excluded, since it was shown experimentally that the composition of the alkali nitrates dissolved in DMS was equal to that of the solvent.

dioxide was evolved from the melt, the displaced H^+ reacting with NO_3^- according to the schematic reaction:

$$2H^+ + 2NO_3^- = H_2O\uparrow + N_2O_4\uparrow + \tfrac{1}{2}O_2\uparrow \tag{1}$$

By percolating fused $NaNO_3$ over ZPH, full conversion to ZPNa was obtained. It must be noted that direct conversion of the hydrogen to the sodium form in fused salts is not possible for the amorphous ZP (ref. 3), owing to its lower thermal stability (condensation to pyrophosphate starts at about 180°). When ZP is converted in salt form, condensation of phosphate groups cannot occur, and the exchanger can be heated at very high temperatures without decomposition. The chemical stability of crystalline ZP was thus checked by contacting for different times 1 g of ZPNa (or ZPK) with 50 g of fused $NaNO_3$ (or KNO_3) at various temperatures.

Both crystalline ZPNa and ZPK were found to be very stable in molten alkali nitrates until about 500°. Above this temperature phosphates were released to the solvent, their amount increasing with the contact time and temperature (see Table I). For this reason, all the ion-exchange experiments were performed at temperatures lower than 500°.

TABLE I

DEGREE OF HYDROLYSIS OF ZPK IN MOLTEN KNO_3 FOR DIFFERENT TIMES AND TEMPERATURES

Temperature (°C)	Time (days)	Degree of hydrolysis[a]
450	30	$< 1\%$
550	1	$\sim 5\%$
550	2	$\sim 7\%$
550	3	$\sim 10\%$
600	1	$\sim 10\%$
650	1	$\sim 20 \div 30\%$
700	1	$80 \div 100\%$

[a] Expressed as: $\dfrac{\text{number of mmoles of phosphate released}}{\text{total number of mmoles of phosphate in the exchanger}} \times 100$

Ion-exchange rate

Since the equilibration time could be dependent on the process under consideration and on the ionic composition of the melt, the time necessary to reach equilibrium for some ionic fractions of the melt was determined before determining isotherm curves.

At $X_K = 0.25$, 0.75 and 0.90, equilibrium was reached in less than two days for both processes, while longer times (about 4 days) were required for the $\overline{Na^+}-K^{+*}$ process at $X_K = 0.50$. It was noted that for $X_K = 0.95$, equilibrium was not reached even after 18 days (Fig. 1). However, if the sample was contacted with the melt for a longer time, the first interplanar distance of the exchanger was increased from 8.7 Å (pure ZPK) to 11.3 Å, and nitrates were found in the exchanger even after prolonged washing with DMS. This phenomenon can be explained assuming that, for very long equilibration times, the melt can penetrate the exchanger. Therefore, to be

* The convention $\overline{Na^+}-K^+$ and $K^+-\overline{Na^+}$ represents Na^+ replacing K^+ in the exchanger and *vice versa*.

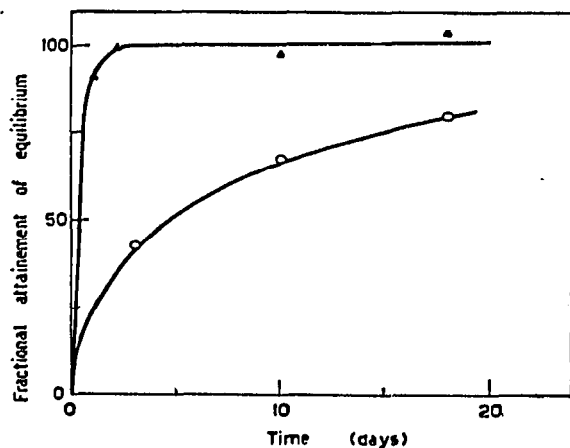sure of the equilibrium and to avoid invasion phenomena, the contact time of the experiments was 10 days.

Fig. 1. Ion-exchange rate of crystalline zirconium phosphate in molten $NaNO_3$–KNO_3 (X_K = 0.95) at 450°. $\bigcirc$, Na^+ displaces K^+ from ZPK; $\blacktriangle$, K^+ displaces Na^+ from ZPNa.

Ion-exchange isotherms

Owing to the stability of the salt forms of crystalline ZP at high temperature, it was possible to study the $\overline{Na^+}$–$\overline{K^+}$ exchange in molten $NaNO_3$–KNO_3 mixtures at 450° over the whole range of composition of this solvent (m.p. of $NaNO_3$, 314°; m.p. of KNO_3, 347°). Further, to ascertain if the ion-exchange hysteresis found for crystalline ZP in aqueous solution at room temperature[6] also occurs at 450°, the $\overline{K^+}$–$\overline{Na^+}$ isotherm was determined.

Fig. 2b shows the results obtained at 450° in fused salts while, for comparison, in Fig. 2a the same isotherms obtained in aqueous solution[6] are reported. In molten nitrates forward and reverse isotherms are practically the same; therefore no appreciable ion-exchange hysteresis takes place at 450°, contrary to what was found at room temperature.
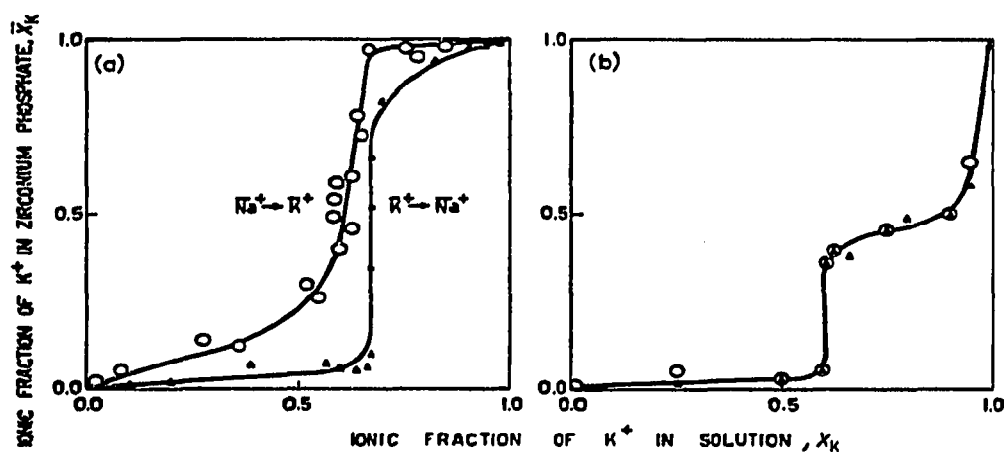

Fig. 2. (a) Forward and reverse ion-exchange isotherms in aqueous solution showing hysteresis. $\blacktriangle$, K^+ displaces Na^+ from ZPNa dried at room temperature; $\bigcirc$, Na^+ displaces K^+ from ZPK dried at room temperature. (b) Forward and reverse ion-exchange isotherms in molten $NaNO_3$–KNO_3 mixtures at 450°. $\bigcirc$, Na^+ displaces K^+ from ZPK; $\blacktriangle$, K^+ displaces Na^+ from ZPNa. (Values for $\overline{X}_K$ at X_K = 0.95 are taken after 18 days of equilibration.)

Another difference between the behavior of crystalline ZP in aqueous solution and in molten nitrates can be seen from Fig. 2. While in aqueous solution Na^+ is preferred only at low X_K values, in molten nitrates the isotherm curve lies entirely below the diagonal of the isotherm plane; therefore Na^+ is always preferred to K^+ over the whole range of the exchanger composition. This result agrees with what is obtained for $\overline{Na^+}-\overline{K^+}$ exchange in the amorphous ZP^2.

In molten nitrates the isotherm curve shows two vertical portions in which the exchanger exhibits different $\overline{X}_K$ values for a same X_K value. In aqueous solution the vertical part of a given isotherm of the crystalline ZP has been related to the co-existence of two immiscible phases, one transforming into the other[6].

X-ray diffraction patterns showed that two diffraction maxima at 7.9 Å and 8.7 Å, respectively, were present in the vertical portion at $X_K = 0.95$ of the isotherm $\overline{Na^+}-\overline{K^+}$. The relative intensities of these peaks were found to vary with time and hence with the degree of the exchanger conversion (Fig. 3).
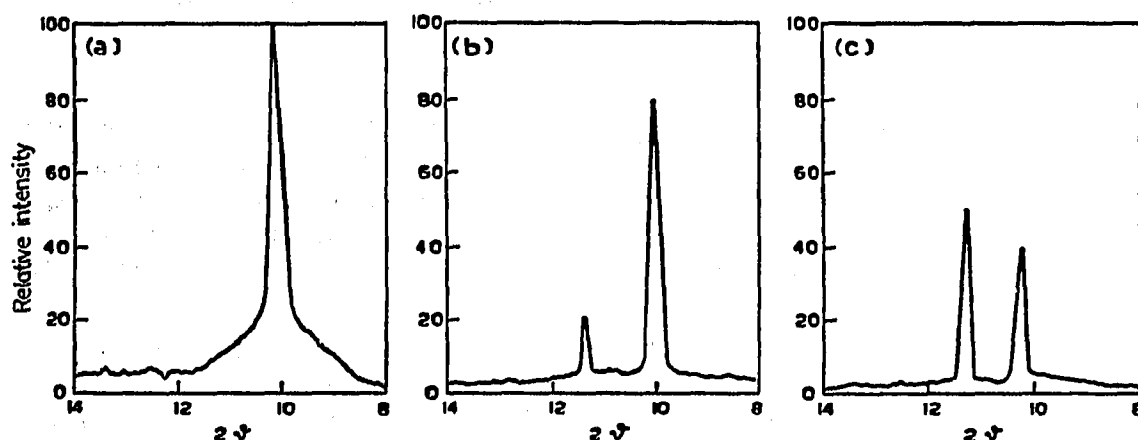

Fig. 3. Modification of X-ray diffraction pattern of crystalline ZPK after 2 and 10 days of equilibration with $NaNO_3-KNO_3$ mixture ($X_K = 0.95$ at 450°). (a) pure ZPK, $\overline{X}_K = 1$; (b) 2 days of equilibration, $\overline{X}_K = 0.83$; (c) 10 days of equilibration, $\overline{X}_K = 0.70$.

Two diffraction maxima at 7.7 Å and 7.9 Å were found also in the vertical portion at $X_K = 0.61$ of the isotherms $\overline{K^+}-\overline{Na^+}$ and $\overline{Na^+}-\overline{K^+}$.

Taking into account that the first interplanar distances of pure ZPNa and pure ZPK are 7.6 Å and 8.7 Å, respectively*, the shape of the isotherm curve $\overline{K^+}-\overline{Na^+}$ can be explained as follows. From $X_K = 0.0$ to $X_K \simeq 0.6$ the exchanger strongly prefers sodium ion; therefore K^+ content increases slowly. At $X_K \simeq 0.6$ two immiscible phases, having the approximate compositions $Zr(Na_{0.95}K_{0.05}PO_4)_2$ and $Zr(Na_{0.6}K_{0.4}PO_4)_2$, respectively, are found.

The composition of the melt remains fixed until the exchanger is completely converted to the latter form. From $X_K \simeq 0.6$ to $X_K \simeq 0.9$, $Zr(Na_{0.6}K_{0.4}PO_4)_2$ becomes richer in K^+ until at $X_K = 0.95$ two immiscible phases having the approximate compositions $Zr(Na_{0.5}K_{0.5}PO_4)_2$ and $Zr(Na_{0.02}K_{0.98}PO_4)_2$, respectively, are formed

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* ZPNa and ZPK obtained from the nitrate melts at 450° exhibit the same X-ray diffraction patterns as ZPNa and ZPK obtained from aqueous solution and heated at 450°.

again. Thus the isotherm curve shows another vertical portion at $X_K = 0.95$ until pure ZPK is obtained.

Similar considerations can also be made for the isotherm $\overline{Na^+}-\overline{K^+}$.

The interplanar distances were determined at room temperature in this work. Therefore to establish for certain the phase transformations occurring at 450°, determinations with a high-temperature X-ray camera, at present not available in our laboratory, will be necessary.

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