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# Potassium-Sodium Ion Exchange Isotherm of Crystalline Zirconium Arsenate

Junko SUGISAWA, Takao YONEZAWA, Kazunori TAKAGUCHI, and Isao TOMITA*
*Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Otsuka, Tokyo 112*

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**Synopsis.** When the forward and reverse $Na^+$–$K^+$ exchange isotherm was investigated for the α-zirconium arsenate ion exchanger, a large hysteresis loop was observed. The interlayer distance of the exchanger decreased with an increase in the ionic fraction of $Na^+$ in the exchanger. The result may be interpreted in terms of the formation of different types of solid solutions during the processes in both directions.

The ion-exchange behavior of alkali metal ions on zirconium bis(monohydrogen orthoarsenate)monohydrate, $Zr(HAsO_4)_2 \cdot H_2O$ (referred to as α-ZA), has been investigated by several authors.[1–3] A recent study has shown that α-ZA can be converted to a half-exchanged phase, $Zr(HAsO_4)(MAsO_4) \cdot xH_2O$, and a fully exchanged phase, $Zr(MAsO_4)_2 \cdot yH_2O$, for each of the lithium, sodium, and potassium ions as the ion exchange proceeds.[3] With regard to a sodium- or potassium-form exchanger, a half-exchanged form is a monohydrate, while a fully exchanged form is a trihydrate. An attempt has been made to study the forward and reverse exchange isotherm by using both disodium and dipotassium form as the starting exchangers.

## Experimental

*Preparation of the Materials.* The α-ZA was synthesized as has been reported previously.[3] The alkali-metal-form exchanger was prepared by titrating α-ZA with a 0.1 M KOH or NaOH solution by the use of a potentiometric titrimeter. The titration was carried out very slowly (for the period of 60 to 70 h) lest the pH of the solution should exceed 9. The hydrolysis of the exchanger could be avoided in this way as much as possible. At the end point the pH was about 8. The prepared materials were filtered and stored over a saturated LiCl solution (the relative humidity was about 10%).

*Ion Exchange.* The ion-exchange reaction, $\overline{K}+Na^+ \rightleftharpoons \overline{Na}+K^+$, was studied, here, the superscript bars refer to the exchanger phase. The experiments were carried out by the batch method, the procedure being as follows. Mixed solutions of 0.1 M NaCl and 0.1 M KCl in various mixing ratios were prepared to give various ionic fractions of $Na^+$ or $K^+$. Each alkali chloride solution had been adjusted to pH 9 by adding a small amount of the corresponding alkali hydroxide solution. Then, 250 mg of α-ZA in the Na or K form was placed in contact with 25 ml of the above-mentioned mixed solution and the slurry was shaken for 4 days at 25 °C. The reaction vessel had been filled with nitrogen gas to avoid the hydrolytic conversion of the salt form into the hydrogen form. The resulting slurry was centrifuged, and the supernatant was analyzed for $K^+$ and $Na^+$ by means of flame photometry. The exchanger phase was subjected to X-ray powder diffractometry and thermal analysis (TG and DSC).

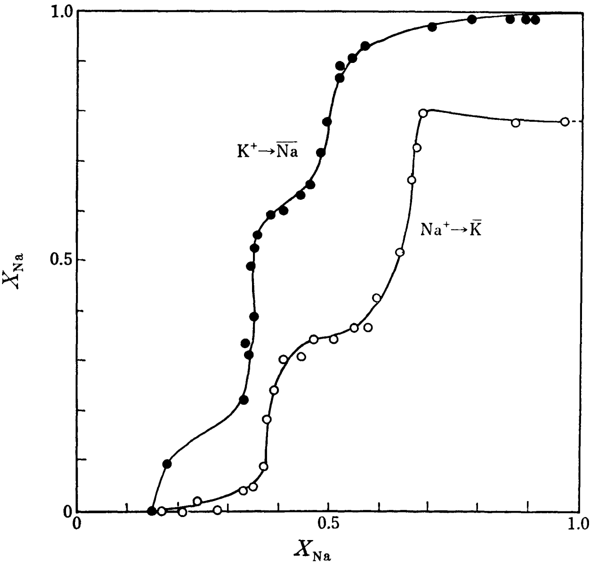

Fig. 1. The forward and reverse $Na^+$–$K^+$ exchange isotherm. $Na^+ \rightarrow \overline{K}$ denotes that $K^+$ ion in the exchanger is replaced with $Na^+$ ion. $K^+ \rightarrow \overline{Na}$ denotes that $Na^+$ ion in the exchanger is replaced with $K^+$ ion.

## Results and Discussion

In Fig. 1 the $Na^+$–$K^+$ ion-exchange isotherm is shown. It should be noted that about 20% of the total $K^+$ could not be released from the exchanger, even when the exchanger in the K form was in contact with the solution containing $Na^+$ ions, *i.e.*, when the ionic fraction of $Na^+$ in the solution ($X_{Na}$) was unity. It has previously been found that $K^+$ could not be released into acidic media with a pH of about 1.5.[3] These facts suggest that the ions with large ionic radii have difficulty in diffusing rapidly inside the exchanger for steric reasons.

In comparison with the $Na^+$–$K^+$ exchange isotherm on crystalline zirconium phosphate (α-ZP), quite a large hysteresis loop was observed in α-ZA. Two vertical portions exist on both the forward and reverse exchange isotherm—at the ionic fraction ($X_{Na}$) of 0.38 and 0.65 for the $Na^+ \rightarrow \overline{K}$ process, while at 0.48 and 0.34 for the $K^+ \rightarrow \overline{Na}$ process. Generally, the presence of vertical portions in the isotherm suggests that two immiscible phases coexist in the exchanger, according to the phase rule.[5] From this point of view, the X-ray powder patterns of the exchanged solid phases were examined carefully. In the $Na^+ \rightarrow \overline{K}$ process, a single (002) reflection peak was observed for each of the samples at various stages of exchange, but the interlayer distance of the exchanger decreased with an increase in $\overline{X}_{Na}$, the ionic fraction of $Na^+$ in the exchanger: 10.83A

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* Present address: Department of Chemistry, The University of Tsukuba, Ibaraki 300-31.

for $\bar{X}_{\mathrm{Na}}=0$, 10.55A for $\bar{X}_{\mathrm{Na}}=0.30$, 10.34A for $\bar{X}_{\mathrm{Na}}=0.43$, and 9.99A for $\bar{X}_{\mathrm{Na}}=0.57$—0.80.

In the K$^+$→$\overline{\mathrm{Na}}$ process, the interlayer distance again decreased with an increase in $\bar{X}_{\mathrm{Na}}$: 10.75A for $\bar{X}_{\mathrm{Na}}=0.09$, 10.55A for $\bar{X}_{\mathrm{Na}}=0.31$, 10.30A for $\bar{X}_{\mathrm{Na}}=0.58$ and 9.35A for $\bar{X}_{\mathrm{Na}}=0.89$. However, here the (002) peak width was somewhat broader than those in the Na→$\overline{\mathrm{K}}$ process, indicating a close overlapping of the two peaks. In fact, at $\bar{X}_{\mathrm{Na}}=0.66$ (the corresponding $X_{\mathrm{Na}}$ is in the vicinity of 0.48), a splitting into two peaks was clearly observed.

Continuous changes in the interlayer distance can usually be explained by the formation of a solid solution. However, this interpretation can not be accepted in the present case, since the phase rule requires the coexistence of two phases in the $\bar{X}_{\mathrm{Na}}$ regions, which give vertical portions in the isotherm. The only possibility is that two kinds of solid solutions with very close interlayer distances are formed. As has been mentioned above, the evidence is found only in the $\bar{X}_{\mathrm{Na}}$ regions, 0.7—0.6, in the K$^+$→$\overline{\mathrm{Na}}$ process, but the possibility can not be excluded in other regions also if one take the unsatisfactory dissolution of X-ray powder diffractometry into account.

The powder patterns of the solid, in which the exchange reaction proceeded to the same extent, but in the opposite direction, gave somewhat different small peaks. The formation of different solid solutions during the forward and reverse processes should result in a hysteresis loop.

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