Potassium–sodium ion exchange on hydrated molybdenum bronze

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The chemistry of potassium–sodium ion exchange on hydrated molybdenum bronzes (ion-exchange isotherms and structural changes during the ion exchange, *etc.*) was investigated. Rather complex ion-exchange behaviour, including hysteresis phenomena, was observed. The behaviour was interpreted based on a discussion of structural changes of the materials and of the solvation and coordination behaviour of the investigated ions. A variety of techniques characterized the properties of the intercalated Na and K ions or their intercalation compounds.

Hydrated molybdenum bronzes are intercalation compounds of layered molybdenum trioxide. Such compounds have been expected to be interesting catalysts with special reaction field and/or ion conductors. However, so far, only specific ions (*i.e.*, alkali-metal ions, alkaline-earth metal ions, and a few transition ions) have been intercalated into the host material. In order to enable a variety of ions to be intercalated, it is important to reveal the factors which control the ion-exchange behaviour or which determine the structure of the intercalation compounds. Generally, ionic radius and charge of guest ions are considered to be factors. Lerf and Schöllhorn showed that there was a simple relation between the charge/radius ratio and the hydration structure for intercalation compounds of layered sulfides.[1,2] However, the problem is more complicated for oxide host materials, since the oxygen of the host takes part into the coordination structure of the guest species. Fig. 1 shows the relation between interlayer spacing and charge/ionic radius ratio for layered molybdenum oxide,[3–5] and by inspection, its complexity is obvious. For vacuum-dried samples of hydrated alkali-metal ion intercalation compounds, which are energetically more stable than the as-prepared or air-dried samples (AD series in Fig. 1), there are two types of structures. One is for smaller ions (*i.e.*, Li and Na), which are six-coordinated by two hydration water molecules and four terminal oxygen ions of the host in the structure [VD (6) series], and the other is for the larger ions (*i.e.*, Rb and Cs) which are eight-coordinated by eight terminal oxygen ions [VD (8) series].[4] The compounds of K with medium radii can adopt both structures, giving VD K(6) and VD K(8) bronzes, respectively. According to our experience, the latter phase might be energetically more stable than the former, but did not always form. We have been trying to delineate the factors which lead to the formation of the different phases over the last few years, considering the chemical composition of the samples, drying conditions, particle size of the host material, *etc.*, but as yet, have not been successful. Here, we investigate the chemistry of potassium–sodium ion exchange on hydrated molybdenum bronzes.

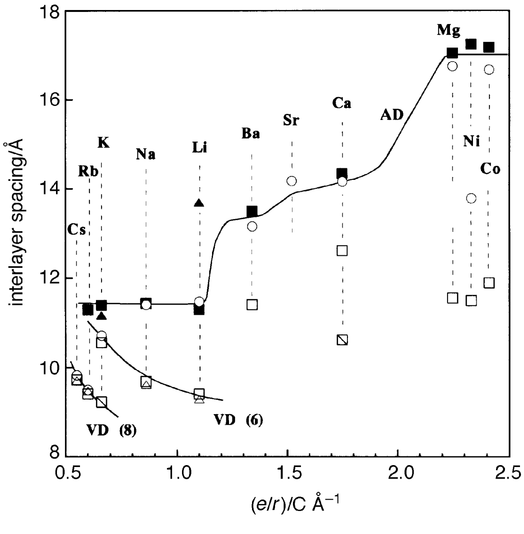

Fig. 1 Plot of the interlayer spacing *vs.* charge:radius ratio (*e*/*r*) for the various hydrated molybdenum bronzes $A_x(H_2O)_y[MoO_3]$ ($x \approx 0.25$ and 0.125 for mono- and bi-valent ions, respectively): ○, Schöllhorn *et al.*;[3] ▲ and ⧅, air-dried and vacuum-dried samples, respectively, from Thomas and McCarron;[4] ■, □ and ⧅, as-prepared, vacuum-dried (first phase) and vacuum-dried (second phase) samples, respectively, from our works

Experimental

Ion exchange

The starting material for the ion exchange was prepared by the method of Thomas and McCarron[4] and its typical composition was $(Na \cdot nH_2O)_{0.25}H_{0.08-0.12}MoO_3$, $n=2$ (VD type) or 5–6 (AD type).† In order to investigate the effects of the interlayer-spacing size on the ion-exchange behaviour, two types of starting materials with a different interlayer spacing (*i.e.*, AD and VD type hydrated bronzes) were used. In a typical ion-exchange procedure, 0.5 g of the starting material was suspended in 200 ml of alkali-metal chloride solution (total alkali-metal concentration = 1 mol dm^{-3}) at 303 K for 24 h. N_2 gas was bubbled through the suspension during exchange.

Measurements and analyses

The structures of the samples were investigated using a Rigaku Rint 1200M diffractometer with Cu-Kα radiation (40 kV, 40 mA). For most cases investigation was on wet samples just after the ion exchange or just after washing to obtain reliable structural information of the samples in suspension. The contribution due to Cu-Kα_2 radiation was removed by computation and the XRD data were analysed by a peak-convolution technique based on the least-squares method, if necessary. The software for the analysis was programmed by one of the authors. The pseudo-Voigt function and eighth-power polynominals were used as the profile function and as the background

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† A partially protonated compound was usually obtained even if the buffer was used to keep the solution neutral according to the preparation method of Thomas and McCarron. We have already investigated the reason why protons are inserted during the preparation and the results will be reported elsewhere.

Table 1 Monitoring of ion-exchange times leading to a steady state system[a]

time/h	K/Mo	Na/Mo
12	0.03	0.20
24	0.03	0.20
48	0.03	0.20
72	0.03	0.20

[a]Results obtained for the AD Na bronze in solution with $X_K = 0.15$. The measured values have an error of ±0.004.

Table 2 Alkali-metal contents of samples after ion exchange[a]

X_K	K/Mo	Na/Mo	A/Mo	Mo^{5+}/Mo
starting material	0.0	0.25	0.25	0.33
0.075	0.02	0.20	0.22	0.33
0.15	0.03	0.18	0.21	0.33
0.3	0.07	0.14	0.21	0.32
0.4	0.13	0.08	0.21	0.33
0.5	0.15	0.06	0.21	0.33
0.6	0.16	0.04	0.20	0.33
0.8	0.20	0.01	0.21	0.33
1.0	0.21	0.0	0.21	0.33

[a]Results obtained for the VD Na bronze. The measured values have an error of ±0.004.

function, respectively. To measure the water content of samples TG and DTA were performed on a MAC Science TG–DTA system 2010 instrument, at a heating rate of 10 K min^{-1}.‡ The Na, K and Mo contents of the samples were measured using a Hitachi atomic absorption spectrophotometer with the 5890.0 Å line of Na, the 7664.9 Å line of K, and the 3132.6 Å line of Mo, respectively. The Mo^{5+} content of the samples was determined by the method of Choain and Marion.[6]

Results

Ion exchange

The K/Na ion exchange proceeded very rapidly and was complete in minutes and a treatment time of 24 h used for the exchange in this work was long enough for the system to reach a steady state (Table 1). The ion-exchange behaviour (*i.e.*, total alkali-metal content of the sample after the exchange, exchange isotherm, *etc.*) varied slightly depending on exchange runs and starting material.§ After the exchange, the total alkali-metal content of the samples, A/Mo, was 0.20–0.23 as listed in Table 2. For the series of runs the total alkali-metal content was constant, but was slightly less than that of the starting material. The Mo^{5+} content retained the value of the starting material, showing that no oxidation occurred during the exchange. These results indicate that some protons were inserted during the ion exchange. The exchange behaviour apparently varied depending on the structure of the starting material, as shown below.

Ion-exchange isotherm

Fig. 2 shows two isothermal curves at 303 K for K/Na ion exchange initiated on AD materials (with a larger interlayer spacing, $d_{020} \approx 11.5$ Å) and VD materials (with a smaller interlayer spacing, $d_{020} \approx 9.6$ Å) hydrated bronzes, respectively. The upward departure of the curve from the dotted line indicates that K ions readily enter the interlayer sites, and *vice versa.* Therefore, for AD bronzes K^+ was predominantly incorporated by ion exchange for the entire molar fraction range of K^+ in solution (x_K). On the other hand the behaviour for VD type bronzes was more complicated. In this case, K^+ was enriched in the samples only in the region of $x_K \geqslant$ *ca.* 0.2 and was evenly incorporated with Na in the lower x_K range.

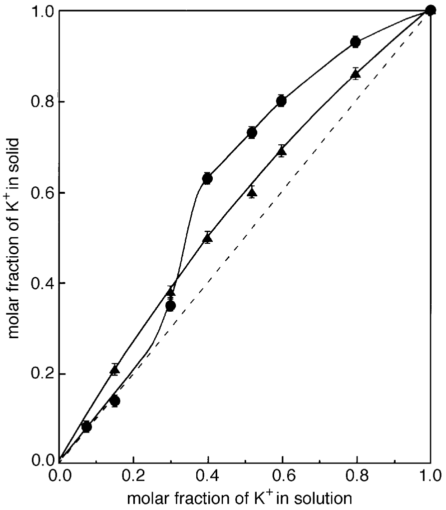

Fig. 2 Isothermal curves for K/Na ion exchange at 303 K. ▲ and ●, ion exchange begun on AD type and VD type hydrated bronzes, respectively.

Fig. 3 shows plots of log $K_{Na}{}^{K}$ (Kielland plots, $K_{Na}{}^{K} \equiv [\bar{K}][Na]/[\overline{Na}][K]$, where $[\bar{A}]$ and [A] refer to the concentration of A in the solid and in solution, respectively) for the above systems. The value of log $K_{Na}{}^{K}$ numerically indicates the ease of ion exchange of K/Na. Log $K_{Na}{}^{K} > 0$ means that K^+ predominates, and *vice versa.* For the AD bronze log $K_{Na}{}^{K}$ showed a small and constant positive value, meaning that K^+ slightly predominated monotonously over the entire range. On the other hand, log $K_{Na}{}^{K}$ had a larger value for the VD bronze than for the AD bronze in the range $x_K \geqslant 0.4$ for which K^+ uptake was more favoured. However, at lower x_K log $K_{Na}{}^{K}$ decreased in magnitude at lower concentrations and became nearly zero at $x_K \leqslant 0.2$, showing that the K/Na ratio in the solid phase was essentially the same as in solution.

Fig. 4 and 5 show the isothermal curves and the Kielland plots, respectively, for the reverse Na/K ion exchange. These

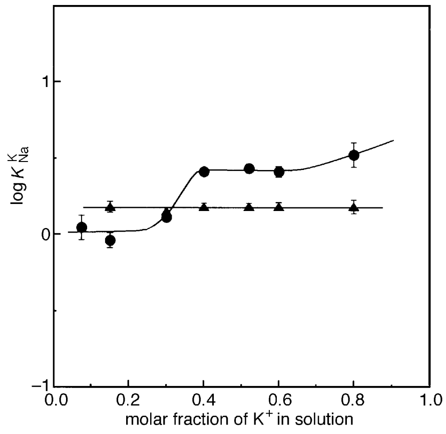

Fig. 3 Kielland plots for K/Na ion exchange at 303 K. ▲ and ●, ion exchange begun on AD type and VD type hydrated bronzes, respectively.

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‡ The hydration water content of the wet samples could not be determined from the TG–DTA results, since it was difficult to distinguish such water from physically adsorbed water or liquid water contained in such samples.

§ The variation was large in the region where the change in ion-exchange behaviour was large, for example, in the range of $0.3 \leqslant x_K \leqslant 0.6$ for VD. Such a deviation seemed to result under non-reversible conditions; we have confirmed that the results were qualitatively reproducible enough to lead the conclusions below.

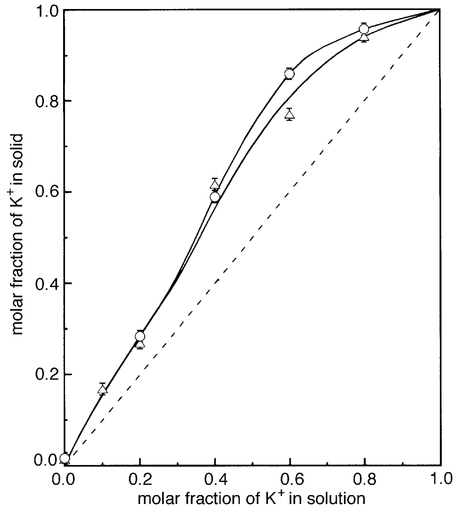

Fig. 4 Isothermal curves for reverse Na/K ion exchange at 303 K. △ and ○, ion exchange begun on AD type and VD type hydrated bronzes, respectively.

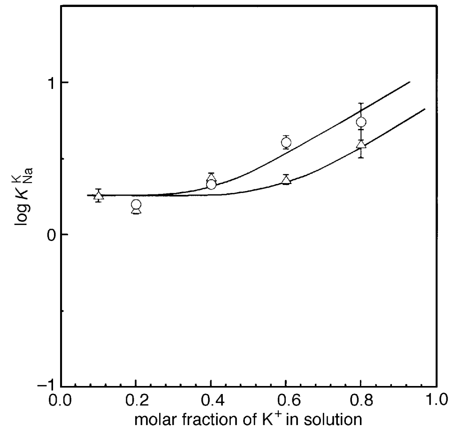

Fig. 5 Kielland plots for reverse Na/K ion exchange at 303 K. △ and ○, ion exchange begun on AD type and VD type hydrated bronzes, respectively.

isothermal curves did not match the corresponding ones for the K/Na ion exchange. The curve on the AD type bronze was similar to the corresponding one for Na/K ion exchange in the range $x_K \leqslant 0.2$, but departed upward above this range ($x_K > 0.2$) while the curve for the VD type bronze was different from that for the K/Na ion exchange, and similar to that for the reverse exchange on the AD type bronze. The Kielland plots confirmed these results, although it should be noted that the $\log K_{Na}{}^{K}$ values for the reverse ion exchange tended to be rather scattered.

Structural changes during ion exchange

In many cases, washing the samples with water led to changes in their XRD diffraction patterns, as shown below. Of course, the behaviour of ion exchange is expected to depend on the structure of the sample in suspension and should be mainly discussed on the basis of the results for unwashed samples. However, changes due to washing reflect the properties of the intercalation compounds or of the intercalated alkali-metal cations, and therefore both types of sample were investigated. For all the samples, the observed peaks were attributed to the hydrated bronzes, except for those at $2\theta = 28.3$ and 31.7°, which were observed only for the unwashed samples and were ascribed to KCl and NaCl used in the solutions, respectively. All the bronzes exhibited three characteristic peaks in the regions $2\theta = 6$–10, 15–20 and 23–29° (Fig. 6–10) which were attributed to 020, 040 and 060 reflections, respectively, and were related directly to the interlayer spacings of the samples. Two of the three peaks (*i.e.*, 020 and 060 reflections) showed large relative intensities and were useful in discussing the changes in structure; they are indicated by symbols in the figures. Moreover, it was reasonable to consider that the phases observed in the ion-exchanged samples were not primary bronzes and were partially substituted; as a consequence the phases were termed AD- or VD-like to distinguish them from the primary ones.

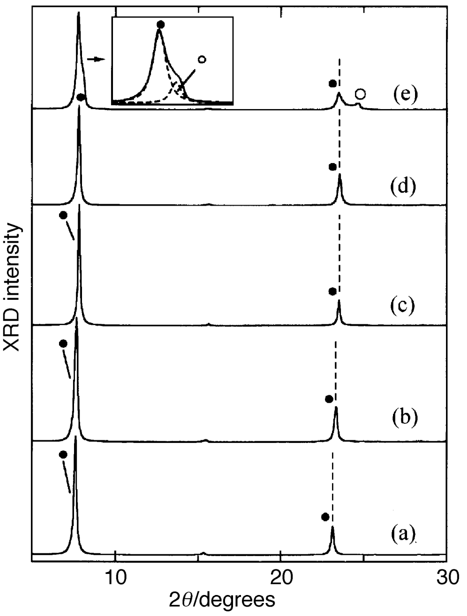

Fig. 6 XRD patterns of (a) the AD Na bronze, and of the as-prepared (unwashed) samples formed by treating the AD Na bronze with solutions of various x_K: (b) $x_K = 0.3$, (c) $x_K = 0.4$, (d) $x_K = 0.8$ and (e) $x_K = 1.0$. ● and ○, AD type and VD K(6)-like bronzes, respectively.

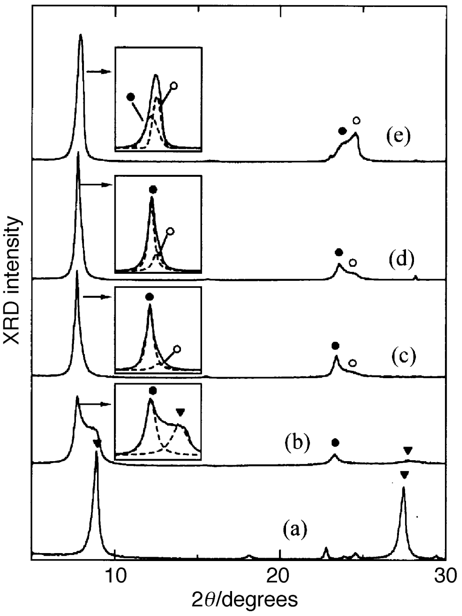

Fig. 7 XRD patterns of (a) the VD Na bronze, and of the as-prepared (unwashed) samples formed by treating the VD Na bronze with solutions of various x_K: (b) $x_K = 0.3$, (c) $x_K = 0.4$, (d) $x_K = 0.8$ and (e) $x_K = 1.0$. ●, ▼ and ○, AD type, VD Na (or VD Na-like) and VD K(6)-like bronzes, respectively.

Fig. 6 shows the XRD patterns of the AD type bronze samples as-prepared upon filtering after ion exchange. The samples showed a typical XRD pattern of the AD type bronze,

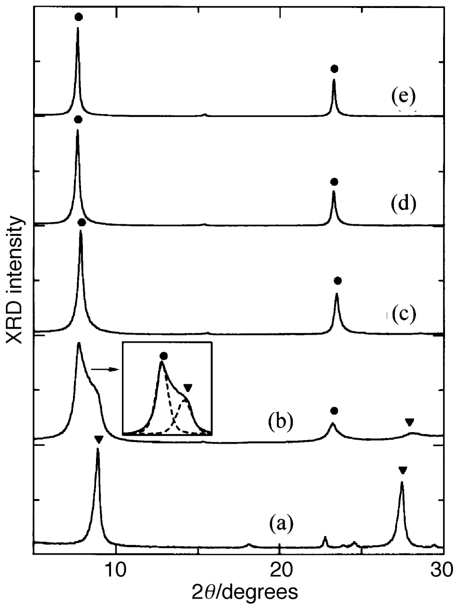

Fig. 8 XRD patterns of (a) the VD Na bronze, and of the samples washed after treating the VD Na bronze with solutions of various x_K: (b) $x_K=0.3$, (c) $x_K=0.4$, (d) $x_K=0.8$ and (e) $x_K=1.0$. ● and ▼, AD-type and VD Na (or VD Na-like) bronzes, respectively.

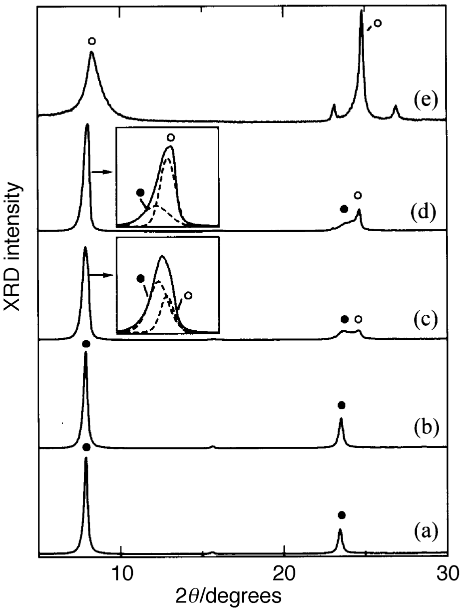

Fig. 9 XRD patterns of the as-prepared (unwashed) samples formed by treating the VD K(6) bronze with solutions of various x_K: (a) $x_K=0.0$, (b) $x_K=0.2$, (c) $x_K=0.6$ and (d) $x_K=0.8$; and of (e) the VD K(6) bronze. ● and ○, AD type and VD K(6) [or VD K(6)-like] bronzes, respectively.

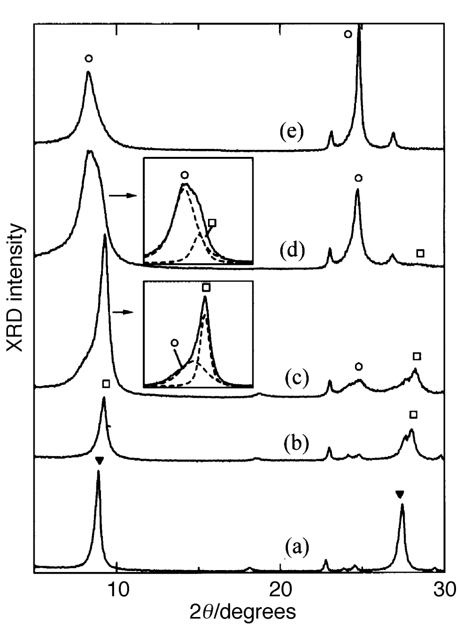

Fig. 10 XRD patterns of (a) the VD Na bronze, and of the samples washed and vacuum-dried after treating the VD Na bronze with solutions of various x_K: (b) $x_K=0.3$, (c) $x_K=0.4$, (d) $x_K=0.8$ and (e) $x_K=1.0$. ▼, ○ and □, VD Na, VD K(6) [or VD K(6)-like] and VD K(8)-like bronzes, respectively.

except for the sample treated at very high x_K (=1.0) and it is suggested that there was no large change in the host layer spacing during the ion exchange for this case. The sample treated with a solution of $x_K=1.0$ showed a portion of VD K(6)-like bronze, indicating that the AD type bronze with a high K^+ content released some hydration water of K^+ to turn into the VD K(6)-like bronze even in aqueous solution (*i.e.*, in water-rich conditions). This finding is important to understand the properties of intercalated K^+ or of the K^+ intercalation compound, and will be discussed later. On the other hand, for the washed samples only the XRD pattern of the AD type bronze was observed without any dependence on the chemical composition of the samples. This result seems to be contradictory to the above finding that the K-rich AD type bronze releases some hydration water of K^+ even in aqueous solution, and this will be discussed later. Moreover, it should be noted that the interlayer spacing of the AD type bronzes varied depending on the K^+ content of the samples, especially for the unwashed samples. This can be seen obviously from the changes in peak position of the 060 reflection,[¶] marked with a dashed line in Fig. 6. The changes indicated that the samples tended to exhibit a smaller interlayer spacing as the K^+ content increased.

For the VD type bronzes, structural changes were complicated (Fig. 7 and 8). According to the results for the unwashed samples (Fig. 7), the VD Na structure of the starting material was retained only in the region of low $x_K(\leqslant 0.3)$. At $x_K \geqslant 0.4$ this structure disappeared, and the AD and the VD K(6)-like bronzes appeared indicating a large change in the interlayer spacing of the sample. The AD type bronze appeared initially and changed into the VD K(6)-like structure as x_K increased. For the washed samples (Fig. 8) only the AD type bronze was observed except for the sample treated with solutions of low $x_K(\leqslant 0.3)$. In the washed sample treated at $x_K \leqslant 0.3$ the VD Na structure was the same as in the unwashed samples prepared by the same ion-exchange treatment, indicating that the structure was stable and did not alter upon washing with water.

Fig. 9 shows the XRD patterns of samples as-prepared by the reverse Na/K ion exchange for the VD type bronzes and the VD K(6) structure was observed in the range $x_K \geqslant 0.6$. However, this structure was never observed for the washed samples for all values of x_K. For the AD type bronze, there were no large structural differences between K/Na exchange and Na/K reverse exchange.

In order to understand the properties of the intercalation compounds, it is of importance to investigate the structure of vacuum-dried samples. Fig. 10 shows the XRD patterns of the ion-exchanged samples, which were vacuum-dried after washing, for the VD Na bronze. It should be noted that the VD K(8)-like bronze was observed for this case. The bronze appeared as a single phase in the range $0.075 \leqslant x_K \leqslant 0.3$, and changed to the VD K(6) type bronze, at larger x_K or as the

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[¶] The peak due to the 020 reflection tended to be rather scattered and was not considered reliable enough to discuss the changes in interlayer spacing precisely.

K^+ content of the sample increased (Table 2). Similar results were observed for the AD type bronzes, although the samples contained a greater portion of VD K(8)-like bronze than for the VD bronze, reflecting the tendency for the samples to exhibit a smaller K^+ content. The vacuum-dried samples for reverse Na/K ion exchange also showed similar structural changes to those for the K/Na ion exchange, depending on their chemical compositions.

Effect of temperature

Fig. 11 shows the log $K_{Na}{}^{K}$ *vs.* temperature plots for the two situations where K^+ is predominantly incorporated at 303 K ($x_K = 0.4$), and where K and Na ions are evenly incorporated at 303 K ($x_K = 0.075$). For the former, log $K_{Na}{}^{K}$ had a rather large positive value at 278 K, but became closer to zero as the temperature increased. On the other hand, for the latter, log $K_{Na}{}^{K}$ was almost zero at 278 K and did not change with the temperature. These results indicate that the ion exchange at higher temperature does not promote the incorporation of Na ions, but makes the K/Na ratio in the sample closer to that in solution.

According to the XRD and compositional analyses of the as-prepared (unwashed) samples formed by treating the VD Na bronze at $x_K = 0.075$ at various temperatures, samples prepared at the lower temperature possessed a larger portion of the AD type bronze, although all the samples had the same alkali-metal content. The change in the AD type portion appears to result from changes in the degree of hydration of the sample with samples prepared at lower temperature having a greater degree of hydration.

Discussion

The reverse Na/K ion exchange did not show the same behaviour as the K/Na ion exchange. This indicates that the equilibrium state was not realized in the timescale used in the present study. However, we have obtained many important findings concerning the chemistry of K/Na ion exchange.

Chemistry of K/Na ion exchange on hydrated molybdenum bronzes

For most cases, the AD type structure was observed mainly during exchange, even with VD type bronzes which turned into the AD type bronze, except at low x_K and for low Na content VD K(6) bronzes. The VD K(6)-like structure also appeared, and this and the AD type structure often coexisted simultaneously. Moreover, in the present work we have observed that the bronzes with K^+ showed a wide range of interlayer spacings, which differed from the sample containing only Na^+ (Fig. 6 and 12). We thus suppose that many states, which are slightly different in their hydration structures, exist for the bronzes. Such a multiplicity in structures and the coexistence of the two phases results in the variation of the ion-exchange behaviour.

More complicated ion-exchange behaviour was observed for the VD Na bronze. As shown previously (Fig. 3), log $K_{Na}{}^{K}$ was constant below $x_K = 0.2$, increased rapidly in the region $0.3 \leqslant x_K \leqslant 0.4$, and then increased gradually at higher x_K. The rapid change was mainly due to the transformation from the VD Na-like structure to the AD type one, and the gradual change resulted from the gradual transformation from the AD- to the VD K(6)-like structure. On the other hand, for the reverse ion exchange on the VD K(6) bronze only the change due to the latter transformation was observed (Fig. 5 and 9).

The behaviour of the two VD structures [VD Na and VD K(6) structures] during ion exchange showed obvious differences. The VD Na structure did not appear spontaneously by transformation from other structures, differing from the VD K(6) structure. Furthermore, the two structures were also different in their behaviour during washing with water with the VD Na structure remaining unchanged upon washing with water, while the VD K(6) structure was transformed readily into the AD structure. Na^+ exhibits a higher surface charge density and the intercalated Na^+ ion is expected to show a larger hydration energy than intercalated K^+. According to geometrical considerations, the Na^+ ion more readily fits into the space formed by the terminal oxygen ions of the Mo—O layer in the VD structure than K^+. It is thus supposed that Na^+ exhibits stronger binding with the terminal oxygen ions. Therefore, the above differences are suggested to result from the fact the large hydration energy and the strong binding energy kinetically hindered transformation between the AD and VD Na structures. The compositional limit where the sample cannot retain the VD Na structure (Table 2 and Fig. 7 and 8) appears to be at Na/Mo *ca.* 0.15. A similar value was observed when the VD Na structure collapsed and was transformed into the hydrogen bronze structure during H/Na ion exchange.[7] This value corresponds to an occupation of 3/5 of the available sites, since the number of possible Na sites in the host structure is equivalent to Na/Mo = 0.25. On the other

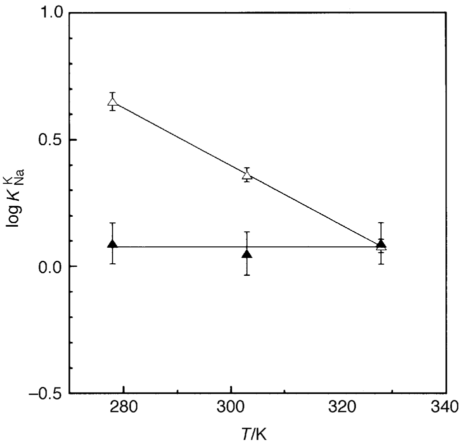


Fig. 11 Dependence of log $K_{Na}{}^{K}$ on temperature for the cases where the VD Na bronze was treated with solutions with $x_K = 0.4$ (△) and $x_K = 0.075$ (▲)

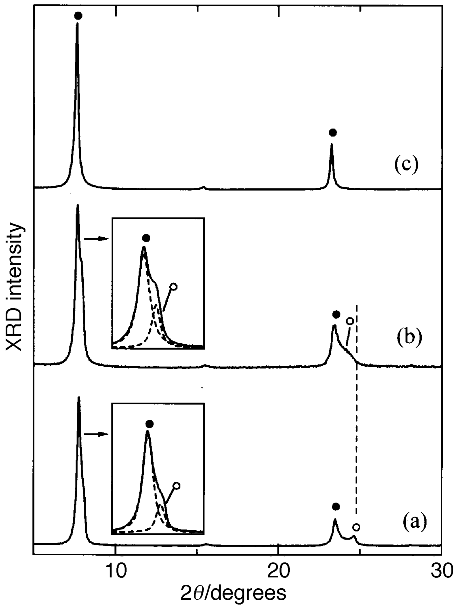


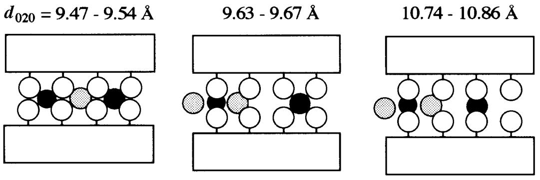
Fig. 12 XRD patterns of the as-prepared (unwashed) samples formed by treating the AD Na bronze with 1 mol dm^{-3} KCl solution (a) and with 0.1 mol dm^{-3} KCl solution (b), and treated with water after ion exchange with 1 mol dm^{-3} KCl solution (c). ● and ○, AD type and VD K(6)-like bronzes, respectively.

hand, the VD K(6) structure behaves curiously, *i.e.* it readily changed to the AD structure upon washing with water, while it appeared spontaneously from the AD structure in suspension. These results initially seem to contradict each other, therefore we carried out a further investigation on the structure of the sample treated with solutions of intermediate concentrations (0.1 mol dm^{-3} total alkali-metal concentration) between 1 and 0 mol dm^{-3} (water). Fig. 12 shows the XRD result together with those of the samples as-prepared by the ion exchange with a 1 mol dm^{-3} solution and washed after the ion exchange with a 1 mol dm^{-3} solution. The sample treated with a 1 mol dm^{-3} solution showed the VD K(6)-like phase, as mentioned above, while the sample treated with the 0.1 mol dm^{-3} solution exhibited a phase with a slightly larger interlayer spacing than that of the VD K(6)-like bronze. We regard this phase as a type VD K(6)-like bronze but with a higher degree of hydration, since this phase shows a larger interlayer spacing. The sample washed with water showed no VD K(6)-like bronze phase. Thus the structural differences are suggested to result from differences in the degree of hydration. The changes in hydration degree of the samples lead directly to changes in the interlayer spacing and simultaneously result in the dilution or concentration of the solution. Therefore, the transformation from the AD to the VD K(6) structure is suggested to be a balance between energy loss due to dehydration, energy gain due to reduction of interlayer spacing resulting from the dehydration, and energy change due to dilution of the solution with dehydrated water. Only a small number of water molecules are involved in the dehydration and the energy change due to the dilution is expected to be small. The present result is an example where a small energy change plays an important role in energy balance to control the structure of the samples.

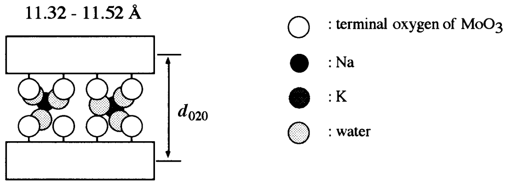
From the present work, the differences in the ion-exchange behaviour between the three bronze structures: AD, VD K(6) and VD Na, have been revealed. In the VD Na structure, Na and K ions were incorporated evenly, but in the other two structures, especially in the VD K(6) structure, K^+ is incorporated predominantly. For the AD type structure it is observed that the bronze with a larger K^+ content showed a smaller interlayer spacing, despite the fact that K^+ is larger than Na^+. It is expected that K^+ binds more weakly with hydration water than does Na^+. We thus suppose that the host favours K^+ which releases some of its hydration water easily and allows the host to have a smaller interlayer spacing; in the VD K(6) structure with a smaller interlayer spacing incorporation of K^+ ion seemed to be more favoured for the same reason. However, we have not yet obtained an explanation as to why Na^+ and K^+ were equally incorporated into the VD Na structure.

Structure of the intercalation compounds

Four types of phases: VD K(8), VD Na, VD K(6) and AD type bronzes, have been observed. According to their interlayer spacings and the ionic sizes of intercalated Na and K, the structural models for the bronzes are given in Fig. 13, together with their observed interlayer spacings. Models where the occupancies of Na and K ions are equal are shown. The occupancies will vary depending on the sample composition. In the VD K(8)-like bronze, both Na and K ions occupy sites where the ions are coordinated by eight terminal oxygen ions of the Mo—O framework. According to the present study this phase was observed for the vacuum-dried samples with a rather large Na^+ content. However, we should state that the VD K(8) bronze obtained previously[8] was a true K^+ intercalation compound without any contamination of Na^+. For the VD Na-like structure the Na ion occupies sites where it is coordinated to four terminal oxygen ions, while the K ion occupies an eight-coordinate site. In the VD K(6)-like bronze both Na and K ions occupy sites coordinated by four terminal oxygen ions. In the AD type bronze Na and K ions are not coordinated directly to terminal oxygen ions.



(a) VD K(8)-like structure (b) VD Na-like structure (c) VD K(6)-like structure



(d) AD type structure

Fig. 13 Schematic models of the four bronzes observed

Conclusion

It was found that the ion-exchange behaviour depended on the structure of the starting material. Owing to kinetic hindrance of certain transformations the behaviour was substantially different between K/Na and Na/K ion exchange. The temperature affected the ion-exchange behaviour and there was a tendency for the K/Na ratios of samples to match the solution values at higher temperatures. As to factors controlling the structure of the hydrated molybdenum bronze during K/Na ion exchange, the following are suggested: (*i*) the energy change due to the change in the interlayer spacing, (*ii*) the energy gain due to the binding of the alkali-metal ion with the terminal oxygen ions of the layer, (*iii*) the energy gain due to hydration of the alkali-metal ion in the bronze and (*iv*) the energy change due to dilution or condensation of the solution.

According to the present study, it is expected that the terminal oxygen–sodium ion bond energy in the VD Na structure is large and that the intercalated K ion shows a rather low hydration energy. Thermodynamic data will be evaluated more fully in the future.

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