Synthetic Inorganic Ion-Exchange Materials LX. Ion Exchange and Chromatographic Separation of Alkali Metal Ions on Cubic Ammonium Molybdate — A Novel Cation Exchanger

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Synopsis. The ion-exchange selectivity of H^+-form of cubic ammonium molybdate (H-CAM) was studied for alkali metal ions in both HNO_3 and NH_4NO_3 media. Ideal ion-exchange reaction was observed in both the media with high selectivity for Rb^+ and Cs^+. The selectivity sequence was found to be $Li^+<Na^+<K^+<Rb^+<Cs^+$ in accordance with the Eisenman sequence-1 in both the media, with separation factors greater than the commercial polystyrene strong acid exchange resin. Efficient separation of alkali metal ions could be achieved on H-CAM column.

The inorganic ion-exchange materials possess significant superiority over the commercial organic ion-exchange resins at high temperatures and ionizing radiations. Some of these materials are very selective showing greater exchange capacity for certain metal ions.[1-4] Abe and Ito[5] studied adsorption properties of various metal oxides and hydrous oxides. An insufficient information about the ion-exchange properties of hexavalent metal hydrous oxides could also be found in the literature.[6] The isopolymolybdates and tungstates have been reviewed by Tytko and Glemser.[7] The heteropoly acid salts of molybdenum have been sufficiently worked on for their ion-exchange properties.[8,9] The acid salts and hydrated compounds of Mo(VI) have drawn a considerable interest for their catalytic properties too. However, less attention has been given to the work concerning the ion-exchange properties of these materials.

The previously reported results[10] indicated that cubic ammonium molybdate (CAM), prepared by the reaction of HNO_3 and hexaammonium heptamolybdate under controlled temperature conditions and reagent specifications, showed a reversible NH_4^+/H^+ exchange reaction. This paper describes the ion-exchange behaviour of H^+-form of CAM (H-CAM) cation exchanger along with some chromatographic separations of alkali metal ions.

Experimental

Synthesis of CAM and H-CAM. CAM was synthesized under optimum conditions and reagent specifications by the reaction of hexaammonium heptamolybdate tetrahydrate and HNO_3 (Wako Pure Chemical Ind., Japan) at 60 °C, following the previously described procedure.[10] The H^+ form (H-CAM) was obtained by conditioning CAM with 0.5 M (M=mol dm^{-3}) HNO_3 by using a column. H-CAM was used throughout the investigations reported here.

Rate of Adsorption and Ion-Exchange Selectivity. The rate of adsorption of alkali metal ions on H-CAM was investigated by equilibrating 0.25 g of the exchanger with 25 cm^3 of 10^{-4} M alkali metal ion solutions containing different concentrations of HNO_3 or $^*NH_4NO_3$ (*=NH_4NO_3 solutions in 10^{-2} M HNO_3).

The distribution coefficients (K_d) for alkali metal ions were determined batchwise by equilibrating 0.10 g of H-CAM with 10 cm^3 of 10^{-4} M alkali metal ions in different concentrations of HNO_3 or $^*NH_4NO_3$ at 30±0.5 °C with intermittent shaking. The metal ion concentrations in the equilibrated solutions were determined by a Varian Techtron-1100 atomic absorption spectrophotometer using air-acetylene flame. The K_d (cm^3 g^{-1}) values were calculated by the following equation,

$$K_d=\frac{\overline{X}}{X}\times\frac{V}{W},$$

where $\overline{X}$ and X are the amounts of metal ion in exchanger and solution respectively. V is the volume of equilibrated solution and W stands for the weight of H-CAM.

Chromatographic Separations. Separations of mixed alkali metal ions were conducted on H-CAM column (2.5—3.5 cm×0.5 cm i.d.). A mixed solution containing 1.0 μmol of each metal ion was loaded at the top of the column, kept for 12—14 h (to assure complete adsorption of metal ions on H-CAM) and then eluted with HNO_3 or $^*NH_4NO_3$ solutions of various concentration. A continuous charging of the eluents was carried out through a high-pressure pump (Nihon Seimitsu Kagaku, model NP-DX-2). The effluent fractions were collected with the help of a fraction collector (Ohtake Works, model UM-160) and analyzed for the metal ion concentrations.

Results and Discussion

Specification of CAM and H-CAM. CAM was a yellowish granular material which could be ground even to <40 mesh size. Characterization of CAM and H-CAM showed the same results as reported previously.[10] Both CAM and H-CAM possessed a body-centered cubic structure with crystal lattice of 12.94±0.005 Å. The chemical formulae of CAM and H-CAM could be represented as $[(NH_4)_{0.78}(NH_4)_2]O_{1.39}\cdot 14.16MoO_3\cdot 6.08H_2O$ and $[H_{0.68}(NH_4)_2]O_{1.34}\cdot 14.16MoO_3\cdot 6.92H_2O$, respectively. The H^+ of H-CAM was found to be reversibly exchanged with NH_4^+ with an exchange capacity of 0.31 mequiv g^{-1} for the latter ion.[10]

Exchange Equilibria and Ion Selectivity. The time required for the equilibration of alkali metal ions was determined through the rate of sorption of these ions on H-CAM in HNO_3 and $^*NH_4NO_3$ media. The exchanger showed a fair rate of adsorption for all the alkali metal ions. The rate of adsorption in $^*NH_4NO_3$ medium was slower for all alkali metal ions by one day as compared to HNO_3 medium. The ion-exchange reaction for all the ions was relatively fast in HNO_3 medium, except Na^+. About 1—2 days were required for ion-exchange equilibria of Li^+, K^+, Rb^+, and Cs^+, whereas for Na^+ it took>2 days.

The ion-exchange reaction where the exchange of micro-amounts of n-valent cations (M^{n+}) follows the stiochiometric ion-exchange mechanism rather than specific adsorption, can be represented as follows,

$$n\overline{H^+} \text{ or } n\ \overline{NH_4^+} + M^{n+} \rightleftarrows \overline{M^{n+}} + n\ H^+ \text{ or } n\ NH_4^+, \quad (1)$$

where bar denotes the exchanger phase then,

$$\log K_d = -n \log\{[H^+] \text{ or } [NH_4^+]\} + \text{const.} \quad (2)$$

The log-log plot of K_d vs. [$^*NH_4NO_3$] (Fig. 1) showed a linear relationship with a slope of -1 for all the alkali metal ions indicating the 1:1 ideal ion-exchange reaction with greater separation factors. The selectivity increased in the order of $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ in accordance with the Eisenman sequence-1.[11]

The above mentioned requirements (Eq. 2), however, are not always met with, either due to the nature of the exchanger[12] or the nature of the small number of groups (contained in the exchanger) which interact specifically with the trace ion.[13] The log-log plot of K_d vs. [HNO_3] (Fig. 2-dotted lines) was also linear with a slope of -1 for all the alkali metal ions except K^+. The selectivity sequence was found to be the same as in $^*NH_4NO_3$ medium with very high K_d values for Rb^+ and Cs^+ even in 8.0 M HNO_3 solution. For K^+ the slope was observed to be <-1 due to its greater exchange affinity for the structural NH_4^+ in H-CAM (irrespective of H^+ concentration of equilibrated K^+ solution) owing to the almost same crystal ionic radii,[14,15] The most probable ion-exchange reaction of the K^+ could be described as,

$$\overline{H^+} + K^+ \rightleftarrows \overline{K^+} + H^+, \quad (3)$$

$$\overline{NH_4^+} + K^+ \rightleftarrows \overline{K^+} + NH_4^+, \quad (4)$$

where $\overline{NH_4^+}$ represents the structural NH_4^+ in H-CAM.

A fractional contribution of the process (4) seems to be responsible for the slope of <-1 for K^+ exchange. Almost same behaviour was expected for Rb^+ too, however the selectivity of ions at SA-site seems to be different for K^+ and Rb^+ (or Cs^+) at low metal ion concentration. The ideal exchange of K^+ (slope -1) and greater separation factor for Rb^+ and Cs^+ in $^*NH_4NO_3$ medium may also be due to the same fact mentioned above. The K_d and separation factors for the alkali metal ions in both the media were found to be greater than that of ion-exchange resin (Table 1).

The K_d values for all the alkali metal ions were observed to be inversely dependent on the initial concentrations of metal ions (Fig. 2) indicating the Langmuir-type ion-exchange reaction.[17] The log-log plots of K_d vs. [H^+] were linear indicating an ideal exchange reaction, however the slope of plots decreased than unity with increasing metal ion concentration. This fact can be explained on the basis of following equations. For the ion-exchange reaction,

$$\overline{nH^+} + M^{n+} \rightleftarrows \overline{M^{n+}} + nH^+, \quad (5)$$

where bar represents the exchanger phase and M^{n+} as n-valent cation, at lower [M^{n+}] e.g. 10^{-4} M [M^{n+}], $[H^+]^n \gg [M^{n+}]$ and $\overline{[H^+]^{n+}} \gg \overline{[M^{n+}]}$ then,

$$K_d = \text{constant} \times \frac{1}{[H^+]^n}, \quad (6)$$

and the slope of equation (6)$=-1$ if $n=1$. However, when [M^{n+}] increases e.g. $10^{-3} \rightarrow 10^{-2}$ etc, $\overline{[M^{n+}]} \gg \overline{[H^+]}^n$ and $\overline{[H^+]}^n$ is a variable depending on $\overline{[M^{n+}]}$ then,

$$K_d = \text{constant} \times \frac{\overline{[H^+]^n}}{[H^+]^n}, \quad (7)$$

and slope of equation (7)<-1 depending on the increase in metal ion concentration.

Similar observations have also been reported by Abe et al.[12,18,19] in the ion-exchange isotherms for some inorganic ion exchangers. This fact indicated the rigid structure of H-CAM. Moreover, the strong dependence of K_d on initial metal ion concentration (Fig. 2) which was observed to be stronger for K^+, Rb^+, and Cs^+ shows that, besides the ordinary exchange site {H^+-site or H^+ exchangeable NH_4^+-site (EA-site) in CAM}, H-CAM also contain an additional functional group {structural NH_4^+-site (SA-site)} of high affinity to certain cations e.g. K^+, Rb^+, and Cs^+.

Chromatographic Separations. In view of the K_d values and separation factors for the neighboring ion pairs, separation of alkali ions was carried out with both HNO_3 and $^*NH_4NO_3$ solutions (eluents) of different concentrations at ambient temperature.

Table 1. K_d Values and Separation Factors (α)[a] on H-CAM and BIO-RAD AG 50W-X8[16]

Exchanger	Medium	Parameter	Li		Na		K		Rb		Cs
H-CAM	1 M HNO_3	K_d	1.23×10^{-1} [b]		2.46×10		6.86×10^2		1.56×10^4		2.0×10^4
		α		2.0×10^2		28		22.8		1.2	
	0.01 M NH_4NO_3 + 0.01 M HNO_3	K_d	*7.2×10^{-3} [b]		6.0		4.9×10		6.4×10^2		4.6×10^3
		α		8.3×10^2		8.2		13.0		7.2	
BIO-RAD AG 50W-X8	1 M HNO_3	K_d	3.9		6.3		11.4		13.4		16.8
		α		1.6		1.8		1.1		1.2	

a) $\alpha = K_{d_B}/K_{d_A}$. b) Extrapolated values to 1.0 M HNO_3.

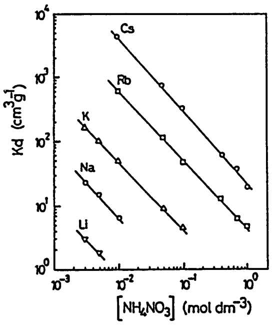

Fig. 1. Distribution coefficients (K_d) for alkali metal ions on H-CAM as a function of [NH_4NO_3] (contained in 0.01 M HNO_3). H-CAM: 0.10 g, Init. [M^+]: 10^{-4} M, Soln vol: 10 cm^3, Temp: 30±0.5 °C.

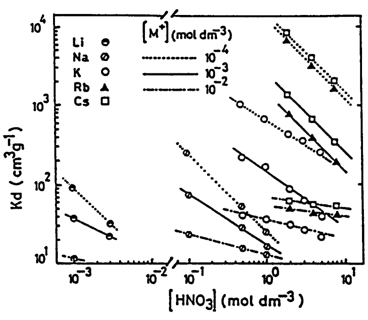

Fig. 2. Distribution coefficients (K_d) for alkali metal ions on H-CAM as a function of HNO_3 concentration and dependence of K_d on the initial concentrations of metal ions. H-CAM: 0.10 g, Soln vol: 10 cm^3, Temp: 30±0.5 °C.

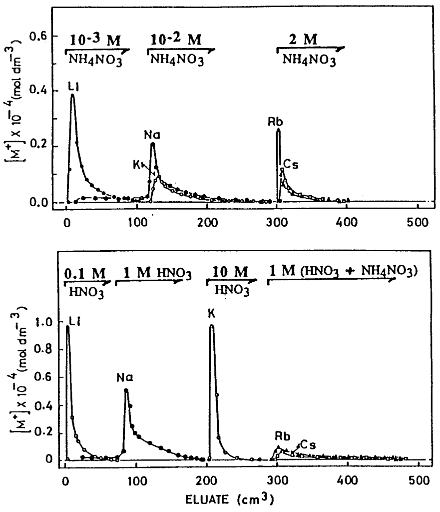

Fig. 3. Chromatographic separations of alkali metal ions on H-CAM. Top—Eluent: NH_4NO_3 soln (in 0.01 M HNO_3), H-CAM: 0.7637 g., Bottom—Eluent: HNO_3, H-CAM: 0.9209 g, Loading: 1 μmol of each M^+, Flow rate: 0.05 $cm^3\,min^{-1}$.

Figure 3(top) indicates the separation chromatogram with *NH_4NO_3 as an eluent. Li^+ was separated with 99% recovery from the Na^+-K^+ and Rb^+-Cs^+ groups with tailing rears. A long leading front was also observed for Na^+.

Successful separation of Li^+, Na^+, and K^+ with a respective recovery of 99.9, 100, and 82% was achieved with HNO_3 of different concentrations (Fig. 3-bottom). A tailing rear was observed for all the ions and long leading front for Na^+ in addition to the tailing rear. The long leading front for Na^+ was observed to be due to some solubility of H-CAM in HNO_3 eluent as well as slow rate of adsorption of the ion on H-CAM.

It has been known that the shape of elution curve depends on the type of ion-exchange isotherm.[20] The retention time may be a function of loading on the exchanger. The peak with a sharp front and a tailing rear (Langmuir type) for the alkali metal ions in the elution curves were evident from the strong dependence of K_d on the initial concentrations of metal ions (Fig. 2).

Complete separation of Rb^+ and Cs^+ was not possible even with concentrated HNO_3 or *NH_4NO_3 solutions. However the recovery of these ions in a mixed eluent {1 M (NH_4NO_3+HNO_3)} was better. The low recovery of Rb^+ (35%) and Cs^+ (25%) with 2.0 M *NH_4NO_3 and 60% and 54% respectively with the mixed eluent may be due to migration of these ions to the less accessible sites, or alternatively that strong bonding forces are involved for low loading.

In conclusion H-CAM (or CAM) can be used as a selective cation exchanger for heavy alkali metal ions even at higher acid concentrations. The very high selectivity of H-CAM towards Cs^+ will enable the latter to be quantitatively removed from the nuclear wastes, rain (fall-out Cs) or even sea water despite a large amount of matrix to Cs^+. It can work as a reliable material for the solid state storage of radioactive cesium at lower cost. H-CAM can be employed to separate K^+ and Rb^+ efficiently which are usualy difficult to do on some of the inorganic ion exchangers.

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