NOTE

SORPTION OF COBALT COMPLEX CATIONS ON HETEROPOLY COLLIDINIUM
TUNGSTO AND MOLYBDOARSENATES

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Sorption of two ammine complex cations, i.e., $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ on the heteropolyacid salt exchangers, collidinium tungsto and molybdo arsenates, which do not show affinity for simple transition metal ions, is investigated and discussed according to their cationic size. On the basis of the studies carried out it is concluded that these exchangers may also be used for the sorption and separation of transition metal ions as ammine complex cations.

The extent of sorption of a metal cation on an exchanger not only depends on its charge, size, polarizability but also is controlled to a great extent by balance of energy change occurring as a result of its electrostatic interaction with exchange sites and change in free energy of hydration when it moves from the bulk solution into the exchanger. It appears that if a hydrated metal cation is not sufficiently adsorbed, this is more likely due to unfavourable, partial/complete free energy change that occurs on dehydration of the cation while moving from the solution and getting adsorbed. In such cases the complex of the metal with neutral ligand which is obviously unhydrated due to large size, is likely to be significantly adsorbed.

Our recent studies on the exchange properties of collidinium molybdoarsenate ($(\text{C}_8\text{H}_{11}\text{NH})_3\text{Mo}_{12}\text{AsO}_{40}^{1)}$ and collidinium tungstoarsenate, ($(\text{C}_8\text{H}_{11}\text{NH})_3\text{W}_{12}\text{AsO}_{40}^{2)}$ have shown them to be poor sorbents for transition metals. In view of the above, it was thought desirable to investigate their sorption on these exchangers in the form of complex cations expecting them to be significantly adsorbed. Thus, the sorption of two ammine complex cations, i.e., $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ on these exchangers has been studied and the results are compared with the sorption of Co^{2+} ions.

EXPERIMENTAL

All the reagents used were of analytical grade. Collidinium nitrate was

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prepared by mixing concentrated nitric acid and distilled 2,4,6-collidine(2,4,6-trimethylpyridine) in equimolar amounts. The white precipitate obtained was crystallized from a water and ethanol mixture and dried in a vacuum desiccator. The exchangers, collidinium molybdoarsenate (CMA) and collidinium tungstoarsenate (CTA) have been prepared and analyzed as already reported.^{1),2)} The two complexes of cobalt, $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ and $\text{Co}(\text{en})_3\text{Cl}_3$ have been prepared by standard methods.³⁾ Infrared spectra of the compounds were examined⁴⁾ and their purity was ascertained by the gravimetric estimation of cobalt(III).⁵⁾

Bausch and Lomb spectronic-20 and Unicam SP-500 were used for spectrophotometric determinations. For sorption studies, 0.1 g of the exchanger (mesh size, 100-200) was taken in a set of pyrex boiling tubes containing 10 cm³ of cobalt complex solution of varying concentrations. The solutions were shaken intermittently and estimated for the complex cations after the attainment of equilibrium (48 h). Amount sorbed was estimated by noting the difference in the absorbances of the colored solutions before and after the sorption.

RESULTS AND DISCUSSION

The dependence of the extent of sorption on the initial concentration of complex cations has been shown in Figs. 1 and 2 on CMA and CTA, respectively, in the form of sorption isotherms. The values of sorption capacity calculated from these Figures for $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ on both the exchangers are given in Table 1. The saturation capacity for $\text{Co}(\text{NH}_3)_6^{3+}$ on CMA is less than its theoretical capacity (1.34 meq of exchangeable collidinium cation per g of exchanger) while it is near to the theoretical capacity (0.91 meq per g) in case of CTA. The uptake of $\text{Co}(\text{en})_3^{3+}$ is much less than that of $\text{Co}(\text{NH}_3)_6^{3+}$ on both the exchangers. The low saturation capacity of $\text{Co}(\text{en})_3^{3+}$ appears to be due to its larger size which hinders its movement through the pores for exchange sites. Moreover, the $\text{Co}(\text{en})_3^{3+}$ ions which have undergone exchange at the easily available sites (at the exterior of the exchangers) during the initial stages of equilibrium may also block the pores in these exchangers, thus preventing the further entry of these ions. This resulted in the low sorption of $\text{Co}(\text{en})_3^{3+}$ on these exchangers.

It is seen that these cobalt complex cations are much more strongly adsorbed as compared to simple cobalt(II) cation. This higher adsorption of complex cations appears due to their larger size which prevents their hydration whereas Co^{2+} is strongly hydrated. The strongly hydrated Co^{2+} ion is not adsorbed on the exchanger, possibly due to unfavourable energy change involved in the dehydration while getting adsorbed. On the other hand, the larger size cobalt complex cations are not only unhydrated but tend to be pushed out from the aqueous solution due to strong cohesive forces between water molecules. This pushing out from bulk solution favors their adsorption on the exchanger. Thus, it is seen that size has become a factor which affects the adsorption of the ion. However, it does not follow from the above that larger is the size of complex cation more would be its adsorption because, above certain optimum size, the entry of the cation into the exchanger gets hindered. This is borne out by the results when the uptake of Co^{2+} , $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ is compared in terms of distribution coefficient

Table 1 Saturation exchange capacity of
exchangers for complex cations

Exchangers	Complex cations; meq g ⁻¹	
	Co(NH ₃) ₆ ³⁺	Co(en) ₃ ³⁺
CTA	0.84	0.19
CMA	0.81	0.30

Fig. 1 Sorption isotherms
of complex cations on
collidinium molybdoarsenate
at 27°C.

△ for Co(en)₃³⁺ and
○ for Co(NH₃)₆³⁺

Fig. 2 Sorption isotherms
of complex cations on
collidinium tungstoarsenates
at 27°C.

△ for Co(en)₃³⁺ and
○ for Co(NH₃)₆³⁺

(Kd) values at $0.002 \text{ mol dm}^{-3}$. The uptake follow the order $\text{Co}^{2+} (\text{Kd}=6)^{2)} < \text{Co}(\text{en})_3^{3+} (\text{Kd}=91) < \text{Co}(\text{NH}_3)_6^{3+} (\text{Kd}=1234)$ on CTA and $\text{Co}^{2+} (\text{Kd}=4)^{1)} < \text{Co}(\text{en})_3^{3+} (\text{Kd}=43) < \text{Co}(\text{NH}_3)_6^{3+} (\text{Kd}=300)$ on CMA. These results suggest the existence of a optimum size for which the exchange would be maximum on these exchangers. If the size of the cation undergoing exchange is smaller or greater than the optimum size, exchange would be reduced. It appears that the size of $\text{Co}(\text{NH}_3)_6^{3+}$ is close to the optimum size in case of CTA as the maximum adsorption approaches theoretical exchange capacity. These complex cations can readily be desorbed by a mixture of 2.0 mol dm^{-3} each of nitric acid and collidinium nitrate.

Thus, it can be concluded that the exchangers CTA and CMA can be used even for the sorption of poorly adsorbed simple ions^{1),2)}, i.e., Co(II) , Ni(II) , Cu(II) , Zn(II) , Cd(II) and Ag(I) in cation complex form. These metals can then be separated from those metals (alkali, alkaline earth, Al(III) and Fe(III)) which are neither adsorbed nor form complexes with the neutral ligands under consideration. Separation of metal complex cations of different sizes is also possible.

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