

A STUDY ON THE CATION EXCHANGE OF [Co(NH₃)₆]³⁺ FROM H-Co (NH₃)₆-VERMICULITE BY INORGANIC AND QUATERNARY AMMONIUM IONS

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Abstract—The exchange of [Co(NH₃)₆]³⁺ from its vermiculite complex has been carried out with a number of inorganic and alkyl quaternary ammonium ions of varying ionic sizes. The distribution and selectivity coefficients of the desorbing ions increase in the order: Li < Na < NH₄ < K < Rb < H < Cs for the monovalent, Ca < Mg for the bivalent and (C₂H₅)₄N < (CH₃)₄N ≪ CTA (cetyl trimethyl ammonium) < CP (cetyl pyridinium) for the organic ions. The ΔG° values of some of the cation exchange reactions have been calculated by an equation of Kielland (1935).

INTRODUCTION

The interaction of inorganic (Barshad, 1954; Wild and Keay, 1964) and organic ions (Weiss, Mehler and Hofmann, 1956; Sutherland and MacEwan, 1961; Garrett and Walker, 1962) with vermiculite has not been so extensively investigated as other clay minerals. Recently some interesting exchange studies have been reported by Das Kanungo and Chakravarti (1971), where monovalent and bivalent cations were the exchanging and exchangeable ions. No systematic study has been reported so far on the exchange of inorganic trivalent complex ions, such as hexamine cobalt (III), [Co(NH₃)₆]³⁺, by different inorganic and organic ions. The work reported here involves a study of the cation exchange behavior of hexamine cobalt (III) ion on vermiculite by inorganic and quaternary ammonium ions. The experimental results have been analysed in the light of the approach of Kielland (1935).

EXPERIMENTAL

The vermiculite was obtained from the Geological Survey of India, Calcutta, and judged to be pure from X-ray powder diffraction studies. A fraction < 2.0 μm was isolated and collected by the usual method of dispersion and sedimentation. The fractions so collected were then treated with dilute HCl and 6% H₂O₂ to remove traces of organic matter, if any. After boiling to decompose the organic matter and excess H₂O₂, the clay fractions were washed two or three times with distilled water to remove the soluble impurities. The clays were then converted to the H-form by appropriate treatment with exchanger resins (Dowex 50 w × 8 and Dowex 2 × 8). Its cation exchange capacity (CEC) was found to be 120 m-

equiv./100 g by titration with Ba(OH)₂ in the presence of 1M BaCl₂ solution with phenolphthalein as indicator.

About 20 g of the H-vermiculite was then mixed with Co(NH₃)₆Cl₃ in concentrations approximately 400 m-equiv./100 g of clay. After 24 hr the excess salt was washed out until the leachate had zero optical density. The resulting clay was then resuspended in water. The percentage of clay-Co(NH₃)₆ complex was determined by drying a definite volume at 105°C for 24 hr. For the desorption studies 10 ml portions of a 1.925% suspension were placed in a number of Pyrex bottles and different amounts of electrolytes were added. The total volume of the suspension was made up to 15 ml in each case by adding the requisite amount of water. The bottles were shaken and kept overnight to attain equilibrium. The supernatant liquid was centrifuged (2000 rpm) for about 15 min and analysed for [Co(NH₃)₆]³⁺ content with a photoelectric grating colorimeter (Spekol of Carl Zeiss). The measurements were done at 470 nm.

RESULTS AND DISCUSSION

The maximum exchange of Co(NH₃)₆³⁺ on H-vermiculite corresponds to about 119 mequiv./100 g which compares well with the cation exchange capacity of the mineral (120 m-equiv./100 g). The results of desorption are shown in Figs. 1-3 and Tables 1-2.

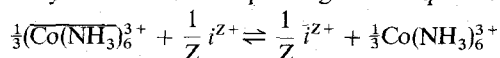
The distribution coefficients were calculated according to the equation $\lambda_i = \bar{m}_i/m_i$ where \bar{m}_i and m_i are the molal concentrations of the species i in the clay and solution phases respectively. The selectivity coefficients have been calculated at different concentrations of the desorbing ions according to the equation,

$$K_{\text{Co(NH}_3)_6^{3+}}^i = \frac{[i^{z+}]^{1/z} a_{\text{Co(NH}_3)_6^{3+}}^{\dagger}}{[\text{Co(NH}_3)_6^{3+}]^3 a_i^{1/z} Z +}$$

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where the bracketed terms and the a and z terms represent the molal concentration, activities and valency of the ions corresponding to the equilibrium



It should be pointed out that in the calculation of the selectivity coefficients, activities have been used in all cases, except when quaternary ammonium ions were used for desorption. The activity coefficient of the inorganic desorbing ions have been taken from the literature (Conway, 1952) and that of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ in solution has been estimated by a formula used by Kielland (1937), taking an ionic radius of $[\text{Co}(\text{NH}_3)_6]^{3+}$ as 2.77\AA (Jenkins and Monk, 1951). However, the mutual influence, if any, on the mean activity coefficients in mixed solution has not been taken into account.

The data presented in Table 1 and Figs. 1 and 2 make it clear that according to the order of preference the desorbing ions may be placed in the following sequence: $\text{Li} < \text{Na} < \text{NH}_4 < \text{K} < \text{Rb} < \text{H} < \text{Cs}$ for the monovalent, $\text{Ca} < \text{Mg}$ for the bivalent and $(\text{C}_2\text{H}_5)_4\text{N} < (\text{CH}_3)_4\text{N} \ll \text{CTA} < \text{CP}$ for the quaternary ammonium ions. The greater exchangeability of Mg^{2+} than Ca^{2+} was also noted by other workers (Wild and Keay, 1964; Beckett, 1964; Peterson, Rhodes, Arca and Coleman, 1965) and has been ascribed to the change in its hydration relative to other bivalent cations. The anomalous behaviour of H^+ in exchange and other colloid chemical reactions is quite common (Hendricks and Alexander, 1940). The greater exchangeability of H^+ than the bi- or even the trivalent ions has been explained by assuming H^+ to be present as a bare proton in the exchange

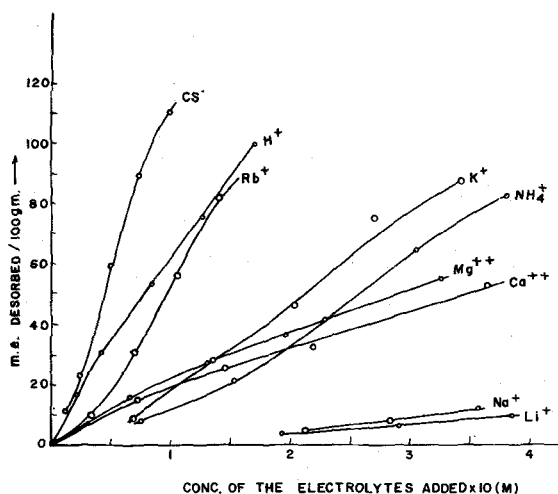


Fig. 1. Exchange of $[\text{Co}(\text{NH}_3)_6]^{3+}$ from $\text{H-Co}(\text{NH}_3)_6$ -vermiculite by inorganic ions.

reactions, as a result of which it has greater accessibility to the exchange sites (De, 1968).

The influence of the size of the desorbing ions is more evident in the case of vermiculite than montmorillonite. The latter swells considerably so that the sizes of the desorbing ions assume less importance, whereas in vermiculite the interlamellar space is limited to the thickness of about two water layers (4.98\AA) (Gruner, 1934). Hence the influence of the size becomes pronounced here. In this case it is observed that $(\text{CH}_3)_4\text{N}^+$, having an ionic diameter 6.94\AA (Ram Gopal and Rastogi, 1966), desorbs larger amounts of $[\text{Co}(\text{NH}_3)_6]^{3+}$ than $(\text{C}_2\text{H}_5)_4\text{N}^+$ with ionic diameter 8.00\AA (Ram Gopal and Rastogi, 1966). Because ion exchange inherently requires a "two-way traffic" and cannot take place in a "one-way street" (Helfferich, 1962), the interlamellar space may be too narrow for a $(\text{CH}_3)_4\text{N}^+$ or $(\text{C}_2\text{H}_5)_4\text{N}^+$ to pass another ion and the results can be explained in terms of the space requirements as shown by Barrer, Buser and Grütter (1956). It is very likely that in this cation exchange process $(\text{C}_2\text{H}_5)_4\text{N}^+$ experiences more steric hindrance than $(\text{CH}_3)_4\text{N}^+$ and the exchange takes place from the edges and exterior surfaces of the mineral only. Das Kanungo and Chakravarti (1971) observed similar results in the exchange of Mg^{2+} by these ions from Mg -vermiculite. That the exchange efficiency of CP^+ is greater than CTA^+ may be due to the fact that at the initial stage the desorption is the result of exchange between CP^+ and CTA^+ mainly in their monomeric forms with the clay bound $[\text{Co}(\text{NH}_3)_6]^{3+}$. At higher concentrations the desorption is effected by micelles of CP^+ having a lower critical micelle concentration than CTA^+ (Das Kanungo and Chakravarti, 1971). The detergent properties of the latter ions also may be operative in the exchange process (Ghosal and Mukherjee, 1972).

The thermodynamic equilibrium constants of some of the exchange reactions have been evaluated (Fig. 3 and Table 2) with the help of the equation proposed

Table 1. Exchange characteristics of $[\text{Co}(\text{NH}_3)_6]^{3+}$ with respect to different ions from $\text{H-Co}(\text{NH}_3)_6$ -vermiculite

Electrolyte used	Concentration of electrolyte	Distribution Coefficient	Selectivity Coefficient
<i>1:1 electrolyte</i>			
LiCl	$2.25 \times 10^{-1}(\text{M})$	0.20	0.020
	2.75 "	0.20	0.021
	3.5 "	0.23	0.028
NaCl	$2.25 \times 10^{-1}(\text{M})$	0.24	0.027
	2.75 "	0.27	0.035
	3.5 "	0.31	0.046
NH_4Cl	$1.5 \times 10^{-1}(\text{M})$	1.35	0.229
	2.0 "	1.68	0.353
	2.5 "	1.99	0.521
	3.0 "	2.17	0.677
KCl	$1.25 \times 10^{-1}(\text{M})$	2.13	0.403
	1.75 "	2.35	0.554
	2.25 "	2.50	0.710
	2.75 "	2.71	0.946
RbCl	$0.50 \times 10^{-1}(\text{M})$	3.77	0.546
	0.75 "	4.81	0.952
	1.0 "	5.68	1.460
	1.25 "	6.17	1.995
	1.25 "	6.17	1.995
<i>Quaternary ammonium salt</i>			
$(\text{CH}_3)_4\text{NBr}$	$40 \times 10^{-2}(\text{M})$	5.93	0.447
	80 "	2.93	0.419
$(\text{C}_2\text{H}_5)_4\text{NBr}$	40 "	2.31	0.232
	80 "	1.85	0.221
	80 "	1.85	0.221
CTABr	$40 \times 10^{-3}(\text{M})$	315.2	47.39
	80 "	194.5	38.13
	40 "	688	110.4
CPCI	40 "	441.7	95.41
	80 "	441.7	95.41

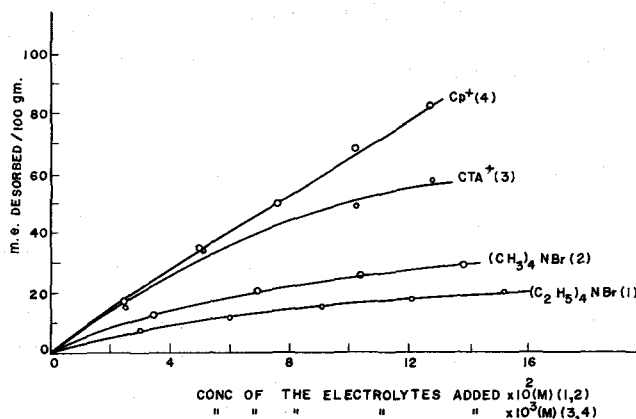
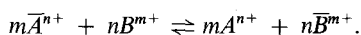


Fig. 2. Exchange of $[\text{Co}(\text{NH}_3)_6]^{3+}$ from $\text{H-Co}(\text{NH}_3)_6$ -vermiculite by quaternary ammonium ions.

by Kielland (1935) as an empirical relationship for the exchange of ions of any valency according to the general reaction



Bars refer to the exchanger phase.

Thus

$$\log K = \log \mathcal{K} + C [n - 2n\bar{x}_B + (n - m)\bar{x}_B^2]$$

where

K = selectivity coefficient

\mathcal{K} = thermodynamic equilibrium constant

\bar{x}_B = equivalent ionic fractions of B in the exchanger phase

C = a constant.

Recently this equation has been given a sounder theoretical foundation by Barrer and Falconer (1956). They derived the Kielland equation (1935) by using

Table 2. Evaluation of thermodynamic quantities from Kielland's equation at 25°C

Exchange system	Thermodynamic equilibrium constant	ΔG° Cal/mole
$K_{\text{Co}(\text{NH}_3)_6}^{\text{NH}_4}$	0.8913	68.19
$K_{\text{Co}(\text{NH}_3)_6}^{\text{K}}$	1.0	0
$K_{\text{Co}(\text{NH}_3)_6}^{\text{Rb}}$	2.291	-490.9
$K_{\text{Co}(\text{NH}_3)_6}^{\text{Cs}}$	4.467	-886.3
$K_{\text{Co}(\text{NH}_3)_6}^{\text{H}}$	2.042	-422.8
$K_{\text{Co}(\text{NH}_3)_6}^{\text{Mg}}$	0.3802	572.7
$K_{\text{Co}(\text{NH}_3)_6}^{\text{Ca}}$	0.3311	654.5

statistical mechanical arguments for the special case when both the cations of the exchanging pair are univalent.

Gibbs free energy change at 25°C, which is a measure of the relative affinities of the ions for the mineral, has been calculated from the relation $\Delta G^\circ = -RT \ln \mathcal{K}$ and is shown in Table 2.

CONCLUSION

The release of $[\text{Co}(\text{NH}_3)_6]^{3+}$ from $\text{H-Co}(\text{NH}_3)_6$ -vermiculite by various ions follows the order: $\text{Li} < \text{Na} < \text{NH}_4 < \text{K} < \text{Rb} < \text{H} < \text{Cs}$ for the monovalent, $\text{Ca} < \text{Mg}$ for the bivalent and $(\text{C}_2\text{H}_5)_4\text{N} < (\text{CH}_3)_4\text{N} \ll \text{CTA} < \text{CP}$ for the alkyl quaternary ammonium ions. The approximate upper limit of concentration for the desorbing electrolytes are as follows: for LiCl and NH_4Cl , 0.375 M; NaCl and KCl , 0.35 M; HCl , 0.175 M; RbCl , 0.15 M; CsCl , 0.1 M; CaCl_2 and MgCl_2 , 0.35 M; $(\text{CH}_3)_4\text{NBr}$ and $(\text{C}_2\text{H}_5)_4\text{NBr}$, 0.15 M; CPCl and CTABr , 0.013 M. The fact that $(\text{C}_2\text{H}_5)_4\text{N}^+$ exchanges less than $(\text{CH}_3)_4\text{N}^+$ may be due to the larger size of the former and also to the limited c -axis expansion of vermiculite. CP^+ is a better desorbing agent than CTA^+ because of its lower critical micelle concentration value. The exchange data obtained with most of the inorganic ions show obedience to the Kielland's equation from which the values of the thermodynamic equilibrium constants have been evaluated.

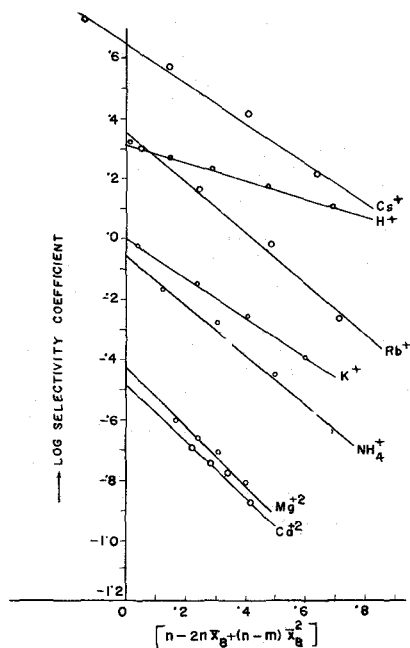


Fig. 3. Plot of log selectivity coefficient against $n - 2n\bar{x}_B + (n - m)\bar{x}_B^2$ in the exchange of $[\text{Co}(\text{NH}_3)_6]^{3+}$ from $\text{H-Co}(\text{NH}_3)_6$ -vermiculite by different ions.

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