June, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **55**, *1947—1948 (1982)* 1947

The Thermodynamics of Ion Exchange of Singly Charged Cobalt(III) Complex with Sodium Ions on Cation Exchange Resin

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(Received April 25, 1981)

Synopsis. Thermodynamic values of the ion exchange of $[Co^{III}L_4B_2]^+$ (L=NH_3, ethylenediamine/2 (=en/2), or dimethylglyoximato(1−) anion/2 (=dmgH/2); B=NO_2^-, NCS^-, $CO_3^{2-}/2$, NH_3, or $C_2H_5NH_2$) with Na^+ on Dowex AG 50W-X2 resin were determined at 25 °C by measurements of selectivity coefficient and heat of exchange. Heats and entropies are negative for the uptake of $[Co(NH_3)_4(NO_2)_2]^+$ and $[Co(en)_2B_2]^+$, while they are positive for the uptake of $[Co(dmgH)_2(C_2H_5NH_2)_2]^+$.

In our previous paper,[1] we determined thermodynamic values of ion exchange of trivalent metal complex ions and pointed out that heats and entropies of ion exchange, which are related to the interaction of these ions with water, are functions of polarization charge densities at the surface of these ions. On the other hand, several investigators have reported affinities of some singly charged cobalt(III) complex ions against ion exchange resins.[2–4] However, the thermodynamics of these ion exchange reactions have not yet been studied. In this paper, thermodynamic values of ion exchange of singly charged cobalt(III) complex ions on Dowex AG 50W-X2 are determined and interactions of these ions with water are discussed.

Experimental

Materials. The poly(styrenesulfonic acid) cation exchange resin (Dowex AG 50W-X2, 50—100 mesh, Bio Labo.) was obtained in the sodium form after conditioning, and dried in air current. Cobalt(III) complex chlorides were prepared by the literature methods.[5,6]

Equilibrium Measurements. Batch method was employed to measure the selectivity coefficient; 0.2 g of sodium form resin was equilibrated with 40 cm^3 of 0.04 mol dm^{-3} mixed salt solution containing the complex and sodium chlorides of several compositions (ionic strength of equilibrium solution is 0.04). Equilibration was achieved within a few hours by agitating at 25±0.1 °C. Concentrations of complex and sodium ions in aqueous phase were determined from optical absorbance and from radioactivity of ^{22}Na, respectively.

Heat of Exchange. A twin type conduction calorimeter of a commercial model (Lesca Co., Tokyo, CM-204S) was employed to measure the heat of ion exchange; 0.2—1.0 g of sodium form resin was weighed into sample holding tubes of sample and reference calorimeters, and then added 5 cm^3 of water to eliminate the heat of swelling, while 40 cm^3 of 0.05 mol dm^{-3} salt solution and water were introduced into the sample and reference cells. After thermal equilibrium, the resins in sample holding tubes were mixed with the salt solution and water in the cells. The heat evolved was recorded as a differential electromotive force.

Results and Discussion

The selectivity coefficient of ion exchange, $X^+ + NaR = Na^+ + XR$, can be defined as

$$K_c' = N_X m_{Na} / N_{Na} m_X,$$

where N and m are the mole fraction in resin and the molality of solution of subscript ions, X^+ and Na^+, respectively. Selectivity coefficients plotted against the mole fraction of complex ion in resin (*i.e.*, Kielland plots) are shown in Fig. 1. All of the Kielland plots are nearly linear. The preferential uptake of $[Co(en)_2(NO_2)_2]^+$, $[Co(en)_2(NCS)_2]^+$, $[Co(NH_3)_4(NO_2)_2]^+$, and $[Co(dmgH)_2(NH_3)_2]^+$ increases with increasing mole fraction of these ions in resin, that is, the slope of Kielland plots of these ions is positive. This trend can be explained in terms of the cluster formation of these ions and resin matrix.[7,8]

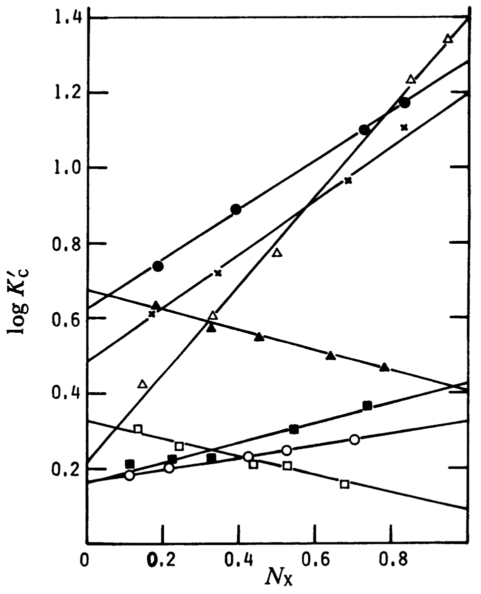

Fig. 1. Selectivity coefficients as functions of ionic compositions in resin.
●: *cis*-$[Co(en)_2(NO_2)_2]^+$, ○: *trans*-$[Co(en)_2(NO_2)_2]^+$, ▲: $[Co(en)_2CO_3]^+$, △: *cis*-$[Co(en)_2(NCS)_2]^+$, ×: *cis*-$[Co(NH_3)_4(NO_2)_2]^+$, ■: $[Co(dmgH)_2(NH_3)_2]^+$, □: $[Co(dmgH)_2(C_2H_5NH_2)_2]^+$.

The free energy $\Delta G°$ and entropy $\Delta S°$ of ion exchange are calculated by

$$\Delta G° = -RT\int_0^1 \ln K_c'[\gamma(Na^+)/\gamma(X^+)]dN_X$$

$$\Delta G° = \Delta H° - T\Delta S°.$$

Since the ionic strength of aqueous phase is sufficiently low (0.04), the values of $\gamma(Na^+)/\gamma(X^+)$ are approximated to 1. Standard heats of exchange $\Delta H°$ are approximated to heats of exchange ΔH, since the heat content terms are small. Thermodynamic values of ion exchange are

Table 1. Thermodynamic values of ion exchange for $A^+ + NaR = AR + Na^+$ on Dowex AG 50W-X2 at 25 °C ($I=0.04$)

Cation	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
cis-$[Co(NH_3)_4(NO_2)_2]^+$	−4.81	−11.92	−23.8
cis-$[Co(en)_2(NO_2)_2]^+$	−5.52	−8.99	−11.7
trans-$[Co(en)_2(NO_2)_2]^+$	−1.38	−3.77	−8.0
trans-$[Co(en)_2(NCS)_2]^+$	−4.39	−8.74	−14.6
$[Co(en)_2CO_3]^+$	−3.05	−5.61	−8.4
$[Co(dmgH)_2(NH_3)_2]^+$	−1.67	−1.59	+0.4
$[Co(dmgH)_2(C_2H_5NH_2)_2]^+$	−1.17	+3.14	+14.6

presented in Table 1.

The exothermic heats cause the preferential uptake of $[Co(NH_3)_4(NO_2)_2]^+$ and $[Co(en)_2B_2]^+$ (Table 1). This trend can be explained in terms of strong interaction between these ions and resin matrix. *cis*-$[Co(en)_2(NO_2)_2]^+$ has a larger dipole moment than *trans*-$[Co(en)_2(NO_2)_2]^+$. This causes the more exothermic heat and stronger affinity of the former than those of the latter.

It was recognized that ions are classified into three groups on the basis of ion-water interaction: (a) Electrostrictive structure makers such as Na^+, (b) structure breakers such as Cs^+, and (c) hydrophobic structure makers.[9,10] Since the structure maker increases the structural order of water near itself, its removal from aqueous phase gives a positive entropy. Furthermore, as an ion of the same charge becomes more structure making, the water content of its form resin increases, that is, the extent of dehydration of ion by transfer from the aqueous to resin phase decreases.[1,11–13] These facts suggest that the sign and magnitude of the entropy of ion exchange gives a reliable indication of the structure altering property of an ion.

Table 1 shows that the values of ΔS° for $[Co(dmgH)_2B_2]^+$ are positive and they become more positive with alkyl chain. A similar behaviour was shown in ion exchanges of tetraalkylammonium ions.[13] The alkyl (hydrophobic) groups of the dmgH ligands are in contact with water. Furthermore, the dmgH ligands coordinated in plane are hydrogen bonded with one another and therefore, the anionic groups are not localized. These facts suggest that $[Co(dmgH)_2B_2]^+$ has a hydrophobic structure making property which causes its preferential uptake against the resin.

The values of $-\Delta S^\circ$ of $[Co(en)_2B_2]^+$ and $[Co(NH_3)_4(NO_2)_2]^+$ are larger than that of Cs^+ with Na^+ on Dowex 50 (2% DVB).[12] This fact shows that $[Co(en)_2B_2]^+$ and $[Co(NH_3)_4(NO_2)_2]^+$ are structure breakers. Interestingly, it has been shown that $[Co(en)_3]^{3+}$ is a hydrophobic structure maker.[10] Water dipoles near an anion are oriented in the opposite direction to those near a cation. Therefore, the water structure near anion ligands of $[Co(en)_2B_2]^+$ should be disturbed in a wide range. Thus, $[Co(en)_2B_2]^+$ as well as $[Co(NH_3)_4(NO_2)_2]^+$ acts as a structure breaker. The order of structure breaking tendencies of $[Co(en)_2B_2]^+$ is $NCS^- > NO_2^- > CO_3^{2-}/2$. This order seems to accord with the structure breaking tendencies of these anions. *cis*-$[Co(NH_3)_4(NO_2)_2]^+$ is more structure breaking than *cis*-$[Co(en)_2(NO_2)_2]^+$, since $-\Delta S^\circ$ of the former is larger than that of the latter. This trend accords with the relation between $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$.[1]

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