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Ion-exchange Properties of Anion-exchanger Containing Cobalticinium Cations

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Selectivity coefficients of various anions *vs.* chloride or nitrate and water uptake at a saturated vapor pressure with polymeric pentamethylene cobalticinium exchanger were calculated from the experimental data and compared with those of anion-exchange resins. The selectivity coefficient sequence was nearly identical with that for quaternary ammonium type anion-exchangers, and the position of hydroxide ion indicated that the cobalticinium type anion-exchanger was a strong base type. Inspection of selectivity coefficients data revealed that strong base anion-exchangers were more selective than weak base anion-exchangers. The cobalticinium type anion-exchanger was found to have a high selectivity coefficient of iodide *vs.* bromide, even in comparison with strong base anion-exchange resins. Column separation of bromide and iodide using the cobalticinium type anion-exchanger was easily accomplished. The separation factor was three times that of the quaternary ammonium type anion-exchanger. The water uptake at a saturation vapor pressure by the cobalticinium type anion-exchanger in a given form increased with decreasing selectivity coefficient for the same anion. These trends were similar to those for quaternary ammonium type anion-exchanger. The relation between selectivity coefficient sequence of various anions *vs.* a common anion, and solubilities of the salt whose cation was the ionogenic group and anion adsorbed ion was discussed.

One of the weakest points of quaternary base anion-exchange resins is their instability toward heat. In order to exploit possible thermostable anion-exchangers, we synthesized polymeric olygomethylene cobalticinium anion-exchangers and investigated their properties (stability toward reagents and heat).1)

In this paper, the ion-exchange properties of the anion-exchanger are investigated and compared with those of anion-exchange resins.

Experimental

Preparations and Conditionings of Anion-exchangers. The method of synthesis and procedure for conditioning cobalticinium type anion-exchanger were identical with those of a previous paper.1) Among the series of olygomethylene compounds, pentamethylene compounds (Cl form) were used, being most stable against reagents. Anion-exchange resins (Dowex 1 X-1, Dowex 1 X-8, Amberlite IR-45 and Amberlite IR-4B) were obtained commercially and conditioned in the same manner. Anion-exchangers were converted to the desired salt forms with column operations.

Measurement of Selectivity Coefficients and Distribution Coefficients. The selectivity coefficient K_c is defined in the system of ion-exchange toward uni-valent ions as follows:

$$K_c = K_{\rm B}^{\rm A} = \left(\frac{m_{\rm A}}{m_{\rm B}}\right)_r \Big/ \left(\frac{m_{\rm A}}{m_{\rm B}}\right)_w$$

where $K_{\rm B}^{\rm A}$ is the selectivity coefficient in the case of the displacement of anion B in the exchanger by anion A in the solution, r refers to the concentration of anion in the exchanger phase and ω the concentration of anion in the solution phase. The mole fraction of a particular anionic state of the exchanger is designated $X_{\rm A}^{\rm B}(=(m_{\rm A}/(m_{\rm A}+m_{\rm B}))_r)$.

Selectivity coefficients were determined by the batch equilibrium method at 25.00±0.01°C using 0.250 g of exchanger. After shaking for 24 hr, concentrations of halogenide ions in the solution were determined with the potentiometric titration method using a solution of 0.1 N silver nitrate and a silver electrode. The anion-exchange systems were arranged in such a way that selectivity coefficients could be obtained by determining the concentration of halogenide ions. Other ions could be calculated by subtracting the amount of halogenide ions from the total amount of anion-exchange capacity.

The distribution coefficient of solute A (a trace constituent) is defined as the total amount of solute A per gram of dry exchanger divided by the total amount of solute A in one milliliter of external solution. Distribution coefficients for perchlorate, thiocyanate, iodide, bromide and chloride ions (trace constituents) against hydroxide ion were measured by the batch method at room temperature. The concentration of trace constituents was 10^{-3} M and that of hydroxide varied from 0.04 M to 2 M. Column operation was used for iodate, bromate, chloride, bromide and iodide ions against nitrate ion, and for iodide and thiocyanate ions against perchlorate ion. Distribution coefficients were calculated according to the following formula for column operation:2)

$$V = I + mK_d$$

where V is the peak elution volume (ml), I the void space of the column (ml), m the mass of the dry exchanger (g) and K_d the distribution coefficient (ml/g). Determination of micro-amounts of anions was carried out by the colorimetric method3) after a large excess of hydroxide ion was removed with Dowex 50W (H form) columns.

Measurements of the Amount of Water Adsorbed on the Cobalticinium Type Anion-exchanger in Various Anion Forms. After the cobalticinium type anion-exchanger in various forms were dried over silica gel to constant weight, they were equilibrated with saturated water vapor at room temperature. Then the amount of water adsorbed was calculated.

Solubilities of Cobalticinium and Tetramethylammonium Salts. Cobalticinium salts were obtained by converting the picrate into the desired salt form with Amberlite IRA-410 columns. Tetramethylammonium halogenides were obtained commercially. The halogenate was obtained by converting the chloride in the same manner as cobalticinium salts. The solubility was measured at 0°C and halogenide ions were determined by potentiometric titration with 0.1 N silver nitrate solution using a silver electrode. Halogenate ions were determined as chloride ion after converting them to chloride with Amberlite IRA-410 columns (Cl form).

Results and Discussion

Selectivity coefficients obtained are shown in Table 1. The selectivity coefficient sequence for the cobalticinium type anion-exchanger resembles that for strong base type anion-exchange resins,4-6) particularly with respect to the position of hydroxide

TABLE 1. SELECTIVITY COEFFICIENTS OF VARIOUS ANIONS *vs.* BROMIDE WITH POLYMERIC PENTAMETHYLENE COBALTICINIUM EXCHANGER

Ion	$X_{\rm A}^{\rm Br}$	$K_{\rm Br}^{\rm A}$
BF_4^-	0.987	9.67
NO_3^-	0.926	1.45
Benzoate	0.925	1.44
ClO_3^-	0.924	1.41
NO_2^-	0.847	0.581
BrO_3^-	0.746	0.270
HCO_3^-	0.687	0.184
OH^-	0.672	0.158
HSO_4^-	0.653	0.147
CH_3COO^-	0.519	0.0664
$H_2PO_4^-$	0.444	0.0417
F^-	0.357	0.0237

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1) T. Ito and T. Kenjo, This Bulletin, **41**, 614 (1968).

2) E. Glueckauf, *Trans. Faraday Soc.*, **51**, 34 (1955).

3) David F. Boltz (Ed.), "Colorimetric determination of nonmetals," Interscience Pub. Inc., New York (1958).

4) R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **41**, 1265 (1949).

5) M. Kikindal, *Compt. rend.*, **237**, 250 (1953).

6) H. P. Gregor, J. Belle and R. M. Marcus, *J. Am. Chem. Soc.*, **77**, 2713 (1955).

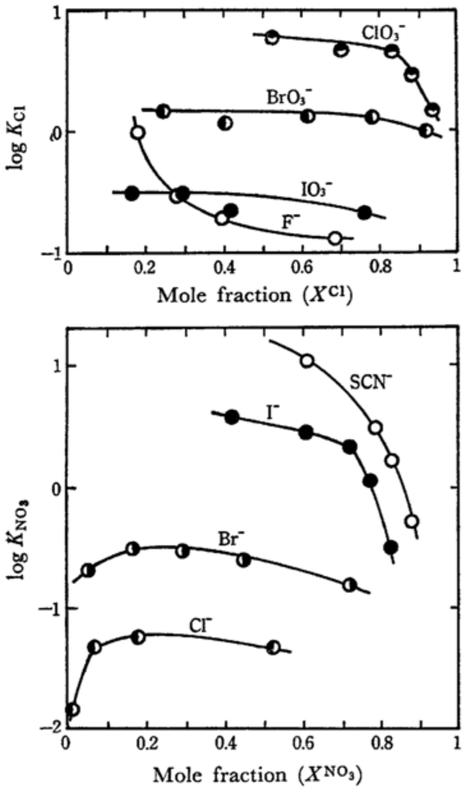

Fig. 1. Selectivity coefficients of various anions *vs.* chloride and nitrate with polymeric pentamethylene cobalticinium exchanger.
upper: fluoride (○) iodate (●) bromate (◐) chlorate (◓)
lower: chloride (◐) bromide (◑) iodide (●) thiocyanate (○)

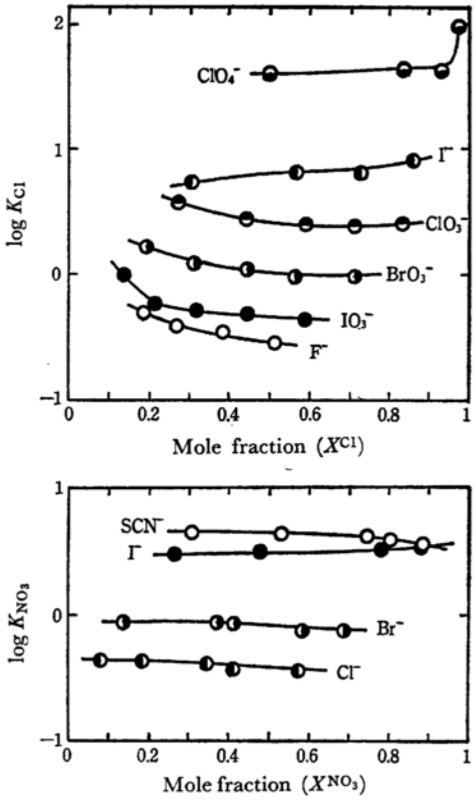

Fig. 2. Selectivity coefficients of various anions *vs.* chloride and nitrate with Dowex 1 X-1.
upper: fluoride (○) iodate (●) bromate (◑) chlorate (◓) iodide (◐) perchlorate (◒)
lower: chloride (◐), bromide (◑) iodide (●) thiocyanate (○)

ion. This fact indicates that cobalticinium type anion-exchanger is a strong base type, which is consistent with an observation that cobalticinium cations form a strong base.⁷⁾

Respective selectivity coefficients on the polymeric pentamethylene cobalticinium exchanger, Dowex 1 X-1, Dowex 1 X-8, Amberlite IR-45 and Amberlite IR-4B are given in Figs. 1 to 5. Great differences in selectivity coefficients with strong base anion-exchangers (cobalticinium, Dowex 1) compared with those with weak base anion-exchangers (Amberlite IR-45 and Amberlite IR-4B) suggest that strong base anion-exchangers are more selective than weak base anion-exchangers. As regards selectivity coefficients for halide ions, cobalticinium type anion-exchanger is more selective than Dowex 1, particularly with respect to the difference between bromide ion and iodide ion. Figure 6 also indicates there is a large difference between bromide and iodide ion in the distribution coefficient, and ion-exchange ideality[*1] is evidenced by straight lines with negative unit slopes. Distribution coefficients for various anions are summarized in Table 2. These values are consistent with the tendency seen in selectivity coefficients. The separation of bromide and iodide ion with a column using cobalticinium ion-exchanger was effected more readily than with

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7) G. Wilkinson and F. A. Cotton, "Progress in Inorganic Chemistry," Vol 1, ed. by F. A. Cotton, International Pub., New York, N. Y. (1959), p. 13.

[*1] The selectivity coefficient for uni-valent anion-exchange is defined by the equation written in the experimental section. If one of the adsorbed ions (A) is in trace concentration, and if ion-exchange reactions occur ideally, the composition of the exchanger is essentially independent of the concentration of the adsorbed trace ion. Then the equation simplifies to

$$K_{d(A)}m_{B(w)} = \text{constant}$$

where $K_{d(A)}$ is the distribution coefficient for A and $m_{B(w)}$ the concentration of B in external solution; $m_{B(w)}$ is equal to the concentration of hydroxide ion in this case. According to the equation, a plot of $\log K_{d(A)}$ *vs.* $\log m_{B(w)}$ should be a straight line with a negative unit slope. This relation has been taken to show ion-exchange ideality.⁸⁾

8) K. A. Kraus, H. O. Phillips, T. A. Carlson and J. S. Johnson, Paper P/1832 Intern. Conference on Peaceful Uses of Atomic Energy, 2nd, Cof. (1958).

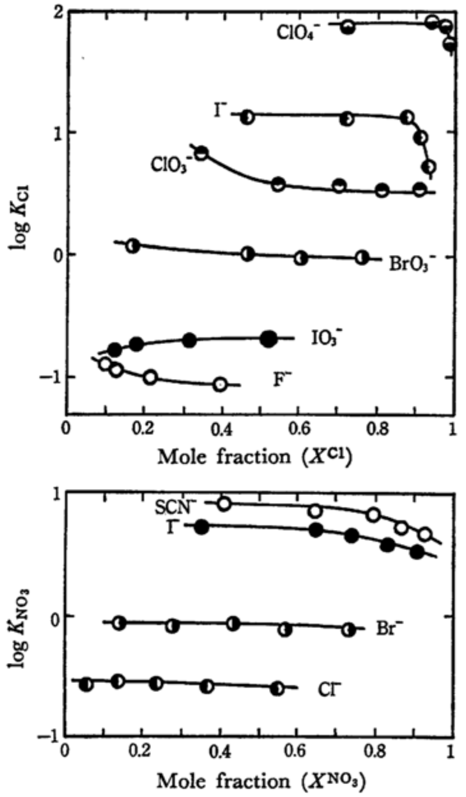

Fig. 3. Selectivity coefficients of various anions *vs.* chloride and nitrate with Dowex 1 X-8.
upper: fluoride (○) iodate (●) bromate (◑) chlorate (◓) iodide (◐) perchlorate (◒)
lower: chloride (◐) bromide (◑) iodide (●) thiocyanate (○)

Table 2. Distribution coefficients for anions on polymeric pentamethylene cobalticinium exchanger (PPC) and anion-exchange resins

Ion	PPC (m*l*/g) (OH form)	Amberlite IRA-410 (m*l*/g) (OH form)	Amberlite IR-45 (normalized to the value for IO_3^-) (NO_3 form)
IO_3^-	15.4	9.80	1.0
Cl^-	26.8	33.5	1.45
BrO_3^-	26.8	33.5	1.67
Br^-	54.2	111	2.97
I^-	575	644	10.8
SCN^-	990	1290	28.1
ClO_4^-	2000	—	—

ion-exchange resins (Fig. 7). The separation factor calculated by dividing the distribution coefficient of iodide ion by that of bromide ion was about 10, from Fig. 7, which agrees well with the value of Table 2, and is three times that of strong base anion-exchangers.[9]

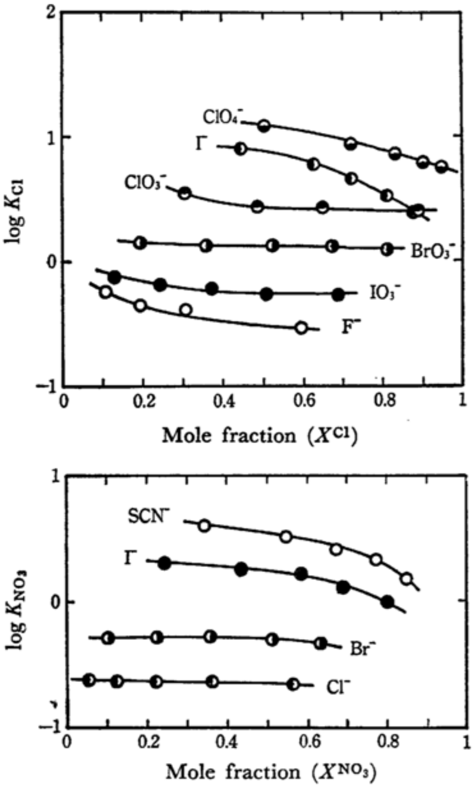

Fig. 4. Selectivity coefficients of various anions *vs.* chloride and nitrate with Amberlite IR-45.
upper: fluoride (○) iodate (●) bromate (◑) chlorate (◓) iodide (◐) perchlorate (◒)
lower: chloride (◐) bromide (◑) iodide (●) thiocyanate (○)

Table 3. The water uptake of polymeric pentamethylene cobalticinium exchanger in various salt forms
(mmol H_2O/meq. exchanger)

IO_3^-	11.31	Cl^-	11.78
BrO_3^-	9.28	Br^-	9.80
ClO_3^-	9.25	I^-	7.40
ClO_4^-	7.30	SCN^-	6.40
		OH^-	13.44

It may be seen from Table 3 that the water uptake at a saturated vapor pressure by cobalticinium type anion-exchanger in various forms increases with decreasing selectivity coefficient of anions *vs.* nitrate or chloride ion. These tendencies are analogous to that of a quaternary ammonium type exchanger.[10] The results can be understood if the selectivity is assumed caused by the difference in the two different anions adsorbed in their affinity to ionogenic groups. One of the most typical theories, suggesting an interaction

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9) W. Rieman III, S. Lindenbaum, *Anal. Chem.*, **24**, 1199 (1952).

10) G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

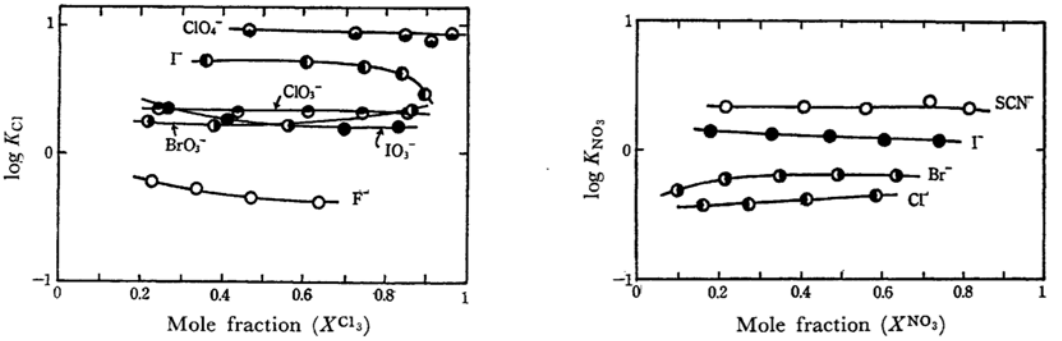

Fig. 5. Selectivity coefficients of various anions *vs.* chloride and nitrate with Amberlite IR-4B.
upper: fluoride (○) iodate (●) bromate (◑) chlorate (◓) iodide (◐) perchlorate (◒)
lower: chloride (◐) bromide (◑) iodide (●) thiocyanate (○)

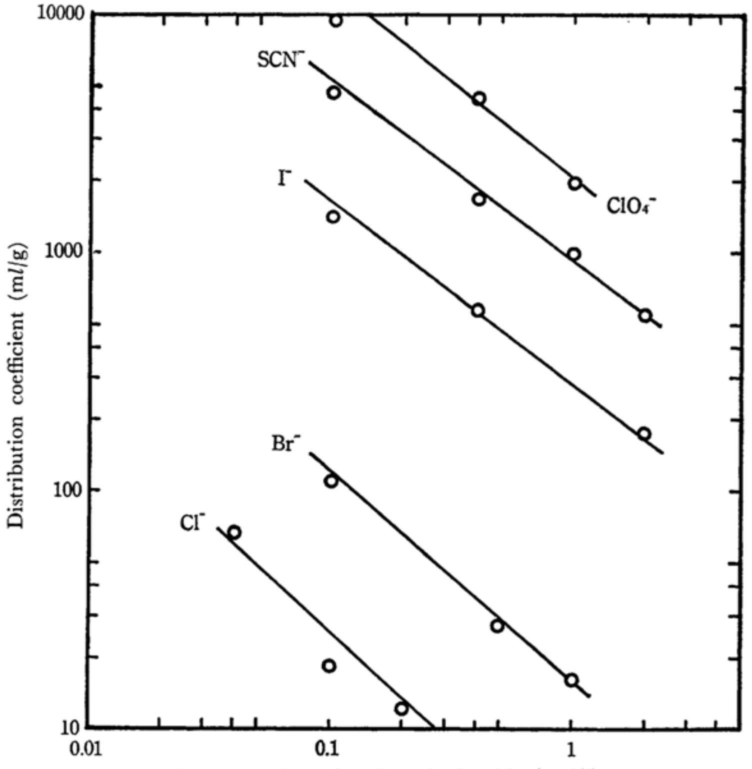

Fig. 6. Distribution coefficients for several anions on polymeric pentamethylene cobalticinium exchanger as a function of sodium hydroxide concentration.

between an ionogenic group and a counter ion was proposed by Gregor.[11] He assumed a dissociation equilibrium between ionogenic groups and adsorbed ions as follows;

$$RA \rightleftharpoons R^+ + A^-$$
$$RB \rightleftharpoons R^+ + B^-$$

where R's refer to the ionogenic group and A and B to adsorbed ions. The dissociation constants for A (D_A) and B (D_B) are given by

$$D_A = \frac{[R^+][A^-]}{[RA]}, \qquad D_B = \frac{[R^+][B^-]}{[RB]}$$

where the brackets refer to the molality of each species. Neglecting strain energy effects, the molality of unpaired ions in the exchanger phase is related to that of these ions in the external solution according to the Donnan equilibrium condition, or $[A^-]_r/[B^-]_r = [A^-]_w/[B^-]_w$, where the *r*'s refer

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[11] H. P. Gregor, J. Belle and R. A. Marcus, *J. Am. Chem. Soc.*, **77**, 2713 (1955).

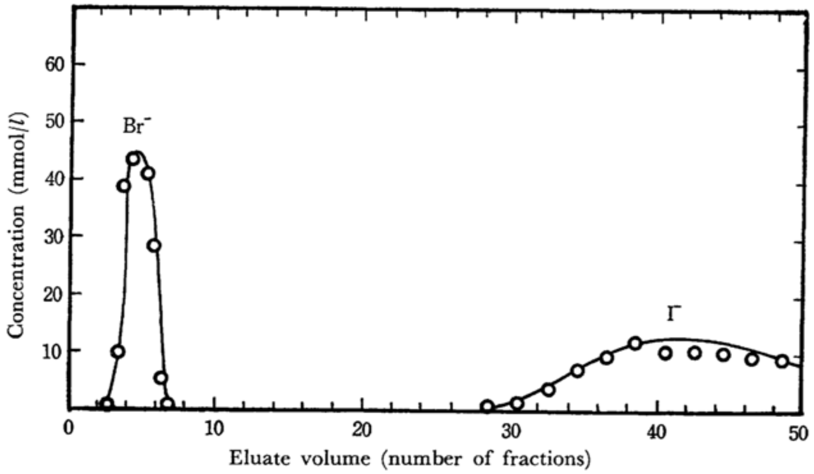

Fig. 7. Separation of bromide from iodide by polymeric pentamethylene cobalticinium exchanger with 0.25 M nitric acid.
Column: 10×111 mm; Flow rate: 0.64 ml/min
Volume of fraction: 4.8 ml

to the exchanger phase and *w*'s to the external solution phase. Then the selectivity coefficient of A *vs.* B (K_A^B) can be related to the dissociation constants as follows:

$$K_A^B = \frac{[A^-]_w D_A + [A^-]_w (D_B - D_A)x}{[A^-]_w D_B - [B^-]_w (D_B - D_A)x}$$

$$\text{where } x = \frac{-D_A + \sqrt{D_A{}^2 + 4[A^-]_w D_A + \dfrac{4D_A{}^2[B^-]}{D_B}}}{2\left(1 + \dfrac{[B^-]_w D_A}{[A^-]_w D_B}\right)}$$

and $[A^-]_w$ and $[B^-]_w$ refer to the molality of anions A and B in the external solution phase, respectively. The above equation indicates that the selectivity coefficient of B *vs.* A increases with decreasing D_B/D_A at a given molality of A or B in the external solution phase. Accordingly, the relation between the water uptake and the selectivity coefficient may be interpreted as the hydration of unpaired ions in the exchanger phase, because unpaired ions may adsorb a greater amount of water than paired ions. These relations between the ionogenic group and the adsorbed ion can be compared to those between the solid phase and solution phase of the salt whose cation is the ionogenic group and anion the adsorbed ion. As shown in Table 4, the solubilities of halogenide salts decrease in the order $Cl^- > Br^- > I^-$, while selectivity coefficients of halogenide ions *vs.* common anion increase in the order $Cl^- < Br^- < I^-$. These results may show the validity of the above mentioned prediction. The solubilities of both cobalticinium and tetramethylammonium halogenates, however, decrease in the order $ClO_3^- > BrO_3^- > IO_3^-$, while the selectivity coefficients of halogenate ions *vs.* a common anion decreased in the order $ClO_3^- > BrO_3^- > IO_3^-$. Considering the Coulomb force, it is expected that the affinities to ionogenic groups decrease in the order $ClO_3^- > BrO_3^- > IO_3^-$ if the structures of the ions in water are the same as that in a crystalline state. These opposite tendencies, presumably, suggest some differences in the nature of interaction (*e. g.*, direction or distance) between the anion-exchangers and the corresponding salts in the crystalline state.

TABLE 4. SOLUBILITIES OF COBALTICINIUM AND TETRAMETHYLAMMONIUM SALTS IN WATER (0°C)

	Cobalticinium (mol/l)	Tetramethylammonium (mol/l)
Cl^-	3.76	6.67
Br^-	3.44	3.04
I^-	1.41	0.104
IO_3^-	3.01	1.00
BrO_3^-	3.60	2.14
ClO_3^-	4.77	2.64