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Studies of the Separation Mechanism in Ion-exchange Chromatography. II. Inversion of the Elution Order of Tri- and Divalent Complex Cations with Increasing Concentration of the Eluent

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Synopsis. Two pairs of tri- and divalent complex cations $[Co(en)_3]^{3+}$, $[Ni(en)_3]^{2+}$ and $[Co(phen)_3]^{3+}$, $[Fe(phen)_3]^{2+}$ were chromatographed through the SP-Sephadex cation-exchange column using various concentrations of aqueous KBr and K_2SO_4 solutions as eluent, and the inversion of the elution order was observed for the pair of the phen complexes when eluted with KBr and for that of the en complexes when eluted with K_2SO_4.

In the first paper of this series,[1] it was reported for *cis* and *trans* isomeric pairs of some complex cations that the usual elution order in ion-exchange chromatography was reversed with the addition of dioxane to the eluent. This was interpreted as a result of the enhancement of the electrostatic interaction in the moving phase which overtook the interaction in the fixed phase. If this interpretation is valid, the inversion of the elution order is expected also for the pairs of differently charged cations under suitable conditions. This expectation was ascertained in the present study.

Experimental

All the complexes were prepared according to the literature, and identified by UV absorption spectra. Complexes used were $[Co(en)_3]Cl_3$, $[Ni(en)_3]Cl_2$, $[Co(phen)_3]Cl_3$, and $[Fe(phen)_3]Cl_2$. All the works were carried out on a laboratory-built chromatographic unit at room temperature. The column size was 10.8 cm long and 1.1 cm in diameter. SP-Sephadex C-25 (K^+-form) was used as a packing material. The detector was operated at an appropriate wavelength in the visible region for each complex. The adjusted retention volume was measured from the elution curve thus obtained. Blue dextran 2000 was used as a marker.

Results and Discussion

Figure 1 shows the adjusted retention volumes of the en and phen complex pairs as a function of KBr concentration. At low KBr concentration, both trivalent complexes, $[Co(en)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ show greater retention volumes than the corresponding divalent complexes, $[Ni(en)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$. This means that the trivalent complex is adsorbed more strongly on the $-SO_3^-$ group of the resin than the corresponding divalent complex. However, the retention volume of the tri- and divalent complexes decreases with increasing concentration of the eluent, and the rate of decrease in the retention volume is much larger for the trivalent complex than for the divalent complex. Thus, the inversion of the elution order can be expected for both pairs above a certain eluent concentration.[2] Here, it is worth noting that this critical concentration at which the inversion takes place is different for different pairs; while the inversion takes place at 0.3 mol dm^{-3} KBr for the phen complex pair, it does not even at 1 mol dm^{-3} KBr for the en complex pair. On the contrary, as shown in Fig. 2, when K_2SO_4 solution is used as eluent, the inversion takes place at *ca.* 0.18 mol dm^{-3} for the en complex pair, but it does not even

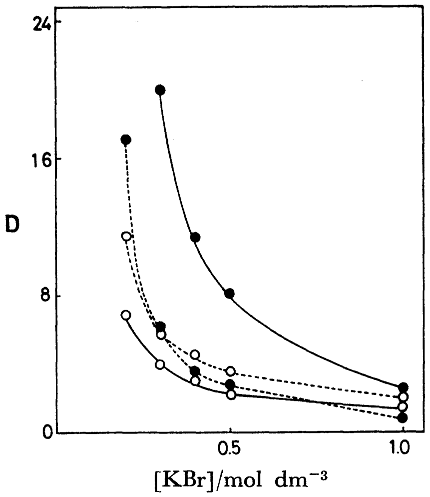

Fig. 1. Plots of *D vs.* concentration of KBr used as an eluent.
$[Co(en)_3]^{3+}$ (●—●), $[Ni(en)_3]^{2+}$ (○—○), $[Co(phen)_3]^{3+}$ (●---●), $[Fe(phen)_3]^{2+}$ (○---○).

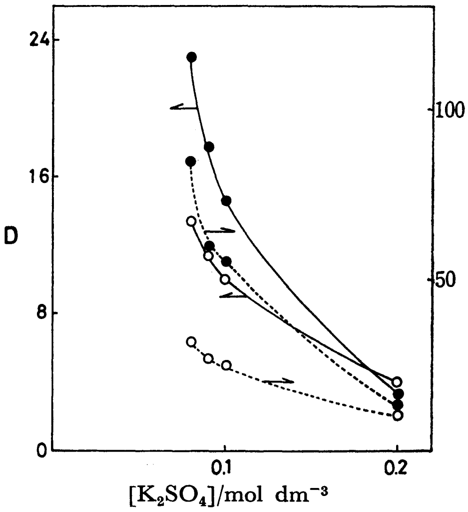

Fig. 2. Plots of *D vs.* concentration of K_2SO_4 used as an eluent.
$[Co(en)_3]^{3+}$ (●—●), $[Ni(en)_3]^{2+}$ (○—○), $[Co(phen)_3]^{3+}$ (●---●), $[Fe(phen)_3]^{2+}$ (○---○).

at 0.20 mol dm^{-3} for the phen complex pair. These trends can be interpreted in the following way.

In quantitative consideration, it is convenient to use the distribution coefficient D, the ratio of the concentration of a sample ion in the resin phase to that in the moving phase, which has been demonstrated[3] to equal the adjusted retention volume per unit resin volume. Thus, we have

$$D = [\mathrm{M}]_\mathrm{R}/[\mathrm{M}] = V_\mathrm{adj}/V_\mathrm{resin}$$

where $[\mathrm{M}]_\mathrm{R}$ and $[\mathrm{M}]$ represent the concentration of a sample ion M^{m+} in the resin phase and in the moving phase, respectively, and V_adj and V_resin represent the adjusted retention volume and the volume of the ion-exchange resin packed in the column, respectively. If it is assumed that a small amount of a sample ion M^{m+} is distributed between the B^+-formed resin and the aqueous solution of an electrolyte $\mathrm{B}_n\mathrm{X}$ used as an eluent, D is given by

$$D = K_\mathrm{B}^\mathrm{M}([\mathrm{B}]_\mathrm{R})^m/[\mathrm{B}]^m$$

where K_B^M is the selectivity coefficient of M^{m+} relative to B^+.[3] When the ion-association between M^{m+} and X^{n-} is taken into account, the distribution coefficient D of M^{m+} is expressed as[3]

$$D = K_\mathrm{B}^\mathrm{M}([\mathrm{B}]_\mathrm{R})^m/\{[\mathrm{B}]^m(1+\beta[\mathrm{X}])\} \qquad (1)$$

where β is the association constant. With this final equation, the elution order of the tri- and divalent complex cations can be compared.

Let D_3 and D_2, $K(3)$ and $K(2)$, and $\beta(3)$ and $\beta(2)$ represent the distribution coefficients, the selectivity coefficients, and the ion-association constants for tri- and divalent complexes, respectively. If we take the ratio of these distribution coefficients D_3 and D_2 for a particular pair, we obtain

$$D_3/D_2 = (K(3)/K(2))([\mathrm{B}]_\mathrm{R}/[\mathrm{B}])(1+\beta(2)[\mathrm{X}])/(1+\beta(3)[\mathrm{X}]). \qquad (2)$$

Here, $K(3)$ is in general larger than $K(2)$. At low concentration of $\mathrm{B}_n\mathrm{X}$, $[\mathrm{B}]_\mathrm{R}$ is larger than $[\mathrm{B}]$, and $\beta[\mathrm{X}]$ can be neglected in Eq. 2. Therefore, the value of D_3/D_2 is larger than unity, indicating that the trivalent ion is adsorbed on the resin more strongly than the corresponding divalent ion. However, as the concentration of $\mathrm{B}_n\mathrm{X}$ increases, the value of $[\mathrm{B}]_\mathrm{R}/[\mathrm{B}]$ becomes smaller and smaller and finally it becomes less than unity so as to make its product with $K(3)/K(2)$ very close to unity at fairly high concentration of $\mathrm{B}_n\mathrm{X}$. Thus, in principle, the value of D_3/D_2 for a particular pair can be smaller than unity at very high eluent concentration. However, when the ion-association effect is added, D_3/D_2 becomes smaller than unity at relatively low eluent concentration, since the value of $(1+\beta(2)[\mathrm{X}])/(1+\beta(3)[\mathrm{X}])$ in Eq. 2 is always smaller than unity for a particular pair. Using Eq. 2, our experimental results can now be explained in the following way.

Bromide anion is poorly hydrated in aqueous solution because of its large size and low electric charge, and therefore is considered to be a water-structure breaker.[4] Such a structure-breaking anion is antagonistic[4] to a water-structure-making cation like $[\mathrm{M(en)_3}]^{m+}$ which attracts many water molecules with its many N–H bonds, and has little tendency toward association with $[\mathrm{M(en)_3}]^{m+}$. Thus, the effect of ion-association need not be considered for the en complex pair when eluted with KBr solution and the elution order is not reversed in the ordinary concentration range of the eluent. On the other hand, $\mathrm{SO_4}^{2-}$ is strongly hydrated and has a great tendency to associate with a strongly hydrated complex cation like $[\mathrm{M(en)_3}]^{m+}$ through S–O⋯H–N–M hydrogen bonds.[5] Thus, when the en complexes are eluted with $\mathrm{K_2SO_4}$, the effect of ion-association, that is, the term $(1+\beta[\mathrm{X}])$ becomes dominant in Eq. 2. Since the term $(1+\beta(2)[\mathrm{X}])/(1+\beta(3)[\mathrm{X}])$ is less than unity, the value of D_3/D_2 will become smaller than unity from a certain concentration of $\mathrm{K_2SO_4}$ solution, resulting in the reversed elution order.

For the elution of the phen complex pair, we have to consider a reverse situation. Since the phen complex has no N–H bonds for hydrogen bonding and its size is large, it is poorly hydrated and is known to be a typical hydrophobic ion.[4] Such a hydrophobic cation has a big tendency toward association with a hydrophobic anion or a water-structure-breaking anion. Thus, the ion-association takes place to a considerable extent with Br^- ion, resulting in the inversion of the elution order from a certain concentration of KBr solution. On the other hand, there is little tendency toward association between a hydrophobic cation and a hydrophilic anion.[5] So, for the phen complex pair eluted with $\mathrm{K_2SO_4}$ solution, the value of D_3/D_2 does not become smaller than unity, that is, the inversion of the elution order does not take place.

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