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A Cation-exchange Study of Cerium(III) and Thulium(III) Tartrate Complexes

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Synopsis. The tartrate complexes of Ce(III) and Tm(III) were studied by the cation-exchange method, where a series of solutions prepared so as to keep the [Htart$^-$] value nearly constant, while the [tart^{2-}] value was varied, was used for the estimation of the protonated complexes. Three kinds of complexes, M(Htart)$_2{}^+$, M(Htart)(tart), and M(tart)$_2{}^-$, were found in the lower pH region of the solutions.

When we use some dibasic or tribasic acids as complexing agents, there must be various kinds of protonated complexes equilibrated in a solution. However, most investigators seem to have neglected or underestimated these protonated complexes. Potentiometry can not be used for these studies since it is difficult to analyze various protonated complexes from a pH titration curve indicating a high degree of overlapping of the successive equilibria. In these cases, it is useful to estimate the amounts of free metal and ligand species equilibrated in a solution. As has previously been reported, it has been found that the citrate complexes of some lanthanoids1) and actinoids2,3) involving various types of protonated complexes could readily be analyzed by the cation-exchange method using a series of solutions prepared so as to keep the amount of one of the protonated ligands constant, while the other one was varied. In this note, we will discuss how we applied this method to the study of tartrate complexes of Ce(III) and Tm(III).

Experimental

Materials. The tracers, ^{144}Ce and ^{170}Tm in the chloride form, were obtained from the New England Nuclear Corporation. To a portion of each of the tracer solutions, a carrier was added to prepare stock solutions of 10^{-3} M (1 M= 1 mol dm^{-3}). A cation exchanger, Dowex 50W-X8 (100—200 mesh), in the sodium form was used. All the chemicals used were of a G. R. grade. Tartrate solutions were made in the following way: (1) To 0.1 M NaHtart solution, various amounts of H$_2$tart were added to prepare solutions containing a nearly constant amount of Htart$^-$ and various quantities of tart^{2-}. The ionic strength governed by the amount of the salt, NaHtart, was also maintained at 0.1 M. The compositions of the solutions are given in Table 1. The acid-dissociation constants used for the calculation of the respective ion concentrations were pK_1=2.88±0.02 and pK_2=4.02±0.02, which were determined by potentiometric titration at I=0.1 M and 25 °C. (2) Solutions containing various amounts of tartrate at the constant pHs of 2.74 and 3.90 were prepared by diluting a mixture of equal volumes of 0.1 M Na$_2$tart and 0.34 M H$_2$tart, and one of 0.1 M Na$_2$tart and 0.05 M H$_2$tart, with a 0.1 M NaClO$_4$ solution.

Table 1. The compositions of tartrate solutions prepared so as to maintain [Htart$^-$] nearly constant (0.1 mol dm^{-3})

pH	[H$_2$tart] mol dm^{-3}	[Htart$^-$] mol dm^{-3}	[tart^{2-}] 10^{-3} mol dm^{-3}
2.12	0.595	0.104	1.31
2.21	0.476	0.102	1.59
2.32	0.359	0.099	1.99
2.49	0.239	0.098	2.92
2.59	0.182	0.095	3.52
2.74	0.124	0.091	4.78

Procedure. The cation-exchange experiments were carried out in a manner similar to that described previously.2) The distribution coefficient, K_d, was calculated as follows:

$$K_d = \frac{\text{Activity in the resin phase}}{\text{Activity in the solution phase}} \times \frac{\text{Volum of solution (ml)}}{\text{Mass of dry resin (g)}}. \tag{1}$$

Results and Discussion

Considering the formation of M(Htart)$^{2+}$ and M(tart)$^+$, the adsorption of these species on the cation exchanger was studied at I=0.1 and 0.2 mol dm^{-3} and was found to be negligible compared with that of the M^{3+} species.4) Thus, the following equation is derived:

$$\begin{aligned} K_d^0/K_d - 1 = &\sum K_{\mathrm{M(Htart)}_i}[\mathrm{Htart}^-]^i \\ &+ \sum K_{\mathrm{M(Htart)}_j\mathrm{(tart)}_k}[\mathrm{Htart}^-]^j[\mathrm{tart}^{2-}]^k \\ &+ \sum K_{\mathrm{M(tart)}_l}[\mathrm{tart}^{2-}]^l \end{aligned} \tag{2}$$

where K_d^0 denotes K_d in the absence of the complexing agent, and where $K_{\mathrm{M(Htart)}_i}$, $K_{\mathrm{M(Htart)}_j\mathrm{(tart)}_k}$, and $K_{\mathrm{M(tart)}_l}$ are the formation constants of the M(Htart)$_i$, M(Htart)$_j$(tart)$_k$, and M(tart)$_l$ respectively. If we can set conditions so as to keep [Htart$^-$] nearly constant and to vary [tart^{2-}], Eq. 2 may be written as a function of [tart^{2-}] alone, thus:

$$\begin{aligned} K_d^0/K_d - 1 = &A + B\sum K_{\mathrm{M(Htart)}_j\mathrm{(tart)}_k}[\mathrm{tart}^{2-}]^k \\ &+ \sum K_{\mathrm{M(tart)}_l}[\mathrm{tart}^{2-}]^l, \end{aligned} \tag{3}$$

where A and B are constant. From a plot of $K_d^0/K_d - 1$ *vs.* [tart^{2-}], we can conclude which of the two species, Htart$^-$ and tart^{2-}, is the actual complexing ligand. It is difficult, however, to decide the type of complexes formed from only this plot. For example, if the plot shows a straight line with an intercept, we can not conclude whether k=1, l=0; k=0, l=1, or k=l=1. To make the difference clear, it is necessary to know the ratio of metal to ligand; this can be found by studying the relation between $K_d^0/K_d - 1$ and [tartrate]$_{\text{total}}$ at a constant pH.

Figure 1 shows the plots of $K_d^0/K_d - 1$ *vs.* [tart^{2-}], where [Htart$^-$] is kept constant (nearly 0.1 mol dm^{-3} for Ce(III) and Tm(III)). The fact that straight lines are obtained indicates the presence of two different type of complexes; one consists of only Htart$^-$, and while in the other the ratio of the metal to the ligand, tart^{2-}, is 1:1. As is shown in Fig. 2, the plots of log ($K_d^0/K_d - 1$) *vs.* log[tartrate]$_{\text{total}}$ at pH 2.74 give straight lines with the slope of 2, indicating that all

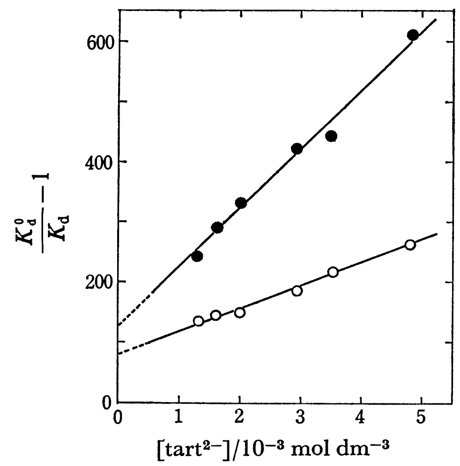

Fig. 1. Plots of (K_d^0/K_d-1) *vs.* [$tart^{2-}$] at [$Htart^-$]$\simeq$0.1 mol dm^{-3}.—○— Ce(III), —●— Tm(III).

Table 2. Formation constants of Ce(III) and Tm(III) tartrate complexes I=0.1 mol dm^{-3}, 25 °C

Metal ions	$\log K_{M(Htart)}$	$\log K_{M(Htart)_2}$	$\log K_{M(tart)}$	$\log K_{M(Htart)(tart)}$	$\log K_{M(tart)_2}$
Ce(III)	2.54±0.03[a]	3.89±0.05	5.5±0.2[b] 3.84[c] 3.09[d]	5.60±0.05[e] 5.58±0.05[f]	6.03±0.05 8.4±0.2[b] 6.72[c]
Tm(III)		4.10±0.05	5.3[g]	5.99±0.05[e] 5.97±0.05[f]	6.35±0.05

a) Ref. 6. b) Ref. 7. c) Ref. 8, I; variable. d) Ref. 9, I=0.2 mol dm^{-3}. e) The values obtained from the plot in Fig. 1. f) The values obtained from the plot of $\log(K_d^0/K_d-1-A)$ *vs.* $\log[H^+]$. g) Ref. 5. I=0 mol dm^{-3}.

the complexes formed in this pH region have a 1:2 metal-to-ligand ratio. On the basis of this, the two complexes, $M(Htart)_2^+$ and M(Htart)(tart), for Ce(III) and Tm(III) are considered. Their formation constants, $K_{M(Htart)_2^+}$ and $K_{M(Htart)(tart)}$, calculated from the intercepts and the slopes of the straight lines in Fig. 1, are listed in Table 2. Equation 3 can be simplified and reformed in this case:

$$K_d^0/K_d - 1 = A + BK_{M(Htart)(tart)}[tart^{2-}], \qquad (3')$$

$$\log(K_d^0/K_d-1-A) = \log B^2k_2K_{M(Htart)(tart)} - \log[H^+], \qquad (4)$$

where $k_2=[H^+][tart^{2-}]/[Htart^-]$. The $K_{M(Htart)(tart)}$ values are also obtained from the intercepts of the straight lines obtained from the plots of $\log(K_d^0/K_d-1-A)$ *vs.* $\log[H^+]$. These values, also listed in Table 2, are found to be close to those presented above.

To examine another type of complexes, the experiments were carried out at a pH of 3.90. The plots of $\log(K_d^0/K_d-1)$ *vs.* $\log[tartrate]_{total}$ given in Fig. 2 indicate the presence of 1:2 complexes, that is, $M(Htart^-)(tart^{2-})$ and $M(tart^{2-})_2$. The intercepts of the plots in Fig. 2 correspond to $\{K_{M(Htart)(tart)}k_1^2k_2\times[H^+]+K_{M(tart)_2}\times(k_1k_2)^2\}/([H^+]^2+k_1[H^+]+k_1k_2)^2$, where $k_1=[H^+][Htart^-]/[H_2tart]$.

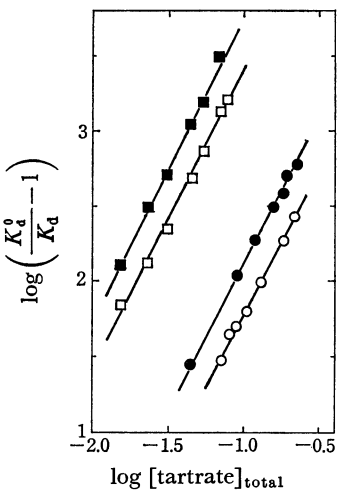

Fig. 2. Plots of $\log(K_d^0/K_d-1)$ *vs.* $\log[tartrate]_{total}$ at constant pHs of 2.74 and 3.90.
—○— Ce(III), —●— Tm(III) at pH 2.74; —□— Ce(III), —■— Tm(III) at pH 3.90.

Since the $K_{M(Htart)(tart)}$ values are already known, the formation constants of $Ce(tart)_2^-$ and $Tm(tart)_2^-$ are determined to be as listed in Table 2. To confirm the reliability of these formation constants, we tried to obtain the relationships between $\log(K_d^0/K_d-1)$ and $\log[tartrate]_{total}$ at pH 2.74, using these values for the calculation. The results are in good agreement with the solid lines shown in Fig. 2. The formation constants of other types of complexes reported in the literature are also listed in Table 2. It is of interest that, for both Ce(III) and Tm(III), the two complexes, M(Htart)(tart) and $M(tart)_2^-$, have stabilities of the same order. From this, M(Htart)(tart) is found to be the predominant species in solutions of the lower pH region.

The complex of the $M(tart)^+$ type, whose formation constants for Ce(III) and Tm(III) are listed in Table 2, was not found under these experimental conditions. There are no protonated couples other than $Ce(Htart)^{2+}$ in the literature. From our results, the type of M(Htart)(tart) is found to be appreciably stable. If this species is neglected in the estimations of other species, the resulting formation constants may involve a considerable error. This might be one of the reasons why there has been a remarkable disagreement among the values reported for the formation constants of $Ce(tart)^+$ and $Ce(tart)_2^-$.

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