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PREPARATION OF OPTICALLY ACTIVE CATION EXCHANGERS WITH L-TARTRATE GROUPS AND ITS APPLICATION TO THE RESOLUTION OF $[Co(en)_3]^{3+}$ ION *

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Two types of optically active Sephadex cation exchangers, in which L-tartrate groups were linked to form ether or ester, were prepared by simple methods for the first time. These cation exchangers were effectively applied to a direct chromatographic resolution of $[Co(en)_3]^{3+}$.

L-Tartrate has been used as a very useful resolving agent of some metal complexes for many years, and was also used as the eluent for the chromatographic resolution of $[Co(en)_3]^{3+}$ on SE- and SP-Sephadex columns1). However, direct chromatographic resolution of metal complexes with ion exchangers containing optically active exchanging groups has not been carried out.

We attempted to prepare optically active Sephadex cation exchangers with L-tartrate residue as the exchanging group, which are in the following denoted by TA-Sephadex. Two types of TA-Sephadex were successfully prepared, and they were applied to the column chromatographic resolution of $[Co(en)_3]^{3+}$.

[I] Preparation of TA-Sephadex

In this experiment, Sephadex was used as the base of ion exchanger. Sephadex contains many hydroxyl groups in a molecule2) and is capable of reacting as a secondary alcohol. L-Tartaric acid, on the other hand, is expected to undergo reaction with Sephadex as a secondary alcohol or a carboxylic acid,

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resulting in the formation of ether or ester. The two types of resulting TA-Sephadex are denoted by TA(ET)-Sephadex and TA(ES)-Sephadex, respectively. Figure 1 shows schematically the structure of each TA-Sephadex.

TA(ET)-Sephadex TA(ES)-Sephadex

Fig. 1 Schematic representation of TA-Sephadex (SD : Sephadex).

TA(ET)-Sephadex Sixty grams of Sephadex(G-10) was added to 120 ml of diethyl L-tartrate and the mixture was stirred well with a magnetic stirrer. Two milliliters of concentrated sulfuric acid was added dropwise, and then the mixture was heated on a hot plate with continuous stirring at *ca.* 60 °C for about 80 hours. The heating was stopped before the reaction mixture turned brown. The product was filtered, washed with water, and then treated with 0.1 M NaOH. Thus diethyl L-tartrate groups of the product were hydrolyzed to yield sodium form of the exchanger. Then, after being washed with ethanol and dried below 80 °C, the product was measured for the ion exchange capacity. The capacity was 0.12 mmol $[\mathrm{Co(en)}_3]^{3+}$/g. To raise the capacity, the procedure mentioned above was repeated using the partially etherfied Sephadex instead of Sephadex(G-10). The TA(ET)-Sephadex obtained after a total of three times of etherification reactions was slightly yellowish and its capacity was 0.24 mmol $[\mathrm{Co(en)}_3]^{3+}$/g. The results of this and other runs are summarized in Table 1.

TA(ES)-Sephadex Forty grams of Sephadex(G-25, fine)*** was added to 160 ml of a 5 M (or saturated) L-tartaric acid aqueous solution. The mixture was stirred well until full swelling, and filtered. The residue was dried and esterified by heating at 110 °C or below for about 4 hours in an oven. Then, the product was washed well with water, filtered, washed with ethanol, and dried below 80 °C. The capacity measured was 0.21 mmol/g for $[\mathrm{Co(en)}_3]^{3+}$. Then, the above procedure was carried out again using the partially esterified product. The TA(ES)-Sephadex obtained was almost white, and its capacity was 0.31 mmol $[\mathrm{Co(en)}_3]^{3+}$/g.

*** The degree of cross linking of Sephadex(G-25) is lower than that of Sephadex(G-10). After full swelling with water, the former occupied 2.5 times as large a volume as that of the latter.

This H-form of TA(ES)-Sephadex was changed to the Na-form with 0.5 M Na_2SO_4 before it was used for column chromatography.

Table 1 Capacity of TA-Sephadex for $[Co(en)_3]^{3+}$ (m mol/g)

TA(ET)-Sephadex			
react.times	1	2	3
run 1	0.12	——a)	0.24
run 2	——a)	0.17	0.22

TA(ES)-Sephadex		
	1	2
run 1	0.21	0.31

a) Capacity was not measured.

[II] Application to the resolution of $[Co(en)_3]^{3+}$

Two ϕ1.5 × 78 cm columns were prepared with TA(ET)-Sephadex (capacity : 0.24 m mol / g) and TA(ES)-Sephadex (capacity : 0.31 m mol / g), respectively. $[Co(en)_3]^{3+}$ was sorbed at the top of each column and was eluted with an NaBr aqueous solution.

Elution curves are shown in Figs. 2 and 3 for the TA(ET)- and TA(ES)-Sephadex columns, respectively.

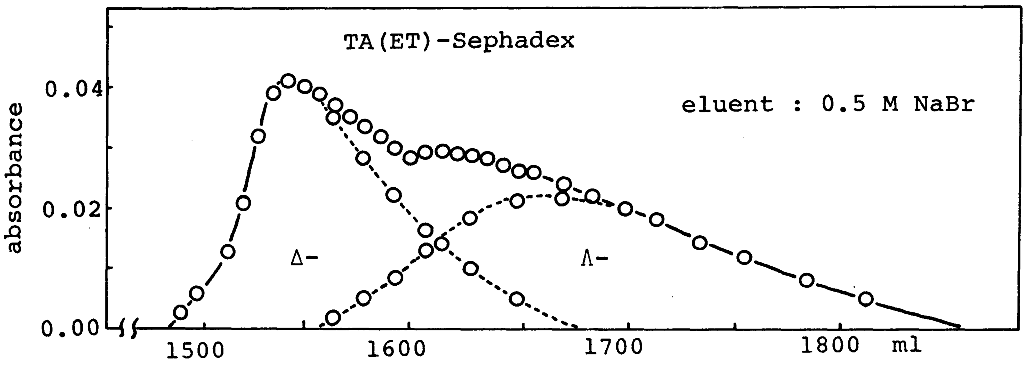

Fig.2 Elution curve of $[Co(en)_3]^{3+}$ on a TA(ET)-Sephadex column.

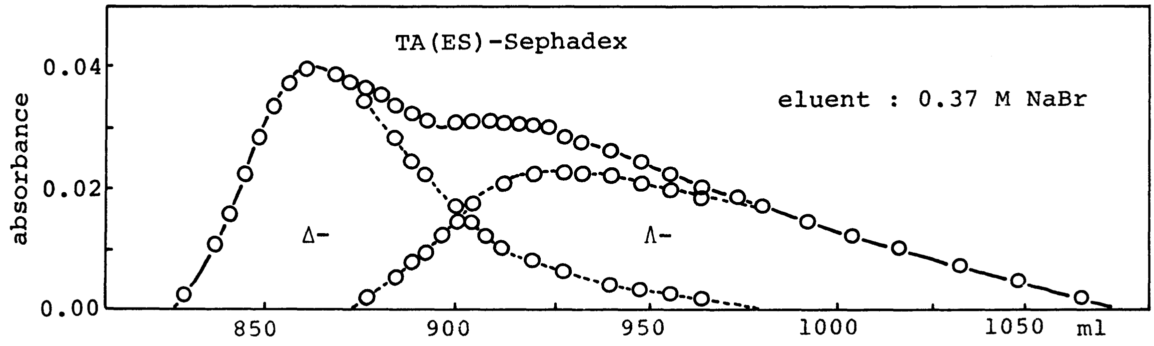

Fig.3 Elution curve of $[Co(en)_3]^{3+}$ on a TA(ES)-Sephadex column.

Δ-$[Co(en)_3]^{3+}$ was eluted faster than Λ-$[Co(en)_3]^{3+}$ on both the TA(ET)- and the TA(ES)-Sephadex columns. This elution order is the one expected from a previous finding that L-tartrate(2-) ions interact with Λ-$[Co(en)_3]^{3+}$ more strongly than with the Δ-form of the complex$^{3)\sim5)}$. From the intensity of circular dichroism measured at 490 nm and the absorbance at 470 nm, the resolution percentage in each fraction was estimated. These values were used to draw the dotted curves (in Figs. 2 and 3) showing the elution of Δ- and Λ-$[Co(en)_3]^{3+}$.

The results show that efficient resolution of $[Co(en)_3]^{3+}$ can be effected with either of TA(ET)- and TA(ES)-Sephadex, and that the efficiencies of the two columns are comparable with each other. However, considering the fact that the exchange capacity was greater for the TA(ET)- than for the TA(ES)-Sephadex column by a factor of 2.5, TA(ES)-Sephadex should have much greater stereoselectivity than TA(ET)-Sephadex. Thus TA(ES)-Sephadex is preferred as the ion exchanger to resolve $[Co(en)_3]^{3+}$, for reasons of simpler preparation and higher efficiency.

The higher efficiency of TA(ES)-Sephadex is consistent with our previous result from a circular dichroism study of the stereoselective interaction of anions of hydroxy acids with Λ- and Δ-$[Co(en)_3]^{3+}$. In that study, we found that existence of two hydroxyl groups and one of the carboxyl groups is essential for a marked stereoselective change of the circular dichroism spectrum of Λ-$[Co(en)_3]^{3+}$ 6).

The newly prepared optically active ion exchangers are expected to be of use for the resolution of other metal complexes and organic bases, and for rapid detection of molecular assymetry of unknown substances. The experiments are in progress and the results will be reported elsewhere.

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