CHEMISTRY LETTERS, pp. 473-474, 1975. Published by the Chemical Society of Japan

HIGHLY EFFICIENT CHROMATOGRAPHIC RESOLUTION OF $[Co(en)_3]^{3+}$ ION WITH A COLUMN OF TA(ES)-SEPHADEX CONTAINING D-TARTRATE GROUPS

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Sephadex cation exchanger with D-tartrate groups was newly prepared. This cation exchanger was applied to column chromatographic resolution of $[Co(en)_3]^{3+}$ and complete resolution was accomplished with high efficiency using an aqueous solution of sodium L-tartrate as the eluent.

In a previous paper,[1)] we reported the preparation of two types of new cation exchanger with L-tartrate groups and their application to the chromatographic resolution of $[Co(en)_3]^{3+}$. Recently we prepared TA(ES)-Sephadex (denoting the Sephadex with tartrate groups of ester type as the functional group) of a higher ion-exchange capacity, and achieved complete resolution of $[Co(en)_3]^{3+}$ with a column of this exchanger using a sodium sulfate solution as the eluent.[2)]

In order to develop a more efficient method for the column chromatographic resolution of metal complexes, we prepared a Sephadex cation-exchanger with D-tartrate groups in place of L-tartrate groups of ordinary TA(ES)-Sephadex, and applied to the column chromatographic resolution of $[Co(en)_3]^{3+}$ using a sodium L-tartrate solution as the eluent.

Preparation of D-TA(ES)-Sephadex (TA(ES)-Sephadex with D-tartrate groups)

D-TA(ES)-Sephadex was prepared in a similar way to that previously described for TA(ES)-Sephadex with natural or L-tartrate groups. Forty grams of Sephadex (G-25, fine) was made to react twice with 160 ml of a 2.6 M D-tartaric acid** solution to yield a partially esterified Sephadex in the H-form, which was then converted to the Na-form by the addition of a 0.5 M NaOH solution with stirring to the pH of about 6. The resulting D-TA(ES)-Sephadex was yellowish white and its exchange capacity for $[Co(en)_3]^{3+}$ was 0.17 mmol/g.

Column chromatographic resolution of $[Co(en)_3]^{3+}$ ions

A ϕ 1.5 × 77 cm column was prepared with D-TA(ES)-Sephadex. $[Co(en)_3]^{3+}$ was sorbed at the top of the column and eluted with a sodium sulfate solution (as a reference) or with a sodium L-tartrate solution. Figures 1 and 2 show elution curves respectively with a 0.04 M Na_2SO_4 and with a 0.06 M sodium L-tartrate as the eluent. The Λ-isomer of $[Co(en)_3]^{3+}$ was eluted faster than Δ-isomer in each case. Figure 2 shows that $[Co(en)_3]^{3+}$ was completely resolved into its

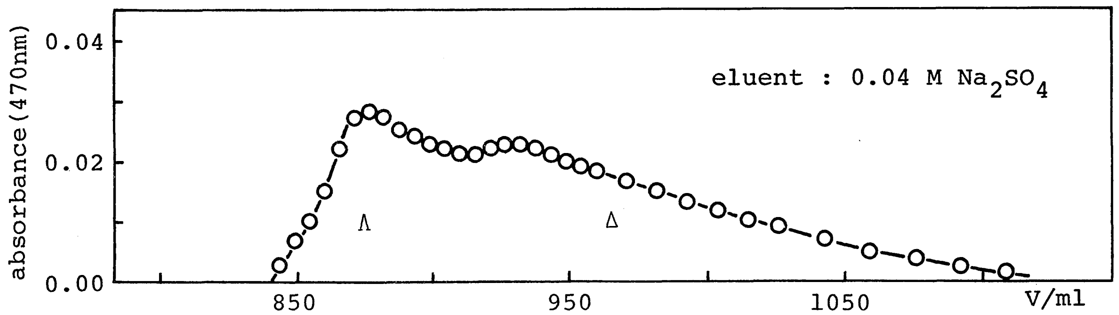

Fig.1 Elution curve of $[Co(en)_3]^{3+}$ on a D-TA(ES)-Sephadex column.

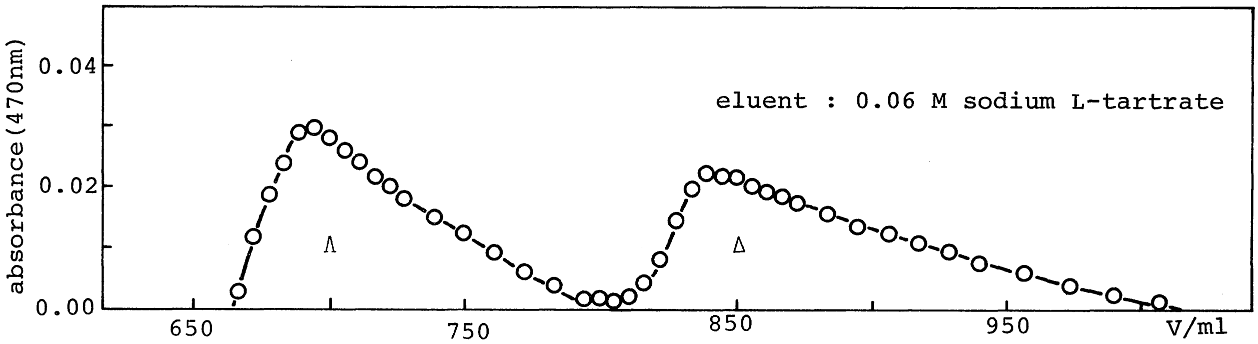

Fig.2 Elution curve of $[Co(en)_3]^{3+}$ on a D-TA(ES)-Sephadex column.

antipodes in spite of the very low ion-exchange capacity of this cation exchanger. Yoshikawa and Yamasaki have achieved complete resolution of this complex with a ϕ 1.1 × 120 cm column of ordinary SE-Sephadex (0.65 mmol $[Co(en)_3]^{3+}$/g) using a 0.15 M sodium L-tartrate as the eluent.[3] Comparison with their result shows that the present method is of surprisingly high efficiency. This high efficiency can be ascribed to the double stereoselective effects of D- and L-tartrates on $[Co(en)_3]^{3+}$. The L-tartrate ion in the eluent interacts more strongly with Λ-$[Co(en)_3]^{3+}$ than with Δ-$[Co(en)_3]^{3+}$, tending to easier elution of the Λ-isomer; whereas the D-tartrate groups of D-TA(ES)-Sephadex hold back the Δ-isomer more firmly than the Λ-isomer, tending to less easy elution of the Δ-isomer. Thus, Λ-$[Co(en)_3]^{3+}$ is eluted much faster than the Δ-isomer.

Applications to the resolution of other metal complexes are in progress and the results will be reported elsewhere.

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** Ammonium sodium D-tartrate was kindly supplied by Nippon Peroxide Co. Ltd. Tokyo, Japan.

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(Received April 10, 1975)