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## Note

### Separation of optical isomers of metal complexes by paper electrophoresis in mixtures of aluminium chloride and tartrate

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The first paper dealing with the electrophoretic separation of optical isomers is that of Yoneda and Miura<sup>1</sup> who separated the two optical forms of  $\text{Co(en)}_3^{3+}$  using a mixture of optically active disodium tartrate and aluminium chloride as electrolyte.

This work was then extended to tris-ethylenediamine complexes of rhodium and chromium<sup>2</sup>. These separations have one feature in common, they all have rather large differences in electrophoretic movement and the slower band is always much longer than the faster band.

The same mixture of tartrate and aluminium salts also produced separation of the optical forms of  $\text{Co(en)}_3^{3+}$  in chromatography on silica gel. Again the slower spot is rather an elongated trail and the faster spot well-defined and close to the liquid front<sup>3</sup>.

While Yoneda states that with his electrophoretic technique (low potential: 250 V/34 cm for 2-3 h) no separations of optical isomers were observed in tartrate solutions in the absence of aluminium, Ossicini and Celli<sup>4</sup> did obtain separations in tartrate alone with high-voltage electrophoresis. In tartrate alone both spots are round and of the same size, and the separation distance is always much lower than in the tartrate-aluminium mixtures.

The high-voltage separations were then extended by Cardaci *et al.*<sup>5</sup> to numerous metal complexes and to a number of optically active electrolytes. The separations in, for example, antimony tartrate or arsenic tartrate were all similar to those in tartrate *i.e.* with rather round spots and small differences in mobility. Thus so far the tartrate-aluminium system was found to be unique both for large separation factors and elongated spots.

We therefore wanted to extend this work with the hope of discovering something about the mechanism of the separations in tartrate-aluminium solutions and our results are reported here.

## EXPERIMENTAL

### Chromatographic experiments

We found that the separations described by Yoneda and Baba<sup>3</sup> were highly reproducible and even improved on Merck silica gel thin layers for high-performance

thin-layer chromatography. We then also noted that these separations are independent of the support and are obtained both on cellulose thin layers and paper strips. Typical results are shown in Fig. 1. Thus the mechanism is unlikely to involve specific adsorption on silica gel. We have also chromatographed some other Co(III) complexes on Whatman No. 3MM paper.  $\text{Co}(\text{NH}_3)_6^{3+}$ , which precipitates as a long trail,  $\text{Co}(\text{pn})_3^{3+}$ ,  $\text{Co}(\text{tn})_3^{3+}$ ,  $\text{Co}(\text{dip})_3^{3+}$  and  $\text{Co}(o\text{-phen})_3^{3+}$  all move close to the liquid front when developed with 0.2 M ammonium *d*-tartrate + 0.1 M  $\text{AlCl}_3$ .

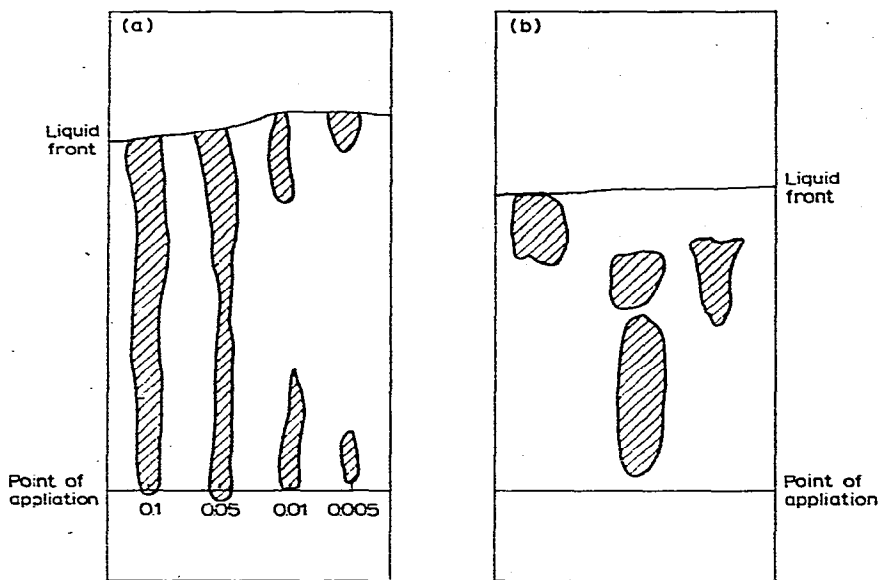


Fig. 1. Typical chromatograms on Whatman No. 3MM paper developed ascendingly with an aqueous solution of 0.2 M ammonium-*d*-tartrate and 0.1 M  $\text{AlCl}_3$ . (a) Various concentrations of  $\text{Co}(\text{en})_3\text{Cl}_3$  solution chromatographed side by side. With 0.1 and 0.05 M solutions only long streaks are formed. With 0.01 and 0.005 M solutions good separations are obtained. (b) Several complexes are chromatographed side by side: (from left to right)  $\text{Co}(o\text{-phen})_3^{3+}$ ,  $\text{Co}(\text{en})_3^{3+}$  and  $\text{Co}(\text{pn})_3^{3+}$ .

#### Paper electrophoretic experiments

In paper electrophoretic experiments if one carries out a separation and then reverses the current for the same length of time, all spots should return to the origin unless they were altered chemically during the electrophoretic run.

In tartrate-aluminium solutions we observed that the faster round spot did indeed return to the origin on reversing the current, while the slower elongated spot remained where it was. Thus the species did not migrate in the normal manner in solution.

#### Mixing the electrolyte and the solution of $\text{Co}(\text{en})_3^{3+}$

When the two solutions were mixed a cloudy appearance was noticed immediately and a rather gelatinous precipitate formed within seconds. We have prepared this precipitate using various ratios of the two solutions. It is always gelatinous and does not show any crystalline structure under a low power microscope even on

aging and drying. The analyses for the Co-Al ratio varied with the ratio of the  $\text{Co(en)}_3^{3+}$ -electrolyte mixed to prepare it.

Typical results obtained are:

(1) The precipitate formed by mixing  $\text{Co(en)}_3\text{Cl}_3$  and a solution of 0.4 M ammonium *d*-tartrate and 0.2 M  $\text{AlCl}_3$  (12.1% Al; 8.1% Co).

(2) The precipitate formed by mixing  $\text{Co(en)}_3\text{Cl}_3$  and a solution of 0.1 M ammonium tartrate and 0.05 M  $\text{AlCl}_3$  (3.22% Al; 4.58% Co).

(3) The precipitate formed by mixing  $\text{Co(en)}_3\text{Cl}_3$  and a solution containing 0.2 M ammonium *d*-tartrate and 0.1 M  $\text{AlCl}_3$  (7.95% Al; 4.96% Co).

#### CONCLUSIONS

Our observations seem to indicate that the separations obtained in tartrate-aluminium solutions are best described as a form of precipitation chromatography specific for an optical configuration. The gelatinous nature of the precipitate would suggest that there is some form of hydrolytic process in which the addition of the cobalt complexes starts a small pH change and a gelatinous aluminium hydroxide-tartrate then preferentially adsorbs one of the optically active forms of the  $\text{Co(en)}_3^{3+}$ .

#### REFERENCES

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