

Note

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Thin-layer chromatography of an optically active complex

In a recent publication in this journal, YONEDA AND BABA¹ reported the resolution of racemic tris(ethylenediamine)cobalt(III) cation by means of thin-layer chromatography (TLC) on silica gel. The resolution was affected using an aqueous solvent system containing the *d*-tartrate anion and aluminum chloride. This study suggested that resolution of this racemic cation was based on the different degree of ion-pair formation for *d*-[Co(en)₃]³⁺, *d*-tartrate and *l*-[Co(en)₃]³⁺, *d*-tartrate.

We reported on the possible use of optically active quartz for the TLC separation of racemic K[Co(EDTA)] (ref. 2). The present work was undertaken to study the chromatographic behavior of racemic [Co(en)₃]³⁺ using optically active quartz incorporated into the TLC plate containing an adsorbent of microcrystalline cellulose. Early investigators³⁻⁵ observed that when solutions of a racemic mixture of certain complexes were stirred or shaken with *d*- or *l*-quartz, they showed optical activity, and KARAGUNIS AND COUMOULOS⁶ have described a partial resolution of Cr(en)₃·3.5 H₂O on a column of quartz.

Experimental

Plate preparation. Plain plates having only microcrystalline cellulose were prepared as previously reported^{2,7}. Plates containing *d*-quartz were prepared by blending 40 g of adsorbent with 10 g of *d*-quartz and 218 ml of distilled water. The slurry was spread on 20 × 5 cm plates at 0.75 mm thickness. Plates containing Na,K *d*-tartrate were prepared by blending microcrystalline cellulose, Na,K *d*-tartrate, and water in the ratio of 50 g:10 g:218 ml. Similarly, plates containing both *d*-quartz and Na,K *d*-tartrate were prepared by blending microcrystalline cellulose, water, *d*-quartz, and Na,K *d*-tartrate in the ratio of 40 g:218 ml:10 g:5 g.

Solution and solvent preparation. The following salts were prepared in 4-6% (w/v) aqueous solution: *d,l*-Co(en)₃Cl₃, *d*-Co(en)₃I₃·H₂O, *l*-Co(en)₃I₃·H₂O, *d*-Co(en)₃Cl (*d*-tartrate). The solvent system (100 ml) consisted of various aqueous mixtures of Na,K *d*-tartrate and/or AlCl₃. Detection was made by spraying a freshly made 10% (w/v) Na₂S solution.

Results and discussion

In agreement with YONEDA AND BABA it was found that a TLC separation on microcrystalline cellulose of racemic [Co(en)₃]³⁺ could be accomplished only when AlCl₃ and Na,K *d*-tartrate are present in the solvent system. Taken individually the isomers had *R_F* values of almost 1.00 on plain and *d*-quartz plates when chromatographed in a solvent system containing only 0.2 *M* AlCl₃. With a Na,K *d*-tartrate plate, a considerable amount of tailing was observed with a 0.2 *M* solvent. This indicated that the ion pairs *d*-complex *d*-tartrate and *l*-complex *d*-tartrate must move with the solvent front. No separation was observed using the various types of plates in a system containing distilled water. A separation of the isomers was observed in a solvent containing 0.3 *M* Na,K *d*-tartrate and either 0.15 *M* or 0.20 *M* AlCl₃. With a plain plate the racemic mixture gave *R_F* values of 0.92 (0.15 *M* AlCl₃)

and 0.90 (0.20 *M* AlCl₃) for the *d*-isomer and 0.50 (0.15 *M* or 0.20 *M* AlCl₃) for the *l*-isomer. The *l*-isomer showed considerable tailing, but this was corrected by using a plate having *d*-quartz mixed with the microcrystalline cellulose. A sharp separation on the *d*-quartz plate was obtained with the tartrate-AlCl₃ solvent system, with the *d*-isomer having an *R_F* value of 0.46 (0.15 *M* AlCl₃) and 0.50 (0.20 *M* AlCl₃) and the *l*-isomer having an *R_F* value of 0.25 (0.15 *M* AlCl₃) and 0.28 (0.20 *M* AlCl₃). These respective *R_F* values were reproducible on *d*-quartz plates for the following mixtures: *d*-[Co(en)₃]I₃·H₂O and *d*-[Co(en)₃]Cl (*d*-tartrate); *l*-[Co(en)₃]I₃·H₂O and *d*-[Co(en)₃]Cl (*d*-tartrate); *d,l*-[Co(en)₃]Cl₃ and *d*-[Co(en)₃]I₃·H₂O; *d,l*-[Co(en)₃]Cl₃ and *d*-[Co(en)₃]Cl (*d*-tartrate).

The asymmetric environment produced by the *d*-quartz interacted with both diastereo ion pairs to lower the *R_F* as compared to a plain plate. The separation was very good with the *l*-isomer, showing a more compact spot as compared to that obtained on a plain plate. It was also noted that one additional spot found near the top of the plate was due to overloading. This was eliminated when 10 μg or less of the racemic mixture were applied per plate. Furthermore it was also observed that the grain size of the *d*-quartz greatly affected the separations. For plates containing *d*-quartz in the range of 177 to 250 μ some tailing of the *d*-isomer and a large tailing of the *l*-isomer occurred; whereas, with plates containing *d*-quartz in the range of 149 to 177 μ only tailing of the *l*-isomer was noted. The *R_F* values for a separation on these plates were similar to that of a plain plate. Only on plates containing *d*-quartz smaller than 140 μ was the separation sharp with *R_F* values as previously noted. It is also interesting to note that the microcrystalline cellulose also passes a 140-μ mesh.

The role of AlCl₃ in the solvent system appears to be very important as salts such as the chlorides of sodium, barium, strontium, zinc, iron(II) and iron(III), when substituted for the AlCl₃, gave no separation. Some dehydration of the *d*- and *l*-cation must occur on the plate through the use of the high hydration energy of the Al(III) ion. The *d*-tartrate ion now interacts differently with the racemic mixture to produce diastereo ion pairs which can be chromatographed. We have shown that this resolution is greatly improved by the use of *d*-quartz for which the ion pairs interact differently with this asymmetric environment. Resolution was not achieved when the developer has a pH value below 2 or above 3.5. Other resolving agents such as *d*-10-champhor-sulfonic acid could not be substituted for the *d*-tartrate ion in the developer.

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