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Studies of thin-layer chromatography of inorganic salts

V. Resolution of the racemic trisethylenediaminecobalt(III) complex by means of thin-layer chromatography on silica gel

Since TSUCHIDA *et al.*[1] reported the partial resolution of racemic complexes using quartz powder, the technique of resolution by the use of asymmetric adsorbents has been widely adopted. KREBS AND RASCHE[2] have shown several examples of the resolution of racemic complexes using a starch column. FUJISAWA[3] and others[4] resolved racemic tyrosine-3-sulphonic acid by paper chromatography without using an optically active solvent. YOSHINO *et al.*[5] resolved racemic complexes using common ion-exchange resins saturated with optically active substances. These methods are all based on the tendency of the optically active adsorbent to adsorb one enantiomer in preference to the other.

Recently YONEDA AND MIURA[6] have succeeded in resolving the racemic $[Co(en_3)]^{3+}$ complex by means of electrophoresis. This method was based on the different degrees of ion-pair formation of the *d*-$[Co(en_3)]$-*d*-tartrate and *l*-$[Co(en_3)]$-*d*-tartrate systems in a solution containing aluminium ions. Against this, in studies on the thin-layer chromatography of inorganic salts[7], it was found that the complex cation can be adsorbed on the negatively charged surface of silica gel and is eluted through ion-pair formation. Thus, the resolution obtained by electrophoresis suggests that resolution by means of thin-layer chromatography might be possible. The successful result obtained is described here.

Experimental

Material. Samples tested were *dl*-$[Co(en_3)]Cl_3 \cdot 3H_2O$, *d*-$[Co(en_3)]Cl$(*d*-tartrate)$\cdot 5H_2O$ and *l*-$[Co(en_3)]Cl$(*l*-tartrate)$\cdot 5H_2O$. These salts were dissolved in water to $1/50$ *M*, and 2.5 μl of the solution was applied to the thin-layer.

Chromatography. As an adsorbent, Merck's Silica Gel H prepared for thin-layer chromatography was used without further purification. This was spread on glass plates of 20 cm length at a thickness of 0.25 mm.

Aqueous solutions containing sodium *d*-tartrate and aluminium chloride in various concentrations were used as a developer. Development was carried out at room temperature (20–22°). Sodium sulphide solution was sprayed for visualisation of the developed spot.

Results and discussion

When only sodium *d*-tartrate was used as the developer, the racemic form of the complex always appeared in one spot, irrespective of the concentration of the developer. This means that the resolution was not successful. However, when aluminium chloride was dissolved at a suitable concentration in the sodium *d*-tartrate solution, the racemic form was completely separated into two spots, as can be seen in Fig. 1C and D. This should be taken as a resolution, because the sample of the *d*-form alone showed a spot in the same position as the upper spot of the racemic form, and the *l*-form alone showed a spot corresponding to the lower spot of the racemic form.

In order to find required concentration of aluminium chloride for resolution, five developers each containing 0.3 *M* sodium *d*-tartrate and various concentrations of aluminium chloride were used. The composition of the developers is listed as follows;

(A) 0.05 *M* $AlCl_3$
(B) 0.10 *M* $AlCl_3$
(C) 0.15 *M* $AlCl_3$
(D) 0.20 *M* $AlCl_3$
(E) 0.30 *M* $AlCl_3$
} plus 0.3 *M* Na *d*-tartrate.

The chromatograms using the above-listed developers are shown in Fig. 1. In this figure, the letters *r*, *d* and *l* represent the racemic and the *d*- and *l*-forms of the $[Co(en_3)]^{3+}$ complex, respectively. From these chromatograms, it is easily seen that complete resolution was achieved in the case when 0.15 *M* or 0.20 *M* $AlCl_3$ and 0.30 *M* sodium *d*-tartrate was used as a developer. Resolution proved to be unsuccessful when the concentration of $AlCl_3$ is below 0.10 *M* and above 0.30 *M*.

In order to see the effect of the pH of the developer, various kinds of developers prepared by adding small amounts of sodium hydroxide solution to developer D were used. The result is shown in Table I. It is noteworthy that resolution was not achieved with a developer whose pH is above 4.

Lastly, we should like to refer to the role of the aluminium salt in the resolution. Suppose the complex is developed with an aqueous solution which contains only sodium *d*-tartrate. A small amount of the *d*- and *l*-forms of the complex cation is eluted by the *d*-tartrate anion through ion-pair formation. In the case where the developer is a dilute solution of sodium *d*-tartrate, the complex cation and the *d*-tartrate anion are both supposed to be highly hydrated. Therefore, the *d*-tartrate anion is

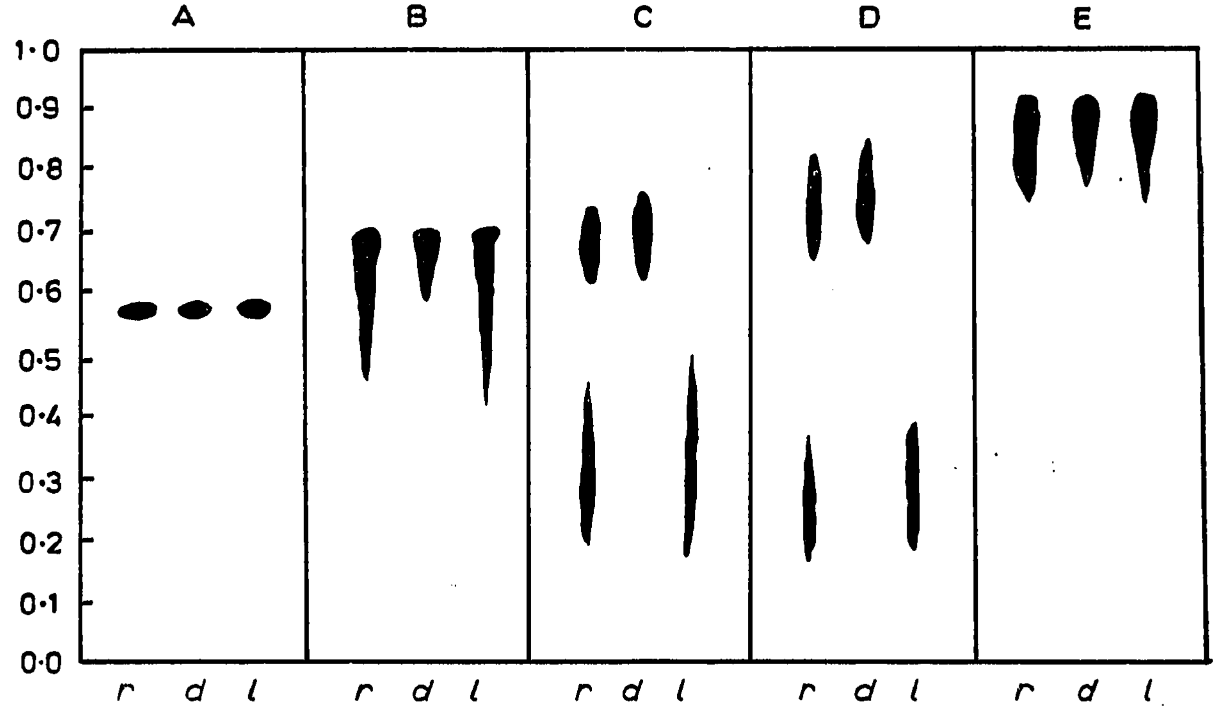

Fig. 1. Chromatograms of the *d*, *l* and racemic forms of $[Co(en_3)]^{3+}$ developed with the mixed solutions of Na *d*-tartrate and $AlCl_3$.

TABLE I

EFFECT OF THE pH OF THE DEVELOPER UPON THE R_F VALUES

Sample	*pH*					
	2.5	*3.0*	*4.0*	*5.0*	*6.0*	*7.0*
Racemate	0.67 0.23	0.58 0.35	0.53	0.55	0.61	0.63
d-form	0.70	0.60	0.53	0.56	0.58	0.60
l-form	0.20	0.35	0.56	0.59	0.58	0.60

only affected by the electrostatic attraction of the tervalent complex cation and cannot detect the enantiomeric difference between the *d*- and *l*-forms of the complex cation. For the *d*-tartrate anion to be able to distinguish between the *d*- and *l*-forms of the complex, it is necessary to reduce the degree of hydration of each ion in solution. The use of a concentrated solution of sodium *d*-tartrate seems to satisfy this requirement. However, in such a case, although the number of hydrating water molecules per ion is actually decreased by the increase of the tartrate concentration, the existence of a large number of tartrate anions shifts the equilibria

$$d\text{-}[\mathrm{Co(en_3)}]^{3+} + d\text{-tartrate} \rightleftharpoons \text{ion-pair}$$
$$l\text{-}[\mathrm{Co(en_3)}]^{3+} + d\text{-tartrate} \rightleftharpoons \text{ion-pair}$$

nearly completely towards ion-pair formation. Therefore, both the *d*- and *l*-forms show large R_F values indistinguishable from each other. Thus, resolution by chromatography is not achieved in this case either.

Therefore, we have to reduce the degree of hydration of each ion without increasing the tartrate concentration. The addition of aluminium salt to the developer will do this, because the large hydration energy of the tervalent aluminium ion will cause dehydration of the complex cation. In this way, the *d*-tartrate anion can distinguish between the *d*- and *l*-forms of the complex cation in the poorly hydrated state.

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