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Note

Paper electrophoretic study of ion-pair formation

XIII. Behaviour of anionic trisoxalatocobalt(III) and trisoxalatochromium(III) in optically active electrolytes

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Many metal complexes, especially those with a charge of 3, form strong ion pairs or outer-sphere complexes in solution. Such cation-anion interactions have been used for obtaining separations in high-voltage electrophoresis^{1,2}.

It was also found that optically active cations will form outer-sphere complexes with optically active anions, mobility differences depending on their optical form and it was possible to obtain separations, *e.g.*, of the *d*- and *l*-forms of Co(en)_3^{3-} using tartrate, arsenyl tartrate and antimonyl tartrate as electrolytes^{3,4}.

We have not found any reference in the literature to the separation of optically active anionic complexes, with the exception of an unsuccessful attempt to separate the optical forms of Co(ox)_3^{3-} (where ox = oxalate) with *l*-strychnine as electrolyte⁵.

In this paper we report the electrophoretic behaviour of anions of the type M(ox)_3^{3-} [where M = cobalt(III) or chromium(III)] using solutions of the acetates of brucine, cinchonine and quinine as electrolytes.

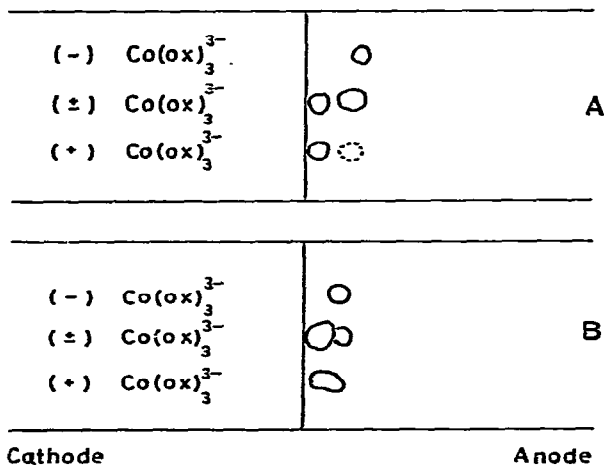


Fig. 1. Separation of the optical isomers of Co(ox)_3^{3-} using acetic acid containing 15% (w/v) of brucine as electrolyte. Whatman No. 1 paper at 2000 V for 1½ h. Acetic acid concentration: (A) 0.3 N; (B) 0.2 N.

EXPERIMENTAL AND RESULTS

We have used the Camag high-voltage paper electrophoresis apparatus with (unless stated otherwise) Whatman No. 1 filter-paper with electrophoretic runs of 1-1½ h at 2000 V. The cooling table of the apparatus was kept at 6-8°C.

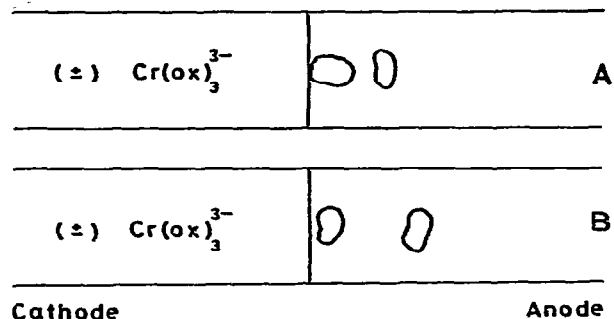


Fig. 2. Separation of the optical isomers of Cr(ox)_3^{3-} using acetic acid containing 15% (w/v) of brucine as electrolyte. Whatman No. 1 paper at 2000 V for 1½ h. Acetic acid concentration: (A) 0.2 N; (B) 0.3 N.

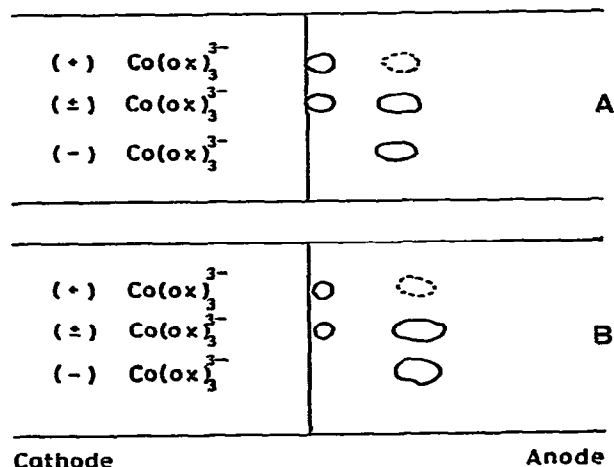


Fig. 3. Separation of the optical isomers of Co(ox)_3^{3-} using Whatman No. 1 paper at 2000 V for 1½ h with the following electrolytes: (A) 0.3 N acetic acid containing 10% (w/v) of quinine; (B) 0.3 N acetic acid containing 20% (w/v) of quinine.

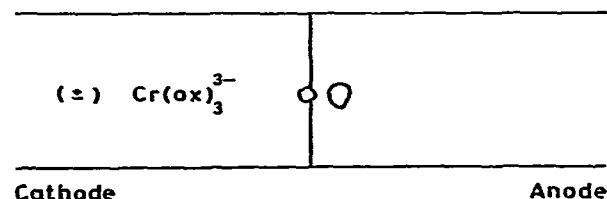


Fig. 4. Separation of the optical isomers of Cr(ox)_3^{3-} by high-voltage electrophoresis (2000 V for 1½ h with Whatman No. 1 paper) in 0.3 N acetic acid containing 20% (w/v) of quinine as electrolyte.

Sodium cobalti(III) oxalate and sodium chromium(III) oxalate were prepared and resolved into their optical isomers as described in the literature^{6,7}. We always placed the racemic mixture side-by-side with the two resolved optical forms.

The cobalt complexes were detected by spraying with ammonium sulphide solution and the chromium complexes with alcoholic ammoniacal 8-hydroxyquinoline. The electro-osmotic movement was measured by running a spot of dilute hydrogen peroxide along with the complexes. In the figures the distances shown are already corrected for electro-osmotic flow.

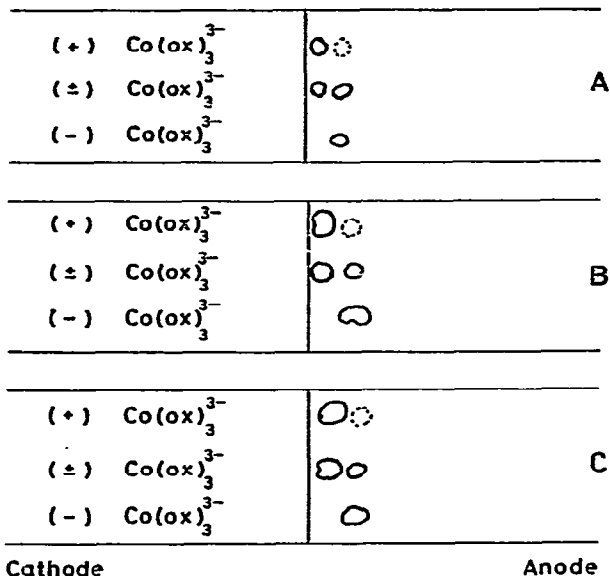


Fig. 5. Separation of the optical isomers of Co(ox)_3^{3-} using cinchonine acetate as electrolyte with Whatman No. 1 paper at 1500 V for 1 h. Cinchonine acetate concentration: (A) 0.2 N; (B) 0.3 N; (C) 0.5 N.

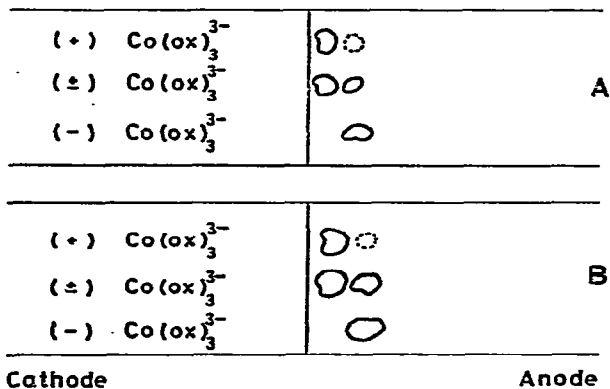


Fig. 6. Separation of the optical isomers of Co(ox)_3^{3-} using 0.3 N cinchonine acetate as electrolyte with Whatman No. 1 paper: (A) 1500 V for 1 h; (B) 2500 V for 45 min.

Figs. 1-7 show the results obtained. It is possible to separate the optical isomers of $\text{Co}(\text{ox})_3^{3-}$ and of $\text{Cr}(\text{ox})_3^{3-}$ in brucine, cinchonine and quinine acetates if the concentration of these bases is between 10 and 20% in solution. It is also evident that only the (-)-form of the cobalt(III) oxalate resolved is electrophoretically pure while the (+)-form still contains appreciable amounts of the (-)-form.

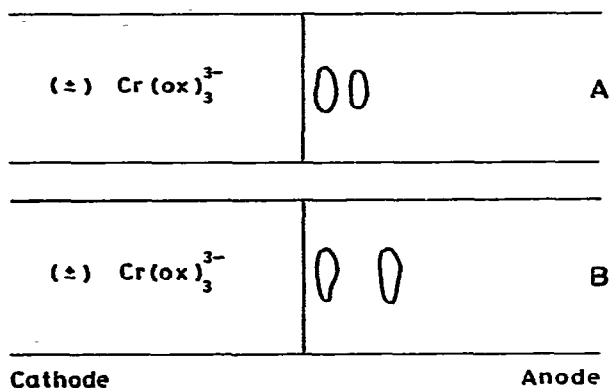


Fig. 7. Separation of optical isomers of $\text{Cr}(\text{ox})_3^{3-}$ using 0.5 N cinchonine acetate as electrolyte with Whatman No. 1 paper: (A) 1500 V for 1 h; (B) 2500 V for 45 min.

The separations of chromium(III) complexes can be improved by increasing the concentration of the optically active cation (see, e.g., Fig. 2) or by increasing the voltage (e.g., Fig. 7), but in all instances the spots moved only very short distances; it seems that strong ion pairs are formed.

To summarize, we have recorded conditions under which some anionic complexes can be separated into their optically active forms. It seems that for each case the conditions for separation differ and have to be established by trial and error. In order to obtain separations conditions must be chosen under which the anions move only very little, but as they yield compact spots complete separations were possible even with mobility differences of less than 8 mm.

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