SHORT COMMUNICATIONS

Curious Adsorptive Power of Alumina upon Inert Cobalt(III) Complexes in Thin-layer Chromatography

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Previously[1] we studied the separation mechanism of inorganic salts in paper chromatography using twenty-three kinds of inert cobalt(III) complexes as samples and an ethylamine aqueous solution as a developer. It was found that the R_f values of the complexes increase with the decrease in their positive ionic charges, reaching nearly unity in the case of the complex anions. A similar trend in variation of R_f values was observed in thin-layer chromatography in which silica gel was used as an adsorbent.[2] Therefore, it is natural to assume that paper and silica gel are charged negatively when in contact with water and that the difference in R_f values is mainly due to the difference in the electrostatic interaction (attraction or repulsion) between the complex and the adsorbent.

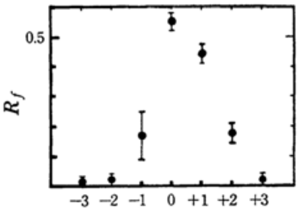

Fig. 1. Cobalt(III) complexes developed with distilled water, placed in order of the ionic charge (−3, −2, −1, 0, +1, +2, +3).

−3 $Na_3[Co(NO_2)_6]$
−2 $Na_2[Co(NO_2)_5NH_3]$
−1 $Na[Co(SO_3)_2 en_2]$
0 $[Co(gly_3)]$
+1 *cis*$[Co(CH_3CO_2)_2 en_2]NO_3$
+2 $[Co(CH_3CO_2)(NH_3)_5](ClO_4)_2$
+3 $[Co(NH_3)_6](ClO_4)_3$

However, when alumina[3] was used as an adsorbent, a quite different pattern of R_f-value variation was obtained. Here, we used distilled water as a developer and several cobalt(III) complexes with different charges, 3, 2, 1, 0, −1, −2 and −3, as samples. As is clearly shown in Fig. 1, the R_f value was found to be largest in the neutral complex and to decrease nearly symmetrically with the increase in the absolute values of the ionic charges of the complexes. This result suggests that alumina is charged negatively against complex cations and positively against complex anions.

It has been well known that alumina adsorbs either cations or anions, depending upon the pH of the solution. There are examples in which this amphoteric nature of alumina has been used in the separation of various ions by adjusting the pH of the solution.[4] In such cases alumina changes the sign of electric charges on its surface from positive to negative or *vice versa*, depending upon the pH of the solution. The result obtained in the present case appears to have no similarity to the amphoteric nature of alumina; still, it seems to originate from the amphoteric nature of the adsorbent. Whether this pattern of R_f value variation holds in other amphoteric oxides is now being investigated.

The details of this investigation will be reported in the near future.

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[1] Presented at the 10th Symposium of Coordination Chemistry, Kyushu University, Fukuoka, October, 1959.

[2] Unpublished paper.

[3] In this experiment, Merck's aluminum oxide H, prepared for thin-layer chromatography according to Stahl's method, was used without further purification.

[4] L. Sacconi, *Discussions Faraday Soc.*, **7**, 173 (1940); W. D. Tucker *et al.*, Brookhaven Natl. Lab. Report BNL-3746 (1958).