Studies of Thin-layer Chromatography of Inorganic Salts. I. The Separation of Inert Metallic Complexes by Means of Thin-layer Chromatography on Silica Gel[1]

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Two kinds of equilibrium, partition and adsorption, can be considered as the main types of retention of solutes onto adsorbing material during development. In paper chromatography, partition mechanism has been widely accepted because adsorption sites of paper are covered with water or hydrophilic solvent, so that the direct adsorption of solute molecules is considered to be negligible. However, one of the present authors[4] studied the paper chromatography of inert cobalt(III) complexes having different ionic charges using an aqueous ethylamine solution as a developer and found that the R_f values of the complexes increase with the decrease of their positive ionic charge to reach nearly unity in the case of complex anions. Thus an adsorption mechanism was established at least in the case where inorganic salts are developed with an aqueous solution.

A similar kind of adsorption mechanism is expected in thin-layer chromatography. In this case, one can select adsorbents as well as developers so that one can carry out the development under much wider range of conditions than in paper chromatography. Therefore much more informations can be expected from the study of thin-layer chromatography. The present paper will discribe the results obtained in thin-layer chromatography, in which inert metallic complexes were developed on silica gel with aqueous solutions of simple inorganic salts.

Experimental

As an adsorbent, Merck's silica gel H, prepared for thin-layer chromatography according to Stahl's method was used without further purification.

The compounds developed in this investigation were inert metallic complexes having various ionic charges: $[Co(NH_3)_6](ClO_4)_3$, $[CoCH_3CO_2(NH_3)_5](ClO_4)_2$, *cis*-$[Co(CHCO_3)_2en_2]NO_3$, α-$[Cogly_3]$, $Na[Co(S_2O_3)_2en_2]$, $Na_3[Co(NO_2)_6]$ and $K_3[Crox_3]$, where *en*, *gly* and *ox* denote ethylenediamine, glycinate anion and bivalent oxalate anion, respectively. The development was carried out at room temperatures of 22—25°C. The spots of the cobalt complexes were detected by spraying a potassium sulfide solution, while the spot of the chromium complex could be easily identified by its characteristic blue color.

Results and Discussion

Figure 1 shows the chromatogram developed with distilled water. A marked contrast can be seen between the behavior of the anionic and the neutral complexes and that of the complex cations; $[Crox_3]^{3-}$, $[Co(NO_2)_6]^{3-}$, $[Co(S_2O_3)_2en_2]^-$ and $[Co\,gly_3]^0$ show large R_f values, while $[Co(NH_3)_6]^{3+}$, $[CoCH_3CO_2(NH_3)_5]^{2+}$ and $[Co(CH_3CO_2)_2en_2]^+$ remained near the origin. This fact indicates that the adsorptive power of silica gel is acting selectively upon the complex cations but not upon the complex anions and the neutral complex.

Next, in order to palliate the strong adsorption of the complex cations and to see the effect of the different ionic charges, the

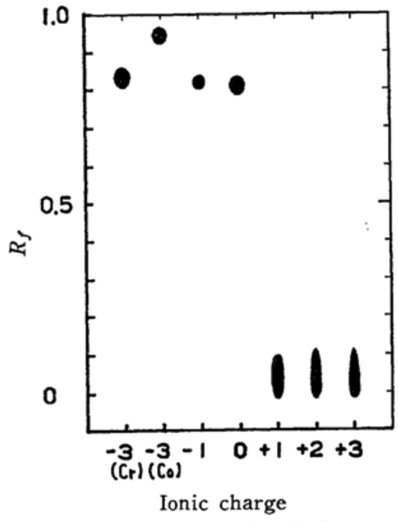

Fig. 1. Chromatogram for distilled water system.

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[4] H. Yoneda, This Bulletin, **40**, 2442 (1967).

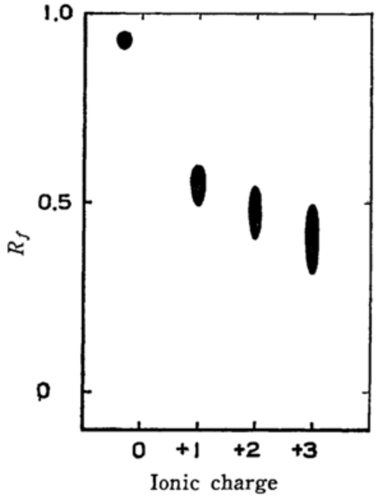

Fig. 2a Chromatogram for 0.1 M KCl system.

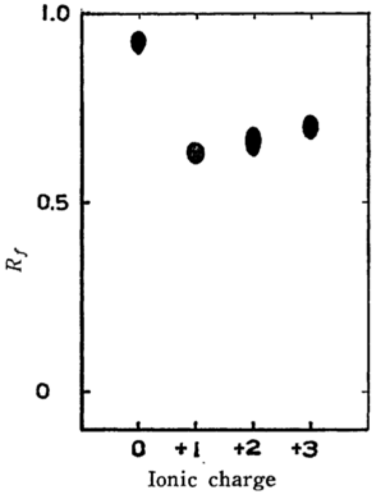

Fig. 2b Chromatogram for 0.2 M KCl system.

development was carried out with several potassium chloride solutions of stepwisely varied concentration. Thus the complex cations moved from the origin, and their R_f values increased with the increase of the salt concentration. At low concentrations up to 0.1 M, the R_f values of the complex cations showed a regular increase with the decrease of the ionic charge as can be seen in Fig. 2a (+1> +2>+3). However, this regular trend in variation of R_f values became irregular above 0.1 M, and at 0.2 M the order of the R_f values was completely reversed as is seen in Fig. 2b (+3>+2>+1). This order of the R_f values (+3>+2>+1) was maintained above 0.2 M and at 0.5 M all the R_f values became near 0.9. A similar variation of R_f value was also observed in the case of ammonium chloride solution.

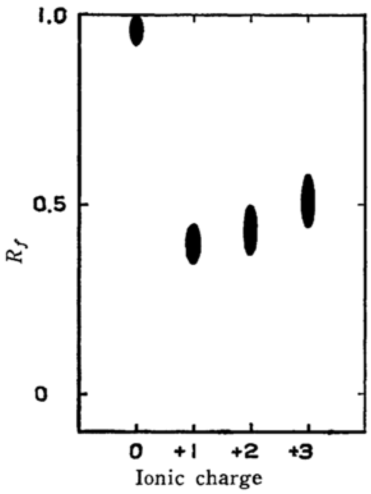

Fig. 3. Chromatogram for 0.05 M Na_2SO_4 system.

When sodium sulfate solutions were used as developer, the above-mentioned phenomena were observed at much lower concentrations; at 0.01 M the complex cations moved from the origin, and the order of the R_f values was +1>+2>+3, and at 0.05 M this order was completely reversed as is seen in Fig. 3.

The R_f value of the neutral $[Co\mathit{gly}_3]^0$ complex was always about 0.9 and did not show the salt effect.

These results can be explained as follows. Since silica gel is charged negatively in contact with water, it adsorbs strongly the complex cations. This kind of electrostatic attraction can be reduced by the addition of an electrolyte such as potassium chloride or sodium sulfate. The R_f value of the complex cation increases with the decrease of positive ionic charge, which reflects decrease of the electrostatic attraction. As the electrolyte concentration increases, association of anions around the complex cation takes place to a considerable extent to result in appreciable decrease of the apparent charge of the complex cation. Since such association proceeds to a greater extent at higher concentrations of the salt anions and for higher positive ionic charges of the complex cation, the order of the apparent charges of the complex cations $[Co(NH_3)_6]^{3+}$, $[CoCH_3CO_2(NH_3)_5]^{2+}$ and $[Co(CH_3CO_2)_2\mathit{en}_2]^+$ becomes reverse to their ionic charges. Thus the electrostatic adsorption onto silica gel is in the order of $[Co(CH_3CO_2)_2\mathit{en}_2]^+$-anions > $[CoCH_3CO_2(NH_3)_5]^{2+}$-anions > $[Co(NH_3)_6]^{3+}$-anions, and the reverse of the R_f value order can be understood.