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Studies of Thin-layer Chromatography of Inorganic Salts. II. Separation of Inert Cobalt(III) Complexes by Means of Thin-layer Chromatography on Alumina[1]

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We were interested in the chromatographic behavior of inert metallic complexes and wrote two papers concerning the mechanism of separation of complexes both in paper[4] and in silica gel thin-layer[5] chromatography. According to these reports, complex salts are developed separately as cations and anions on the negatively charged surface of an adsorbent, so that the R_f value of the complex increases with the decrease of its positive ionic charge and reaches nearly unity in the case of complex anions.

In order to see whether a similar separation mechanism holds in other adsorbents, we studied the chromatographic behavior of twenty-two kinds of inert cobalt (III) complexes on alumina and found interesting features characteristic of alumina thin-layer chromatography.

Experimental

As an adsorbent Merck's alumina H, prepared for thin-layer chromatography according to Stahl's method was used without further purification. The compounds studied are listed in Table 1. The development was carried out at room temperature of 22—23°C. Spots of cobalt(III) complexes were detected by spraying potassium sulfide solution.

Results and Discussion

The R_f values of the complexes are summarized in Table I. As is seen from these data, the chromatographic behavior of the complex cation on alumina is in general similar to that on silica gel. All complex cations show R_f values smaller than those of neutral complexes. This indicates that alumina is charged negatively in contact with water and adsorbs complex cations more strongly than neutral complexes. On silica gel, all complex cations including monovalent ions are strongly adsorbed and remained nearly at the origin when developed with distilled water. However, the present R_f values obtained with alumina layers are 0.5—0.8 for monovalent cations and 0.8—0.9

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

[5] T. Baba, H. Yoneda and M. Muto, *ibid.*, **41**, 1965 (1967).

TABLE 1. R_f VALUES OF COBALT(III) COMPLEXES DEVELOPED ON ALUMINA

(The R_f value was measured at the front of the spot.)

Sample	Developer		
	Distilled water	0.5M HCOOH aq.	0.5M $(CH_3)_2NH$ aq.
$[Co(NH_3)_6](ClO_4)_3$	0.03	0.06	0.01
$[CoH_2O(NH_3)_5]Cl_3$	0.04	0.05	0.02
$[CoCH_3CO_2(NH_3)_5]$-$(ClO_4)_2$	0.09	0.20	0.09
$[CoCHCl_2CO_2(NH_3)_5]$-$(ClO_4)_2$	0.08	0.18	0.08
$[CoCCl_3CO_2(NH_3)_5]$-$(NO_3)_2$	0.06	0.14	0.05
$[CoCF_3CO_2(NH_3)_5]$-$(NO_3)_2$	0.12	0.22	0.10
$[CoCH_3CH_2CO_2$-$(NH_3)_5](NO_3)_2$	0.12	0.21	0.11
$[CoNCS(NH_3)_5](NO_3)_2$	0.05	0.13	0.05
$[CoCN(NH_3)_5]Cl_2$	0.05	0.09	0.03
$[CoCl(NH_3)_5]Cl_2$	0.06	0.15	0.08
trans-$[Co(CH_3CO_2)_2$-$(NH_3)_4]ClO_4$	0.78	0.72	0.85
cis-$[Co(CH_3CO_2)_2$-$(NH_3)_4]NO_3$	0.52	0.53	0.68
cis-$[Co(CHCl_2CO_2)_2$-$(NH_3)_4]ClO_4$	0.53	0.54	0.61
[Co ox en_2]NO_3	0.47	0.53	0.69
trans-$[Co(NCS)_2$ en_2]Cl	0.78	0.73	0.85
trans-$[Co(NO_2)_2$ $en_2]NO_3$	0.73	0.71	0.81
cis-$[Co(NO_2)_2$ $en_2]NO_3$	0.60	0.64	0.78
[Co gly_3]	0.79	0.66	0.84
$[Co(NO_2)_3(NH_3)_3]$	0.88	0.75	0.89
$[Co(NO_2)_3$ den]	0.90	0.79	0.91
$Na[Co(SO_3)_2$ en_2]	0.64	0.37	0.90
$Na(Co(NO_2)_4$ en]	0.77	0.72	0.82

for neutral complexes. Therefore it is supposed that alumina has less negative charge than that of silica gel.

While on silica gel the R_f value shows a monotonic increase in going from cations, through neutral species, to anions, a trend in R_f value variation on alumina has a maximum in neutral species and shows a decrease in anions. This suggests that the complex anion is more strongly adsorbed than the neutral complex and can be explained by assuming positively charged sites besides the negatively charged ones. We attribute this to the amphoteric nature of alumina. This idea of the coexistence of the positive and negative sites finds support from Schwab's report.[6] He showed that alumina adsorbed both NH_3 (base) and BF_3 (acid). In order to ascertain our idea, the complexes were developed with 0.5M HCOOH and 0.5M $(CH_3)_2NH$ aqueous solutions. With an acidic developer, hydrogen ions are expected to cover the negative sites of an adsorbent, so that the adsorptive power of alumina is expected to decrease towards cations and to increase towards anions, compared to those with a neutral developer. On the other hand, with a basic developer, hydroxide ions are expected to cover the positive sites, so that the adsorptive power of alumina is expected to increase towards cations and to decrease towards anions. As is seen in Fig. 1, this expectation is almost fulfilled. The R_f value varies regularly with the pH of developers. The R_f value increases in the order basic < neutral < acidic in the cases of tri- and divalent cations, and in the order acidic < neutral < basic in the case of monovalent anions.

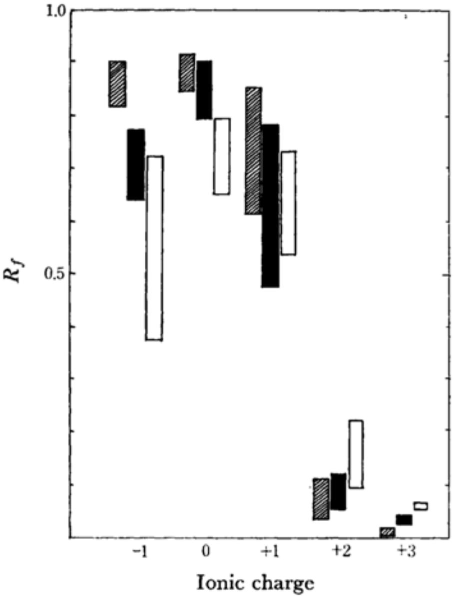

Fig. 1. pH dependency of R_f values. (Each block represents a range of R_f values.)
☐ developed with 0.5M HCOOH
▨ developed with 0.5M $(CH_3)_2NH$
■ developed with distilled water

As is seen in Table 1, the cis diacido complexes show always smaller R_f values than those of the corresponding trans complexes. The trans complex has no dipole moment, while the cis complex must have a dipole moment. Therefore, this finding is acceptable if we assume that the adsorption is caused mainly by electrostatic attraction.

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[6] G. M. Schwab and H. Kral, 3rd. Internl. Congr. Catalysis (Amsterdam), 1964.