Paper Chromatography of Inert Cobalt(III) Complexes

Hayami YONEDA

Chemistry Department, Wakayama University, Masagocho, Wakayama

(Received March 17, 1967)

The developers used in inorganic paper chromatography are, in most cases, mixtures of water and an organic solvent which is mixed freely with water. In these cases, however, it is difficult to assume the partition of samples between the developer and the paper-impregnated water. In addition, since a developer also acts as a complexing agent toward samples, the incessant formation and dissociation of complexes must take place in the process of development. Because of this complicated situation, the selection of a suitable developer is difficult; indeed, it may be said to depend only on the experience and intuition of individual researchers. Most works in this field have focussed on practical applications, that is, on empirical searches for suitable conditions for the analysis of inorganic samples. The present investigation was undertaken in order to clarify the nature of the mechanism of the separation of samples in inorganic paper chromatography.

The most rational way to clarify this complicated phenomenon is to seek the factors dominating the separation of samples under as simple conditions as possible. In the present study inert cobalt(III) complexes which are not subjected to structural change in the process of development were used as samples; aqueous solutions were used as developers in order to exclude any possibility of the partition of samples between a developer and the paper-impregnated water. As a result, only the adsorption of ions by filter paper was closed up, and the electrostatic nature of adsorption was revealed.

Experimental

The samples tested were the twenty-three kinds of cobalt(III) complexes listed in Table 1.

The aqueous solution of ethylamine as the developer[2] was prepared by heating a commercial 33% ethylamine solution and by absorbing the gas thus evolved in the distilled water. The concentration was adjusted to 1 N.

The filter paper used was Toyo Filter Paper No. 50. A strip of filter paper (2 cm×40 cm) was stained by a sample solution at a point 15 cm from the end; from there an area of about 15 cm was developed. The time required for the development was about 7 hr.

The developed spot was identified by spraying a sodium sulfide solution. In the case of hexacyanocobaltate, it was necessary to devise a special method of detection, because the spot of the sample was colorless and was not changed to dark brown by a sodium sulfide solution. In this case, a strip of filter paper was dipped into a pink solution of cobalt(II) chloride to produce the insoluble cobaltous salt of hexacyanocobaltate at the spot developed, and then dipped into 6 N hydrochloric acid to wash away the excess cobalt(II) chloride adsorbed by the filter paper.[3] Thus quite a clear spot of pink color was obtained.

---

1) Presented at the 9th Symposium of Coordination Chemistry, Kyushu University, October, 1959.

[2] Similar good results can be obtained with a methylamine solution. The use of an ethylamine solution in the present investigation had no special significance.

[3] An acid solution lowers the power of filter paper to adsorb cations.

Table 1. R_f values of cobalt(III) complexes developed with 1 N ethylamine solution

Ionic charge	Complex	R_f values
+3	$[Co(NH_3)_6]Cl_3$	0.13
	$[Co\ en_3]Cl_3$	0.15
+2	$[CoCl(NH_3)_5]Cl_2$	0.23
	$[CoOH(NH_3)_5]Cl_2$	0.25
	$[CoNO_2(NH_3)_5]Cl_2$	0.25
	$[CoNCS(NH_3)_5]Cl_2$	0.22
+1	*cis*-$[Co(NO_2)_2(NH_3)_4]Cl$	0.43
	cis-$[CoClNO_2(NH_3)_4]Cl$	0.55
	cis-$[Co(NO_2)_2en_2]NO_3$	0.50
	trans-$[Co(NO_2)_2en_2]NO_3$	0.50
	trans-$[Co(NCS)_2en_2]NO_3$	0.57
	$[CoCO_3en_2]Cl$	0.60
	$[CoC_2O_4en_2]Cl$	0.60
0	α-$[Co(NH_2CH_2CO_2)_3]$	0.84
	$[Co(NH_2CH_2CH_2O)_3]$	0.85
	$[Co(NO_2)_3(NH_3)_3]$	0.72
−1	$NH_4[Co(NO_2)_4(NH_3)_2]$	0.89
	$K[Co(NO_2)_4]$	0.90
	$K[Co(NO_2)_2CO_3(NH_3)_2]$	0.90
	$K[Co(NO_2)_2C_2O_4(NH_3)_2]$	0.90
	$K[Co(NO_2)_2dgH_2]$	0.83
−3	$Na_3[Co(NO_2)_6]$	0.96
	$K_3[Co(CN)_6]$	1.00

Results and Discussion

The chloride, bromide, nitrate, perchlorate, acetate, and sulfate of the $[Co(NH_3)_6]^{3+}$ complex were developed using distilled water as a developer. All the salts gave quite similar patterns, diffused from the point of origin to a point corresponding to R_f=*ca.* 0.9. A similar diffuse pattern was obtained in the case of the $[CoCl(NH_3)_5]^{2+}$ complex also. With a 1 N solution of such electrolytes as HCl, NaCl, KBr, $NaNO_3$, $NaClO_4$ and Na_2SO_4 as developers, no such diffuse pattern appeared, and in every case quite a clear spot was obtained at R_f=*ca.* 0.9. Here the kind of electrolyte did not affect the R_f value.

Next, the $[Co(NH_3)_6]^{3+}$ complex was developed with 1 N pyridine and ethylamine. In both cases, though the tailing of a spot did not completely disappear, a marked decrease in the R_f value was observed. This decrease was especially marked in the case of an ethylamine solution (a stronger base than pyridine), and the R_f value was 0.13.

When $[Co(NH_2CH_2CO_2)_3]^0$ and $[Co(NO_2)_4(NH_3)_2]^-$ complexes were developed with distilled water, and 1 N solutions of electrolytes and amines, quite a distinct spot was obtained at R_f=0.8—0.9 in every case. In these cases no change in the R_f value with the variation in developers was observed.

All these results suggest the existence of an electrostatic force acting between the complex and filter paper. As the complex cation reacts more sensitively to any variation in the kind of developer than do the neutral and anionic complexes, it may be presumed that filter paper is charged negatively when in contact with an aqueous solution. This presumption is very reasonable, considering that cellulose is built up by the condensation of glucose molecules, which contain many hydrogen atoms exchangeable with deuterium. Thus, when filter paper comes in contact with water, some protons are dissociated from hydroxyl groups with an increase in the pH of a developer; consequently, the paper should be charged more negatively. Such negatively-charged filter paper will attract cations and repel anions.

The small R_f values of $[Co(NH_3)_6]^{3+}$ and $[CoCl(NH_3)_5]^{2+}$ complexes can thus be understood. If this interpretation is correct, it is possible to determine the ionic charge of a complex by developing it with a 1 N ethylamine aqueous solution. To test this possibility, twenty-three kinds of cobalt(III) complexes were developed. The results are listed in Table 1. These results completely fulfilled expectations.

Previously Yamamoto, Nakahara, and Tsuchida[4] studied the paper chromatography of a series of nitroammine cobalt(III) complexes, $[Co(NH_3)_6]^{3+}$, $[CoNO_2(NH_3)_5]^{2+}$, *cis*- and *trans*-$[Co(NO_2)_2(NH_3)_4]^+$, $[Co(NO_2)_3(NH_3)_3]^0$, $[Co(NO_2)_4(NH_3)_2]^-$ and $[Co(NO_2)_6]^{3-}$. They found that the best separation of these complexes was obtained with a developer containing methanol : acetone : 33% ammonia in a 7 : 2.5 : 1 volume ratio. With this developer, the R_f value was found to increase regularly with an increase in the number of nitro groups within the complex. This finding is in good agreement with the results of the present study.

---

[4] Y. Yamamoto, A. Nakahara and R. Tsuchida, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 114 (1954).