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Study of Hydration and Association of Ions in Solution. I. Chromatographic and Electrophoretic Behaviors of Hexamminetype Cobalt(III) Complexes in Aqueous Solutions of Various Electrolytes

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The dissolved state of ions in solution was investigated through the study of separation mechanism of a series of tervalent hexammine-type cobalt(III) complexes in thin-layer chromatography and in electrophoresis. The results obtained are summarized as follows. In the case of strongly hydrated complexes, a strongly hydrated anion has a greater tendency towards association than a weakly hydrated anion. On the contrary, in the weakly hydrated complexes, a weakly hydrated anion is associated more easily than a strongly hydrated anion. From these findings, ionic association was presumed to occur through direct contact of a complex cation and an anion.

We have been studying the dissolved state of ions by use of inert metal complexes. The reasons for our using inert metal complexes instead of simple salts are as follows: 1) In the case of simple cations, *i. e.*, Mg^{2+}, Fe^{2+}, Ni^{2+}, *etc.*, both direct and solvent-separated associations of anions take place simultaneously around a cation, so that a migrating cationic species changes its structure even at the first coordination sphere. In contrast to this, when inert complex salts are used, only the outer sphere association of anions around a complex cation has to be considered, because the first coordination sphere remains unchanged. Thus, the analysis of the phenomenon is expected to be much simpler. 2) In the case of complex salts, there are a series of related compounds which differ from each other in certain properties, *i. e.*, ionic charge, ionic size, number of N–H bonds, *etc.*, so that the use of such related compounds enables us to find out the effect of the property upon the phenomenon concerned.

In this paper we would like to report the results of experiments with thin-layer chromatography and paper electrophoresis in which a series of tervalent hexammine-type cobalt(III) complexes were used as samples and to discuss the relation between hydration and association of ions in solution.

Results and Discussion

Thin-layer Chromatography on Alumina. The hexammine-type cobalt(III) complexes used in chromatography are $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4en]Cl_3$, $[Co(NH_3)_4pn]Cl_3$, $[Co(NH_3)_2en_2]Cl_3$, $[Co\ en_3]Cl_3$, $[Co\ tn_3]Cl_3$, $[Co\ pn_3]Cl_3$, $[Co\ dip_3]Cl_3$, and $[Co\ phen_3]Cl_3$. When these complexes were developed with distilled water, they all remained at the starting point. This is not surprising when we remember that alumina has negatively charged sites on its surface and adsorbs complex cations. However, when aqueous soultions of 0.2M NaCl and $NaClO_4$ were used as a developer, these complexes began to move and showed a regular increase of R_f values in the decreasing order of the number of N-H bonds within the complex. Further, the results from chromatograms developed in 0.2M Na_2SO_4 aqueous solution are worthy of note.

While the spots of the complexes having many N–H bonds show nearly the same R_f values both in NaCl and in Na_2SO_4 developers, the R_f values of $[Co\ dip_3]^{3+}$ and $[Co\ phen_3]^{3+}$ developed with Na_2SO_4 solution are definitely smaller than those developed with the NaCl solution (See Fig. 1).

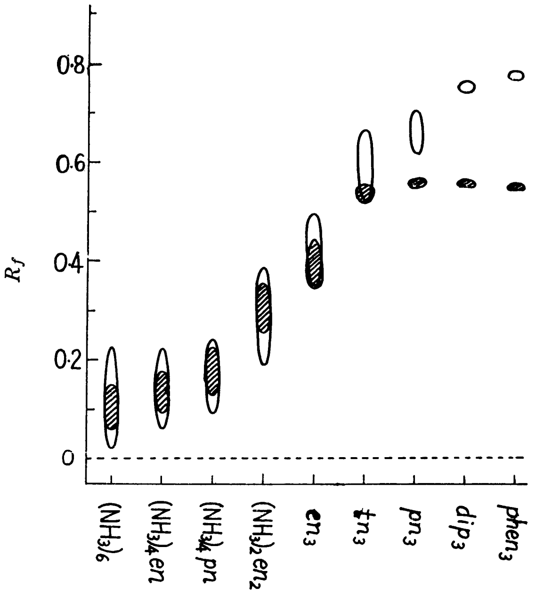

Fig. 1. Chromatogram of hexammine-type cobalt(III) complexes.
○: developed with 2M NaCl
▨: developed with 2M Na_2SO_4
adsorbent: alumina

This can be interpreted in terms of ionic association. Through such ionic association, the complex cation reduces its apparent positive charge, which results in the decreased adsorption on alumina and in the increased R_f value. Since hydration of the complex cation is presumed to take place not only by ion-dipole attraction but also through hydrogen bonds between the N–H bonds and solvent water molecules, the degree of hydration is expected to decrease with the decreasing number of N–H bonds within the complex. Thus, the present results are summarized as follows. 1) Ionic association proceeds more easily when the complex has a lower

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[2] T. Baba, M. Muto, and H. Yoneda, This Bulletin, **42**, 2697 (1969).

number of N–H bonds within itself, that is, when the complex is less hydrated.

2) As far as weakly hydrated complexes such as [Co dip$_3$]$^{3+}$ or [Co phen$_3$]$^{3+}$ are concerned, a univalent anion like Cl$^-$ or ClO$_4^-$ forms an ion-pair more easily than bivalent anion like SO$_4^{2-}$ does.[3] In other words, the more weakly an anion is hydrated, the more easily it forms an ion-pair with a weakly hydrated complex.

Electrophoresis. Although information concerning hydration and association of ions in solution can be obtained through chromatography by use of a simple device, the analysis of the result is not always simple, because adsorption plays an essential role in the process of development. In fact, the above mentioned chromatographic behavior of the complexes can be explained in terms of adsorption also. If we assume that adsorption on alumina is caused not only by the mere electrostatic attraction but also through the Al–O···H–N–Co type hydrogen bonds to a large extent, it is easily understood that the complex having more N–H bonds is adsorbed more firmly and shows a smaller R_f value than the complex having less N–H bonds. Thus, it may be reasonable to assume that both mechanisms, association and adsorption, work together in the actual development process. In this respect, electrophoresis has an advantage of facilitating the analysis of the result, because adsorption can be eliminated by selecting suitable conditions.

The electrophoresis of tervalent hexammine-type cobalt(III) complexes were studied by Mazzei and Lederer.[4] They measured the mobilities of [Co(NH$_3$)$_6$]$^{3+}$, [Co en$_3$]$^{3+}$, [Co dip$_3$]$^{3+}$ and [Co phen$_3$]$^{3+}$ in several kinds of salt solutions and showed a marked effect of ionic association upon the mobility of the complex. However, they did not give a detailed discussion of the mechanism of association. We have carried out a similar measurement using a wide variety of background electrolytes in order to find the mechanism of association.

Figure 2 shows a part of the results. Hexammine-type cobalt(III) complexes are represented with their ligands NH$_3$, en, tn, dip, and phen and arranged in the decreasing order of hydration from left to right. Anions shown at the sides of the curves represent the background electrolytes which were used in electrophoresis. Sodium salts were used in all cases. The ordinate corresponds to the mobility of the complex. (Here the mobility is defined as the relative migrating distance of a complex, when the migrating distance of [Co en$_3$]$^{3+}$ in 0.1M NaCl is taken to unity.)

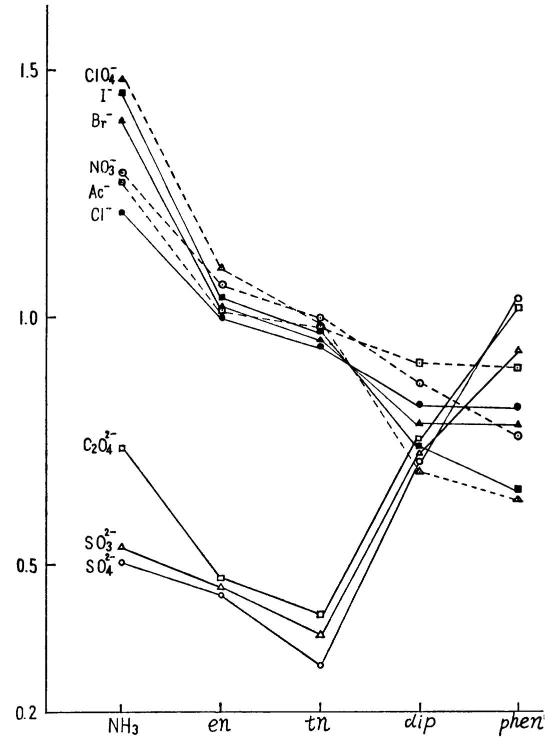

Fig. 2. Electrophoretic migration of hexammine-type cobalt (III) complexes in various background solutions.

potential gradient	500 V/34 cm
time	about 1 hour
temperature	25°C
concentration of a background electrolyte	0.1M

Let us consider the behavior of the [Co(NH$_3$)$_6$]$^{3+}$ complex. This complex is presumed to be most highly hydrated through many hydrogen bonds between the coordinating NH$_3$ and solvent water. In this case, it should be noted that the mobility of the complex is definitely larger in solutions containing univalent anions than in solutions containing bivalent anions. In other words, migration of the complex cation is retarded to a greater extent by bivalent anions than by univalent ones. Such difference in mobility is observed also in the cases of [Co en$_3$]$^{3+}$ and [Co tn$_3$]$^{3+}$, though less markedly. However, in the case of [Co dip$_3$]$^{3+}$ and particularly of [Co phen$_3$]$^{3+}$, the situation is the reverse. The complex cation migrates more easily in a solution containing bivalent anions than in a solution containing univalent ones.

Let us next consider the trend of mobilities of the complexes in a certain salt solution from the highly hydrated [Co(NH$_3$)$_6$]$^{3+}$ complex to the poorly hydrated [Co phen$_3$]$^{3+}$ complex. In the case of a salt solution containing univalent anions, the mobility of the complex decreases in the decreasing order of hydration of the complex. On the other hand, a reversed trend is observed in the case of a solution containing bivalent anions, the mobility increasing with the decrease of hydration.

Such a variation of mobility can be attributed to various degrees of the electrostatic withdrawing effect of anions. However, it is more effective to consider the phenomenon in terms of ionic association

$$\text{Complex cation} + \text{anion} \rightleftarrows \text{ion-pair}$$

Through such association, the complex cation reduces its apparent positive charge. This results in the decrease of mobility. Thus, it can be concluded that the more the mobility is decreased, the more the equilibrium can be considered to be shifted towards ion-pair forma-

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[3] The hydration number of ions can be estimated by various methods. As an example, Padova estimated the hydration number of Cl$^-$, ClO$_4^-$ and SO$_4^{2-}$ to be 1.1 and 4, respectively, from the amount of Volume decrease of an ionic solution due to hydration (J. Padova, *J. Chem. Phys.*, **39**, 1552 (1963)).

[4] M. Mazzei and M. Lederer, *J. Chromatog.*, **31**, 1965 (1967).

tion. The present results can be summarized as follows. In the highly hydrated complex such as $[Co(NH_3)_6]^{3+}$, the bivalent anion is associated with it more easily than the univalent anion is. However, in the weakly hydrated complex such as $[Co\ phen_3]^{3+}$, the situation is reverse. The univalent anion can form an ion-pair more easily than the bivalent anion. In certain salt solution containing univalent anions, the association takes place more easily in a less hydrated complex, and in a certain salt solution containing bivalent anions, association takes place more easily in the more hydrated complex.

The results are in good agreement with the interpretation of the chromatographic behavior of the complexes. As to the hydration of anions, it is reasonably assumed that the bivalent anion is more strongly hydrated than the univalent anion. Thus, we can state as follows. In a strongly hydrated complex, association with a strongly hydrated anion takes place more easily than that with a weakly hydrated anion, and in a weakly hydrated complex, association occurs with a weakly hydrated anion more easily than with a strongly hydrated anion. In either case, ionic association is presumed to take place not in a solvent-separated state but rather by the direct contact of an anion and a complex cation. The strength of hydration is considered to correspond to the tendency towards hydrogen bonding. Thus, a strongly hydrated anion is expected also to form a strong hydrogen bond with the N–H bond of a strongly hydrated complex. This is regarded as the main cause of ionic association in a strongly hydrated complex. In fact, the strength of the hydrogen bonds between the N–H bonds and the outer-sphere anions is estimated from the shift of the N–H stretching frequency of the $[Co(NH_3)_6]^{3+}$ and $[Co\ en_3]^{3+}$ complexes (hydrogen bonding is expected to weaken N–H bond and shift the N–H stretching band to a lower frequency). The infrared data[5] indicate that the strength of the hydrogen bonds is in the order $Cl^- > Br^- > I^-$. This is in good agreement with the present results.

A weakly hydrated complex has no tendency towards hydrogen bonding. Thus, a strongly hydrated anion has little tendency towards association, because the removal of the solvating water molecules from the anion is not compensated for by the hydrogen bonding with the complex. Thus, a weakly hydrated univalent anion has an advantage for association because the energy required for the removal of the solvating water molecules in less as compared with the case of the more strongly hydrated bivalent anion.[6] This trend is observed not only between the uni- and bivalent anions, but also among univalent anions. Thus, the mobility data indicate that ionic association takes place in the order $I^- > Br^- > Cl^-$ in the case of a weakly hydrated complex such as $[Co\ dip_3]^{3+}$ and $[Co\ phen_3]^{2+}$. This is just the reverse order of the hydration energies of these halide ions.

TABLE 1. MOBILITIES OF COMPLEX CATIONS IN A SERIES OF ELECTROLYTE SOLUTIONS

The mobility of the $[Co\ en_3]^{3+}$ complex in 0.1M NaCl solution is taken as standard.

Anion	[Co-$(NH_3)_6]^{3+}$	[Co-$en_3]^{3+}$	[Co-$tn_3]^{3+}$	[Co-$dip]^{3+}$	[Co-$phen_3]^{3+}$
1) In 0.1M electrolyte solutions					
Cl^-	1.21	1.00	0.94	0.82	0.84
Br^-	1.40	1.02	0.95	0.78	0.80
I^-	1.46	1.03	0.96	0.73	0.64
Ac^-	1.29	1.01	0.96	0.90	0.90
ClO_4^-	1.49	1.10	0.98	0.68	0.63
NO_3^-	1.29	1.04	0.99	0.86	0.76
$C_2O_4^{3-}$	0.73	0.45	0.39	0.78	1.03
SO_3^{2-}	0.53	0.43	0.35	0.76	0.93
SO_4^{2-}	0.50	0.43	0.29	0.74	1.03
2) In 0.5M electrolyte solutions					
Cl^-	1.00	0.65	0.64	0.61	0.60
Br^-	1.03	0.72	0.65	0.53	0.52
I^-	1.16	0.75	0.67	0.40	0.34
Ac^-	0.98	0.68	0.67	0.66	0.57
ClO_4^-	1.05	0.73	0.72	0.30	0.27
NO_3^-	0.97	0.77	0.75	0.50	0.48
$C_2O_4^{2-}$	0.55	0.53	0.36	0.62	0.69
SO_3^{2-}	0.35	0.26	0.25	0.55	0.58
SO_4^{2-}	0.33	0.24	0.23	0.61	0.64

The above discussion is based on the mobility data of the complexes in 0.1M electrolyte solutions. The same conclusion can be drawn when 0.5M electrolyte solutions are used as a background, as can be seen in Table 1. However, comparison of the two sets of data obtained in 0.1M and 0.5M solutions revealed that the mobility order of a complex in a series of background solutions in the both cases showed a slight difference from each other. Thus, the mobility of the $[Co(NH_3)_6]^{3+}$ complex in 0.5M solutions decreases in the order

$$I^- > ClO_4^- > Br^- > Cl^- > Ac^- > NO_3^-$$

while the mobility of the same complex in 0.1M solutions decreases in the order

$$ClO_4^- > I^- > Br^- > NO_3^- > Ac^- > Cl^-$$

Therefore, the association tendency in 0.5M solutions is presumed to increase in the order

$$I^- < ClO_4^- < Br^- < Cl^- < Ac^- < NO_3^-$$

while the association tendency in 0.1M solutions is presumed to increase in order

$$ClO_4^- < I^- < Br^- < NO_3^- < Ac^- < Cl^-$$

Thus, the order of association tendency concerning the $[Co(NH_3)_6]^{3+}$ complex in a certain series of electrolyte solutions various with the concentration of an electrolyte solution. This can be explained in the following way. With the increases of the concentration of a solution, the number of the solvating water molecules per one complex cation is presumed to decrease, and the complex is presumed to become poorly hydrated. Owing to such sort of dehydration, the highly hydrated $[Co(NH_3)_6]^{3+}$ in 0.1M background electrolyte solution be-

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[5] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, **78**, 3295 (1956).

[6] Among univalent anions, the acetate ion is considered to be strongly hydrated. Thus, the mobility of the $[Co\ dip_3]^{3+}$ and $[Co\ phen_3]^{3+}$ in the acetate solution is fairly large, compared with that in the halide solution.

comes poorly hydrated in the more concentrated background solution, and the hydrated state of the $[Co(NH_3)_6]^{3+}$ becomes similar to that of the less hydrated species like $[Co\ en_3]^{3+}$ and $[Co\ tn_3]^{3+}$ or even to that of the least hydrated $[Co\ dip_3]^{3+}$ and $[Co\ phen_3]^{3+}$ in 0.1M solution. The change in the order of the association tendency with variation of the background electrolyte concentration can thus be understood.

The association constants of the $[Co(NH_3)_6]^{3+}$ and $[Co\ en_3]^{3+}$ with the halide ions are in the order $I^- < Br^- < Cl^-$.[7-9] On the other hand, the solubility of $[Co(NH_3)_6]X_3$ and of $[Co\ en_3]X_3$ (X=Cl, Br, and I) is in the order $I^- < Br^- < Cl^-$. These two trends contradict each other. If we regard the undissolved complex salt which is in equilibrium with the saturated solution, as the final product of ionic association, it is expected from the data of the association constant that the solubility should increase in the order $Cl^- < Br^- < I^-$. However, this is not the case. This apparent discrepancy can be understood by the above consideration. In other words, the hydrated state of $[Co(NH_3)_6]^{3+}$ and $[Co\ en_3]^{3+}$ in the saturated solution is presumed to be similar to that of $[Co\ dip_3]^{3+}$ and $[Co\ phen_3]^{3+}$ in solution, for example in a 0.1M background electrolyte solution. In the latter case, the association constant is presumed to increase in the order $Cl^- < Br^- < I^-$, which is just the same order of decreasing solubility of $[Co(NH_3)_6]X_3$ and $[Co\ en_3]X_3$ (X=Cl, Br, and I).

Concerning the behavior of the perchlorate ion, it is believed that the perchlorate ion has little tendency toward complex formation with a metal ion and also has little associating ability with a complex cation. Consequently, sodium perchlorate is often used to keep the ionic strength of a series of solutions constant in the determination of the formation constant and of the association constant. However, although the tendency of the perchlorate ion toward association with $[Co(NH_3)_6]^{3+}$ and $[Co\ en_3]^{3+}$ is least among univalent anions, it is almost the same as that of the iodide ion as can be seen in Fig. 2. Furthermore, the order of the associating ability of the perchlorate and iodide is reversed in the case of 0.5M background solution. In addition, the association tendency of the perchlorate ion with the hydrophobic complex cations like $[Co\ dip_3]^{3+}$ and $[Co\ phen_3]^{3+}$, is the largest among univalent anions studied. Thus, we must re-examine the validity of the use of the perchlorate for adjustment of ionic strength in the study of an association equilibrium.

Addition of the perchlorate ion to the equilibrium system, *i. e.*,

$$[Co(NH_3)_6]^{3+} + \text{anion } X^- \rightleftarrows \text{ion-pair}$$

gives vise to a new equilibrium

$$[Co(NH_3)_6]^{3+} + ClO_4 \rightleftarrows \text{ion-pair}$$

which causes a big change in the first equilibrium, if the associating ability of the perchlorate ion is comparable to or larger than that of the anion X^-.

The association constants of the $[Co(NH_3)_6]^{3+}$ and $[Co\ en_3]^{3+}$ complexes with the halide and sulfate ions were determined by various methods. For instance Evans and Nancollas[7] determined spectrophotometrically the association constants of the $[Co(NH_3)_6]^{3+}$ with the halide ions, whereas King *et al.*[8] obtained the different values of the association constants of the same ion-pair. Tanaka *et al.*[9] redetermined the association constants of these two complexes with the halide and sulfate ions by the spectrophotometric method under the same ionic strength as by Evans and Nancollas. However, they got quite different values. They attributed this to the inaccurate measurement of optical density by Evans and Nancollas. However, this does not seem to give an explanation. If we assume the big influence of the perchlorate ion upon the equilibrium, the difference can be explained. Although both groups of workers used the same ionic strength, the conditions under which they worked were quite different. Evans and Nancollas worked with very low concentrations and Tanaka *et al.* much higher concentrations of the halide ions as compared with the complex ion. This makes the equilibrium quite different. Thus, it becomes clear that the association constant is of little value unless the disturbing effect of the perclorate ion is taken into consideration.

Experimental

Thin-layer Chromatography on Alumina. As an adsorbent, Merck's aluminum oxide H prepared for thin-layer chromatography was used without further purification. This was spread in 250 μ thickness over a glass plate of 20 cm length. Solutions were applied at a starting point 5 cm above the lower edge of the plate and development was carried out to a distance of 14 cm above the starting point. A sodium sulfate solution was sprayed for visualization of the spot.

Paper Electrophoresis. A migration apparatus with multicompartment cells was used, so that ten samples could be run at the same time. A paper strip was dipped uniformly in the background electrolyte solution and then the excess of the solution was removed by hanging the strip. After that, about 5 μl of a sample solution was placed on the paper strip (Toyoroshi No. 51 A, 2×40 cm). Samples were run for about one hour under a potential gradient 500 V/34 cm, keeping the temperature of the migrating box at 25°C. The spot of the sample was detected in the same way as in thin-layer chromatography.

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[7] M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

[8] E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

[9] N. Tanaka, Y. Kobayashi, and M. Komoda, This Bulletin, **40**, 2839 (1967).