*Nitrogen Isotopic Equilibria between Ammonia and Metal-ammine Complex Ions in Aqueous Solution**

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The isotopic exchange of ions or molecules dissolved in solution with those coordinated in complex ions have been studied on the carbon isotopes between carbonate or bicarbonate ion and the carbonate coordinated in the cobalt complex ions[1,2], the oxygen isotopes between water as solvent and that in cobalt complex ion[3], and the nitrogen isotopes between ammonia as solvent and metal-ammine complex ions in liquid ammonia[4]. These studies have given data on the nature of the bond in complex ions. This paper reports on the nitrogen isotope effect in the formation of a series of metal-ammine complex ions with ammonia in aqueous solution. Copper-, zinc-, cadmium-, silver- and nickel-ammine complex ions were studied. The experimental method using ion exchangers[5] has been employed. A theoretical relation has been derived between the isotopic equilibrium constant and the first dissociation constant of the complex ion of the stable form.

Experimental

Using the nitrogen compound with natural isotopic abundance, the equilibrium to be measured is written as

$$\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH_3})^{+p}+{}^{15}\mathrm{NH_{3(aq)}}$$
$$=\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})^{+p}+{}^{14}\mathrm{NH_{3(aq)}} \qquad K_1 \quad (1)$$

where $\mathrm{M(NH_3)}_n{}^{+p}$ represents a metal-ammine complex ion, K_1 the equilibrium constant. The cation exchanger of the metal-ammine complex ion form can be brought to isotope equilibrium with the metal-ammine complex ion or ammonia in solution The equilibria are written by the equations:

$$\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})^{+p}$$
$$+\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH_3})\mathrm{R}$$
$$=\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH_3})^{+p}$$
$$+\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})\mathrm{R}, \qquad K_2 \quad (2)$$

$$\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH})\mathrm{R}+{}^{15}\mathrm{NH_{3(aq)}}$$
$$=\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})\mathrm{R}+{}^{14}\mathrm{NH_{3(aq)}} \qquad K_3 \quad (3)$$

where $\mathrm{M(NH_3)}_n\mathrm{R}$'s represent the metal-ammine complex ions adsorbed on the cation exchanger, K_2 and K_3 the equilibrium constant for Eqs. 2 and 3, respectively.

The following quantity can be measured conveniently:

$$\delta=\frac{(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{solution}}-(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{resin}}}{(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{resin}}} \qquad (4)$$

where $(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{resin}}$ and $(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{solution}}$ are the ratio of the nitrogen isotopes in resin and solution, respectively. The value of δ for Eq. 2 can be measured directly for the system of the complex ion adsorbed on the resin and the solution of the complex ion, if the complex ion is stable without free ammonia or with a negligible amount of the excess ammonia. The equilibrium constant for Eq. 2 can be written

$$K_2=\frac{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})\mathrm{R}}{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH_3})\mathrm{R}}\Big/\frac{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})^{+p}}{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH_3})^{+p}}$$
$$\simeq(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{resin}}/(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{solution}}$$
$$=1/(1+\delta_2) \qquad (5)$$

Eq. 3 describes the equilibrium of the complex ion adsorbed on the resin with excess ammonia in aqueous solution. Using the symbols δ_3 for this case, the equilibrium constant of Eq. 3, K_3, is given by the following equation:

$$K_3=\frac{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})\mathrm{R}}{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH_3})\mathrm{R}}\Big/\frac{^{15}\mathrm{NH_{3(aq)}}}{^{14}\mathrm{NH_{3(aq)}}}$$
$$\simeq n(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{resin}}/(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{solution}}$$
$$=n/(1+\delta_3) \qquad (6)$$

In this equation, $(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{resin}}$ is assumed to represent the isotope ratio in only the exchanged complex ions, since the amount of the free ammonia in the resin is negligibly small compared with that of ammonia coordinated in the exchanged compelx ions. It is not necessary to consider ammonium ion in this equilibrium if the pH of the aqueous solution is high.

Now, K_1 is given with δ_2 and δ_3;

$$K_1=\frac{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{15}\mathrm{NH_3})^{+p}}{\mathrm{M}(^{14}\mathrm{NH_3})_{n-1}(^{14}\mathrm{NH_3})^{+p}}\Big/\frac{^{15}\mathrm{NH_{3(aq)}}}{^{14}\mathrm{NH_{3(aq)}}}$$
$$=K_3/K_2=n(1+\delta_2)/(1+\delta_3)$$

The value of the fractionation factor, $(1+\delta_2)/(1+\delta_3)$, can be experimentally obtained.

The metal-ammine complex ion may undergo successive dissociations. However, many of the complex ions, in general, have one stable form

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[1] D. R. Stranks and G. W. Harris, *J. Chem. Phys.*, **19**, 257 (1951); *J. Phys. Chem.*, **56**, 906 (1952).

[2] P. E. Yankwich and J. E. McNamara, *J. Chem. Phys.*, **20**, 1325 (1952).

[3] A. Rutenberg and H. Taube, ibid., **20**, 825 (1952).

[4] H. U. D. Wiesendanger, W. H. Jones and C. S. Garner, ibid., **27**, 668 (1957).

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TABLE I. FRACTIONATION FACTORS OF NITROGEN ISOTOPES BETWEEN METAL-AMMINE COMPLEX IONS AND AMMONIA IN AQUEOUS SOLUTION AT 30°C

Complex ion	Composition of solution, M		$\delta\times10^3$	$\frac{K_1}{n}$
	Complex ion	Ammonia		
(I) Experiments using cation exchanger				
$Cu(NH_3)_4{}^{2+}$	0.259	0.00024	$\delta_2=-\ 0.4\pm0.1$	
	0	0.236	$\delta_3=-11.9\pm0.4$	1.0117
$Zn(NH_3)_4{}^{2+}$	—	—	$\delta_2\equiv0$	
	0	0.270	$\delta_3=-11.5\pm0.4$	1.0116
$Cd(NH_3)_4{}^{2+}$	—	—	$\delta_2\equiv0$	
	0	0.270	$\delta_3=-10.2\pm0.9$	1.0103
$Ag(NH_3)_2{}^{2+}$	0.250	0	$\delta_2=-\ 0.1\pm0.3$	
	0	0.237	$\delta_3=-\ 9.3\pm0.6$	1.0093
(II) Experiments by salting out complex ions				
$Cu(NH_3)_4{}^{2+}$	0.0455	0.276	$\delta=-11.9\pm0.4$	1.0120
$Ni(NH_3)_n{}^{2+}$	0.250	0.540	$\delta=-\ 7.4\pm0.3$	1.0076

which exists predominantly in aqueous solution. In such a case, the isotopic equilibrium constant measured will present the equilibrium constant of the stable form of the complex ion.

Copper quadrammine sulfate was prepared[6] and its solution was made by dissolving the prepared crystal in a very dilute ammonia solution. The other complex solutions: zinc, cadmium and silver complex solution were made by dissolving the slight excess of metal sulfate in an ammonia solution and filtering the insoluble residue out. The cation exchanger used was Dowex 50, X-8. The exchanger of a complex ion form was made by passing the metal-ammine complex- ammonia solution through the exchanger column. The exchangers were washed with ammonia solution on the glass filter with a suction of water jet pump.

The general procedures were the same as described in the previous report[5]. The exchanger of the complex ion form was added to the solution of the complex ion or ammonia and allowed to stand in the constant temperature bath at 30°C over one or two nights. The periods may be long enough for the attainment of the equilibria of the exchange reactions in this experiment, which are supposed to be rapid by the rapid exchanges of ammonia between solvent liquid ammonia and copper-, silver- or nickel-ammine complex ion[4]. After the attainment of the equilibria, the exchangers were separated from the solution with suction filtration, and washed with a limited amount of water to avoid the hydrolysis of the exchanged complex ions. The washed exchanger was put into the sulfuric acid solution to convert to the metal ion and ammonium ion. Then, the exchanger and the solution were poured on the exchanger column in the hydrogen form. The ammonium ion was recovered by eluting with 0.5 N potassium sulfate-0.5 M sulfuric acid solution. Through this process, the greater part of the metal ion was removed. The ammonia solution separated from the exchanger at equilibrium was acidified with sulfuric acid solution and used for the isotopic analysis. The complex ion solution was acidified with sulfuric acid solution and treated by the same procedure as described for the complex ion exchanged.

For copper and nickel complex ions, the complex ions were separated from the complex-ammonia mixed solutions by salting out the complex salts with the addition of the large amount of alcohol and centrifuging the complex salts. The isotopic measurements were carried out for the supernatant solution and complex salts centrifuged.

The isotope ratio measurements were made in the same way as described in the previous report[5].

Results

The experimental results are shown in Table I with the experimental conditions. In the experiments of cadmium and zinc complex ion, the value of δ_2 could not be measured since these complex ions were not stable in aqueous solution without a large excess of ammonia. Their equilibrium constants were calculated by assuming the value of δ_2 to be zero. This assumption seems to be reasonable since the equilibrium constant of isotopic ions between the exchanger and solution phase is nearly unity.

The experiments were carried out by the technique of salting out the complex ion from the complex ion-ammonia mixture solution with the addition of alcohol for copper and nickel complex ions. In this technique, the equilibrium constant can be readily obtained from the measured value of δ:

$$\delta=[({}^{15}N/{}^{14}N)_{\mathrm{solution}}-({}^{15}N/{}^{14}N)_{\mathrm{salt}}]/({}^{15}N/{}^{14}N)_{\mathrm{salt}}$$

The results are also shown in Table I. Both the techniques of using cation exchanger and

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[6] G. Brauer, "Handbuch der Praeparativen Anorganischen Chemie", Ferdinand Bnke Verlag, Stuttgart (1954), p. 757.

salting out the complex ion gave a good agreement on the value of K_1. The agreement shows that the technique with cation exchanger can be efficiently used in measurements of this kind.

Theoretical and Discussion

A theoretical relationship can be derived between the isotopic equilibrium constant of Eq. 1, K_1, and the first dissociation constants of the stable ammine complex ions, k and k' for the dissociations:

$$\mathrm{M}({}^{14}\mathrm{NH}_3)_{n-1}({}^{15}\mathrm{NH}_3)^{+p} = \mathrm{M}({}^{14}\mathrm{NH}_3)_{n-1}{}^{+p} + {}^{15}\mathrm{NH}_{3(\mathrm{aq})} \qquad k \quad (8)$$

$$\mathrm{M}({}^{14}\mathrm{NH}_3)_{n-1}({}^{14}\mathrm{NH}_3)^{+p} = \mathrm{M}({}^{14}\mathrm{NH}_3)_{n-1}{}^{+p} + {}^{14}\mathrm{NH}_{3(\mathrm{aq})} \qquad k' \quad (9)$$

The value which is defined as a ratio of the partition functions of isotopic molecules by Biegeleisen and Mayer⁷⁾, is written as,

$$\frac{s}{s'} f = 1 + \Sigma_i G_i \Delta u_i \qquad (10)$$

where s and s' are the symmetry number of isotopic molecules. The primed notation refers to the light molecule. The G function relates to the difference in free energy of the formation of isotopic molecules from the isolated gaseous atoms⁷⁾:

$$\frac{\Delta F^0 - \Delta F^{0\prime}}{\boldsymbol{RT}} = -\Sigma_i G_i \Delta u_i + \ln \frac{s}{s'} \qquad (11)$$

The following equation can be obtained from Eqs. 10 and 11:

$$f = \frac{s'}{s}\left(1 - \frac{\Delta F^0 - \Delta F^{0\prime}}{\boldsymbol{RT}} + \ln \frac{s}{s'}\right) \qquad (12)$$

Then Eq. 12 is applied to the isotopic complex ions in aqueous solution, the ratio of their symmetry numbers, s'/s, can be replaced by the number of the ammonia molecules coordinated in the stable complex ions. Further, if Eqs. 8 and 9 are compared the difference of the free energies of formation of the complex ions becomes

$$\Delta F^0{}_c - \Delta F^{0\prime}{}_c = \Delta F^0{}_a - \Delta F^{0\prime}{}_a - \boldsymbol{RT} \ln(k'/k) \quad (13)$$

where the subscripts c and a refer to the complex ion and ammonia, respectively. The f function of the complex ion is written as

$$f_c = n\left(1 + \ln k'/k - \frac{\Delta F^0{}_a - \Delta F^{0\prime}{}_a}{\boldsymbol{RT}} - \ln n\right) \quad (14)$$

For the isotopic ammonia molecules, the ratio of the symmetry numbers is one and its f function is given by

$$f_a = 1 - \frac{\Delta F^0{}_a - \Delta F^{0\prime}{}_a}{\boldsymbol{RT}} \qquad (15)$$

With Eq. 15, the f function of the complex ion is rewritten as

$$f_c = n(\ln k'/k + f_a - \ln n) \qquad (16)$$

Now the equilibrium constant, K_1, which is the ratio of the f function of the complex ion to that of ammonia, can be expressed with the dissociation constants of the stable complex ions, k and k':

$$K_1 = n\left[1 + \ln\left(\frac{k'}{n} \Big/ k\right) \Big/ f_a\right] \qquad (17)$$

The quantity of k'/n in this equation is equivalent to k if the probabilities of the dissociations of the isotopic complex ions are taken into account. Both k'/n and k are a measure of the strength of the bond between metal and nitrogen in the complex ions which appeared at the first dissociation.

The measured fractionation factors can be compared with the relationship of Eq. 17, provided a form of the complex ion among the successively dissociated ions is predominantly stable. The successive dissociation constants have been measured⁸⁾. The values of the dissociation constants are listed with the measured fractionation factors in Table II. Copper, zinc, cadmium and silver complex ions have one stable form. However, in the case of nickel complex ion, the successively dissociated ion may exist with comparable concentrations and they effect the value of the measured fractionation factor as an average.

TABLE II. FRACTIONATION FACTORS AND THE FIRST DISSOCIATION CONSTANTS OF COMPLEX IONS

Complex ion	$\frac{K_1}{n}$	$\log k'$	$\log \frac{k'}{n}$
$\mathrm{Cu(NH_3)_4{}^{2+}}$	1.0117	−2.13	−2.73
$\mathrm{Zn(NH_3)_4{}^{2+}}$	1.0116	−2.15	−2.75
$\mathrm{Cd(NH_3)_4{}^{2+}}$	1.0103	−0.93	−1.53
$\mathrm{Ag(NH_3)_2{}^{2+}}$	1.0093	−3.83	−4.13
$\mathrm{Ni(NH_3)_{\mathit{n}}{}^{2+}}$	1.0076	−0.03 for $n=6$	−0.81
		−0.75 for $n=5$	−1.45
		−1.19 for $n=4$	−1.79

In Table II, the tendency is noted that the smaller value of k' causes the greater fractionation factor or the greater value of the ratio of k'/n to k. An exception is in the case of the silver complex ion although the reason is not clear. The greater isotope effect is found in the more tightly bound complex ion which agrees with the general rule of the isotope effects.

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7) J. Biegeleisen and M. C. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

8) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

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