Studies on Silver Cyanide Complexes in Aqueous Solution

Akio SAITO*, Yasuharu MIGITA**,
Akihiro YAMAGUCHI*** and Toshiaki TSURU***

水溶液中における銀—シアン錯体の研究

斉藤明夫*, 右田泰治**, 山口昭浩***, 津留壽昭***

Key Words : Infrared Absorption, Silver Cyanide Complexes, Aqueous solution, Free CN^-

Introduction

Although cyanide is poisonous, silver cyanide complex bath has been used in silver electroplating for a long time because of its excellent properties. However, the composition of the main silver cyanide complexes in the bath is not well known. L. H. Jones and R. A. Penneman investigated the infrared absorption of silver cyanide complex ions in aqueous solutions. They suggested that the dissociation constant for the tetra-cyanide complex into the tri-cyanide one becomes smaller rapidly with increasing the concentration of free CN^- above about $1.5\text{M}^{1)}$.

In the present work, the effects of the concentrations of Ag(I) and free CN^- on the formation of the silver cyanide complex from the next lower complex ion have been investigated by measuring the infrared absorption spectra of aqueous silver cyanide solutions.

Experimental

Analytical grade AgCN , KCN and KAg(CN)_2 were used. KAg(CN)_2 was used only in preparing aqueous solution with the CN/Ag ratio of 2.

FTIR spectra were obtained by use of a Nihon Bunko FT/IR-5300 FTIR spectrometer with the single-beam. Window materials of cell was CaF_2 with the thickness of 3 mm. The thickness of Lead spacers used was $25\mu\text{m}$.

Results and discussion

Fig. 1 shows the infrared absorption spectra of aqueous silver cyanide solutions at 0.1M Ag(I)

Fig. 1 Infrared absorption spectra of aqueous silver cyanide complexes at 0.1M Ag(I) , and of aqueous KCN .

with various ratios of CN/Ag , and of aqueous KCN . According to L. H. Jones and R. A. Penneman, Ag(CN)_2^- , Ag(CN)_3^{2-} , Ag(CN)_4^{3-} and CN^- have infrared absorption peaks at 2135 ± 1 , 2105 ± 1 , 2092 ± 1 and $2081 \pm 1\text{ cm}^{-1}$, and the extinction coefficients of 264 ± 12 , 397 ± 23 , 556 ± 83 and $29 \pm 1\text{ mole}^{-1}\text{ liter cm}^{-1}$ respectively²⁾. As shown in Fig. 1, the absorption peak due to Ag(CN)_4^{3-} at 2091 cm^{-1} was not observed at any CN/Ag ratios. The intensity of the peaks due to Ag(CN)_3^{2-} at 2105 cm^{-1} increased with an increase of the CN/Ag ratios, but decreased with increasing the CN/Ag ratios above 13. The intensity of the peaks due to Ag(CN)_2^- at 2135 cm^{-1} decreased with an increase of the CN/Ag ratios, and the peak was not observed in the range over the CN/Ag ratio of 13. Very small absorption peak due to CN^- appeared at 2081 cm^{-1} in the CN/Ag ratio of 6, and its intensity increased with an increase of the CN/Ag ratios. Therefore Ag(CN)_4^{3-} was thought to be formed in the range over the CN/Ag ratio of 13 though

* Kyushu National Industrial Res. Inst. (807-1, Shukumachi, Tosu-shi, Saga, 841 Japan)
九州工業技術研究所

** Migita Engineer's Office (188-36, Noma, Okagaki-machi, Onga-gun, Fukuoka, 811-42 Japan)
右田技術士事務所

*** Kyushu Sangyo Univ. (Matsukadai, Higashi-ku, Fukuoka-shi, Fukuoka, 813 Japan)
九州産業大学

Table 1 The concentration equilibrium constants of silver cyanide complexes in the solutions with various concentrations of Ag(I) and free CN⁻.

CN/Ag ratios	[Ag(I)]*	[CN] ⁻ *	[Ag(CN) ₂] ⁻ *	[Ag(CN) ₃] ²⁻ *	[Ag(CN) ₄] ³⁻ *	K _{2,3} **	K _{3,4} ***
3	0.1	0.076	0.076	0.024	—	4.15	—
	0.5	0.187	0.187	0.313	—	8.95	—
	1	0.295	0.295	0.705	—	8.1	—
4	0.5	0.565	0.093	0.379	0.028	7.21	0.131
	1	1.005	0.11	0.785	0.105	7.1	0.133
7	0.5	1.762	0.017	0.228	0.255	7.61	0.634
	1	3.214	0.01	0.194	0.796	6.03	1.276

*, Concentration=M, **, K_{2,3} = [Ag(CN)₃]²⁻/[Ag(CN)₂]⁻[CN]⁻, ***, K_{3,4} = [Ag(CN)₄]³⁻/[Ag(CN)₃]²⁻[CN]⁻

Fig. 2 Infrared absorption spectra of aqueous silver cyanide complexes at 1M Ag(I).

its absorption peak was not observed because it overlapped with the absorption band due to CN⁻.

Fig. 2 shows the infrared absorption spectra of 1 molar Ag(I) solutions. The absorption peak due to Ag(CN)₄³⁻ at 2092 cm⁻¹ was observed in the CN/Ag ratio of 4, and its intensity increased rapidly with an increase of the CN/Ag ratios.

At first the calibration curve for the concentrations of Ag(CN)₂⁻ was determined on the basis of the infrared absorption data in the case of CN/Ag ratio of 2. Then by using this curve together with the stoichiometry and the infrared absorption data in the CN/Ag ratio of 3, the calibration curve for the concentrations of Ag(CN)₃²⁻ was determined. The concentrations of CN⁻, Ag(CN)₂⁻, Ag(CN)₃²⁻ and Ag(CN)₄³⁻ in the solutions were calculated from the infrared absorption data, the calibration curves and the stoichiometry. The errors of the calculated concentrations were within 5% in the CN/Ag ratio of 3, and within 10% in the CN/Ag ratios of 4 and 7. The results are shown in **Table 1**. The concentration formation constants (K_{2,3} and K_{3,4}) of the reactions below were calculated from these concentrations, and are also shown in **Table 1**.

The values of K_{2,3} agreed approximately with each other except the condition of the low concentrations of both Ag(I) and free CN⁻, under which its value was lower than those under the other conditions. The constant value of K_{3,4} was obtained in the case of the CN/Ag ratio of 4. However, its values increased as the CN/Ag ratio increased to 7, and were different from each other. For these reasons, it was thought that the activity coefficient of each ion in reactions of (1) and (2) above changed remarkably with changes of the ionic strengths under the condition of the low concentrations of both Ag(I) and free CN⁻, or of the high concentrations of both Ag(I) and free CN⁻.

Conclusion

The effects of the concentrations of Ag(I) and free CN⁻ on the formation of silver cyanide complexes in aqueous solution were investigated. It was found that K_{2,3} decreased under the condition of the low concentrations of both Ag(I) and free CN⁻, and that K_{3,4} increased under the condition of the high concentrations of both Ag(I) and free CN⁻. Consequently the concentrations of Ag(CN)₄³⁻ were high under the condition of the high concentrations of both Ag(I) and free CN⁻.

We are grateful to Dr. S. SUKIMOTO for his suggestions in measuring the infrared absorption of silver cyanide complexes in aqueous solution.

(Received August 8, 1996; Accepted November 20, 1996)

References

- 1) Llewellyn H. Jones and Robert A. Penneman; *J. Chemical Physic*, **22**, 965 (1954)
- 2) Llewellyn H. Jones and Robert A. Penneman; *J. Chemical Physic*, **22**, 965 (1954)