Articles

Spectrophotometric Investigation of Silver Complex Solution with Thiomicher's Ketone

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The reaction between silver (I) and thiomicher's ketone (TMK) was sensitive at pH 5 and 8 in the presence of non-ionic or anion surfactant. We studied the complex solution and determined the properties by beta-correction spectrophotometry, which included the complex ratio and the stability constant of the complex. The results showed that complex Ag(TMK) was formed in the presence of alkylphend ethoxylates (emulsifier OP) and Ag(TMK)$_2$ was formed in the presence of sodium dodecyl benzene sulfonate (SDBS). Their real absorptivities are as follows: $\varepsilon_{Ag(TMK)}{}^{540}=5.23 \times 10^4$, $\varepsilon_{Ag(TMK)2}{}^{555}=1.05 \times 10^5$ Lmol^{-1}cm^{-1} both at pH 5 and $\varepsilon_{Ag(TMK)2}{}^{555}$ $=7.52 \times 10^4$ lmol^{-1}cm^{-1} at pH 8. The stability constant of complex Ag(TMK) was equal to 1.23×10^5 at pH 5, and that of Ag(TMK)$_2$ 8.29×10^9 at pH 5 and 1.15×10^{11} at pH 8.

Introduction

Silver is one of the precious metal elements. It can react with many chromogenic agents or ligands such as azo compounds,[1,2] acidic and basic dyes,[3,4] porphyrin compounds,[5] etc. Some of them are used to determine[6-8] trace amounts of silver in geological, wastewater and metal materials. The ligand, thiomichers ketone (TMK) is one of the sulfodyes, and it is sensitive to complex silver (I). It has been used to determine trace silver in mining.[9] This report describes the updated determination of the properties of Ag-TMK complex solution, which include the complex ratio, the real (not apparent) absorptivity and the stability constant of the complex by beta-correction spectrophotometric method[10,11] instead of common spectrophotometry. The beta-correction spectrophotometric method gives the respective absorption of the excess TMK and Ag-TMK complex product. This allows the simpler operation, which gives a more acceptable result for the determination of the properties of the Ag-TMK complex compared with the conventional method such as molar ratio[12] and Yatzimirsky.[13]

Principle

From the following expression,[11] the real absorbance (A_c) of the complex (ML_γ) formed in the reaction between metal (M) ion and ligand (L) is calculated.

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta}$$

where ΔA and $\Delta A'$ are the absorbances of the mixed solution of ML_γ and L measured at wavelengths λ_2 and λ_1 against the reagent blank (only L solution), respectively. Both α and β are named correction factors and they are calculated with the following expressions.

$$\alpha = \frac{\varepsilon_{ML_\gamma}{}^{\lambda 1}}{\varepsilon_{ML_\gamma}{}^{\lambda 2}}$$

and

$$\beta = \frac{\varepsilon_L{}^{\lambda 2}}{\varepsilon_L{}^{\lambda 1}}$$

where $\varepsilon_{ML_\gamma}{}^{\lambda 1}$, $\varepsilon_{ML_\gamma}{}^{\lambda 2}$, $\varepsilon_L{}^{\lambda 1}$ and $\varepsilon_L{}^{\lambda 2}$ are the molar absorptivities of ML_γ and L at wavelengths λ_1 and λ_2, respectively.

It is well known that the apparent absorptivity ($\varepsilon_{a-ML_\gamma}{}^{\lambda 2}$) of ML_γ at wavelengths λ_2 can be obtained from the measured absorbance (ΔA). Therefore, its real absorptivity ($\varepsilon_{r-ML_\gamma}{}^{\lambda 2}$) should be calculated from the real absorbance (A_c).

$$\varepsilon_{r-ML_\gamma}{}^{\lambda_2} = \frac{A_c}{\delta C_M} \quad \text{and} \quad \varepsilon_{a-ML_\gamma}{}^{\lambda_2} = \frac{\Delta A}{\delta C_M}$$

The ratio (γ') of L to complex M in reaction may be expressed as follows.

$$\gamma' = \eta \times \frac{C_L}{C_M}$$

where

$$\eta = \frac{\alpha \Delta A - \Delta A'}{(1 - \alpha \beta) A_o'}$$

where η indicates the reacted percentage of ligand, and C_M, C_L indicate the molar concentration of M and L at the beginning of the reaction, respectively. The term δ indicates the thickness of the used cell and A_o is the measured absorbance of the reagent blank at wavelength λ_2. If γ' reaches maximum and remains constant, it is thought that $\gamma = \gamma'$. The symbol γ is a natural number taken as the stoichiometric ratio of the complex produced. In addition, the following expression was established for the stability constant (K) of

Table 1. The operation condition of the method and the calculation result of the correction factors for the reaction between Ag(I) and TMK

M-L reaction	λ_1 nm	λ_2 nm	α	β	Ac=
Ag-TMK-OP at pH 5	440	540	0.350	0.082	$1.03(\Delta A-0.082\Delta A')$
Ag-TMK-SDBS at pH 5	420	555	0.388	0.479	$1.23(\Delta A-0.479\Delta A')$
Ag-TMK-SDBS at pH 8	420	555	0.446	0.291	$1.15(\Delta A-0.291\Delta A')$

complex ML_γ from the reaction: $M + \gamma L = ML_\gamma$.

$$K = \frac{\gamma'}{(\gamma - \gamma')[C_L(1 - \eta)]^\gamma}$$

Experimental Section

Apparatus. Absorption spectra were measured on a Model UV-265 spectrophotometer (Shimadzu, Japan) with 1.0 cm cells.

Reagents. TMK solution (0.500 mmol/L) was prepared by dissolving 0.142 g TMK (Shanghai Third Reagents) in 1000 mL of acetone (Shanghai Reagents). It was stored in a dark bottle at less than 5 °C. Silver (I) standard, 100.0 mg/L, was prepared with silver nitrate (A. R., Shanghai Reagents) and 10.0 mg/L Ag (I) solution was obtained by diluting the above standard. A pH 5 buffer solution was prepared using acetic acid (A. R., Beijing Chemicals) and sodium acetate (A. R., Shanghai Chemicals). Two buffer solutions, pH 8 and pH 10, were prepared using ammonia water and ammonium chloride (A. R., Beijing Chemicals). The following surfactant solutions were prepared to increase reaction sensitivity: alkylphend ethoxylates (emulsifier OP, Shanghai Reagents) solution, SDBS (Shanghai Reagents) solution and cetyltrimethyl-ammonium bromide (CTMAB) solution. All were 5%.

Recommended procedure. 20.0 μg silver was transferred to a 25-mL calibrated flask, and 2 mL of buffer solution and 1 ml of surfactant solution were added. Also added was a known volume of TMK solution. The contents of the flask were diluted to the mark with distilled water and mixed well. The absorbances were measured between 10 and 20 min at two wavelengths (shown in Table 1), respectively. Finally, A_c, α and β were calculated.

Results and Discussion

Absorption spectra. The absorption spectra of TMK and the Ag-TMK reaction solution are shown in Figure 1 at pH 5 or 8 and in OP presence or SDBS presence. The measured wavelengths were selected at the peak absorption and the valley absorption because this gave the maximal sensitivity. From *x-c* curves, the measured wavelengths of the three reactions and the results are listed in Table 1. From curves *x-a* and *x-b*, β and α of each solution were calculated, respectively (Table 1). The Ac expression of each reaction was obtained, as also shown in Table 1.

Effect of TMK concentration. Figure 2 shows the measurement absorbances of Ag (0.80 mg/L)-TMK reaction solution obtained by varying the addition of TMK solution.
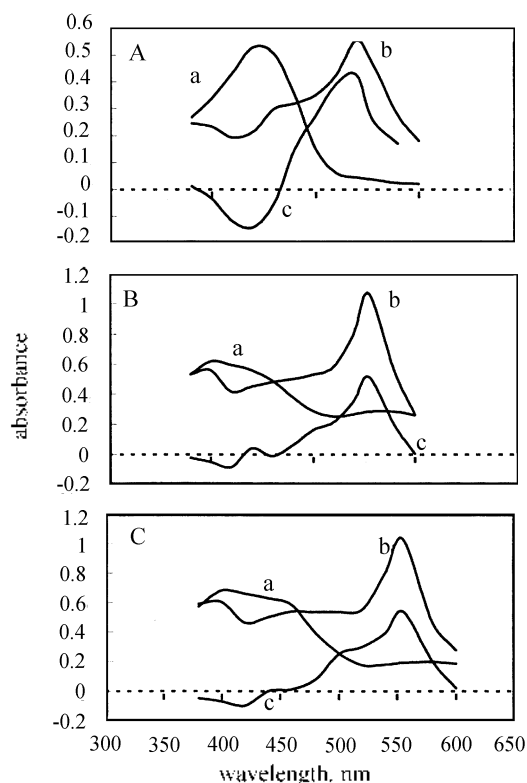
Figure 1. Absorption spectra of TMK and Ag-TMK solution : A-, in the presence of OP at pH 5; B-, the presence of SDBS at pH 5; C-, same as B- but at pH 8; curve a: TMK solution. b: Ag-TMK complex (no free TMK) solution. c: Ag-TMK reaction (containing excess TMK) solution.
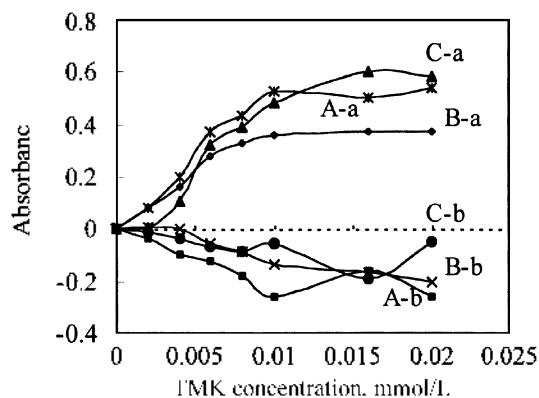
Figure 2. Effect of TMK concentration on the Ag (0.80 mg/L)-TMK solution: A-a, in the presence of OP at pH 5 at 540 nm; A-b, same as A-a but at 440 nm; B-a, in the presence of SDBS at pH 5 at 555 nm; B-b, same as A-a but at 420 nm; C-a and C-b, same as B-a and B-b but at pH 8, all against reagent blank
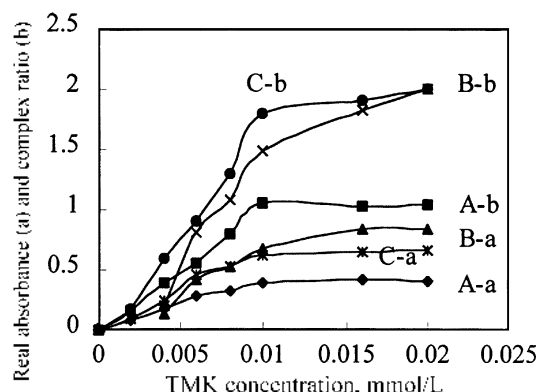
Figure 3. The real absorbance (a) and the complex ratio γ (b) curves: A-. in the presence of OP at pH 5: B- in the presence of SDBS at pH 5: C-. same as B- but at pH 8.

From curves x-a, the positive absorption approaches to maximum when the concentration of TMK is more then 0.010 mmol/L. From curves x-a, the complex ratio of TMK to Ag(I) was difficult to calculate by the molar ratio method[12] because the inflection points are not clear. From the curves above, the real absorbance (Ac) and the complex ratio (γ') of each solution were obtained and the results are shown in Figure 3. From curves x-b, the real molar absorptivity ($\varepsilon^{\lambda 2}$) of Ag-TMK complex was computed as follows: $\varepsilon_{Ag(TMK)}^{540}$ = 5.23 × 10^1 L · mol^{-1} · cm^{-1} at pH 5, $\varepsilon_{Ag(TMK)2}^{555}$ = 1.05 × 10^5 L · mol^{-1} · cm^{-1} at pH 5 and $\varepsilon_{Ag(TMK)2}^{555}$ = 7.52 × 10^4 L · mol^{-1} · cm^{-1} at pH 8. The reaction between Ag(I) and TMK had a higher sensitivity in the presence of SDBS than in the presence of OP. The Ag-TMK-SDBS ternary complex had a higher absorption at pH 5 than at pH 8. From curves x-a in Figure 2, we obtained their respective apparent absorp-
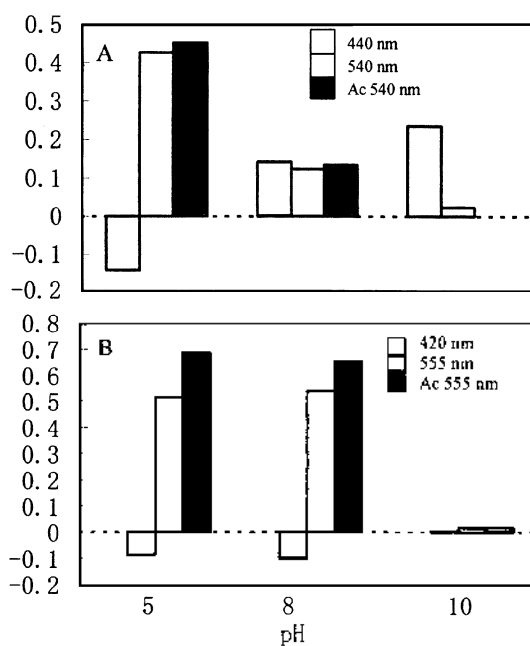
tivities as follows: 4.90 × 10^4, 7.56 × 10^4 and 6.19 × 10^4 L · mol^{-1} · cm^{-1}. The differences between the apparent and real values ranged from 0.33 × 10^4 to 2.94 × 10^4 L · mol^{-1} · cm^{-1}. The ratio γ' approached 1 from curve A-b in Figure 3 and 2 from curves B-b and C-b when the TMK concentration was more than 0.01 mmol/L. The following complexes were formed: Ag(TMK) in the presence of OP at pH 5, Ag(TMK)$_2$ in the presence of SDBS at pH 5 and 8.

Effect of pH. The results or varying the pH or the reaction solution are shown in Figure 4. The reaction hardly proceeded at pH 10 because the real absorbance of the complex approached zero. From Figure 4(A), the real absorption of the Ag-TMK solution in the presence of OP at pH 8 is only one-fourth that of the solution at pH 5. It was found that pH 5 in the presence of OP or SDBS and pH 8 in the presence of SDBS gave the highest sensitivity. In this work, pH 5 and pH 8 buffer solutions were used.

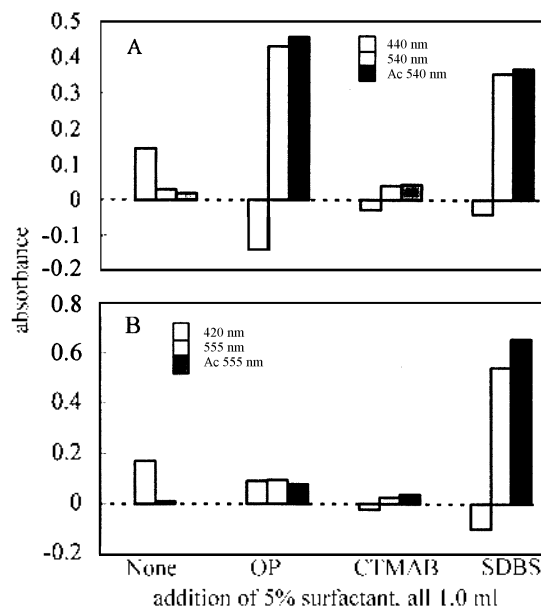**Effect of surfactant.** The ternary complex reaction

Figure 5. Effect of surfactants on absorption of the Ag (0.80 mg/L)-TMK solution: A-. pH 5: B-. pH 8.

Figure 4. Effect of pH on absorption of the Ag(0.80 mg/L)-TMK solution: A-. in the presence of OP: B-. in the presence of SDBS.
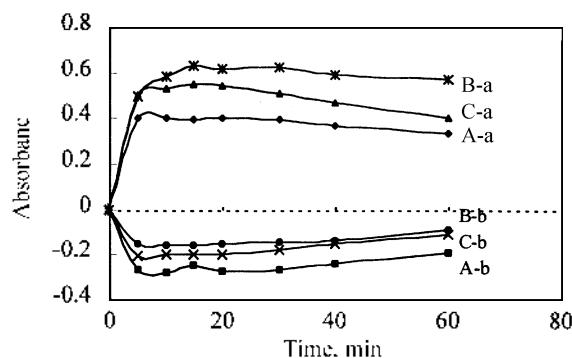

Figure 6. Effect of time on absorption of the Ag (0.80 mg/L)-TMK solution: A-. in the presence of OP at pH 5: B-. in the presence of SDBS at pH 5: C-. same as B- but at pH 8. a- peak absorption and b- valley absorption.

Table 2. The stability constant of Ag-TMK complex in ion strength 0.001 and at temperature 25 °C

Reaction	Absorbance at λ_1	Absorbance at λ_2	η, %	γ'	K
Ag-TMK-OP at pH 5	0.339	-0.185	71.8	0.712	1.07×10^6
	0.336	-0.193	74.1	0.741	1.38×10^6
	0.347	-0.182	72.8	0.728	1.23×10^6
					mean: 1.23×10^6
Ag-TMK-SDBS at pH 5	0.248	-0.028	34.9	0.349	7.79×10^9
	0.237	-0.035	35.8	0.358	8.27×10^9
	0.263	-0.026	36.8	0.368	8.82×10^9
					mean: 8.29×10^9
Ag-TMK-SDBS at pH 8	0.318	-0.061	69.1	0.691	7.86×10^{10}
	0.319	-0.072	74.4	0.744	1.41×10^{11}
	0.331	-0.071	72.6	0.726	1.19×10^{11}
					mean: 1.15×10^{11}

between a metal-ligand binary complex and a surfactant usually happens and it was applied to improve the analytical sensitivity. In this study, the effect of OP, CTMAB and SDBS on Ag-TMK reaction are shown in Figure 5. From the column height shown in Figure 5, the real absorption of the Ag(0.80 mg/L)-TMK complex was less than 0.05 in the presence of CTMAB or in the absence of surfactant, which was only one-tenth the absorption in the presence of SDBS and OP. The Ag-TMK reaction at pH 5 gave higher sensitivity in the presence of OP and SDBS than the reaction without the surfactant and in the presence of CTMAB. The same result was obtained from the Ag-TMK reaction at pH 8 in the presence of SDBS. Therefore, the surfactants OP and SDBS were used in this study to give sensitivity about 10 times as high as what would be observed in the absence of surfactant.

Effect of time. The absorption of Ag (0.80 mg/L)-TMK solution was measured at different time intervals. The effect curve of the reaction time on absorbance is shown in Figure 6. All reactions were complete in 15 min. However, slow fading of solution color was found when reaction time exceeded 30 min. This was possibly due to the oxidation or decomposition of the Ag-TMK complex. Hence, the measurement of absorbance should be made between 10 and 30 min for the best result.

Determination of stability constant, K. The following solution was prepared and measured for the determination of the stability constant of the Ag-TMK complex: 0.200 μmol Ag (I) with 0.200 μmol TMK. The stability constants, K's, were calculated and the results are listed in Table 2. The complex Ag(TMK)$_2$ formed at pH 8 in SDBS presence was most stable because its stability constant (K) was about 12 times that of Ag(TMK)$_2$ formed at pH 5 and about 10^5 times that of Ag(TMK) at pH 5 in the presence of OP.

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