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A NOVEL METHOD OF PHOTOMETRIC DETERMINATION OF SILVER (I) BY ADSORPTION OF ITS 1-ALLYL-3-(5-CHLORO-2-PYRIDYL) THIOUREA COMPLEX ON MICROCRYSTALLINE NAPHTHALENE

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ABSTRACT

An accurate and simple method for the photometric determination of silver (I) by using 1-allyl-3-(5-chloro-2-pyridyl) thiourea as organic reagent has been described. Silver (I) formed a stable, water insoluble complex with 1-allyl-3-(5-chloro-2-pyridyl) thiourea. This complex was adsorbed on microcrystalline naphthalene. The adsorbed complex was dissolved in dimethylformamide. The absorbance of the solution was measured at 430 nm against the reagent blank. Beer's law was obeyed in the concentration range 7-120 µg of silver (I) in 10 ml of dimethylformamide. The molar absorptivity was found to be 3.18 x 10^4 1 mol^{-1} cm^{-1} and sensitivity being 1.591 x 10^{-2}µg cm^{-2} of silver for the absorbance of 0.001. The effect of various parameters such as pH, reagent and naphthalene concentration and volume of buffer solution have been investigated.

KEYWORDS: Pyridylthiourea, Microcrystalline Naphthalene, Absorbance

First synthesized by Neucki, (Hawa *et al.* 1986) thiourea and its derivatives hold wide range of applications in the field of agriculture, medicine and analytical chemistry thioureas show hypoglycemic hyperlipemic (Mocanu and Axenia ;1972), anticancer (Mrinal and Majumdar; 1970) antiulcer (Mathur and Bhandan; 1970) antitubercular (Mealor and Townshend; 1968), antimicrobial (Searle; 1986) antifungal (Sukhveer Singh; 1986) antipesticidal (Sataka and Singh; 1982) analgesic (Vasilev *et al.* 1978), anticonvulsant (Jain *et al.* 1988) and hypnotic activities (Weiping *et al*. 1989). In the field of analytical chemisty thiourea derivatives are used for extraction of many metals owing to their capability of forming complex with many metals.

Thiourea derivatives are used as analytical reagents for calorimetric determination of various metals (Philip *et al.* 1987). Looking to the versatility of pyridyl substituted thiourea (Rao and Shrinivasan 1970; Young and Eyre, 1901). 1-allyl-3(5-chloro-2-pyridyl) thiourea has been prepared and its analytical application as photometric reagent for the determination of silver (I) has been studied.

Using an effective method called "Analysis of metals by 'Solid-Liquid' separation after 'Liquid-Liquid' extraction" has been used for the determination of trace amount of silver.

EXPERIMENTAL

Standard Silver (I) Solution

A stock standard solution (1000 ppm) of silver (I) was prepared by dissolving requisite amount of silver nitrate in distilled water. A 10 ppm solution of silver (I)was prepared by diluting10ml of stock solution of silver nitrate to 1000 ml with distilled water. Amount of silver (µg) present in sample solution was determined gravimetrically.

1-allyl-3-(5-chloro-2-pyridyl) thiourea Solution

A 0.2% solution of 1-allyl-3-(5-chloro-2-pyridyl) thiourea was prepared by dissolving 0.2g of this reagent in 100 ml of ethanol.

Naphthalene-Acetone Solution

A 20% naphthalene solution was prepared by dissolving 20g of naphthalene in 100 ml of acetone.

Buffer Solution

Buffer solutions of different pH values were prepared by mixing 1M acetic acid and 1 M ammonium acetate solution for pH range 3-6 and 1M aqueous ammonia and 1M ammonium acetate solution for pH range 8-11. All the reagent used were of analytical reagent grade.

APPARATUS

A Toshniwal spectrophotometer (Model Cl-10) was used for all absorbance measurements.

All pH measurements were taken with Toshniwal pH meter model (CL-43) equipped with glass and calomel electrodes.

PROCEDURE

An aliquot of standard sample solutions of silver (I) containing 10-120 µg of silver, was taken in a dry, clean, tightly stoppered Erlenmeyer flask. To it ,3ml of acetate buffer solution was added to adjust the pH of the solution to 6.0 and then 3.0 ml of 0.2% 1-ally1-3-(5-chloro-2-pyridyl) thiourea solution was mixed. The contents of the flask were kept standing in hot water bath (50^0-60^0C) for 25 minutes. Then, 3 ml of 20% naphthalene solution were added to the solution of silver (I) complex and shaken vigorously for four minutes. The silver (I) complex of 1-allyl1-3-(5-chloro-2-pyridy1) thiourea was adsorbed on microcrystalline naphthalene. It

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was filtered off, washed with water and dried in an oven at 50^0-60^0C. This dried solid was dissolved in dimethylformamide and diluted to 10 ml. The absorbance measurements of silver (I) complex were taken at 430 nm wavelength against the reagent blank which was prepared similarly.

RESULTS AND DISCUSSION

Absorption Spectra

A sample solution containing 90 µg of silver (I), 3.0 ml of 0.2% 1-allyl-3-(5-chloro-2-pyridyl) thiourea solution, and 3.0 ml of acetate buffer solution, pH 6.0, was treated according to the recommended procedure. The silver (I) complex, so formed was adsorbed on microcrystalline naphthalene on vigorous shaking for 4 minutes. The solid mixture of naphthalene and silver (I) complex was dissolved in dimethylformamide and the absorbance of the solution was measured at wavelength between 380-600nm. The data of absorbance was plotted against the wavelengths and absorption spectra of silver (I) complex solution was obtained against the reagent blank . The silver (I) complex had the maximum absorption at 430 nm wavelength whereas the reagent blank had negligible absorption at this wavelength. Therefore, all absorbance measurements were carried out at 430 nm wavelength (γ max).

Effect of pH

The effect of pH on the absorbance of the silver (I) complex containing 90 µg of silver was investigated at different pH ranging between 2-10 at 430 nm wavelength. The results are shown in Table. It was found that the absorbance of the silver (I) complex in dimethylformamide solution was dependent on pH. The maximum absorbance was obtained in the pH range 4.5-10.0 and decreased rapidly beyond pH 10.0. Therefore, the pH of the sample solution of silver (I) was adjusted to 6.0 for all absorbance measurements.

Effect of Buffer Solution

The effect of addition of varying amounts of the buffer solution on absorbance of silver (I) complex was studied. The results are given in Table 2. The addition of 1.0 to 5.5 ml of the buffer solution brought out the same absorbance and therefore, 3.0 ml of the buffer solution was chosen as the most suitable amount for out investigations.

Effect of Concentration of 1-ally1-3-(5-chloro-2-pyridyl) thiourea

In order to investigate the effect of the reagent concentration on the absorbance of silver (I) complex solution, different amounts of the reagent solutions were added to the sample solution containing 90 µg of silver (I) at pH 6.0. The results are shown in Table 3. The addition of 0.5 to 7.0 ml of the reagent solution gave the maxima and almost the same absorbance. Hence 3.0 ml of the reagent solution was considered the appropriate quantity to be used for all absorbance measurements.

Effect of Naphthalene Concentrations

The effect of naphthalene concentration on the absorbance measurements was determined by adding different amounts of naphthalene solution to the solution containing silver (I) complex of 1-ally-3-(5-chloro-2-pyridyl) thiourea. The results are given in table 4. The absorbance increased with the addition of naphthalene solution upto 1.5 ml and achieved is maximum value in the range 1.5-6.0 ml. Hence 3.0 ml of 20% naphthalene solution was taken for all absorbance measurements.

Calibration Curve for Silver (I)

Under the optimum conditions as specified in the recommended procedure, the calibration curve was obtained. The results are shown in table 5. Beer's law was obeyed in the range 7-120 µg per 10 ml of dimethylformamide. The molar absorptivity was found to be 3.185×10^41 mol^{-1} cm^{-1} at 430 nm and sensitivity being 1.595×10^{-2}µg cm^{-2} of silver for the absorbance of 0.001.

Precision

The precision of the proposed method was estimated with ten samples of silver (I) complex solution containing 90 µg of silver, which gave a mean absorbance of 0.566 with a standard deviation of 0.27%.

Table 1: Effect of pH on Absorbance

pH	Absorbance 430 nm
2.0	0.375
2.5	0.385
3.0	0.425
3.5	0.435
4.0	0.480
4.5	0.510
5.0	0.545
5.5	0.562
6.0	0.560
6.5	0.561
7.0	0.565
7.5	0.567
8.0	0.564
8.5	0.565
9.0	0.563
9.5	0.565
10.0	0.565
10.5	0.530
Silver (I) : 90 µg; Naphthalene : 0.6 gm	

Table 2: Effect of Buffer solution

Buffer solution ml	Absorbance 430 nm
1.0	0.566
1.2	0.561
1.5	0.562
1.8	0.565
2.0	0.567
2.3	0.568
2.5	0.562
2.8	0.563
3.0	0.562
3.3	0.565
3.5	0.564
3.7	0.567
4.0	0.566
4.2	0.565
4.5	0.568
4.7	0.565
5.0	0.568
5.3	0.567
5.5	0.569

Table 3: Effect of Reagent concentration

0.2% Reagent ml	Absorbance 430 nm
0.0	0.245
0.5	0.482
1.0	0.560
1.5	0.562
2.0	0.565
2.5	0.567
3.0	0.561
3.5	0.568
4.0	0.564
4.2	0.572
4.5	0.574
4.8	0.577
5.0	0.576
5.3	0.535
5.5	0.517
5.8	0.478
6.0	0.465
Silver : 90 µg; pH : 6.0; Naphthalene : 0.6 gm	

Table 4: Effect of Naphthalene concentration

20% Naphthalene ml	Absorbance 430 nm
0.5	0.426
1.0	0.478
1.5	0.564
2.0	0.565
2.5	0.567
2.7	0.562
3.0	0.563
3.2	0.568
3.5	0.566
3.7	0.571
4.0	0.573
4.3	0.576
4.5	0.578
4.8	0.572
5.0	0.570
5.3	0.562
5.5	0.565
6.0	0.568
Silver : 90 µg, pH : 6.0; Napthalene : 0.6 gm	

Table 5: Calibration Data for Silver (I)

Silver (I) Concentration µg	Absorbance 430 nm
10	0.0
20	0.146
30	0.189
40	0.241
50	0.327
60	0.375
70	0.440
80	0.512
90	0.565
100	0.624
110	0.686
120	0.752
130	0.809
140	0.865
150	0.898
0.2% Reagent : 3.0 ml; pH 6.0; Naphthalene : 0.6 gm	

REFERENCES

A Dean Philip, J. JagdeseVittal and S. Radhey Srivastava, 1987. Con. J. Chem; **65**: 2628.

Car WeipingYaoguoOnyancy and Xu Yingon, 1989. FenxiHuaxne; **17**: 20.

D. Mealor and A. Townshend, 1968. Talanta, **15**, 131.

George Young and William Eyre, 1901. J. Chem. Soc., **79**: 54.

K. Das Mrinal and A.K. Majumdar, 1970. Micro. Chem. J., **15**: 540.

M. Neucki, ZurKenntniss des sulfoharstaffs, Deuschen Chemischen Gesellschaft, **6**(1): 598-600.

M. Sataka and H.B. Singh, 1982. Def. Sci., **32**: 207.

P.L. Searle, 1986. Aust. J. Soil Res., **24**: 193.

Qi Wnbi and Luo xiongshanFenxiShiganshi, **7**, (1988).

Ralucg Mocanu and Axenia Marculescu, 1972. An. Stiint, Uni. Al. I. Cuza Lassi, Sec. 1, 18, 4.

S.K. Hawa, B.K. Sharma, S.P. Mathur and Saroj Sharma, 1986. Oriented J. Chem., **2**:51.

S.K. Jain, B.K. Puri A.L. Singh and J.A.L. Rao, 1988. Zn Anal Khim, **2**: 2164.

S.P. Mathur and M.R. Bhandan, 1970. Chem. J., **15**: 540.

Sukhveer Singh et. al., 1986. Chem. Acta Turc, **14**: 380.

U. Ranga Rao and V.R. Shrinivasan, 1970. Ind. J. Chem., **8**: 5009.

V.P. Vasilev, V.I. Shorokhova, S.V. Kanova and A.V., Katroutseve, 1978. Zaved. Lab, **44**: 263.