ASIAN JOURNAL OF CHEMISTRY

Extraction and Determination of Copper(II) from Wastewater with Hydrophilic Ionic Liquid-Salt Aqueous Two-Phase System

Ou Sha[*], Yun Zhou and Wei-Xing Ma

School of Chemistry and Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P.R. China

*Corresponding author: Tel: +86 518 85895063; E-mail: shaou7993259@hhit.edu.cn

In this paper, a novel method of extraction and spectrophotometric determination of copper in ionic liquid aqueous two-phase system(ATPS) formed by a hydropilic ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate $[C_2mim][ESO_4]$ and K_2HPO_4 was developed. In the ionic 1iquid aqueous two-phase system of pH 8, the complex formed by acid chromium blue K and Cu^{2+} had a high absorbance with the maximum absorption of 541 nm. The effects of ionic liquid dosage, solution acidity, the dosages of acid chromium blue K and salt on the extraction determination of copper were studied. Beer's law was obeyed in the range of 0.040-2.0 μg/mL Cu^{2+}. The method has been applied to the determination of copper in electroplating wastewater and standard copper sample GBW(E)08036.

Key Words: Hydrophilic ionic liquid, Aqueous two-phase, Extraction, Copper.

INTRODUCTION

The determination of heavy metals in the environment water is of great interest, since their toxic effects on the ecosystem and human health depend on their dose and toxicity. Copper as one of the heavy metals is on one hand important for life but on the other hand, it is highly toxic for organisms like algae, fungi and many bacteria or viruses[1]. Therefore, determination of trace amounts of copper in water samples is an important analytical task.

Aqueous two-phase system (ATPS) is a very promising technology for novel separation and pretreatment[2,3]. Aqueous two-phase system is usually formed by combining either two incompatible polymers or a polymer and a salt in water above a certain critical concentration[4]. Compared with the traditional organic solvent extraction and solid phase extraction, ATPS is considered to be environmentally friendly due to the bulk of both phases consist of water and no use of volatile organic solvent in the whole process. However, most of phase-formation polymers in ATPS have high viscosity, form an opaque solution and sometimes interfere with the analytes.

As a kind of novel green solvent, Room temperature ionic liquids (RTILs) have been paid ever increasing attentions in RTIL-based extraction for metal separation, since they have many unique properties, such as non-volatile and non-flammable. Many of them are known that melt below room temperature[5]. A new type of ATPSs consisting of ionic liquids and salts were reported by Rogers and co-workers[6]. The IL-salt ATPS (IL-ATPS) has many advantages, such as low viscosity, little emulsion formation, no need of using volatile organic solvent, quick phase separation, high extraction efficiency and gentle biocompatible environment[7-9].

In this work, we have studied the extraction of Cu(II)-acid chromium blue K (ACBK) complex with IL-ATPS system formed by a hydropilic ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate($[C_2mim][ESO_4]$) and K_2HPO_4 system and applied this proposed system to the spectrophotometric determination of Cu^{2+} in standard copper sample GBW(E)08036 and electroplating wastewater.

EXPERIMENTAL

UV-2501 spectrophotometer (Shimadzu, Japan); MT-31 YAMATO Touch mixer(Yamato Scientific Co., Ltd). All the other chemicals were analytical grade reagents and all the solutions were prepared from deionized water. Diethyl sulfate (Beijing Chemical Reagent Corporation, China); toluene (Beijing Chemical Reagent Corporation, China); 1-methylimidazole (99 %, Shanghai Darui Finechemical Co., Ltd, China).

Stock solution for copper ions was prepared from appropriate amounts of the $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, Darmstadt, Germany) as 1000 mg/L in deionized water and diluted daily for obtaining working solutions prior to use; standard copper sample GBW(E)08036 (National reference materials, China); Acid chrome blue K: 5×10^{-4} mol/L; Britton-Robinson buffer solutions (B-R) were prepared by mixing the mixed acid (composed of 0.12 mol/L H_3PO_4, CH_3COOH and H_3BO_3) with 0.6

mol/L NaOH in proportion. The buffer solutions were prepared to adjust the acidity of the system.

The ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate [C₂mim][ESO₄] used in this work was synthesized in our laboratory according to the literature[10]. Diethyl sulfate was added dropwise to a solution of 1-methylimidazole in toluene cooled in an ice-bath under dinitrogen at a rate to maintain the reaction temperature below 40 ℃. After addition of the diethyl sulfate, the reaction mixture was stirred at room temperature for 1 h. The upper, organic phase was decanted and the lower, ionic liquid phase was washed with toluene, dried with heating at 75 ℃ under reduced pressure to remove residual organic solvents and finally *in vacuo* to yield the resulting 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid as a colourless hygroscopic liquid free from starting materials.

General procedure: Appropriate volumes of the standard solution of copper (or the water sample after preparation) in the linear concentration range were placed in a 10 mL centrifuge tube comparison tube equipped with plug and treated with 1.00 mL 2×10^{-4} mol/L ACBK solution, 2.00 mL pH = 8.0 B-R buffer solution, 1.00 mL [C₂mim][ESO₄] and diluted to 10 mL with distilled water and mixed. Then 9 g of K₂HPO₄ were added to the centrifuge tube. The mixture was shaken for 3 min. After complete phase separation was performed, the Cu²⁺-ACBK complex was extracted into the upper-rich phase. The upper phases were separated and placed in a 5 mL centrifuge tube. Then the upper phase was diluted to 5 mL with 1 mL B-R buffer solution and distilled water. After the solution was placed for 10 min, the concentrations of Cu²⁺ was determined by spectrophotometry against corresponding reagent blank, which was prepared with the same procedure without Cu²⁺ added. Meanwhile the absorbance of the unextraction system of Cu²⁺-ACBK-[C₂mim][ESO₄] was also determiner against the corresponding reagent blank. The extraction behaviour described in this work was evaluated as extraction efficiency (E %), which is defined as:

$$E\ (\%) = \frac{A_e}{A_o} \times 100 \tag{1}$$

where A_e is the absorbance of upper-rich phase diluted to 5 mL with B-R buffer solution and distilled water against the corresponding reagent blank and A_o is the absorbance of unextraction system of Cu²⁺-ACBK-[C₂mim][ESO₄] against the corresponding reagent blank.

RESULTS AND DISCUSSION

Choice and dosage of salt: Different salts were tested for the formation of typical aqueous two-phase systems (ATPS) with [C₂mim][ESO₄]. Results show that ATPS can be formed by adding appropriate amount of these salts, such as KOH, K₂HPO₄, NaOH, Na₂HPO₄, while adding acidic or neutral salts, such as KH₂PO₄, (NH₄)₂SO₄, NaCl or KCl can not drive [C₂mim][ESO₄] solution to separate into two phases. Accordant with that of salting-out ability of anion. K₂HPO₄ was chosen in the following studies. One reason was that K₂HPO₄ led to effective phases isolation between [C₂mim][ESO₄] and salt enriched solutions and the other was that K₂HPO₄, compared with other phase-forming salts, resulted in an appropriate pH

to determine the copper concentration. It was found optimum amount of K₂HPO₄ to lead to rapid phase separation was in the range of 8.2-10 g so dosage of K₂HPO₄ was kept at 9 g.

Spectra of Cu²⁺-ACBK containing [C₂mim][ESO₄]: In the alkali medium Cu²⁺ and acid chrome blue K could form a red dark chelate complex and the molar ratio of Cu²⁺-ACBK complex obtained by employing mole ratio method in our laboratory was 1:1. When the complex was extracted into the upper ionic liquids phase of an aqueous two-phase system containing [C₂mim][ESO₄] and K₂HPO₄. The absorption spectrum of the complex before and after the extraction has a peaks at wavelengths of 541 nm (Fig. 1) and the absorbance was also kept stable in 3-40 min. Therefore, maintain at 541 nm and 10 min after the solution mixed were recommended for spectrophotometric determination in the subsequent experiments.
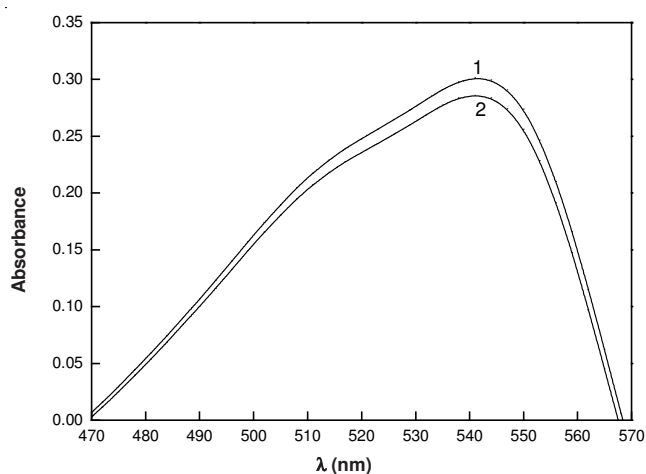

Fig. 1.   Absorption spectra of Cu²⁺-ACBK complex (1) the absorption after the extraction against corresponding reagent blank; (2) the absorption before the extraction against corresponding reagent blank

Effect of pH: The effect of pH on the extraction of Cu²⁺-ACBK complex was examined over the range from pH 6-11. The result was shown in Fig. 2. The extractability of Cu-ACBK complex into the upper ionic liquids phase showed a maximum at pH = 8. Therefore, the extraction was formed at pH = 8 hereinafter.
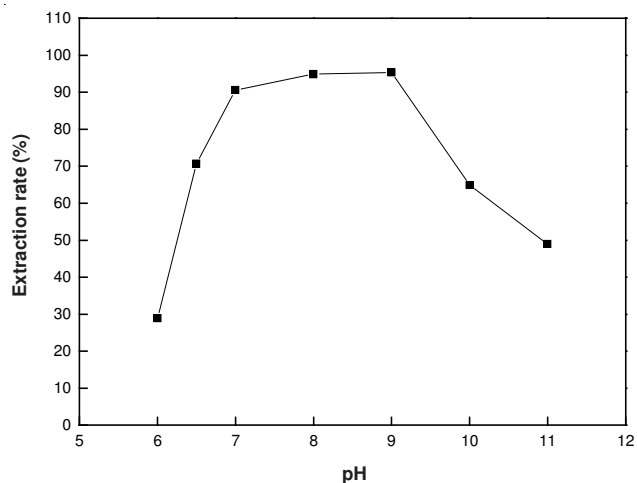

Fig. 2. Effect of pH

	TABLE-1				
	DETERMINATION RESULTS OF SAMPLES (MEAN ± SD, n = 6)				
Sample	Determination value (µg/mL)	Certified value (mg/L)	Added (µg/mL)	Found (µg/mL)	Recovery (%)
Electroplating wastewater 1	0.178	–	1.00	1.04	104
Electroplating wastewater 2	0.165	–	1.50	1.47	98.0
GBW(E)08036	508 ± 0.084	500	0.50	0.49	98.0%

Effect of the dosage of [C₂mim][ESO₄]: The effect of the dosage of $[C_2mim][ESO_4]$ was examined. The extraction rate of Cu^{2+}-ACBK extracted into the upper phase was found to above 90 % when the dosage of $[C_2mim][ESO_4]$ was in the range of 1.0-1.4 mL (Fig. 3). When ionic liquid dosage less than 0.6 mL, interphase boundary was not clear and extraction was not complete. Therefore, the volume ratio of $[C_2mim][ESO_4]$/ sample solution was kept at 1 mL/10 mL in the subsequent experiments.
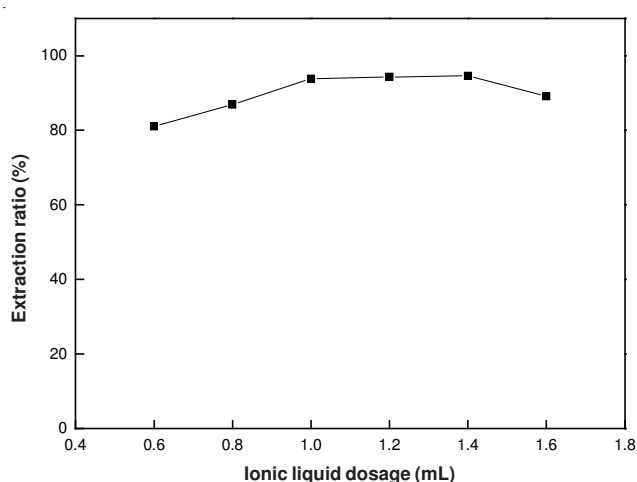

Fig. 3. Effect of the dosage of $[C_2mim][ESO_4]$

Effect of the amount of acid chromium blue K: The effect of the amount of added ACBK in the systems has been investigated on the extraction efficiency of Cu(II) and the results are illustrated in Fig. 4. As indicated in this figure, when the dosage of ACBK was in the range of 0.6-1.2 mL, the extracion rate was constant and the Cu^{2+} could be extracted quantitative. So in this work, 0.8 mL dosage of ACBK was adopted.
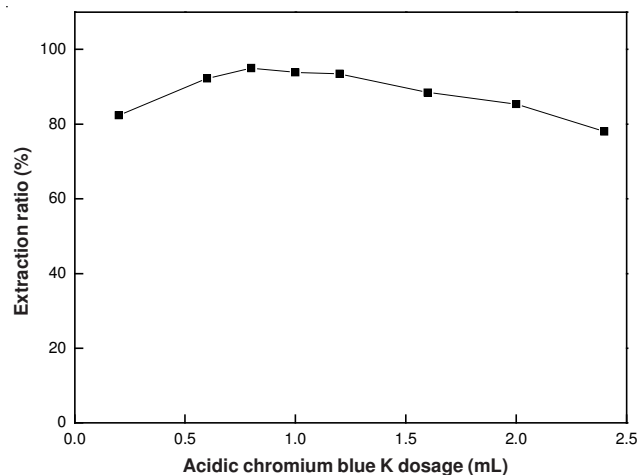

Fig. 4. Effect of the amount of ACBK

Interferences: Determination of Cu(II) 1.0 µg/mL in the presence of foreign substances was investigated. With a relative error of less than ± 5 %, the tolerance limit for various foreign substances were as follows (tolerance ratio in mass): Na^+, K^+, Cl^-, HPO_4^{2-}, $H_2PO_4^-$, NO_3^- (1000); Fe(II), Mn(II), Cr(III), Cr(VI) (50); Fe(III), Cd(II), Mo(VI), Ca(II), Mg(II) (10).

Analytical parameters: The calibration concentration range for the spectrophotometric determination of Cu(II) was linear 0.040-2.0 µg/mL. The linear equation was A = 0.2375C (µg/mL)-0.01033, the corresponding coefficient of correlation was 0.9919. The relative standard deviation was 2.34 % (n = 6, c = 1.0 µg/mL). The limit of detection by the described procedure was 20 ng/mL.

Sample analysis: In order to demonstrate the applicability of the proposed method to real samples, the ionic liquid-salt-ATPS was applied to determine Cu(II) in electroplating waste-water from electroplating industry by standard addition method. Standard copper sample GBW(E)08036 was also determined under the optimal conditions by standard curve method and standard adding method, respectively (Table-1). This method has been successfully applied to the analysis of real samples with satisfactory results. The contents of Cu(II) in the national reference materials were in agreement with the certified value.

Conclusion

The use of aqueous two-phase system based on ionic liquid for preconcentration of copper ions with Cu^{2+}-ACBK complex in water samples is proposed as a prior step to their determination by spectrophotometry. This method is simple, rapid, sensitive and cheap and has low toxicity, since only very small amounts of an ionic liquid as a 'green extraction solvent' is used instead of environment damaging organic solvents.

REFERENCES

1. T. Mayr, I. Klimant, O.S. Wolfbeis and T. Werner, *Anal. Chim. Acta*, **462**, 1 (2002).
2. A.M. Azevedo, P.A.J. Rosa, I.F. Ferreira, A.M.M.O. Pisco, J. de Vries, R. Korporaal, T.J. Visser and M.R. Aires-Barros, *Sep. Purif. Technol.*, **65**, 31 (2009).
3. J.S. Becker, O.R.T. Thomas and M. Franzreb, *Sep. Purif. Technol.*, **65**, 46 (2009).
4. L. Li, F. Liu, X.X. Kong, S. Su and K.A. Li, *Anal. Chim. Acta*, **452**, 321 (2002).
5. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
6. K.E. Gutowski, G.A. Broker, H.D. Willauer, J.G. Huddleston, R.P. Swatloski, J.D. Holbrey and R.D. Rogers, *J. Am. Chem. Soc.*, **125**, 6632 (2003).
7. M. Gharehbaghi, F. Shemirani and M. Baghdadi, *Int. J. Environ. Anal. Chem.*, **89**, 21 (2009).
8. H. Abdolmohammad-Zadeh and G.H. Sadeghi, *Anal. Chim. Acta*, **649**, 211 (2009).
9. S.R. Youse and F. Shemirani, *Anal. Chim. Acta*, **669**, 25 (2010).
10. J.D. Holbrey, W.M. Reichert, R.P. Swatloski, G.A. Broker, W.R. Pitner, K.R. Seddon and R.D. Rogers, *Green Chem.*, **4**, 407 (2002).