912 *J. Chem. Eng. Data* **2010,** *55,* 912–918

Study on the Cloud Point Extraction of Copper(II) from an Aqueous Sulfate Medium with *N*,*N*′-Bis(salicylideneaminoethyl)amine Polydentate Schiff Base into a Nonionic Surfactant Phase

Hasnia Reffas, Tayeb Benabdallah,* Mohamed Hadj Youcef, and Hocine Ilikti

Laboratory of the Chemistry and Electrochemistry of the Organo-metallic Complexes, Department of Chemistry, Faculty of Sciences, University of the Sciences and Technology of Oran (U.S.T.O.MB), BP-1505 Oran El-M'naouer, Algeria

A novel polydentate Schiff base extractant, *N*,*N*′-bis(salicylideneaminoethyl)amine (H_2L), was successfully used in a cloud point extraction of copper(II) from aqueous sulfate solutions. The extraction process is based on the formation of a hydrophobic complex of copper(II)−H_2L, which is subsequently extracted into the nonionic surfactant *p*-octylpolyethyleneglycolphenylether (Triton X-100) rich phase at a temperature above the cloud point temperature (CPT). The phase diagrams of the binary system, water−surfactant (Triton X-100), and the ternary systems, water−surfactant−salt (Na_2SO_4), were determined. The effects of the main experimental parameters such as pH, extractant concentration, and nonionic surfactant concentration on the extraction behavior of copper(II) with *N*,*N*′-bis(salicylideneaminoethyl)amine were studied. The percentage extraction was found to be significantly dependent on the aqueous solution pH. The extraction of copper(II) was observed in the pH range of (3 to 11). The stoichiometry of the extracted species of copper(II) was ascertained by the Yoe−Jones mole ratio method to have a composition of 1:1 (Cu:H_2L). The optimum conditions of the extraction of copper(II) have been established as the following: (1) $2 \cdot 10^{-3}$ mol·L^{-1} extractant; (2) 5 % (by weight) surfactant; (3) pH of 9; (4) 0.49 mol·L^{-1} Na_2SO_4; and (5) temperature of 65 °C.

Introduction

Surfactants form a unique class of chemical compounds which have found important practical applications in almost every area of chemistry.[1] They contain a hydrophilic headgroup and hydrophobic chain (tail), which make possible molecular aggregate dissolution in water solutions.[2,3] These amphiphilic molecules form microheterogeneous structures in solutions, namely, micelles, which make the solubilization of water-insoluble molecules in the aqueous matrix possible.

Micellar systems or other organized molecular assemblies have great potential application in analytical chemistry as well as in separation science and technology. Aqueous solutions of most nonionic and zwitterionic surfactants, when heated or cooled, become cloudy over a narrow temperature range due to the diminished solubility of the amphiphile in water.[4−6]

This critical temperature is called the "cloud point". Above the cloud point (CP), the solution separates into two isotopic liquid phases: one very small in volume, the surfactant-rich phase (coaservate), and the other, the dilute aqueous phase, in which the surfactant concentration is close to its critical micelle concentration.[7]

The CP phenomenon of the nonionic surfactant is reversible and can be influenced by many factors such as its own concentration[8,9] and the number of ethylene oxide units in its molecules[10] as well as additives like electrolytes.[11−13] It has been demonstrated that the surfactant-rich phase, thus separated under cloud point conditions, is able to extract and separate a wide range of organic and inorganic species from the aqueous phase. The use of the cloud point extraction process (CPEP) offers an interesting alternative to conventional extraction systems. Compared with conventional liquid−liquid solvent extraction, CPEP uses water and avoids the use of huge amounts of expensive, toxic, and flammable volatile organic solvents. Besides, CPEP can lead to higher extraction efficiency and a large concentration factor because the presence of the surfactant can minimize losses of analytes due to their adsorption into the container.[14−17]

The CPEP technique has been used for extractive preconcentration,[18] separation, and/or purification of metallic species,[19,20] metal chelates,[21] biomaterials,[22] and organic compounds.[23]

Extractions of metal ions by CPEP have been achieved in the absence of chelating extractants,[24,25] but metal ion separation could be improved by the formation of sparingly water-soluble hydrophobic complexes in the surfactant micellar solution. Since Watanabe and Tanaka pioneered work[7] on nickel and zinc extraction, several chelating extractants such as dithizone,[26,27] 1-(2-thiazolylazo)-2-naphthol (TAN),[28−30] 1-(2-pyridylazo)-2-naphthol (PAN),[31,32] diethyldithiocarbamate (DDTC),[33] 8-hydroxyquinoline (HQ),[34] and *o*,*o*-diethyldithiophosphate (DDTP) have been used to extract metal ions in many procedures.[35,36]

The Schiff bases constitute another family of powerful chelating extractants. Indeed, they are well-known as extractants that are easy to be synthesized and have structural rigidity, and they are also used in selective solvent extraction of several kinds of metal cations.[37−41]

However, they have been rarely utilized in cloud point extraction.[42] Therefore, this paper is concerned with the cloud point extraction of copper(II) employing a polydentate Schiff base, *N*,*N*′-bis(salicylideneaminoethyl)amine (H_2L) as extractant and Triton X-100 as a nonionic surfactant (Figure 1). The pentadentate Schiff base (H_2L), which contains in its structure mixed O−N type donor atoms, was chosen as the chelating

---

* Corresponding author. E-mail: reffas26@yahoo.fr.

10.1021/je900522g

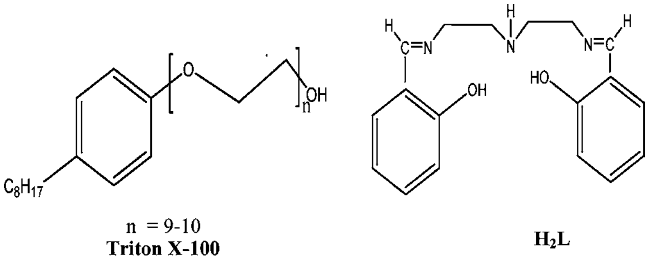


Figure 1. Structures of chelating extractant and surfactant used.

extractant because it forms more stable complexes than either O−O or N−N types.[43] Another advantage to select this kind of extractant is its stability in dilute acidic solutions and high hydrophobicity.[38,44] The copper(II) metallic ion was used as an example because it constitutes a perpetual toxic threat to the environment. Besides, the extraction-recovery of this metal coincides with the goals of the waste management strategy since it could provide some economical revenue and solve a pollution problem. In addition to the optimization of the use of *N*,*N*′-bis(salicylideneaminoethyl)amine in cloud point extraction and the assessment of its application for the removal of copper, the effects of some variables such as pH, extractant concentration, and surfactant concentration were investigated.

Experimental Section

Reagents and Solutions. All reagents used were of the highest available purity and analytical grade. The nonionic surfactant polyethylene glycol *p*-isooctyl phenyl ether (Triton X-100) with 9 to 10 oxyethylene units was purchased from Alfa Aesar. This surfactant was chosen for the formation of the surfactant-rich phase because it had many advantages. After settling, the two phases were easy to separate without cooling by an ice bath. Moreover, this reagent had a high capacity to solubilize the Schiff base. The initial concentration of analyte, $[\mathrm{Cu}^{2+}] = 1.57 \cdot 10^{-3}\ \mathrm{mol \cdot L^{-1}}$, was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (Fluka) in double distilled water. Na_2SO_4 (Prolabo) was used to aid phase separation ($[Na_2SO_4] = 0.49\ \mathrm{mol \cdot L^{-1}}$), and H_2SO_4 [(0.1 to 0.5) $\mathrm{mol \cdot L^{-1}}$] (Merck) and NaOH [(0.1 to 0.5) $\mathrm{mol \cdot L^{-1}}$] (Prolabo) were used to adjust the pH to the desired value.

Synthesis of Extractant. The quinquedentate extractant Schiff base *N*,*N*′-bis(salicylideneaminoethyl)amine (H_2L) was prepared according to the literature through a well-known method:[45] diethylenetriamine (0.2 mol) was mixed with salicylaldehyde (0.4 mol) in 100 mL of ethanol. The stirred mixture was kept reacting for 120 min at 60 °C under reflux. The product was obtained as a deep yellow oily mass. The purity was checked by IR and ^{1}H NMR spectra.

H_2L: Yellow oil; yield 70 %; IR (KBr pellet, $\mathrm{cm^{-1}}$) 1631 (C═N); ^{1}H NMR ($CDCl_3$, δ ppm) 13.20 (s, 2H, OH), 8.35 (s, 2H, CH═N), 6.80−7.32 (m, 8H, aromatic-H), 2.99 (t, 4H, ═N−C−CH_2−), 3.71 (t, 4H, ═N−CH_2−C−).

This extractant is very stable in the surfactant solution. It has three nitrogen atoms and two hydroxyl groups in complexation with copper (Figure 1).

Instrumentation. A Shimadzu 1202 model UV-visible spectrophotometer with 10 mm quartz cells was used for the determination of the concentration of metal. The pH values were measured using a Schott-Gerate model CG820 pH-meter, equipped with a glass-combination electrode. A thermostatted bath maintained at the desired temperature was employed for the cloud point experiments.

Analytical Procedures. Cloud Point Determination. The temperature at which the cloud point phenomenon occurs was determined by the method reported by Carvalbo et al.[46] The method is based on the visual observation of the separation of phases in the micellar solution. The initial aqueous solution (25 mL) was heated in a thermostatted vessel at a specific temperature which was well above its cloud point (turbid solution). Then the solution was cooled gradually. The cloud point was considered as the temperature at which the solution became clear. To verify the results, the opposite process was carried out by gradually heating the clear solution until turbidity appeared. The reported value was the average of these two determinations. In most cases, these two temperatures were identical, within 0.5 °C.

Typical Cloud Point Extraction. Typically, a cloud point extraction experiment was performed as follows: aliquots of 10 mL of the sample solution containing the analyte Cu(II) ($1.57 \cdot 10^{-3}\ \mathrm{mol \cdot L^{-1}}$), Schiff base ($2 \cdot 10^{-3}\ \mathrm{mol \cdot L^{-1}}$), surfactant (Triton X-100) 5 % (by weight), and Na_2SO_4 ($0.49\ \mathrm{mol \cdot L^{-1}}$) were adjusted to the appropriate pH value (pH = 9) with NaOH. Then, the sample was stirred for 5 min in a shaker and kept in a constant temperature bath at 65 °C for 3 h. The copper concentration was determined spectrophotometrically in the water phase. The overall process can be visualized as in Chart 1.

Results and Discussion

Calculations. The distribution coefficient parameter used to describe the degree of metal partitioning from the aqueous to the surfactant-rich phase is given by

$$D_{\mathrm{M}} = \frac{[\mathrm{M}]_{\mathrm{s}}}{[\mathrm{M}]_{\mathrm{w}}} \tag{1}$$

where $[\mathrm{M}]_{\mathrm{s}}$ and $[\mathrm{M}]_{\mathrm{w}}$ are the final metal concentrations in the surfactant-rich phase and in the aqueous phase, respectively.

The percentage of extraction of metal (yield), *R* %, and the efficiency of the process, *E* %, can be expressed as

$$R = 100\frac{[\mathrm{M}]_0 - [\mathrm{M}]_{\mathrm{w}}}{[\mathrm{M}]_0} \tag{2}$$

$$E = 100\frac{D_{\mathrm{M}}}{D_{\mathrm{M}} + \dfrac{V_{\mathrm{w}}}{V_{\mathrm{s}}}} \tag{3}$$

wher, $[\mathrm{M}]_0$ refers to the metal concentration in the original aqueous solution prior to the extraction step and V_{w} and V_{s} are the volumes of dilute aqueous solution and surfactant-rich phase obtained after the extraction step, respectively.

Finally, the concentration factor and the volume fraction of the surfactant-rich phase are given by

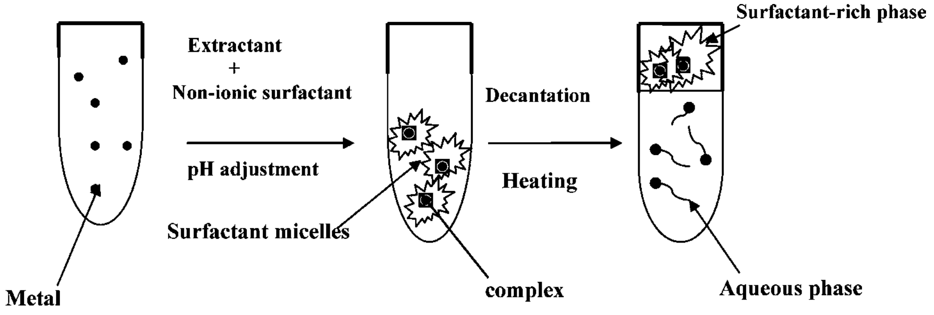
$$C_{\mathrm{f}} = \frac{E}{100\varphi_{\mathrm{s}}} \tag{4}$$

$$\varphi_{\mathrm{s}} = \frac{V_{\mathrm{s}}}{V_0} \tag{5}$$

where V_0 is the volume of the original aqueous solution prior to the extraction step.

Phase Diagrams of Binary Systems. Characterization of the Phase Diagram of the Triton X-100−Water System. The phase diagram of the nonionic Triton X-100 obtained in this study at different aqueous concentrations, ranging from (0.1 to 5) % (by weight), is shown in Figure 2. The shape of the curve coincides with that expected for a typical nonionic surfactant.[47]

Chart 1. Schematic Representation of the Typical CPE Process



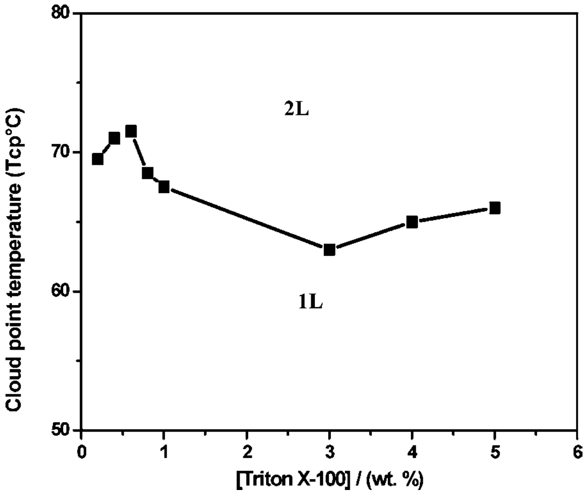


Figure 2. Phase diagram of the Triton X-100−water binary system. 1L, one phase; 2L, two phases.

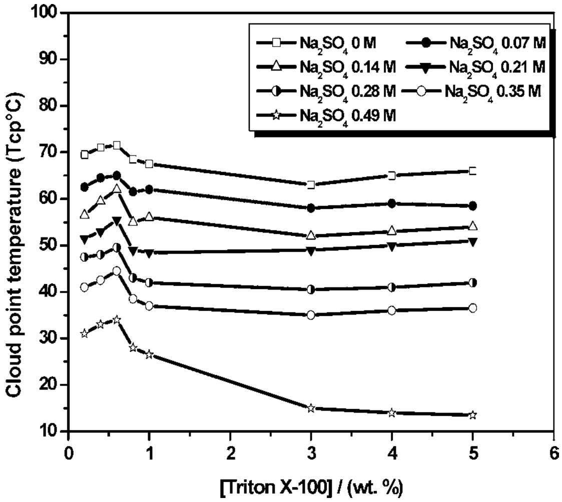


Figure 3. Phase diagram of the Triton X-100−water−Na_2SO_4 ternary system.

Below the curves, micellar solutions (1L) exist, while two-phase regions coexist above the curves (2L).

It has been mentioned by several authors that solutions of nonionic surfactants generally can show different critical temperatures at similar concentrations depending on the experimental conditions and purity of the amphiphiles.[4] Nonionic polyoxylene surfactants are usually synthesized as a mixture of oligomers characterized by an average number of oxyethylene units. Furthermore, the presence or addition of other compounds to the amphiphile solution can lead to a change in the clouding process. Thus, one should not expect complete agreement among the results obtained by different researchers unless the experiments have been carefully controlled and all operating conditions are exactly repeated.

As evident from the phase diagram given in Figure 2, the highest cloud point temperature (T_{cp}) value determined for Triton X-100 was 71.5 °C at the concentration of 0.6 % (by weight), whereas the lowest cloud point temperature was 63 °C at the concentration of 3 % (by weight). Moreover, the cloud point temperature, $T_{cp} = 67$ °C, found at the surfactant concentration of 1 % (by weight) was in good agreement with that reported by Mata,[48] for the micellar solution of Triton X-100 without any additives.

Effect of Sodium Sulfate. The influence of added Na_2SO_4 [(0.07 to 0.49) $mol \cdot L^{-1}$] on the cloud point temperatures of the Triton X-100 micellar solutions was examined at various surfactant concentrations. Figure 3 clearly demonstrates that the addition of sodium sulfate lowers the cloud point curve. This phenomenon can be conveniently explained in terms of a faster dehydration of the ethoxylated chains due to the presence of inorganic ions (sodium sulfate in this case: Na^+ and SO_4^{2-}) competing for interaction with water molecules, i.e., a "salting-out" effect.

Also, it seems that the sodium sulfate lowers the cloud point by a continuous medium change, more than by direct interaction with the ethoxy groups of the surfactant.[49−51]

Figure 3 shows how 0.49 $mol \cdot L^{-1}$ of Na_2SO_4 is able to lower the cloud point of 5 % (by weight) Triton X-100 solutions from (66 to 13.5) °C. Therefore, it is possible to adjust the cloud point to room temperature and facilitate the cloud point extraction process by simply controlling surfactant and salt concentrations. Salt addition can also increase the density of the dilute phase, and this makes the separation of the water- and surfactant-rich phases easy in some nonionic surfactant systems.[7,52,53]

Equilibrium Distribution Coefficients of Copper(II). The cloud point extraction process of copper(II) by *N*,*N*′-bis(salicylideneaminoethyl)amine dissolved in TX-100 nonionic surfactant micellar solutions was investigated over a pH range of approximately 3 to 11. The concentrations of the extractant and TX-100 were between $1.3 \cdot 10^{-4}$ $mol \cdot L^{-1}$ and 10^{-2} $mol \cdot L^{-1}$ and 1 % (by weight) and 7 % (by weight), respectively. The results of the equilibrium distribution coefficients of copper(II) between the dilute aqueous phase and surfactant-rich phase are presented in Tables 1 to 3. As shown in Table 1, it can be seen that the distribution coefficients of Cu(II) are higher in the basic pH range. Because *N*,*N*′-bis(salicylideneaminoethyl)amine Schiff base is the basic extracting agent, copper(II), which is a common Lewis acidic metallic ion, was easily extracted from aqueous sulfate solutions by complex formation. Moreover, the distribution coefficient increased with an increase in pH. This confirms that the CPE process has taken place via a cation exchange

Table 1. Influence of Equilibrium pH on Distribution Coefficients of Copper(II)[a]

equilibrium pH	D_M	% E
3.59	1.78	11.84
4.72	6.02	31.20
5.40	9.03	40.50
6.66	11.34	46.06
7.85	15.75	54.24
8.10	19.42	59.40
8.71	34.35	72.11
9.00	14272.43	99.90
9.47	37.01	73.60
9.69	31.33	70.22
10.47	26.4	66.52
10.93	22.38	62.75

[a] $[Cu^{2+}] = 1.57\cdot10^{-3}$ mol·L^{-1}. $[H_2L] = 2\cdot10^{-3}$ mol·L^{-1}. $[Na_2SO_4] = 0.49$ mol·L^{-1}. [S] = 5 % (by weight). $pH_i = 5.68$. $T = 65°$ C.

Table 2. Influence of Initial Concentration of Extractant on Distribution Coefficients of Copper(II)[a]

initial concentration of extractant mol·L^{-1}	D_M	% E
$1.3\cdot10^{-4}$	6.55	33.04
$2.5\cdot10^{-4}$	18.03	57.60
$5.0\cdot10^{-4}$	46.24	77.68
$7.7\cdot10^{-4}$	91.62	87.33
10^{-3}	141.91	91.44
$2.0\cdot10^{-3}$	14272.43	99.90
$3.08\cdot10^{-3}$	343.56	96.30
$4.11\cdot10^{-3}$	343.56	96.30
$5.0\cdot10^{-3}$	343.56	96.30
10^{-2}	343.56	96.30

[a] $[Cu^{2+}] = 1.57\cdot10^{-3}$ mol·L^{-1}. $[Na_2SO_4] = 0.49$ mol·L^{-1}. [S] = 5 % (by weight). pH = 9. $T = 65$°C.

Table 3. Influence of Initial Concentration of Surfactant on Distribution Coefficients of Copper(II)[a]

initial concentration of surfactant (% (by weight))	D_M	% E
1	23.22	41.80
2	38.50	61.60
3	77.15	80.24
4	123.22	88.87
5	14272.43	99.90
6	69.25	87.26
7	34.86	79.48

[a] $[Cu^{2+}] = 1.57\cdot10^{-3}$ mol·L^{-1}. $[H_2L] = 2\cdot10^{-3}$ mol·L^{-1}. $[Na_2SO_4] = 0.49$ mol·L^{-1}. pH = 9. $T = 65$ °C.

mechanism. At higher pH values, the distribution coefficients decrease, revealing probably metal hydroxide formation. On the other hand, it is obvious from the data given in Tables 2 and 3 that with increasing extractant and surfactant concentrations the distribution coefficients of Cu(II) increase. This result is presumably due to an increase of the complex ligands and solubilzation power of the nonionic surfactant TX-100 micelles.

Optimization of the CPE Process. The dependence of the extraction efficiency upon changes in some experimental parameters was studied. These included solution pH, concentration of the extractant, and concentration of the surfactant. In these studies, extraction process parameters were investigated to find the optimal operation conditions.

Effect of Solution pH. For ionizable solutes, the charge of the solute can greatly influence its extent of binding to a micellar assembly.[54] The ionic form of a molecule normally does not interact with and bind the micellar aggregate as strongly as its neutral form. Indeed, adjustment of the micellar solution pH is the key parameter when controlling experimental variables in a cloud point extraction process.

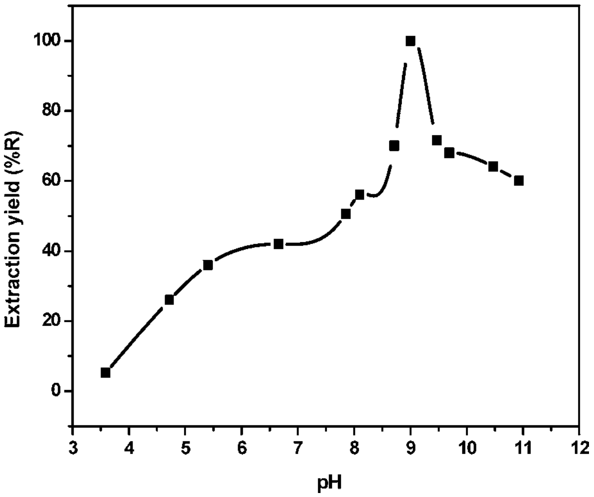


Figure 4. Effect of the pH on the percentage extraction of copper(II). $[Cu^{2+}] = 1.57\cdot10^{-3}$ mol·L^{-1}. $[H_2L] = 2\cdot10^{-3}$ mol·L^{-1}. $[Na_2SO_4] = 0.49$ mol·L^{-1}. [S] = 5 % (by weight). $T = 65$ °C.

An interesting result was obtained in the study of the influence of solution pH on the extraction recovery of the studied cation. In this series of experiments, the solution pH was varied over the range of 3 to 11. The Triton X-100, *N,N′*-bis(salicylideneaminoethyl)amine, copper, and Na_2SO_4 concentrations were kept constant at 5 % (by weight), $2\cdot10^{-3}$ mol·L^{-1}, $1.57\cdot10^{-3}$ mol·L^{-1}, and 0.49 mol·L^{-1}, respectively. The experiments were carried out at the separation temperature of 65 °C. The extraction yield depends on the pH at which complex formation between copper and ligand occurs. It is evident that the $Cu-H_2L$ system is reasonably influenced by the pH, as shown in Figure 4.

The extraction yield reaches the highest amount at pH = 9 for Cu(II). At lower pH values, the formation of complexes is not quantitative, and at higher pH values, the extraction starts to decrease. Therefore, a pH of 9 was selected to perform further extractions.

Effect of Extractant Concentration. To achieve the total extraction and preconcentration of copper(II), a series of experiments were carried out in which the other experimental variables, except extractant concentration, remained constant. The yield of the extraction as a function of the concentration of the extractant over the range ($1.3\cdot10^{-4}$ to 10^{-2}) mol·L^{-1} is presented in Figure 5.

It is shown that the yield of the extraction of copper increases with an increasing concentration of the extractant, *N,N′*-bis(salicylideneaminoethyl)amine (H_2L). An extractant concentration of $2\cdot10^{-3}$ mol·L^{-1} permitted a 100 % extraction efficiency to be reached and to raise the total formation of the complex. On the other hand, when an excess of extractant was used ($3.1\cdot10^{-3}$ mol·L^{-1}), a slight decrease in the yield was observed (96 %). This behavior can be explained because the molecules of the extractant are presumably trapped in the micelles, thus reducing the concentration of the complex.[42]

Effect of Surfactant Concentration. The concentration of surfactant that is used in CPE is a critical factor. A successful cloud point extraction would be that which maximizes the yield of extraction through minimizing the phase volume ratio and thus maximizing its concentrating factor. To obtain the optimal concentration of Triton X-100, the effect of surfactant concentration on the extraction efficiency of the system was investigated over the range of 1 % (by weight) to 7 % (by weight). The results are shown in Figure 6. The optimum concentration of Triton X-100 falls in the range (4 to 6) % (by weight). A

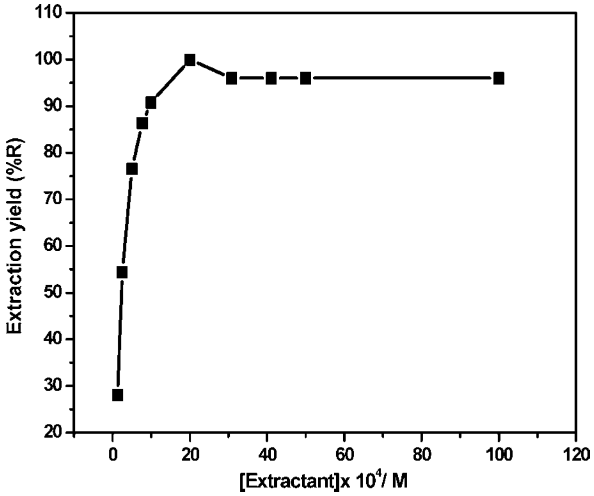


Figure 5. Effect of the extractant concentration on the extraction yield of copper(II). $[Cu^{2+}] = 1.57 \cdot 10^{-3}$ mol·L^{-1}. pH = 9. $[Na_2SO_4] = 0.49$ mol·L^{-1}. [S] = 5 % (by weight). T = 65 °C.

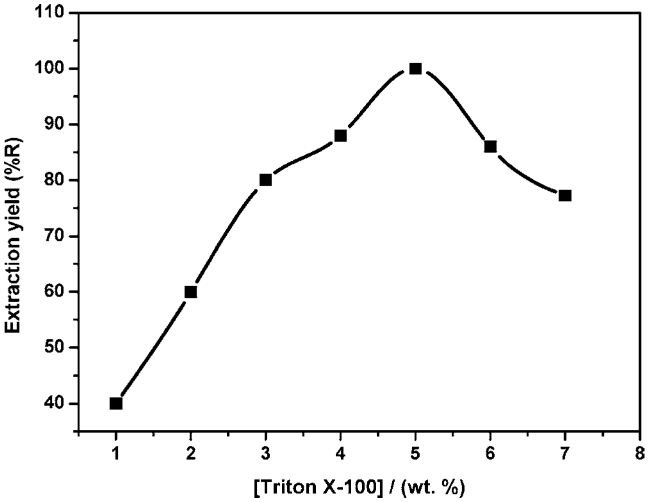


Figure 6. Effect of the Triton X-100 surfactant concentration on the percentage extraction of copper(II). $[Cu^{2+}] = 1.57 \cdot 10^{-3}$ mol·L^{-1}. $[H_2L] = 2 \cdot 10^{-3}$ mol·L^{-1}. pH = 9. $[Na_2SO_4] = 0.49$ mol·L^{-1}. T = 65 °C.

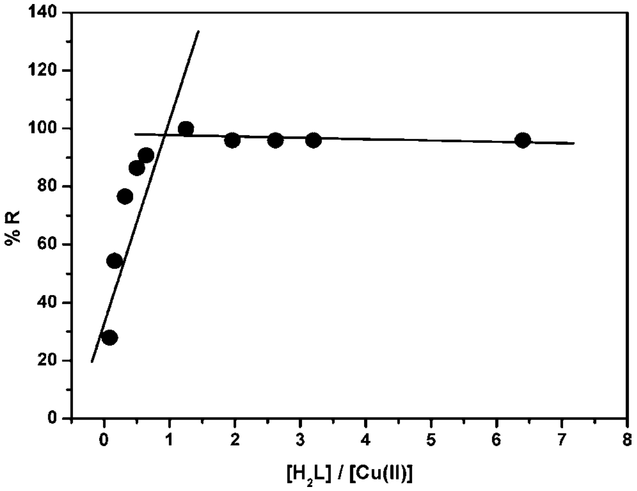


Figure 7. Determination of the stoichiometry of the extracted copper(II)−H_2L complex by the mole ratio method. $[Cu^{2+}] = 1.57 \cdot 10^{-3}$ mol·L^{-1}. pH = 9. $[Na_2SO_4] = 0.49$ mol·L^{-1}. T = 65 °C.

Table 4. Effect of the Surfactant Concentration on the Concentration Factor (C_f) and Surfactant-Rich Phase Volume Fraction (φ_s) of the CPE Process Performance[a]

[S]/% (by weight)	E %	C_f	φ_s
1	41.8	13.97	0.03
2	61.6	15.4	0.04
3	80.24	16.05	0.05
4	88.87	14.81	0.06
5	100	14.29	0.07
6	87.26	9.69	0.09
7	79.48	7.95	0.10

[a] $[H_2L] = 2 \cdot 10^{-3}$ mol·L^{-1}. $[Na_2SO_4] = 0.49$ mol·L^{-1}. pH = 9. T = 65 °C.

concentration of 5 % (by weight) was selected as the optimum concentration for the quantitative extraction of copper. At lower concentrations, the yield of the extraction of the complexes was low because there are few molecules of the surfactant to entrap the complex quantitatively. At higher concentrations of Triton X-100, the yields decrease. This result might be related to the presence of the high quantity of surfactant, resulting in an increment in the volume of the surfactant-rich phase, which in fact increases the loss of the complex in the aqueous phase and minimizes the extractability. Besides, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity.

Concentration Factor, C_f, and Phase Volume Fraction, φ_s. The performance of a CPE process can also be assessed by its surfactant-rich phase volume fraction, φ_s, and concentration factor, C_f. These two parameters are defined in the "Calculation sections". Table 4 illustrates the variation of φ_s, C_f, and extraction efficiency (% E) of copper(II) of the Triton X-100/Na_2SO_4/H_2L CPE process with respect to the concentration of the nonionic surfactant. At a fixed sample volume, C_f initially increases and then decreases as the concentration of the nonionic surfactant increased.

In general, with less surfactant in the solution, the volume of the surfactant-rich phase thus formed becomes smaller, and hence, the concentration of the extracted analyte in the surfactant-rich phase increases. However, further reduction of surfactant concentration will eventually lead to insufficient surfactant in the surfactant-rich phase to efficiently extract the analyte, causing a drop in analyte extraction. From Table 4, it is seen that a concentration of nonionic surfactant of 3 % (by weight) provides a high concentration factor ($C_f = 16.05$) and extraction efficiency (E % = 80 %) with an acceptable surfactant-rich phase volume fraction of $\varphi_s = 0.05$ ($0.02 \le \varphi_s \le 0.1$).[6] On the other hand, the results show that the volume fraction, φ_s of the surfactant increases with increasing concentration of the surfactant TX-100. A similar behavior was observed in other CPE processes using nonionic and ionic surfactants.[55−57]

Composition of the Extracted Species. To determine the composition of the extracted copper(II)−H_2L complex, the Yoe−Jones mole ratio method[58] was carried out by heating at 65 °C for 3 h at pH 9 (Figure 7). The extractant concentration (H_2L) was changed from ($1.3 \cdot 10^{-4}$ to 10^{-2}) mol·L^{-1} with a constant copper(II) concentration ($1.57 \cdot 10^{-3}$ mol·L^{-1}). When the mole ratio of copper(II) to H_2L was above 1, the value of % R was constant, suggesting that copper(II) should be extracted by H_2L in the surfactant-rich phase with the stoichiometry of 1:1. From this result and taking into account that the extraction of Cu(II) proceeds via a cation exchange mechanism in the pH range 6 to 9, the extraction process may be represented by the following equation

$$Cu^{2+}_{(w)} + H_2L_{(w)} \rightleftharpoons CuL_{(s)} + 2H^{+}(w)$$

((w) denotes the spices in the aqueous phase and (s) refers to the spices in the surfactant-rich phase).

Conclusion

In this study, the combined advantages of the cloud point extraction process and the use of a polydentate Schiff base N,N'-bis(salicylideneaminoethyl)amine as extractant were utilized for extraction of copper(II) in aqueous sulfate solutions. From the results obtained, the following conclusions can be drawn: (i) The cloud point extraction is an easy, practical, and very promising process for the extraction and separation of copper(II). It offers an inexpensive and nonpolluting alternative to other separation extraction processes. (ii) The N,N'-bis(salicylideneaminoethyl)amine proved to be an efficient chelating extractant for quantitative cloud point extraction of copper(II). The simple synthesis, the formation of stable complexes, and consistency with the cloud point extraction process are the major advantages of the use of this type of extractant in cloud point extraction of copper. (iii) The extent of extraction is markedly influenced by the pH of the aqueous solution and the concentration of the extractant and nonionic surfactant. (iv) The optimized experimental parameters for quantitative extraction (R % = 100 %) are: (1) $2 \cdot 10^{-3}\ \mathrm{mol \cdot L^{-1}}$ of extractant; (2) 5 % (by weight) surfactant; (3) pH of 9; and (4) temperature of 65 °C. (v) The good biodegradability of the nonionic surfactant[1] and the easy disposal of the small volume fraction of the aqueous surfactant-rich phase[6] are particularly attractive for processes adopting green chemistry practices.

Although the suggested CPE system offers good extraction ability for copper(II), much more work is obviously needed to fully understand the CPE process. These include the following: (1) elucidation of the nature of the interaction and binding between the extracted species with this kind of extractant and the nonionic surfactant micelles; (2) separation of copper ions from copper complex-entrapped surfactant and, hence, the regeneration of the extractant by the application of the pH-switching process; and (3) increase in the selectivity of the CPE process with this type of polydentate Schiff base extractant to accomplish extraction of copper from multimetal solutions.

Literature Cited

(1) Schramm, L. L.; Stasiuk, E. N.; Marangoni, D. G. Surfactants and their applications. *Ann. Rep. Prog. Chem. Sect. (C).* **2003**, *99*, 3–48.

(2) Mittal, K. L.; Lindman, B., Eds. *Surfactants in solution*; Plenum Press: New York, 1984; p705.

(3) Pellizzetti, E.; Pramauro, E. Analytical application of organized molecular assemblies. *Anal. Chim. Acta* **1985**, *169*, 1–29.

(4) Corti, M.; Minero, C.; Degiorgio, V. Cloud point transition in nonionic micellar Solutions. *J. Phys. Chem.* **1984**, *88*, 309–317.

(5) McIntire, G. L. Micelles in Analytical Chemistry. *Crit. Rev. Anal. Chem.* **1990**, *21*, 257–278.

(6) Hinze, W. L. *Annual Report No. 92−269*, Wake Forest University, North Carolina, 1992; p 36.

(7) Watanabe, H.; Tanaka, H. A non-ionic surfactant as a new solvent for liquid extraction of Zinc (II) with 1-(2-pyridylazol)-2-naphlhol. *Talanta* **1978**, *25*, 585–589.

(8) Koshy, L.; Saiyad, A. H.; Rakshit, A. K. The effects of various foreign substances on the cloud point of Triton X 100 and Triton X 114. *Colloid Polym. Sci.* **1996**, *274*, 582–587.

(9) Schott, H. Effect of inorganic additives on solutions of nonionic surfactants. XIV. Effect of chaotropic anions on the cloud point of octoxynol 9 (triton X-100). *J. Colloid Interface Sci.* **1997**, *189*, 117–122.

(10) Schott, H. A linear relation between the cloud point and the number of oxyethylene units of water-soluble nonionic surfactants valid for the entire range of ethoxylation. *J. Colloid Interface Sci.* **2003**, *260*, 219–224.

(11) Schott, H.; Royce, A. E. Effect of inorganic additives on solutions of non-ionic surfactants. VII: Cloud point shift values of individual ions. *J. Colloid Interface Sci.* **1984**, *98*, 196–201.

(12) Schott, H.; Han, S. K. Effect of Inorganic Additives on Solutions of Nonionic Surfactants II. *J. Pharm. Sci.* **1975**, *64*, 658–664.

(13) Schott, H. Comparing the surface chemical properties and the effect of salts on the cloud point of a conventional nonionic surfactant, octoxynol 9 (Triton X-100), and of its oligomer, tyloxapol (Triton WR-1339). *J. Colloid Interface Sci.* **1998**, *205*, 496–502.

(14) Sicilia, D.; Rubio, S.; Pérez-Bendito, D.; Maniasso, N; Zagatto, E. A. G. Anionic surfactants in acid media: a new cloud point extraction approach for the determination of polycyclic aromatic hydrocarbons in environmental samples. *Anal. Chim. Acta* **1999**, *392*, 29–38.

(15) Nascentes, C. C.; Aurélio, M.; Arruda, Z. Cloud point formation based on mixed micelles in the presence of electrolytes for cobalt extraction and preconcentration. *Talanta* **2003**, *61*, 759–768.

(16) Ohashi, A.; Tsugushi, A.; H. Imura, H.; Ohashi, K. Synergistic Cloud Point Extraction Behavior of Aluminum (III) with 2-Methyl-8-quinolinol and 3,5-Dichlorophenol. *Anal. Sci.* **2004**, *20*, 1091–1093.

(17) Afkami, A.; Bahram, M.; Gholami, S. Z. Micelle-mediated extraction for the spectrophotometric determination of nitrite in water and biological samples based on its reaction with p-nitroaniline in the presence of diphenylamine. *Anal. Biochem.* **2005**, *336*, 295–299.

(18) Hinze, W. L.; Pramauro, E. A critical-review of surfactant-mediated phase separation (cloud point extraction)-theory and applications. *Crit. Rev. Anal. Chem.* **1993**, *24*, 133–177.

(19) Stalikas, C. D. Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis. *Trends Anal. Chem.* **2002**, *21*, 343–355.

(20) Hadj Youcef, M.; Benabdallah, T.; Ilikti, H. A study on copper (II) extraction from sulphate medium via cloud- point extraction with N-salicylideneaniline ligand in presence of non-ionic surfactant. *Can. J. Anal. Sci. Spectrosc.* **2006**, *51*, 267–278.

(21) Tani, H.; Kamidate, T.; Watanabe, H. Micelle-mediated extraction. *J. Chromatogr. A* **1997**, *780*, 229–241.

(22) Tani, H.; Kamidate, T.; Watanabe, H. Aqueous micellar two-phase systems for protein separation. *Anal. Sci.* **1998**, *14*, 875–888.

(23) Li, J.; Chen, B.-H. Equilibrium partition of polycyclic aromatic hydrocarbons in a cloud-point extraction process. *J. Colloid Interface Sci.* **2003**, *263*, 625–632.

(24) Akita, S.; Rovira, M.; Sastre, A. M.; Takeuchi, H. Cloud Point extraction of gold (III) with non-ionic surfactant. Fundamental and its application to gold recovery from printed substrate. *Sep. Sci. Technol.* **1998**, *33*, 2159–2177.

(25) Luconi, M. O.; Fernanda Silva, M.; Olsina, R. A.; Fernandez, L. P. Cloud point extraction of lead in saliva via use of nonionic PONPE 7.5 without added chelating agents. *Talanta* **2000**, *51*, 123–129.

(26) Manzoori, J. L.; Karim-Nezhad, G. Development of a cloud point extraction an preconcentration method for Cd and Ni prior to flame atomic absorption spectrometric determination. *Anal. Chim. Acta* **2004**, *521*, 173–177.

(27) Garrido, M.; Di-Nezio, M. S.; Lista, A. G.; Palomeque, M.; Fernadez-Band, B. S. Cloud- Point extraction/preconcentration On-Line Fia Method For Mercury Determination. *Anal. Chim. Acta* **2004**, *502*, 173–177.

(28) Teo, K. C.; Chen, J. Determination of manganese in water samples by flame atomic absorption spectrometry after cloud point extraction. *Analyst* **2001**, *126*, 534–537.

(29) Saitoh, T.; Kimura, Y.; Kamidata, T.; Watanabe, H.; Haragichi, K. Distribution Equilibria of Metal Chelates with Thiazolylazo Dyes between Two Phases Formed from an Aqueous Micellar Solution of a Nonionic Surfactant. *Anal. Sci.* **1989**, *5*, 577–581.

(30) Chen, J.; Teo, K. C. Determination of cobalt and nickel in water samples by flame atomic absorption spectrometry after cloud point extraction. *Anal. Chim. Acta* **2001**, *434*, 325–330.

(31) Nascentes, C. C.; Arruda, M. A. Z. Cloud point formation based on mixed micelles in the presence of electrolytes for cobalt extraction and preconcentration. *Talanta* **2003**, *61*, 759–768.

(32) Doroschuck, V. O.; Lelyushok, S. O.; Ishchenko, V. B.; Kulichenko, S. A. Flame atomic absorption determination of manganese (II) in natural water after cloud point extraction. *Talanta* **2004**, *64*, 853–856.

(33) Yuan, C. G.; Jiang, G. B.; Cai, Y. O.; He, B.; Liu, J. F. Determination of cadmium at the nanogram per liter level in seawater by graphite furnace AAS using cloud point extraction. *At. Spectrosc.* **2004**, *25*, 170–176.

(34) Shimerani, F.; Abkenar, S. D.; Jamali, M. R. Determination of cadmium(II), copper(II) and zinc (II) in water samples by flame atomic absorption spectrometry after cloud point extraction. *Indian J. Chem., Sect. A* **2005**, *44*, 1211–1214.

(35) Manzoori, J. L.; Bavili, A. T. Cloud point preconcentration and flame atomic absorption spectrometric determination of Cd and Pb in human hair. *Anal. Chim. Acta* **2002**, *470*, 215–221.

(36) Manranhao, T. D.; Borges, D. L. G.; DaVeiga, M. A. M. S.; Curtius, A. J. Cloud point extraction for the determination of cadmium and lead in biological samples by graphite furnace atomic absorption spectrometry. Spectrochim. *Spectrochim. Acta, Part (B)* **2005**, *60*, 667–672.

(37) Spinu, C.; Kriza, A. Co(II), Ni(II) and Cu(II) Complexes of bidentate Schiff bases. *Acta Chim. Slov.* **2000**, *47*, 179–185.

(38) Benabdallah, T.; Al-Taiar, A. H.; Reffas, H. Spectrophotometric Studies of the Behaviour of Multidentate Schiff Base Ligands with Copper (II) in Methanol Solution. *South. Afr. J. Chem.* **2004**, *57*, 33–36.

(39) Ohashi, Y. Excitation Energy Dependence of Transient Absorptions of [*N*,*N*′-*o*-Phenylenebis(salicylideneaminato)]cobalt(II) in DMF Solution. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1319–1324.

(40) Cimmerman, Z.; Galic, N.; Bosner, B. The Schiff bases of salicylaldehyde and aminopyridines as highly sensitive analytical reagents. *Anal. Chim. Acta* **1997**, *343*, 145–153.

(41) Hadj Youcef, M.; Barkat, D.; Benabdallah, T. Behaviour Study of Some Bidentate o- Hydroxy Schiff Base Extractants in The Removal of Copper (II) by Solvent Extraction Technique. *J. Saudi Chem. Soc.* **2006**, *10*, 15–20.

(42) Shemirani, F.; Abkenar, S. D.; Mirroshandel, A. A.; Niasari, M. S.; Kozania, R. R. Preconcentration and speciation of chromium in water samples by atomic absorption spectrometry after cloud-point extraction. *Anal. Sci.* **2003**, *19*, 1453–1456.

(43) Sone, K.; Fukuda, Y. *Inorganic Thermochromism (Inorganic Chemistry Concept)*; Springer: Heidelberg, 1987; Vol. 10.

(44) Hirayama, N.; Taga, J.; Oshime, S.; Honjo, T. Sulfonamide-type di-Schiff base ligands as chelate extraction reagents for divalent metal cations. *Anal. Chim. Acta* **2002**, *466*, 295–301.

(45) Agarwal, A. K.; Agarwal, S.; Singh, N.; Kansal, B. D. Copper(II), nickel(II) and cobalt(II) complexes of dibasic tridentate Schiff bases. *J. Chin. Chem. Soc.* **1980**, *29*, 113–118.

(46) Carvalho, B. L.; Briganti, G. Lowering of the miscibility gap in the dioctanoylphosphatidylcholine-water system by addition of urea. *J. Phys. Chem.* **1989**, *93*, 4282–4286.

(47) Akita, S.; Takeuchi, H. Cloud-Point Extraction of Organic Compounds from Aqueous Solutions with Nonionic Surfactant. *Sep. Sci. Technol.* **1995**, *30*, 833–846.

(48) Mata, J. P. Hydrodynamic and Clouding Behavior of Triton X-100 + SDS Mixed Micellar Systems in the Presence of Sodium Chloride. *J. Dispers. Sci. Technol.* **2006**, *2*, 49–54.

(49) Laughlin, R. G. *The Aqueous Phase Behavior of Surfactants*; Academic Press Inc., 1994.

(50) Valaulikar, B. C.; Manohar, C. The mechanism of clouding in triton X-100: the effect of Additives. *J. Colloid Interface Sci.* **1985**, *108*, 403–406.

(51) Lins De Barros Neto, E.; Canselier, J. P. Cloud-point behaviour and phase separation in liquid-coacervate extraction of phenol. *Jorn. Com. Esp. Deterg.* **1998**, *28*, 433–444.

(52) Saito, H.; Shinoda, K. The solubilization of hydrocarbons in aqueous solutions of non- ionic surfactants. *J. Colloid Interface Sci.* **1967**, *24*, 10–15.

(53) Pramauro, E. Concentration and removal of chloroaromatic pollutants using micelle- mediated methods. *Ann. Chim.* **1990**, *80*, 101–109.

(54) Fendler, J. H. Atomic and molecular clusters in membrane mimetic chemistry. *Chem. Rev.* **1987**, *87*, 877–899.

(55) Silva, M. F.; Fernandez, L.; Olsina, R. A.; Stacchiola, D. Cloud point extraction, preconcentration and spectrophotometric determination of erbium(III)-2-(3,5-dichloro- 2-pyridylazo)-5-dimethylaminophenol. *Anal. Chim. Acta* **1997**, *342*, 229–238.

(56) Sicilia, D.; S.Rubio, S.; Pérez-Bendito, D. Evaluation of the factors affecting extraction of organic compounds based on the acid-induced phase cloud point approach. *Anal. Chim. Acta* **2002**, *460*, 13–22.

(57) Sicilia, D.; Rubio, S.; Pérez-Bendito, D.; Maniasso, N.; Zagatto, E. A. G. Anionic surfactants in acid media: a new cloud point extraction approach for the determination of polycyclic aromatic hydrocarbons in environmental samples. *Anal. Chim. Acta* **1999**, *392*, 29–38.

(58) Christian, G. D.; O'Reilly, J. E., Eds. *Instrumental Analysis*; Allyn and Bacon: Boston, 1986; p 186.

Received for review June 22, 2009. Accepted November 13, 2009.

JE900522G