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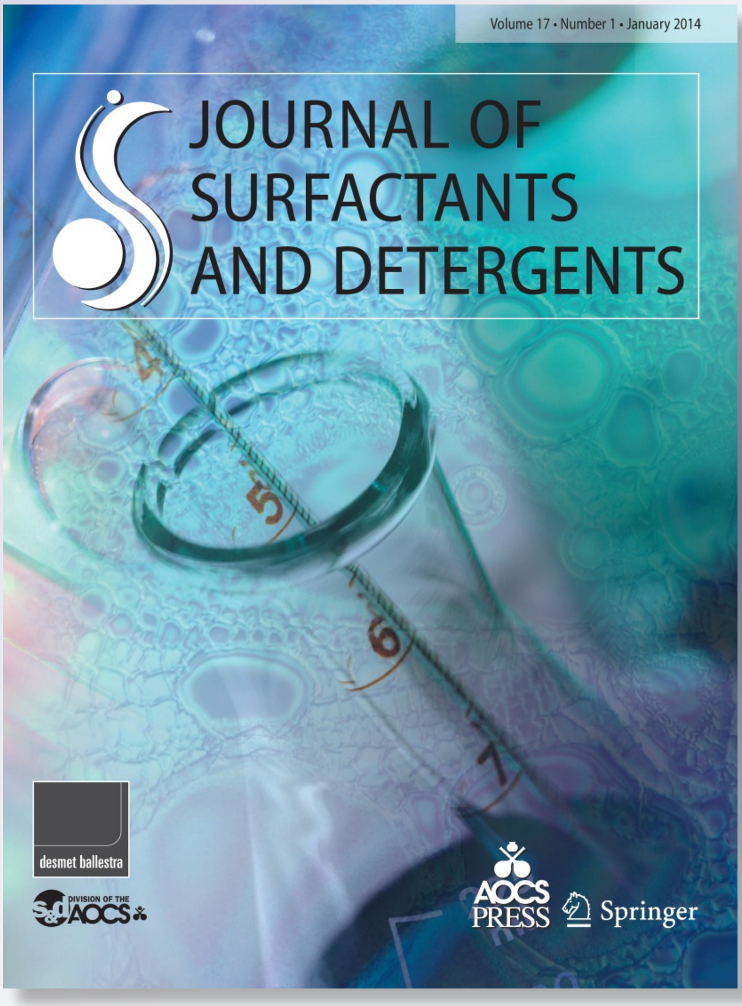

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ORIGINAL ARTICLE

Removal of Copper(II) from a Concentrated Sulphate Medium by Cloud Point Extraction Using an *N*,*N*′-Bis(salicylaldehyde) Ethylenediimine Di-Schiff Base Chelating Ligand

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Abstract Various chelating ligands have been investigated for the cloud point extraction of several metal ions. However, limited studies on the use of the Schiff base ligands have been reported. In this work, cloud point extraction behavior of copper(II) with *N*,*N*′-bis(salicylaldehyde)Ethylenediimine Schiff base chelating ligand, (H_2SALEN), was investigated in aqueous concentrated sulphate medium. The extraction process used is based on the formation of hydrophobic H_2SALEN–copper(II) complexes that are solubilized in the micellar phase of a non-ionic surfactant, i.e. ethoxylated (9.5EO) *tert*-butylphenol. The copper(II) complexes are then extracted into the surfactant-rich phase above cloud point temperature. Different parameters affecting the extraction process of Cu(II), such as equilibrium pH, extractant concentration, and non-ionic surfactant concentration were explored. The extraction of Cu(II) was studied in the pH range of 2–11. The results obtained showed that it was profoundly influenced by the pH of the aqueous medium. The concentration factor, C_f, of about 17 with extraction efficiency of $E\,\% \approx 100$ was achieved. The stoichiometry of the extracted complex of copper(II) was ascertained by the Yoe–Jones method to give a composition of 1:1 (Cu:H_2L). The optimum conditions of the extraction-removal have been established as the following: (1) 1.86×10^{-3} mol/L ligand; (2) 3 wt% surfactant; (3) pH of 8 (4) 0.5 mol/L Na_2SO_4 and (5) temperature of 60 °C.

Keywords Cloud point extraction · Copper(II) · Schiff base chelating ligand · Sulphate media · *N*,*N*′-bis(salicylaldehyde)Ethylenediimine · Alkyl phenol ethoxylate

Introduction

Solvent extraction is one of the most effective separation processes, and is widely used for the separation and recovery of several heavy metal ions [1]. However, this technique has some restrictions and presents drawbacks due to the use of expensive, hazardous and flammable organic solvents. An interesting alternative to traditional solvent extraction is cloud point extraction (CPE), initially developed by Watanabe and co-workers [2].

The process of cloud point extraction is based on the property that an aqueous solution of non-ionic surfactant forms micelles and becomes turbid when heated to a temperature known as the cloud point temperature (CPT). Above this temperature, the micellar solution separates in a surfactant-rich phase of a small volume and diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (CMC). Accordingly, any component originally present in the solution that interacts with surfactant aggregates (micelles) either directly or after chelation by hydrophobic extractant can thus be separated and concentrated in the small surfactant-rich phase [3–6].

The cloud point temperature of the non-ionic surfactant can be affected by many factors such as its own concentration and the number of ethylene oxide units in its molecules as well as additives like electrolytes [7–11].

As novel separation process, CPE offers many advantages over traditional solvent extraction. Indeed, this process uses water and reduces the consumption of and

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exposure to a solvent. Moreover, CPE can contribute to higher recovery efficiency and large concentration factor since the presence of the surfactant can minimize losses of analytes [12–15].

The cloud point extraction has been applied for the extractive preconcentration, separation and/or purification of various inorganic species and organic compounds from different aqueous matrices [16–21].

Extractions of heavy metal ions by CPE have been successfully achieved using various chelating ligands, such as dithizone [22, 23], 1-(2-thiazolylazo)-2-naphthol (TAN) [24–26], 1-(2-pyridylazo)-2-naphthol (PAN) [13, 27], 8-hydroxyquinoline (HQ) [28], di(2-ethylhexyl)phosphoric acid (D_2EHPA) [29], and calixarenes [30].

The Schiff bases constitute another family of powerful chelating ligands. Indeed, they are well known as extractants that are easy to be synthesized and have structural rigidity and stability, and they are also used in selective solvent extraction of several kinds of metal cations [31–35]. However, they have been hardly utilized in cloud point extraction [36–38]. In this context, and as sulphate is a common aqueous medium in many industrial applications, the present work is focused on the study of the cloud point extraction of copper(II) from sulphate media employing the polydentate Schiff base, *N*,*N*′-bis(salicylaldehyde)Ethylenediimine, (H_2SALEN), as a chelating ligand and ethoxylated (9.5EO) *tert*-octyl phenol as a non-ionic surfactant (Fig. 1). The tetradentate Schiff base (H_2L), which contains in its structure mixed O and N type donor atoms, was chosen as the chelating extractant because it forms more stable complexes than either O–O or N–N types [39]. Another advantage for selecting this extractant is its stability in dilute acidic solutions and high hydrophobicity. The copper(II) ion was used as a model metal ion because it constitutes a perpetual toxic threat to the environment and represents a waste of resources. It is also found with other pollutant materials in the waste pickle liquor of the brass industry. Hence, the extraction-removal of this metal coincides with the goals of a waste management strategy since it could provide some economical revenue and simultaneously solve a pollution problem.

In addition to the use of *N*,*N*′-bis(salicylaldehyde)Ethylenediimine extractant in cloud point extraction and its application to the removal of copper, the extraction process was optimized by varying some parameters such as pH, chelating ligand concentration and surfactant concentration. On the other hand, the results obtained were compared with those previously reported in the literature using other chelating ligands from the point of view of the extraction efficiency, concentration factor and separation temperature. Finally, to the best of our knowledge, no such study has been reported on this chelating extractant with copper(II) from an aqueous concentrated sulphate medium.

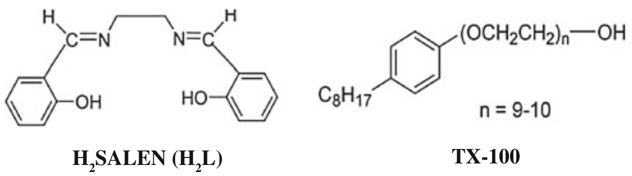

Fig. 1 Structures of chelating ligand and surfactant used

Experimental

Materials

All reagents used were of the highest available purity and analytical grade. The non ionic surfactant *tert*-octyl phenol ethoxylate with 9–10 oxyethylene units (Triton X-100) abbreviated as TOP9.5EO in what follows (Fig. 1) 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 using an ice bath. What is more, this reagent is not very expensive. The initial concentration of analyte, 1.57×10^{-3} mol/L, was prepared by dissolving $CuSO_4\ 5H_2O$ (Fluka) in distilled water. Na_2SO_4 (Prolabo) was used to aid phase separation $[(Na_2SO_4] = 0.49$ mol/L] and H_2SO_4 (Merck) and NaOH (Prolabo) to adjust the pH. A stock solution of chelating extractant was prepared by dissolving appropriate amounts of a Schiff base in absolute ethanol. The Schiff's base *N*,*N*′-bis(salicylaldehyde)Ethylenediimine was synthesized and purified as described below.

Synthesis of the Chelating Extractant

The tetradentate extractant Schiff base *N*,*N*′-bis(salicylaldehyde)Ethylenediimine (H_2SALEN) (Fig. 1) was prepared according to the literature following a well-known method, as follows [40]: A solution of ethylenediimine (0.1 mol) in 50 mL ethanol was slowly added to 0.2 mol salicylaldehyde in 50 mL ethanol. After 2 h at 60 °C under reflux, the precipitate was collected by filtration. The solid product was recrystallized from ethanol and dried for 24 h under reduced pressure at room temperature. The purity was checked by IR and ^1H-NMR spectra.

H_2SALEN: yield 98 %; IR (KBr pellet, cm^{-1}): 1634(C = N). ^1H-NMR (400 MHz, $CDCl_3$, δ/ppm): 13.1 (2H, *s*, OH), 8.47 (2H, *s*, CH = N), 6.90–40 (8H, *m*, aromatic-H), 4.01 (4H, *s*, $=N–(CH_2)_2–$).

The Schiff base is insoluble in water and sparingly soluble in TOP9.5EO. Thus, to increase its solubility in the micellar solution, 2 mL of ethanol was added to each 25-mL sample as an assistant solvent. Moreover, this chelating ligand is very stable in the solid state and in ethanol. On the other hand, it has two nitrogen atoms and hydroxyl groups in complexation with copper.

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 with an accuracy of 0.02 pH units, using a Schott-Geräte model CG820 pH-meter, equipped with a glass-combination electrode. A thermostated bath maintained at the desired temperatures was employed for cloud point experiments.

General Procedures

Cloud Point Determination

The temperature at which the cloud point phenomenon occurs was determined by the method reported by Carvalho et al. [41]. 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 thermostated 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

First, 25 mL of the analytical solution mixture containing 1.57×10^{-3} mol/L Cu(II), 1.86×10^{-3} mol/L Schiff base, 3 wt% TOP9.5EO, and 0.5 mol/L of Na_2SO_4 was adjusted to the appropriate pH value (pH = 8) with NaOH. Then, the system was stirred for 5 min in a shaker and transferred to a 10-mL test tube with a graduated line. After that, the test tube was kept in a constant temperature bath for 6 h at 60 °C. The copper concentration was determined spectrophotometrically in the dilute aqueous phase. The volume of the surfactant-rich phase was registered to an accuracy within ±0.1 mL units.

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:

$$D_M = \frac{[M]_s}{[M]_w} \quad (1)$$

where $[M]_s$ and $[M]_w$ are the final metal concentrations in the surfactant-rich phase and in the aqueous phase, respectively.

The efficiency of process, E %, can be expressed as:

$$E = 100 \frac{D_M}{D_M + \frac{V_w}{V_s}} \quad (2)$$

where, the V_w and V_s refer 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:

$$C_f = \frac{E}{100\ \varphi_s} \quad (3)$$

$$\varphi_s = \frac{V_s}{V_0} \quad (4)$$

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 a Triton X-100 Water System

The phase diagram of the non-ionic surfactant TOP9.5EO obtained in this study at different aqueous concentrations, ranging from 0.1 to 5 wt% is shown in Fig. 2. The shape of

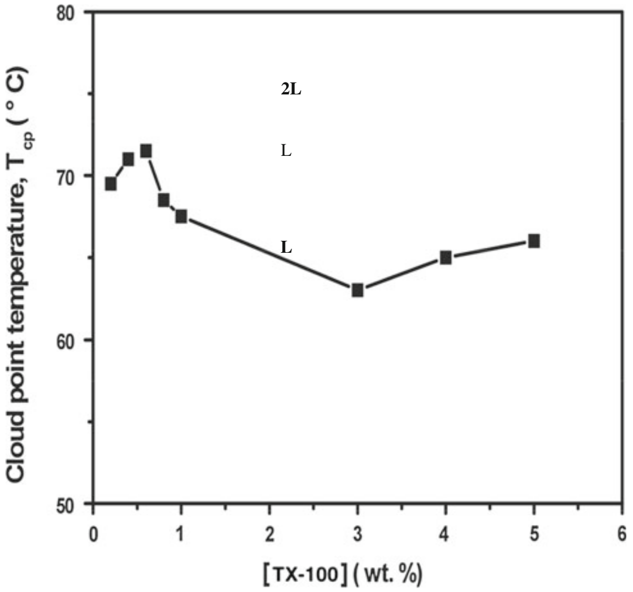

Fig. 2 Phase diagram of a TOP9.5EO—water–binary system. *L* one phase, *2L* two phases

the curve coincides with that expected for a typical non-ionic surfactant [42]. Below the curves, there are micellar solutions (1L), while two-phase regions co-exist above the curves (2L).

It has been mentioned by several authors that solutions of non-ionic surfactants generally can show different critical temperatures at similar concentrations depending upon the experimental conditions and purity of the amphiphiles [4]. Non-ionic polyoxyethylene 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 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 Fig. 3, the lowest cloud point temperature (T_{cp}) value determined for TOP9.5EO was 63 °C at a concentration of 3 wt%. Moreover, the cloud point temperature, $T_{cp} = 67$ °C, found at the surfactant concentration of 1 wt% was in good agreement with that reported by Mata [43], for a micellar solution of TritonX-100 without any additives.

Effect of Sodium Sulphate

The influence of adding Na_2SO_4 (0–0.5 mol/L) on the cloud point temperatures of the TOP9.5EO micellar solutions was examined at various surfactant concentrations. Figure 3 clearly demonstrates that the addition of sodium sulphate lowers the cloud point curve. This phenomenon can be conveniently explained in terms of an earlier dehydration of the ethoxylated chains due to the presence of inorganic ions (sodium sulphate in this case: Na^+ and SO_4^{-2}) competing for the interaction with the water molecules, i.e. a “salting–out” effect.

Also, it seems that sodium sulphate lowers the cloud point by a continuous medium change, more than by direct interaction with the ethoxy groups of the surfactant [42, 44–46].

Figure 3 shows how 0.5 mol/L of Na_2SO_4 is able to lower the cloud point of a 3 wt% Triton X-100 solution from 63 to 15 °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; this makes the separation of both dilute and surfactant rich phases easy in some non-ionic surfactant systems [2, 47].

Equilibrium Distribution Coefficients of Copper(II)

The cloud point extraction process of copper(II) by *N*,*N*′-bis(salicylaldehyde)Ethylenediimine dissolved in TOP9.5EO nonionic surfactant micellar solutions was investigated over a pH range of approximately 2–11. The concentrations of the ligand and TOP9.5EO were between 10^{-4} mol/L and 5×10^{-3} mol/L, and 0.8 and 5 wt%, respectively. The results of the equilibrium distribution coefficients, D_M of copper(II) between the dilute aqueous phase and surfactant-rich phase are presented in Tables 1, 2, 3. As shown in Table 1, it can be seen that the distribution coefficients of Cu(II) are higher in the basic pH

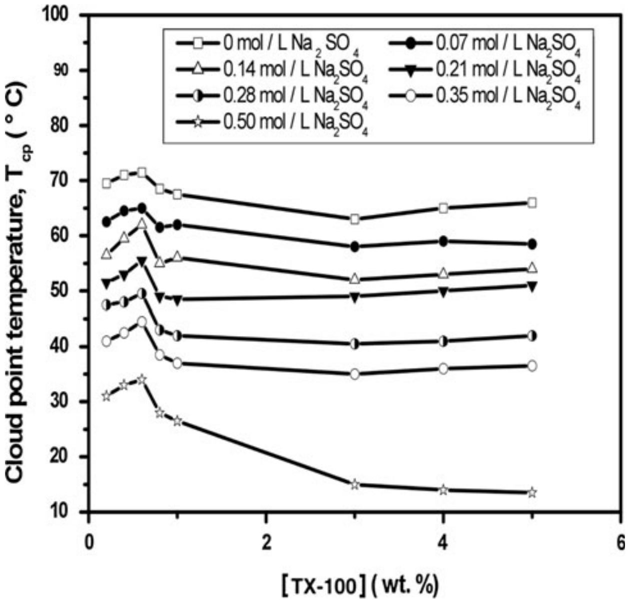

Fig. 3 Phase diagram of TOP9.5EO—water–Na_2SO_4 ternary systems

Table 1 Influence of equilibrium pH on distribution coefficient, D_M and extraction efficiency, *E* % of copper(II)

Equilibrium pH	D_M	*E* %
2.58	3	17
3.37	4	21
4.16	5	25.5
5.02	6	29
6.25	14	47
6.60	22	58
7.03	ND	100
7.53	ND	100
7.81	ND	100
8.02	ND	100
9.29	60	79
11.04	54	77

$[Cu^{2+}] = 1.57 \times 10^{-3}$ mol/L, $[H_2L] = 1.86 \times 10^{-3}$ mol/L, $[Na_2SO_4] = 0.5$ mol/L, $[TOP9.5EO] = 3$ wt%, $T = 60$ °C, $\varphi_s = 0.06$

ND Not determined because of high extractability range. Because *N*,*N*′-bis(salicylaldehyde)Ethylenediimine Schiff base is a basic extracting agent, copper(II), which is a common Lewis acidic metallic ion, was easily extracted from aqueous sulphate 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 mechanism. On the other hand, it is obvious from the data indicated in Tables 2 and 3 that the distribution coefficients of Cu(II) initially increase, and then decrease as the ligand and surfactant concentrations are increased. The increase in D_M is presumably due to the increase in the complex concentration and solubilization power of the non-ionic surfactant TOP9.5EO micelles. A similar conclusion has been reported by Favre-Réguillon et al. [48] for the cloud point extraction of lanthanides(III) by 8-hydroxyquinoline.

Optimization of the CPE Process

The efficiency of the cloud point extraction process of metals depends on a number of parameters, namely concentration of the extractant, concentration of the surfactant and solution pH. In the present study, these parameters were investigated in order to find the optimal operation conditions.

Effect of Solution pH

For ionisable solutes, the charge of the solute can greatly influence its extent of binding to a micellar assembly [49]. The ionic form of a molecule normally does not interact with and bind the micellar aggregate as strongly as does its neutral form. Indeed, adjustment of the micellar solution pH is the key-parameter when controlling experimental variables in the cloud point extraction process.

An interesting result was obtained in the study of the influence of solution pH on the extraction recovery of the studied cations. In this series of experiments, the solution pH was varied over the range of 2–11. The Triton X-100, *N*,*N*′-bis(salicylaldehyde)Ethylenediimine, copper, and Na_2SO_4 concentrations were kept constant at 3 wt%, 1.86×10^{-3} mol/L, 1.57×10^{-3} mol/L, and 0.5 mol/L, respectively. The experiments were carried out at a separation temperature of 60 °C. Table 1 shows the effect of pH on the extraction efficiencies of Cu(II) complexes. It can be seen that extraction was quantitative for copper(II) in the pH range 7–8. At lower pH values, the formation of complexes is not quantitative, and at higher pH values, the extraction starts to decrease. A similar pattern of the pH effect has been reported in the literature for the extraction of copper with different ligands such as 1-(2-pyridylazo)-2-naphthol (PAN), isoleucine and pyrogallol [50–52]. Therefore, based on these findings, an optimised pH of 8 was selected for the CPE system.

Effect of Chelating Ligand Concentration

In order to achieve the total extraction and preconcentration of copper(II), a series of experiments was carried out in which the other experimental variables, except extractant concentration, remained constant. Table 2 highlights the differences in the efficiencies at different extractant concentrations over the range of 10^{-4} to 5×10^{-3} mol/L. It is shown that the efficiencies (*E* %) of the extraction of copper increase with the concentration of the chelating extractant, *N*,*N*′-bis(salicylaldehyde)Ethylenediimine (H_2SALEN). An extractant concentration of 1.86×10^{-3} mol/L permitted us to achieve the total formation of the complex and about 100 % extraction efficiency. On the other hand, when an excess of extractant was used (3×10^{-3} mol/L), a decrease in the efficiency was observed (94 %). This behaviour can be explained because the molecules of

Table 2 Influence of initial concentration of extractant on the distribution coefficient, D_M and extraction efficiency, *E* % of copper(II)

$[H_2L]$/mol/L	D_M	*E* %
10^{-4}	4	21
2×10^{-4}	5	25
3×10^{-4}	12	44
5×10^{-4}	16	51
1.41×10^{-3}	208	93
1.86×10^{-3}	ND	100
3×10^{-3}	245.5	94
4×10^{-3}	232	94
5×10^{-3}	193	92.5

$[Cu^{2+}] = 1.57 \times 10^{-3}$ mol/L, $[Na_2SO_4] = 0.5$ mol/L, [TOP9.5EO] = 3 wt%, pH = 8, $T = 60$ °C, $\varphi_s = 0.06$

ND Not determined because of high extractability

Table 3 Influence of initial concentration of surfactant on the distribution coefficient, D_M and extraction efficiency, *E* % of copper(II)

TOP9.5EO/wt%	D_M	*E* %
0.8	55	53
1	206	86
2	497	95
3	ND	100
4	40	75
5	27	73

$[Cu^{2+}] = 1.57 \times 10^{-3}$ mol/L, $[H_2L] = 1.86 \times 10^{-3}$ mol/L, $[Na_2SO_4] =$ 0.5 mol/L, pH = 8, $T = 60$ °C

ND Not determined because of high extractability extractant are presumably trapped in the micelles, thus reducing the concentration of the complex. Finally, it should be pointed out that similar results were mentioned in other published studies concerning the cloud point extraction of copper and chromium with analogous Schiff base chelating ligands [36, 53].

Effect of Surfactant Concentration

The concentration of surfactant that is used in CPE is a critical parameter. A successful cloud point extraction would be that which maximizes the efficiency of extraction through minimizing the phase volume ratio, and thus maximizing its concentrating factor. To obtain the optimal concentration of TOP9.5EO, the effect of surfactant concentration on the extraction efficiency of the system was investigated over the range of 1–5 wt%. The results are shown in Table 3. A concentration of 3 wt% was selected as the optimum concentration for the extraction of copper. At concentrations below this value, the efficiency of the extraction of the complexes and efficiency of the process were low because there are few molecules of the surfactant to entrap the complex quantitatively. At concentrations higher than 3 wt% of TOP9.5EO, the efficiencies decrease because of the volume and viscosity increases of the surfactant phase. These results are in qualitative agreement with other literature reports investigating the effects of increases in surfactant concentration upon the extraction efficiency of several metal ions [18, 22, 26, 36, 53].

Concentration Factor, C_f and Phase Volume Fraction, φ_s

Performance of a CPE process can be also assessed by its surfactant rich-phase volume fraction, φ_s and concentration factor, C_f. These two parameters are defined in the.

"Calculations" Table 4 reflects the variation of φ_s, C_f, and extraction efficiency, *E* %, of copper(II) of the TOP9.5EO/Na_2SO_4/H_2SALEN CPE process with respect to the concentration of the non-ionic surfactant. At a fixed sample volume, C_f initially increases and then decreases as the concentration of the non-ionic surfactant increases.

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 in the 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 non-ionic surfactant of 1 wt% provides a high concentration factor ($C_f = 29$) and extraction efficiency ($E\ \% \approx 86\ \%$) with an acceptable surfactant-rich phase volume fraction of $\varphi_s = 0.03$ ($0.02 \le \varphi_s \le 0.1$) [54]. On the other hand, the results show that the volume fraction (φ_s) of the surfactant increases with increasing concentration of TOP9.5EO. Similar behaviour was observed in other CPE processes using non-ionic and ionic surfactants [12, 55, 56].

Stoichiometry of the Extracted Complexes

The mole ratio method, resulting in the so-called Yoe–Jones [57] plots, was used to determine the stoichiometry of the complex Cu(II)-H_2SALEN formed. The Yoe–Jones method was performed by heating a series of mixtures of solutions of copper sulphate and extractant at 60 °C for 6 h at pH = 8. The extractant concentration (H_2L) was varied from (10^{-4} to 5×10^{-3}) mol/L with a constant copper(II) concentration (1.57×10^{-3} mol/L). The mole ratio plot showed only one break, corresponding to the formation of a 1:1 complex between copper ion and H_2L (Fig. 4). From this result and taking into account that the extraction of Cu(II) proceeds via a cation exchange mechanism in the pH range 7–8, the extraction process may be represented by the following equation:

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

[(m) denotes the species in the homogeneous micellar solution; (w) and (s) refer to the species in the aqueous and surfactant-rich phases, respectively].

Comparison of Performance of the Present Chelating Ligand with Others for CPE of Copper(II)

For comparison purposes, the extraction efficiency (*E* %), the separation temperature (T_s) and the concentration factor (C_f) of the cloud point extraction of copper(II) by the proposed chelating ligand and those previously reported ligands are given in Table 5 [50, 51, 58–62]. As can be seen, the extraction efficiency (*E* %) and the concentration factor (C_f) of the present chelating ligand in

Table 4 Effect of the surfactant concentration on the concentration factor (C_f) and the surfactant-rich phase volume fraction (ϕ_s) of the CPE process performance: $[H_2L] = 1.86 \times 10^{-3}$ mol/L, $[Na_2SO_4] = 0.5$ mol/L, pH = 8, *T* = 60 °C

TOP9.5EO/wt%	*E* %	C_f	ϕ_s
0.8	53	26.5	0.02
1	86	29	0.03
2	95	24	0.04
3	100	17	0.06
4	75	11	0.07
5	73	8	0.09

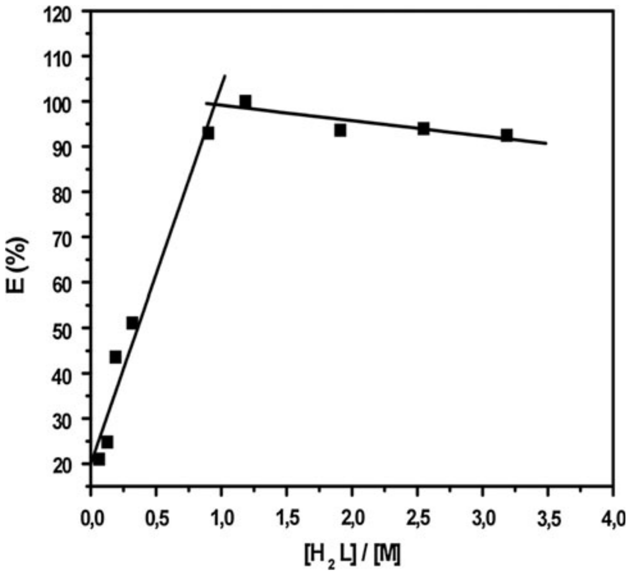

Fig. 4 Determination of the stoichiometry of the extracted copper(II)-H_2SALEN complex by the mole ratio method. $[Cu^{2+}] = 1.57 \times 10^{-3}$ mol/L; pH = 8; $[Na_2SO_4] = 0.5$ mol/L; $T = 60$ °C⇋

this work are superior to those of most other reported ligands. Besides, under the same experimental conditions, it seems that the system H_2SALEN/Triton X-100 exhibits a higher concentration factor and a lower separation temperature ($C_f = 29$, $T_s = 60$ °C) than the system H_2SALDIEN/TOP9.5EO ($C_f = 14$, $T_s = 65$ °C), reported in our previous study [53]. On the other hand, the separation, temperature (T_s) of the extraction process is comparable with, and in some cases lower than the reported ones [50, 51, 59, 62]. Finally, it should be emphasized that chemical structure and cloud point temperature of the non-ionic surfactant employed for extraction can seriously alter the separation temperature of the cloud point extraction of metals [63, 64].

Conclusions

In this study, the combined advantages of the cloud-point extraction process and the use of polydentate Schiff base *N*,*N′*-bis(salicylaldehyde)Ethylenediimine as a chelating ligand were utilized for the extraction of copper(II) in an aqueous sulphate medium. From the results obtained, the following conclusions can be drawn: (1) The cloud point extraction is an easy, practical and a very promising process for the extraction and separation of copper(II). It offers an inexpensive and non-polluting alternative to other separation extraction processes. (2) *N*,*N′*-bis(salicylaldehyde)Ethylenediimine proved to be an efficient chelating ligand 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 ligand in cloud point extraction of copper. (3) The extent extraction is markedly influenced by the pH of the aqueous solution, the concentration of the extractant and non-ionic surfactant. (4) The optimized experimental parameters for quantitative extraction ($E\,\% \approx 100\,\%$) are: (1) 1.86×10^{-3} mol/L of ligand; (2) 3 wt% surfactant; (3) pH of 8 and (4) temperature of 60 °C. (5) The environmental pollution is limited to a small amount of surfactant. This fact is particularly attractive because the “green chemistry” concept can be employed here.

Although the suggested CPE system offers a good extraction ability for copper(II), much more work is obviously needed to fully understand the CPE process. This includes the following: (1) Elucidation of the nature of the interaction and binding between the extracted species with this kind of extractant and the non-ionic 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

Table 5 Comparison of the performance of the present chelating ligand with others for the CPE of copper(II)

Ligand	Surfactant	*E* %	C_f	T_s	References
Monocarboxylic aromatic acids	OP-10	30–90	ND	75	[58]
MPKO	TOP7.5EO	100	30	45	[59]
1-PTSC	TOP7.5EO	97	25	50	[60]
Alizarin red	TOP7.5EO	96	21	70	[61]
Isoleucine	TOP9.5EO	96	22	65	[51]
Me-BDBD	TOP7.5EO	95	14	45	[62]
PAN	TOP7.5EO	96	16	50	[50]
H_2SALDIEN	TOP9.5EO	100	14	65	[53]
H_2SALEN	TOP9.5EO	100	29	60	This work

ND Not determined, *MPKO* methyl-2-pyridylketone oxime, *1-PTSC* 1-Phenylthiosemicarbazide, *Me-BDBD* 6-[2-(6-methyl-benzothiazolylazo)]-1,2-dihydroxy-3,5-benzenedisulfonic acid, *PAN* 1-(2-pyridylazo)-2-naphthol (PAN), *H_2SALDIEN* *N*,*N′*-bis(salicylideneaminoethyl)amine, *H_2SALEN* *N*,*N′*-bis(salicylidene)Ethylenediimine process; (3) increase the selectivity of the CPE process with this type of polydentate Schiff base extractant in order to accomplish extraction of copper from a multimetal solution.

Finally, further work is under way in our laboratory to generalize the cloud point extraction technique with this type of polydentate Schiff base ligand for the separation-removal of other heavy metals such as Ni(II), Cd(II) or Pb(II).

References

1. Rydberg J, Musikas C, Choppin GR (1992) Principles and Practice of Solvent Extraction. Marcel Dekker, New York
2. Watanabe H, Tanaka H (1978) A non-ionic surfactant as a new solvent for liquid extraction of Zinc (II) with 1-(2-pyridylazo)-2-naphthol. Talanta 25:585–589
3. Mittal KL, Lindman B (1984) Surfactants in solution (Lund Proceedings), vol 1. Plenum Press, New York
4. Corti M, Minero C, Degiorgio V (1984) Cloud point transition in nonionic micellar Solutions. J Phys Chem 88:309–317
5. McIntire GL (1990) Micelles in analytical chemistry. Crit Rev Anal Chem 21:257–278
6. Rosen MJ (1978) Surfactants and interfacial phenomena. Wiley-Interscience, New York
7. Koshy L, Saiyad AH, Rakshit AK (1996) The effects of various foreign substances on the cloud point of Triton X 100 and Triton X 114. Colloid Polym Sci 274:582–587
8. Schott H (1997) 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 189:117–122
9. Schott H (2003) 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 260:219–224
10. Schott H, Royce AE (1984) Effect of inorganic additives on solutions of non-ionic surfactants. VII: Cloud point shift values of individual ions. J Colloid Interface Sci 98:196–201
11. Materna K, Cote G, Szymanowski J (2004) Cloud point of aqueous solutions containing oxyethylated methyl dodecanoates: effects of surfactant hydrophilicity, nature of added electrolyte, and water activity. J Colloid Interface Sci 269:466–471
12. Sicilia D, Rubio S, Pérez-Bendito D, Maniasso N, Zagatto EAG (1999) Anionic surfactants in acid media: a new cloud point extraction approach for the determination of polycyclic aromatic hydrocarbons in environmental samples. Anal Chim Acta 392:29–38
13. Nascentes CC, Aurélio M, Arruda Z (2003) Cloud point formation based on mixed micelles in the presence of electrolytes for cobalt extraction and preconcentration. Talanta 61:759–768
14. Ohashi A, Tsugushi A, Imura H, Ohashi K (2004) Cloud point extraction behaviour of aluminum (III) with 2-methyl-8-quinolinol and 3,5-dichlorophenol. Anal Sci 20:1091–1093
15. Afkami A, Bahram M, Gholami SZ (2005) 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 336:295–299
16. Hinze WL, Pramauro E (1993) Critical-review of surfactant-mediated phase separation (cloud point extraction)-theory and applications. Crit Rev Anal Chem 24:133–177
17. Stalikas CD (2002) Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis. Trends Anal Chem 21:343–355
18. Hadj Youcef M, Benabdallah T, Ilikti H (2006) 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 51:267–278
19. Tani H, Kamidate T, Watanabe H (1997) Micelle-mediated extraction. J Chromatogr A 780:229–241
20. Li J, Chen BH (2003) Equilibrium partition of polycyclic aromatic hydrocarbons in a cloud-point extraction process. J Colloid Interface Sci 263:625–632
21. Materna K, Milosz I, Miesiac I, Cote G, Szymanowski J (2001) Removal of phenols from aqueous streams by the cloud point extraction technique with oxyethylated methyl dodecanoates as surfactants. Environ Sci Technol 35:2341–2346
22. Manzoori JL, Karim-Nezhad G (2004) Development of a cloud point extraction and preconcentration method for Cd and Ni prior to flame atomic absorption spectrometric determination. Anal Chim Acta 521:173–177
23. Garrido M, Di-Nezio MS, Lista AG, Palomeque M, Fernadez-Band BS (2004) Cloud-point extraction/preconcentration on-line FIA method for mercury determination. Anal Chim Acta 502:173–177
24. Teo KC, Chen J (2001) Determination of manganese in water samples by flame atomic absorption spectrometry after cloud point extraction. Analyst 126:534–537
25. Saitoh T, Kimura Y, Kamidata T, Watanabe H, Haragichi K (1989) Distribution equilibria of metal chelates with thiazolylazo dyes between two phases formed from an aqueous micellar solution of a nonionic surfactant. Anal Sci 5:577–581
26. Chen J, Teo KC (2001) Determination of cobalt and nickel in water samples by flame atomic absorption spectrometry after cloud point extraction. Anal Chim Acta 434:325–330
27. Doroschuck VO, Lelyushok SO, Ishchenko VB, Kulichenko SA (2004) Flame atomic absorption determination of manganese (II) in natural water after cloud point extraction. Talanta 64:853–856
28. Shimerani F, Abkenar SD, Jamali MR (2005) 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) 44:1211–1214
29. Ohashi A, Hashimoto T, Imura H, Ohashi K (2007) Cloud point extraction equilibrium of lanthanum(III), europium(III) and lutetium(III) using di(2-ethylhexyl)phosphoric acid and Triton X-100. Talanta 73:893–898
30. Mustafina A, Elistratova J, Burilov A, Knyazeva I, Zairov IR, Amirov R, Solovieva S, Konovalov A (2006) Cloud point extraction of lanthanide(III) ions via use of Triton X-100 without and with water-soluble calixarenes as added chelating agents. Talanta 68:863–868
31. Spinu C, Kriza A (2000) Co(II), Ni(II) and Cu(II) complexes of bidentate Schiff bases. Acta Chim Slov 47:179–185
32. Benabdallah T, Al-Taiar HA, Reffas H (2004) Spectrophotometric studies of the behaviour of multidentate Schiff base ligands with copper(II) in methanol solution. S Afr J Chem 57:33–36
33. Ohashi Y (1997) Excitation energy dependence of transient absorptions of [*N*,*N*′-*o*-phenylenebis(salicylideneaminato)]cobalt(II) in DMF solution. Bull Chem Soc Jpn 70:1319–1324
34. Cimerman Z, Galic N, Bosner B (1997) The Schiff bases of salicylaldehyde and aminopyridines as highly sensitive analytical reagents. Anal Chim Acta 343:145–153
35. Hadj Youcef M, Barkat D, Benabdallah T (2006) Behaviour study of some bidentate o-hydroxy Schiff base extractants in the removal of copper(II) by solvent extraction technique. J Saudi Chem Soc 10:15–20

36. Shemirani F, Abkenar SD, Mirroshandel AA, Niasari MS, Kozania RR (2003) Preconcentration and speciation of chromium in water samples by atomic absorption spectrometry after cloud-point extraction. Anal Sci 19:1453–1456
37. Shemirani F, Jamali MR, Kozani RR, Salavati-Niasari M (2006) Cloud point extraction and preconcentration for the determination of Cu and Ni in natural water by flame atomic absorption spectrometry. Sep Sci Technol 41:3065–3077
38. Baghban N, Shabani AMH, Dadfarnia S, Jafari AA (2009) Flame atomic absorption spectrometric determination of trace amounts of cobalt. J Braz Chem Soc 20:832–838
39. Sone K, Fukuda Y (1987) Inorganic Thermochromism. Springer, Heidelberg
40. Aggett J, Richardson RA (1970) Solvent extraction of copper(II) by Schiff's bases. Anal Chim Acta 50:269–275
41. Carvalho BL, Briganti G (1989) Lowering of the miscibility gap in the dioctanoyl phosphatidylcholine-water system by addition of urea. J Phys Chem 93:4283–4286
42. Laughlin RG (1994) The Aqueous Phase Behavior of Surfactants. Academic Press, London
43. Mata JP (2006) Hydrodynamic and clouding behavior of Triton X-100 + SDS mixed micellar systems in the presence of sodium chloride. J Dispers Sci Technol 27:49–54
44. Valaulikar BC, Manohar C (1985) The mechanism of clouding in Triton X100: the effect of Additives. J Colloid Interface Sci 108:403–406
45. De Barros Lins, Neto E, Canselier JP (1998) Cloud-point behaviour and phase separation in liquid-coacervate extraction of phenol. Jorn Com Esp Deterg 28:433–444
46. Saito H, Shinoda K (1967) The solubilization of hydrocarbons in aqueous solutions of non-ionic surfactants. J Colloid Interface Sci 24:10–15
47. Pramauro E (1990) Concentration and removal of chloroaromatic pollutants using micelle-mediated methods. Ann Chim 80:101–109
48. Favre-Réguillon A, Draye M, Lebuzit G, Thomas S, Foos J, Cote G, Guy A (2004) Cloud point extraction : an alternative to traditional liquid–liquid extraction for lanthanides(III) separation. Talanta 63:803–806
49. Fendler JH (1987) Atomic and molecular clusters in membrane mimetic chemistry. Chem Rev 87:877–899
50. Tang AN, Jiang DO, Yan XP (2004) Cloud point extraction preconcentration for capillary electrophoresis of metal ions. Anal Chim Acta 507:199–204
51. Liang P, Yang J (2010) Cloud point extraction preconcentration and spectrophotometric determination of copper(II) in food and water samples using amino acids as the complexing agent. J Food Comp Analysis 23:95–99
52. Shemirani F, Abkenar SD, Khatouni A (2004) Determination of lead and copper in water samples by flame atomic absorption spectrometry after cloud point extraction. Bull Korean Chem Soc 25:1133–1136
53. Reffas H, Benabdallah T, Hadj youcef M, Ilikti H (2010) Study on 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. J Chem Eng Data 55:912–918
54. Hinze WL (1992) Annual Report No. 92-269 P 36. Wake Forest University, North Carolina
55. Silva MF, Fernandez L, Olsina RA, Stacchiola D (1997) Cloud point extraction, preconcentration and spectrophotometric determination of erbium(III)-2-(3,5-dichloro-2-pyridylazo)-5-dimethylaminophenol. Anal Chim Acta 342:229–238
56. Sicilia D, Rubio S, Pérez-Bendito D (2002) Evaluation of the factors affecting extraction of organic compounds based on the acid-induced phase cloud point approach. Anal Chim Acta 460:13–22
57. Yoe JH, Jones JL (1944) Colorimetric determination of iron with disodium-1,2-dihydroxybenzene-3,5-disulphonate. Ind Eng Chem (Anal Ed) 16:111–115
58. Kulichenko SA, Doroschuk VO, Lelyoshok SO (2003) The cloud point extraction of copper(II) with monocarboxylic acids into non-ionic surfactant phase. Talanta 59:767–773
59. Ghaedi M, Shokrollahi A, Ahmadi F, Rajabi HR, Soylak M (2008) Cloud point extraction for the determination of copper, nickel and cobalt ions in environmental samples by flame atomic absorption spectrometry. J Hazard Mater 150:533–540
60. Citak D, Tuzen M (2010) A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry. Food and Chem Toxicol 48:1399–1404
61. Satiroglu N, Arpal C (2008) Cloud point extraction for determination of trace copper in water samples by flame atomic spectrometry. Microchim Acta 162:107–112
62. Lemos VA, Santos MS, Santos MJS, Vieira DR, Novaes CG (2007) Determination of copper in water samples by atomic absorption spectrometry after cloud point extraction. Microchim Acta 157:215–222
63. Quina FH, Hinze WL (1999) Surfactant-mediated cloud point extraction: an environmentally benign alternative separation approach. Ind Eng Chem Res 38:4150–4168
64. Frankewich RP, Hinze WL (1994) Evaluation an optimization of the factors affecting nonionic surfactant-mediated phase separations. Anal Chem 66:944–954

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