

CPE OF URANIUM (VI) USING IONIC LIQUID

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Abstract: Cloud point extraction (CPE) was used to extract uranium (VI) from an aqueous solution in acetate media. The methodology used is based on the formation of uranyl-ionic liquid (I) complexes and uranyl-D2EHPA soluble in a micellar phase of non-ionic surfactant (Triton X-100). The uranium (VI) complexes are then extracted into the surfactant-rich phase at ambient temperature. The ionic liquid (IL) used as a chelating agent was synthesized and characterized in this study. It is composed of N-butyl N'-triethoxy methyl imidazolium cation and diethylhexylphosphate (D2EHPA-H) as anion.

The effect of the IL on the extraction efficiency was studied in presence and in absence of IL's cation in acetate medium.

Keywords: *acetate medium, cloud-point extraction, ionic liquid, Triton X-100, uranium*

INTRODUCTION

Ionic liquids (ILs) have been accepted as a new green chemical revolution which excited both the academia and the chemical industries. ILs consists of bulky inorganic anions paired with highly asymmetric and diffusely charged organic cations, leading to disturbed molecular packing and lower melting points [1 – 2].

This new chemical group can reduce the use of hazardous and polluting organic solvents which leads to have a large variety of their applications such as: electrolytes in batteries, lubricants, plasticizers, solvents and catalysis in synthesis, matrices for mass spectroscopy, solvents to manufacture nanomaterials, gas absorption agents, and extractant agent in environmental chemistry [3].

Conventional techniques of metal ion removal from environmental matrices include the following processes: precipitation, solvent extraction which uses extensive amounts of organic solvents [4, 5], ion exchange [6], adsorption, electrochemical recovery, membrane separation [7] and other techniques that are currently used in treatment techniques [4]. These techniques may be ineffective because they sometimes fail to meet regulation levels for technical and/or economical reasons.

Alternatively, cloud point extraction (CPE) can be used for the extractive pre-concentration, separation and purification of metal ions, metal chelates, biomaterials and organic compounds [7, 8].

The present research paper describes the synthesis and the characterization of a novel ionic liquid molecule and its effect on uranium (VI) extraction efficiency.

The extraction condition studies such as the concentrations of triton X-100, D2EHPA and uranyl ions, and ionic strength, on the cloud point behavior, were investigated in our previous work [9].

EXPERIMENTAL

Instruments

Visible spectra were measured using SPECORD 210/plus UV–Visible spectrophotometer (Tlemcen University). A Bruker Advance 400 spectrometer was used for ^{13}C and ^1H NMR analysis (LCMT CAEN). TLC revelation was executed by Vilber Lourmat UV lamp ($2 \times 6\text{W}$) with two wavelengths (254 and 365 nm).

Reagents

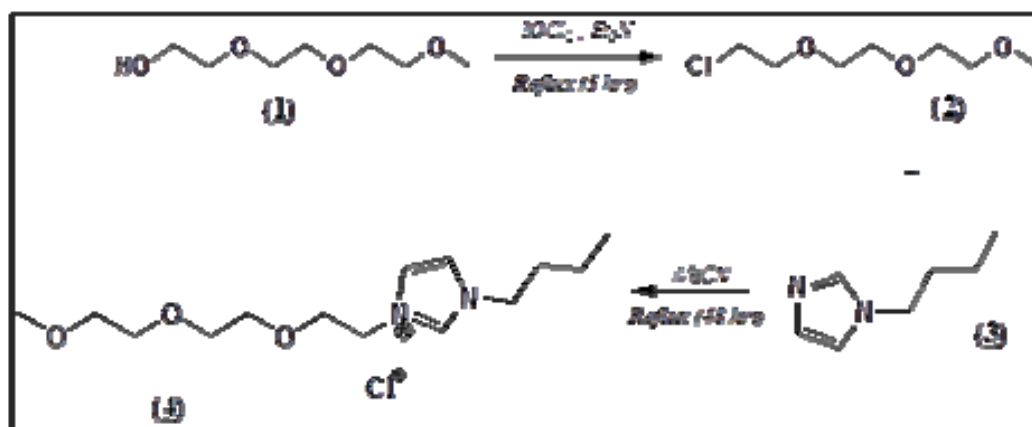
Uranyl acetate dehydrate was obtained from Merck. Triton X-100 (p-octylpolyethyleneglycolphenylether) and D2EHPA (2-(2-ethylhexyl) phosphoric acid) and triethyleneglycolmonoethylether were purchased from Fluka. 1-butylimidazole was obtained from Aldrich Chemistry. Arsenazo III {3,6-bis[(2-azonophenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulphonic acid} was supplied by Alfa Aesar (Johnson Matthey Company). Anhydrous sodium acetate was purchased from Reidel-de-Haen. Triethylamine and silica gel [60 F254, 0.04-0.063 mesh] were purchased from Sigma-Aldrich. Buffer solution at pH equal to 2.0 was prepared by Lambiote (Titrimorm).

Cyclohexane and ethylacetate were obtained from Carlo Erba. Acetonitrile was supplied by Acros Organics. Toluene was supplied by Analar Norma Pur.

Ionic liquid preparation

Synthesis of N-butyl N-(-2-(2-methoxyethoxy)ethoxy)ethyl imidazolium chloride (4)

The synthesis of the imidazolium salt (4) is described in scheme 1.



Scheme 1. N-butyl N- triethoxy methyl imidazolium chloride synthesis

Synthesis of 1-chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane (2)

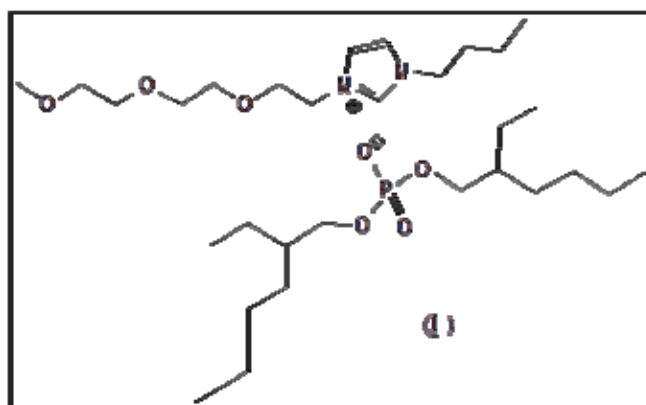
To triethyleneglycol monoethyl ether (1) (7.000 g, 0.042 mol), dried by azeotropic distillation of 300 mL dried toluene, 0.0105 mol of dried triethylamine were added, under stirring, followed by drop wise addition of thionyl chloride (9.993 g, 0.084 mol). The solution was refluxed for 5 h, cooled to room temperature, and filtered from triethyl amine hydrochloride salt. Filtrate was distilled by dryness [10], and then filtered on silica gel by using cyclohexane / ethylacetate mixture as eluent solvent. The filtration was followed by TLC. Once the separation was completed, the eluent was evaporated by dryness. Yield 72 %. R_f = 0.9 (eluent: cyclohexane/AcOEt = 50/50 %).

Synthesis of N-butyl N-(-2-(2-methoxyethoxy)ethoxy)ethyl imidazolium chloride (4)

A 50 mL, two-necked, round-bottomed flask is equipped, with a magnetic stirring heating oil bath, an internal thermometer adapter, and a reflux condenser. The flask is charged with 3.39 g (27.3 mmol, 1 equiv) of N-butylimidazole (3), 10 mL of acetonitrile and 5.00 g (27.3 mmol, 1equiv) of (2), and brought to a gentle reflux (80 °C internal temperature). The solution is heated under reflux for 48 h and then cooled to room temperature. The volatile material is removed from the resulting brown solution under reduced pressure [11]. The residue (7 mL) was taken up in water (2 mL) and washed three times with methylene chloride (3×10 mL). The organic layer was dried and concentrated in vacuum. The residue was obtained with 23.8%.

Preparation of the ionic liquid (I)

The ionic liquid (I) was prepared by substituting the chloride anion of (4) by D2EHPA anion as was shown in scheme 2. It was made by mixing an equimolar quantity (1:1) of each of (4) and D2EHPA. The mixture was brown limpid slightly viscous liquid.



Scheme 2. Ionic liquid structure (I)

Cloud point temperature study

Based on our results obtained in [9], we checked, in this paper, only the influence of the IL (I) on the cloud point temperature of Triton X-100 mixtures.

Influence of the ionic liquid concentration on the cloud point temperature

In graduated cylinders of 10 mL, introduce 10 % (v/v %) of triton X-100, different ionic liquid concentration (4×10^{-3} to 1×10^{-1} mol·L⁻¹) and water. The mixtures were stirred until complete components dissolutions, and then adjusted to 10 mL by adding water. The graduated cylinders were introduced into a thermostatic bath in order to study the mixtures, behaviors according temperature variations.

General extraction procedure

An aqueous solutions containing 10 % (v/v %) of triton X-100, 30 % (w/w.%) of AcONa, ionic liquid (I) at different molar concentrations and the solute (0.15 g·L⁻¹ uranium (U (VI)) in demineralized water were poured into graduated cylinders and kept at room temperature for 24 h to reach equilibrium and $T = 25$ °C. The volumes of both phases were registered and the dilute phase was spectrophotometrically analyzed after the addition of a buffer solution ($pH = 2$) and 0.06 % (wt %) Arsenazo (III). The absorbance of Arsenazo (III) complex of uranium (VI) was measured at 651 nm [11, 12].

RESULTS AND DISCUSSION

The ionic liquid IL (**1**) synthesis is carried out in three steps. First, (**1**) is chlorated to give (**2**) with the use of thionyl chloride in triethylamine medium. Then, this last one was combined with (**3**) by quaternization reaction to lead to (**4**) which was a room temperature ionic liquid. It was characterized by ¹H and ¹³C NMR spectroscopy.

The spectra obtained revealed the presence of the IL (**1**) characteristic peaks which were summarized in the Table 1.

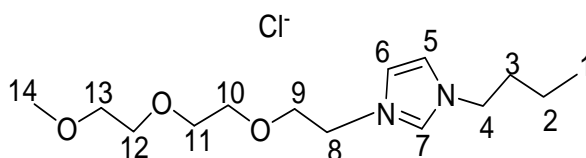


Table 1. Characteristic peaks of IL (**I**)

¹ H NMR (DMSO-d ₆)														
Proton position	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Shift (ppm)	0.90	1.33	1.75	3.95	7.18	7.18	7.71	4.65	4.26	3.64	3.74	3.64	3.54	3.35
Multiplicity *	t	m	m	t	d	d	s	t	t	t	t	t	T	s
* s: singlet, d: doublet, t: triplet, m: multiplet														
¹³ C NMR (DMSO-d ₆)														
Carbon position	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Shift (ppm)	13.33	19.51	32.81	49.41	121.17	123.56	137.31	49.41	71.75	70.1	70.4	70.15	71.67	58.8

The ¹³C NMR characterization revealed the absence of H₂C–Cl (**2**) bond at 42.82 ppm and the appearance of new bonds H₂C=N⁽⁺⁾ (**4**), HC□N⁽⁺⁾ (**4**) and H₂C□N⁽⁺⁾ (**4**) which their shifts are respectively: 137.31, 123.56 and 49.41 ppm. In the other side, ¹H NMR spectroscopy confirmed these results. It indicated the presence of the three new bonds H₂C=N⁽⁺⁾ (**4**), HC□N⁽⁺⁾ (**4**) and H₂C□N⁽⁺⁾ (**4**) at 7.71, 7.18 and 4.65 ppm; and the disappearance of H₂C–Cl (**2**) bond's pic at 3.76 ppm.

Then, the IL (**4**) undergone an anion exchange reaction between chloride ion and diethylhexylphosphate ion in order to have IL (**I**) desired (scheme 2.). ¹³C NMR spectroscopy analyses showed the presence of all the IL (**I**) characteristic bonds shifts which were cited above for the cationic part and 10.9, 14.1, 23.0, 23.3, 29.0, 30.0, 40.1 and 69.6 ppm for the anionic part (diethylhexylphosphate ion).

The use of ionic liquids as an alternative to extract uranyl ions in cloud point extraction processes is possible if the IL in question shows low water solubility. The water solubility of IL based on imidazolium depends on the length of the cations alkaline chain and the number of hydrogens substituted in the imidazolium cation, as well as on the constituent anion. Therefore, the effect of the ionic liquid (**I**) on the cloud point temperature (CPT) of aqueous triton X-100 solution seemed to be an important step to check. This study revealed that there was no change of triton's CPT, at low (**I**) concentration (3 × 10^{−4} mol·L^{−1}). It is probably due to the surfactants micelles stability. But at high concentration (0.1 mol·L^{−1}) of (**I**), CPT of Triton X-100 decreased and the phase's separation took place at ambient temperature. This phenomenon can be explained by the interaction of triton polar head with IL's ions and the formation of mixed micelles in which the lypophilic-lypophilic aggregation was important.

Then, (**I**) was used in the extraction of uranyl ions in acetate medium. Figure 1 shows the separation state of uranium micellaire mixture at ambient temperature. It appears clearly the formation of two distinct phases. The coacervat phase which is rich of TX-100, takes place upon the diluted phase which is poor from TX-100.

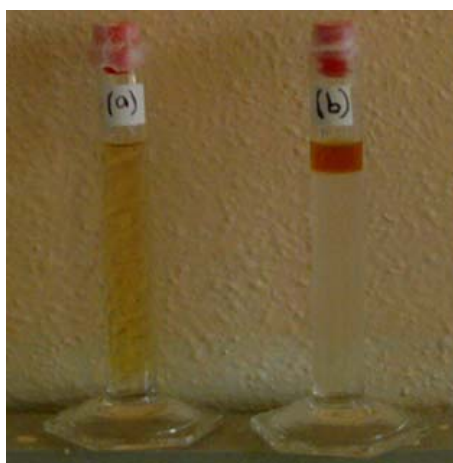


Figure 1. Cloud Point Extraction of uranyl ions in acetate medium, in presence of (**I**)
(a) Before extraction process (b) After extraction process.

Moreover, the uranyl extraction process was expressed in terms of extraction yield. This last was calculated according to equation (1), where C_i and C_a were the initial concentration of uranium and the concentration of uranium in aqueous phase after extraction respectively.

$$Y(\%) = [(C_i - C_a)/C_i] \times 100 \quad (1)$$

Figure 2 demonstrates the effect of both the ionic liquid (**I**) and (**4**) on the uranyl extraction efficiency. It describes the uranyl extraction yield variation versus the extractants concentrations.

Thus, it showed that the extraction efficiency has the same drawing appearance. It increases as the extractants concentrations rises to reach a maximum at 83.6 % with only D2EHPA and 86.5% with only IL (**I**), the uranyl extraction yield behaviour was lower in the presence of ionic liquid (**I**) at small concentrations (0.006-0.02 mol·L⁻¹). But it was slightly higher in presence of D2EHPA at the same concentration rang. In the other side, an opposite behavior was observed at high extractant agent concentration rang (0.02-0.1 mol·L⁻¹). The ionic liquid (**I**) extracted uranyl ions more than D2EHPA alone.

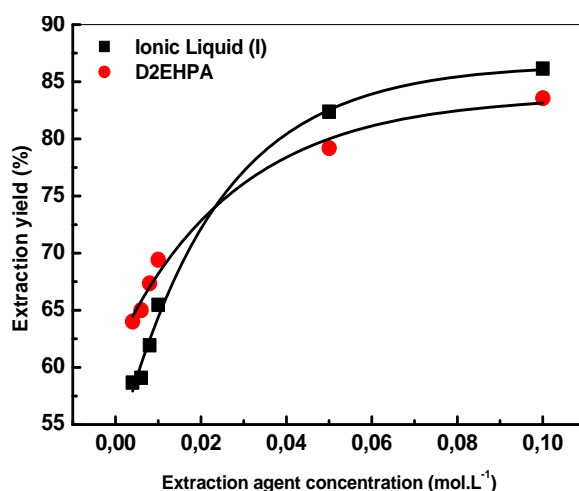


Figure 2. Extraction efficiency of uranyl ions: (■) in presence of IL (**I**). (●) and in presence of D2EHPA, uranium concentration = 0.15 g·L⁻¹, T = 25 °C

These phenomena's can be explained as follows: in the first extraction case, uranyl ions were fixed on the negative micelles' surface [13, 14]. But in the second case, the increase in UO_2^{2+} extraction yield in presence of IL (**I**) is probably due to the formation of big mixed micelles in which UO_2^{2+} was complexed both by phosphate IL anion and acetate anion, as shown in Figure 3.

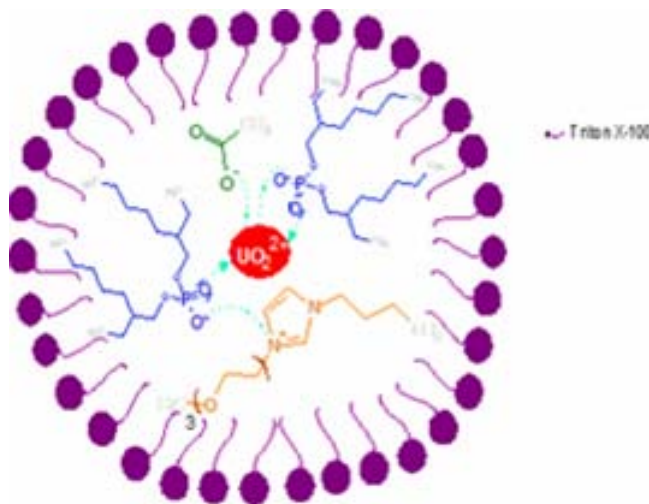


Figure 3. Representation of extraction system

CONCLUSION

This paper describes a new approach to extract the uranyl ions from aqueous solutions by the use of a micellaire mediated extraction (CPE) technique. It is based on the use of an ionic liquid (**I**), previously synthesized and characterized, as a chelating agent in presence of a non-ionic surfactant (triton X-100) in acetate media and under ambient temperature. The research showed that the uranyl extraction yield, in ambient conditions and in acetate medium, is better in presence of ionic liquid (**I**) than D2EHPA alone in the same concentration rang ($0.02 - 0.1 \text{ mol}\cdot\text{L}^{-1}$).

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