Selective cloud point extraction of uranium from thorium and lanthanides using Cyanex 301 as extractant

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ABSTRACT

A cloud point extraction (CPE) process using TX-114 as nonionic surfactant and bis(2,4,4-trimethylpentyl)di-thiophosphinate (Cyanex 301) as extractant was successfully applied to extract UO_2^{2+} selectively and quantitatively in the presence of Th^{4+} and lanthanide ions. The thermodynamic parameters of the interaction between the related metal ions and the micelles were obtained by isothermal titration calorimetry (ITC), and the binding constant followed the order of $UO_2^{2+} > Th^{4+} > La^{3+}$, consistent with the result of extraction selectivity. In the absence of NaCl, the stability constants β_1 and β_2 of the UO_2^{2+}-Cyanex 301 complex in the micellar system were determined *via* UV–vis spectroscopic titration to be 6.3×10^3 and 2.0×10^5, respectively. In the presence of $0.10 \, mol \, L^{-1}$ NaCl, the stability constants β_1 and β_2 were measured to be 5.9×10^3 and 1.0×10^7, separately. It is believed that the combination of UO_2^{2+} and Cyanex 301 leads to the formation of a neutral complex, which enters the micelles and results in a high extraction efficiency.

1. Introduction

Uranium, one of the most abundant natural actinides in the earth crust, is a significant element used as nuclear fuel for electrical power production. Uranium has an appreciable solubility in water, where uranyl ion (UO_2^{2+}) is the most stable chemical form [1]. Considering the important usage as well as the chemical and radiological toxicity of uranium [2], it is necessary to recover and detect UO_2^{2+} in aqueous solutions. Nevertheless, uranium always coexists with thorium, lanthanide, transition metal ions and main group metal ions. The separation of uranium from main group and transition metal ions is relatively easy, while the separation of UO_2^{2+}/Th^{4+} and UO_2^{2+}/Ln^{3+} is difficult. In the traditional liquid-liquid extraction, multi-stage extraction and stripping is indispensable, which produced a large volume of organic wastes and acidic wastewater [3]. Therefore, it is necessary to explore some green extraction methods.

Cloud point extraction (CPE), a micelle-mediated separation process, is one of the most preferred methods to preconcentrate and separate metal ions, owing to its high efficiency, high concentration factor, low cost, safety, environment-friendly nature and versatility [4–6]. By far, CPE has been proved suitable for a variety of metal ions, such as transition metal ions (*e.g.*, Pb(II), Cd(II) and Cu(II) co-extraction [7], Co(II) and Ni(II) co-extraction [8], Cu(II) [9,10], Ni(II) [11]), rare

earth metal ions (*e.g.*, co-extraction of La(III), Nd(III), Gd(III), etc. [12], co-extraction of La(III), Gd(III), Lu(III), etc. [13]) and actinide ions (*e.g.*, U(VI) and Th(IV) co-extraction [14]). With respect to the CPE of UO_2^{2+}, chelating agent (*e.g.*, 8-hydroxyquinoline [15], dibenzoylmethane [16,17]), organic pigments (*e.g.*, chromotrope 2R [18], eriochrome cyanine R [19]), organophosphorus compounds (*e.g.*, P,P-di(2-ethylhexyl)methanediphosphonic acid [20], di-(2-ethylhexyl) phosphoric acid (D2EHPA) [21], trioctylphosphine oxide (TOPO) [22]), etc. [23–27] have been used as the extractant, and high efficiency was achieved. The recovery of uranium by the CPE approach could be useful in some special cases (*e.g.*, recovery of ^{233}U in the presence of Th^{4+}) besides detection. However, most of the extractants could extract not only UO_2^{2+}, but also Th^{4+}, even lanthanide ions. Thus, the simultaneous preconcentration of UO_2^{2+} and Th^{4+} [14,17,28] was inevitable. Table 1 summarized the reported works that considered the influence of Th^{4+} and Ln^{3+} in the CPE of UO_2^{2+}, while others didn't mention. Our research group developed an ionic liquid assisted TOPO/TX-114 (TX-114: polyoxyethylene(8) octylphenyl ether) system to extract UO_2^{2+} selectively in the presence of lanthanide ions [22]. However, this system could not separate UO_2^{2+} from Th^{4+} [29]. Thus, there is still a great challenge.

Bis(2,4,4-trimethylpentyl)dithiophosphinate (Cyanex 301) is an extractant used for the extraction of Co^{2+}, Ni^{2+} [30], UO_2^{2+} [31] and

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Table 1
Summery of the reported CPE methods and our work.

Extractant	Micellar media	Selectivity towards Th^{4+} and Ln^{3+}	Reference
Cyanex 301	TX-114	$S_{U/Th} = 140$, Ln^{3+} could not be extracted	This work
Dibenzoylmethane	TX-114	5 times of Th^{4+} could interfere the detection of uranium	[16]
Dibenzoylmethane	TX-114	UO$_2^{2+}$ and Th^{4+} were co-extracted	[17]
Trioctylphosphine oxide	TX-114	Selective separation of UO$_2^{2+}$/La^{3+}. Th^{4+} was not mentioned	[22]
P,P-di(2-ethylhexyl)methanediphosphonic acid	TX-114 + CTAB	UO$_2^{2+}$ and Th^{4+} were co-extracted	[28]
Trioctylphosphine oxide and N,N,N′,N′-tetraoctyldiglycolamide	TX-114 + SDS	UO$_2^{2+}$ and Th^{4+} were co-extracted and equal amount of La^{3+} could interfere the detection of uranum	[14]
Diglycolamide-capped quantum dot	TX-114	Ln^{3+} did not interfere the detection of uranium. Th^{4+} was not mentioned	[24]
N-propyl-(diphenylphosphoramidate)trimethylammonium bis [(trifluoromethane)sulfonyl]imide	TX-114	Equal amount of Th^{4+} did not affect the detection of uranium	[25]

minor actinide ions [32]. Indeed, Cyanex 301 (pK_a = 2.6 [33]) can dissociate in weak acid solution and act as an anionic surfactant. Therefore, it can form mixed micelles with TX-114 easily, favoring its dissolution in TX-114 solution and the following usage in CPE. Very recently, Akl [34] applied Cyanex 301 as extractant in the mixed micelles of TX-100 and cetylpyridinium bromide for the selective CPE of UO$_2^{2+}$ from transition, alkali and alkaline earth metal ions. However, the separation of UO$_2^{2+}$/Th^{4+} or UO$_2^{2+}$/Ln^{3+} was not investigated. Considering the preferable coordination of Cyanex 301 with "soft" metal ions through two S atoms, it may have a better affinity towards UO$_2^{2+}$ than Th^{4+} and Ln^{3+}, leading to the separation of UO$_2^{2+}$/Th^{4+} and UO$_2^{2+}$/Ln^{3+} by CPE method.

In the CPE process, it is believed that the complex formation between metal ions and extractants incorporated in the micelles had a great influence on the CPE efficiency [35], but the complex formation process was rarely studied. Nispen et al. [36] characterized the binding of multivalent ions to modified pluronic micelles by isothermal titration calorimetry (ITC). Nevertheless, they were not able to get the stability constants. Recently, Saha et al. [25] used ITC to investigate the combination of the extractant (*i.e.*, a task specific ionic liquid bearing phosphoramidate group) with UO$_2^{2+}$ in HNO$_3$ solution to help understanding the CPE mechanism. However, the formation process of complex in the micelles system may be different from that in aqueous solution. Moreover, most of the extractants used in the CPE have a poor solubility in water. Therefore, this method could not well reflect the real interaction between metal ions and extractants in micelles. In the investigation of complex formation, spectroscopic method is powerful. In TX-100 micelles, Verma and coworkers [21] have ever qualitatively confirmed the binding of UO$_2^{2+}$ with D2EHPA by UV–vis spectra. To get the stability constant of complex, spectroscopic titration is often used [37]. However, to the best of our knowledge, the method has not been applied in micelle system. Challenge still exists.

In the present work, we developed a TX-114-based CPE process with Cyanex 301 as extractant to extract UO$_2^{2+}$ selectively in the presence of Th^{4+} and lanthanide ions. Furthermore, the binding thermodynamic parameters (ΔH, ΔG) between metal ions and the mixed micelles as well as the stability constants of the complex formed in the micelles were achieved to help understanding the CPE mechanism.

2. Experimental

2.1. Reagents and instruments

TX-114 (> 98%) and polyoxyethylene(10) octylphenyl ether (TX-100, > 98%) was obtained from Alfa Aesar (China) and used as received. Ammonium bis(2,4,4-trimethylpentyl)dithiophosphinate (Cyanex 301) was purchased from Cytec Industries Inc. (Canada) and purified by recrystallization [38]. Ultrapure water was used throughout the experiment. All other materials used in this work were of analytical grade and used without further purification.

The concentrations of all metal ions were determined by inductively

coupled plasma-atmoic emission spectrometer (ICP-AES, Leeman, USA) with relative standard deviation (RSD) below 5%, whose instrumental and operating conditions were listed in Table S1 (Supporting Information). Dynamic light scattering (DLS) and Zeta potential measurements were performed on a Malvern Nano ZS90 instrument (Malvern Instruments, UK) at 293.2 K and at a scattering angle of 90°. A He–Ne laser (λ = 632.8 nm) with a power of 4 mW was used as the light source. The UV–vis spectra were recorded on a U-3010 spectrophotometer (Hitachi, JP). ITC experiments were operated on a Nano ITC 2G (TA instruments, USA).

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2.2. CPE process

In a typical CPE process, the mixed solution of Cyanex 301 and TX-114 (pH = 3) was firstly added into the UO$_2^{2+}$ solution and the mixture was shaken slightly for about 30 s. Then, NaCl was added and the solution was made up to 10 mL containing 10 mmol L^{-1} TX-114, 1 mmol L^{-1} Cyanex 301, 0.05 mmol L^{-1} UO$_2^{2+}$, 1.0 mmol L^{-1} HCl and 0.1 mol L^{-1} NaCl. After being shaken for 2 h at 25 °C and being placed at 70 °C for 2 h, the mixture was centrifuged for 10 min at 4000 rpm and 70 °C to achieve complete phase separation. The concentration of UO$_2^{2+}$ in the aqueous phase was measured by ICP-AES. The extraction efficiency E was calculated by the following equation:

$$E = \frac{C_i V_i - C_f V_f}{C_i V_i} \times 100\% \tag{1}$$

where C_i (mmol L^{-1}) is the initial concentration of UO$_2^{2+}$ in the micellar solution, C_f (mmol L^{-1}) is the final concentration of UO$_2^{2+}$ in aqueous phase after CPE, V_i (L) is the volume of the micellar solution and V_f (L) is the volume of aqueous phase after CPE.

2.3. Microcalorimetric titration

In a typical titration, 4.0 mmol L^{-1} UO$_2^{2+}$ solution (pH 3.0) in the syringe was injected in a total of 25 drops by each of 10 μL into the measuring cell filled with the mixed micelles solution (1.0 mmol L^{-1} Cyanex 301 and 10 mmol L^{-1} TX-114, pH 3.0) at 293.2 K. The rotational speed of the stirrer was 250 rpm and the equilibrium time between two injections was 600 s. The dilution heat of UO$_2^{2+}$ solution titrated to TX-114 micelles solution (10 mmol L^{-1}, pH 3.0) was determined in a separate run, and was subtracted from the determined heat flow.

The binding parameters were obtained from the ITC data using the NanoAnalyze software (Version 3.7). Data fitting was performed using the independent set of multiple non-interacting sites (MNIS) model [39], in which the total measured heat Q is determined by Eq. (2).

$$Q = \frac{(1 + C_L n K_a + K_a C_M) - [(1 + C_L n K_a + K_a C_M)^2 - 4 C_L n K_a^2 C_M]^{1/2}}{2 K_a / (V \Delta H)} \tag{2}$$

where V is the volume of the calorimeter cell, ΔH is enthalpy, and K_a is the equilibrium binding constant. C_L is the concentration of Cyanex 301 and C_M is the total concentration of metal ions. The n value represents the number of metal ions combined by each Cyanex 301 on average.

2.4. Spectroscopic titration

In a typical titration, 2.00 mL UO_2^{2+}/TX-100 micelles solution was placed in a quartz cuvette with 1.0 cm optical path, into which 0.04 mL Cyanex 301/TX-100 mixed micelles solution was added and mixed for 2 min before the spectra were collected in the wavelength region of 290–500 nm. The solution was maintained at 293.2 K and 26 additions were performed, which generated 27 spectra. The stability constants of UO_2^{2+}/Cyanex 301 were obtained by using the nonlinear regression program HypSpec 2008 [40].

3. Results and discussion

3.1. Optimization of CPE procedure

3.1.1. Effect of salting-out agent

The cloud point of 10 mmol L^{-1} TX-114 with 1.0 mmol L^{-1} Cyanex 301 was not observed at 95 °C. Therefore, it is necessary to adjust the cloud point temperature (CPT). In CPE process, salting-out agent is often added to reduce the CPT and to improve the extraction efficiency. Generally, NaCl, Na_2SO_4 and $NaNO_3$ are often used. Their influence on the extraction efficiency was evaluated (Fig. S1 in Supporting Information). At three identical concentrations of Na^+, the salt type has no significant influence on the CPE efficiency. In our investigation, NaCl was selected.

The effect of NaCl concentration on the CPT of mixed micelles was shown in Fig. 1A (curve a). With the increase of NaCl concentration, the CPT of mixed micelles reduces greatly, favoring the usage of mixed micelles in CPE. More importantly, sufficient NaCl is necessary to improve the extraction efficiency (curve b, Fig. 1A). The extraction efficiency increased with the increase of NaCl concentration and reaches plateau at 50 mmol L^{-1} NaCl. Considering that the addition of NaCl could not alter the coordination environment of UO_2^{2+} (see the discussion in Section 3.3.3), the reason for the phenomenon may be that high NaCl concentration favors the phase separation of the mixed micelles above CPT. To guarantee the extraction efficiency at different conditions, 100 mmol L^{-1} NaCl was used in the following experiments.

3.1.2. Effect of phase separation temperature

Although the CPT of 10 mmol L^{-1} TX-114 with 1.0 mmol L^{-1} Cyanex 301 and 100 mmol L^{-1} NaCl is 8 °C, the separation temperature is not identical to the CPT. The influence of the separation temperature on the CPE efficiency was evaluated from 25 to 75 °C. The result was shown in Fig. 1B. It can be seen that the extraction efficiency increases to about 97% at 35 °C, then decreases to approximately 92% at 55 °C, and finally increases to about 98% when the temperature is higher than 65 °C.

In the temperature range of 25–35 °C, the increase of the extraction efficiency is due to the dehydration of the hydrophilic group of TX-114, which leads to a solubility decrease of mixed micelles. From 35 to 55 °C, the decrease of extraction efficiency may be ascribed to the re-solubilization of Cyanex 301 with the increase of temperature. Similar phenomena was observed by Labrecque and coworkers [20]. When they evaluated the influence of phase separation temperature (15–40 °C) on the CPE efficiency of uranium by mixed micelles of TX-114 and
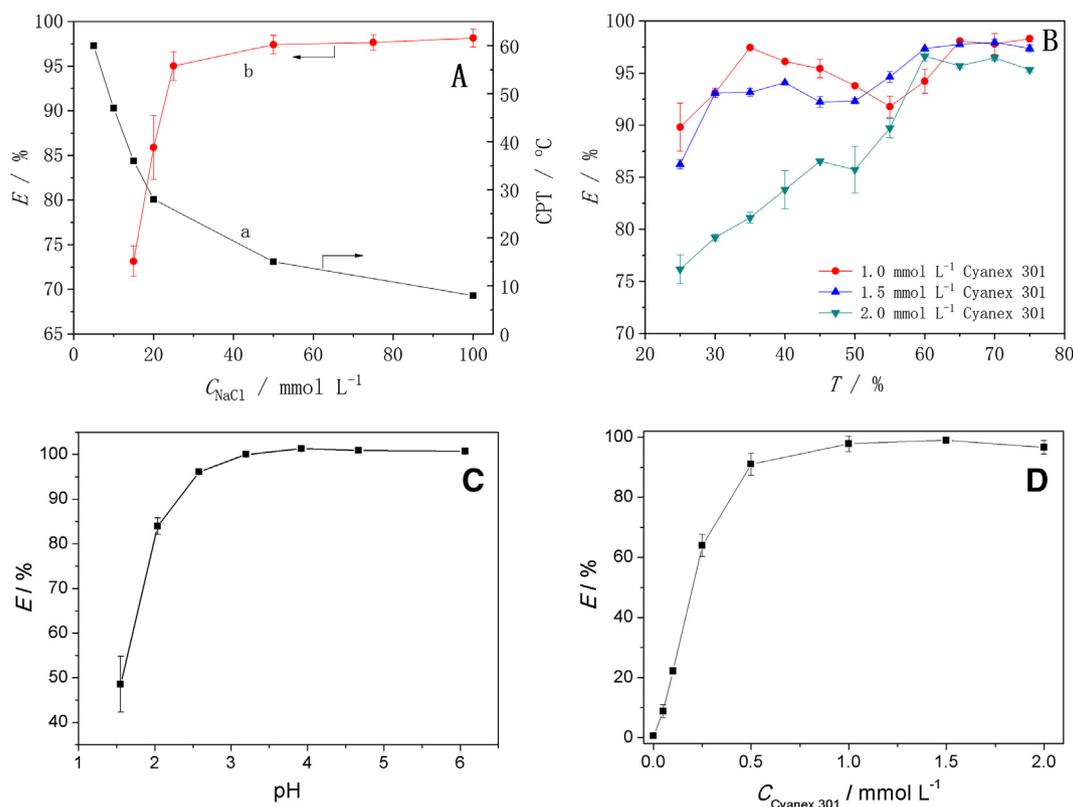

Fig. 1. The effect of NaCl concentration on the CPT (A, curve a) (Conditions: 10 mmol L^{-1} TX-114, 1.0 mmol L^{-1} Cyanex 301). The effects of NaCl concentration (A, curve b), phase separation temperature (B), pH values (C) and Cyanex 301 concentration (D) on the extraction efficiency of UO_2^{2+} (Conditions of A: 10 mmol L^{-1} TX-114, 1.0 mmol L^{-1} Cyanex 301, pH 3.0, 0.05 mmol L^{-1} UO_2^{2+}, phase separation temperature: 70 °C; Conditions of B: 10 mmol L^{-1} TX-114, pH 3.0, 0.05 mmol L^{-1} UO_2^{2+}, 0.1 mol L^{-1} NaCl; Conditions of C: 10 mmol L^{-1} TX-114, 1.0 mmol L^{-1} Cyanex 301, 0.05 mmol L^{-1} UO_2^{2+}, 0.1 mol L^{-1} NaCl, phase separation temperature: 70 °C; Conditions of D: 10 mmol L^{-1} TX-114, pH 3.0, 0.05 mmol L^{-1} UO_2^{2+}, 0.1 mol L^{-1} NaCl, phase separation temperature: 70 °C).

cetyltrimethyl ammonium bromide (CTAB), there appeared a maximum extraction efficiency at 20 °C. It was assumed that CTAB resolubilization occurs at higher temperature. Rub et al. [41] observed a maximum critical micelle concentration (CMC) of the mixed micelles of promethazine hydrochloride and TX-100 when the temperature increased. As to the final increase of the extraction efficiency at the temperature higher than 55 °C in our experiment, it might be related to the decrease of CMC of the mixed micelles.

Labrecque et al. [20] chose 20 °C as the optimal temperature, but they proposed that a system with a different ratio of CTAB and TX-114 would lead to a different optimal temperature. In our experiments, when the molar ratio of Cyanex 301 and TX-114 was altered, the optimal temperature changed (Fig. 1B). When the concentration of TX-114 was fixed at 10 mmol L^{-1} and the concentration of Cyanex 301 increased to 1.5 mmol L^{-1}, the extraction efficiencies reached a plateau over 97% at the temperature above 60 °C, which were obviously higher than those around 35 °C. When the concentration of Cyanex 301 arrived at 2.0 mmol L^{-1}, the plateau around 35 °C disappeared, and there was only one plateau over 95% at the temperature above 60 °C. Thus, 70 °C was used rather than 35 °C in the condition experiments to guarantee the extraction efficiency at different conditions.

3.1.3. Effect of pH

The pH value of the solution has a direct influence on the complexation between UO_2^{2+} and Cyanex 301, because H^+ is able to affect the dissociation of Cyanex 301 and the hydrolysis of UO_2^{2+}. Thus, the effect of acidity on the extraction efficiency was firstly assessed by varying the pH value from 1.5 to 6.0 with HCl (Fig. 1C). The extraction efficiency increases greatly from pH 1.5 to 3.0, then reaches a maximum efficiency close to 100% at the pH range of 3.0–6.0. This may be attributed to the competition of H^+ with UO_2^{2+} to combine with the Cyanex 301 anion. The pK_a of Cyanex 301 is 2.6 [31], so that most of the Cyanex 301 molecules are dissociated at pH > 3, favoring the formation of the complex of UO_2^{2+} and Cyanex 301. The hydrolysis of UO_2^{2+} ions in aqueous solution begins at pH 3.0, leading to the appearance of UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ species at pH > 3.0 [42]. It seems that the hydrolysis of UO_2^{2+} could not decrease the extraction efficiency in the pH range of 3.0–6.0. The influences of pH on the extraction efficiencies of Th^{4+} and La^{3+} were also evaluated. The La^{3+} could not be extracted at the pH range of 1.5–5.2. The extraction efficiency of Th^{4+} increases at the pH range of 1.5–3.5 and then decreased (Fig. S2 in Supporting Information). Considering the CPE efficiency and selectivity towards Th^{4+}, as well as avoiding the hydrolysis of UO_2^{2+} and Th^{4+} that may influence the ITC measurement, pH 3.0 was chosen as the proper pH value.

3.1.4. Effect of Cyanex 301 concentration

To optimize the dosage of Cyanex 301, the effect of Cyanex 301 concentration was studied (Fig. 1D). The extraction efficiency in the absence of Cyanex 301 was 0.6 ± 0.5%, indicating that TX-114 micelles could not extract UO_2^{2+} at pH 3.0. The CPE efficiency increases rapidly before the Cyanex 301 concentration increases to 1.0 mmol L^{-1}, and then remains nearly 100% with further increase of the concentration. In other words, the extraction efficiency reaches nearly 100% when the Cyanex 301 concentration is about 20 times of the UO_2^{2+} concentration, and much more excess Cyanex 301 is applied to guarantee that all UO_2^{2+} ions are coordinated. Since the CPE process is often used at a low UO_2^{2+} concentration, a Cyanex 301 concentration of 1.0 mmol L^{-1} is enough. Besides, since Cyanex 301 can act as an anionic surfactant to form charged mixed micelles with TX-114, a relatively high Cyanex 301 concentration will lead to the increase of TX-114 usage to guarantee the phase separation, which will be discussed in the following section. Thus, 1.0 mmol L^{-1} Cyanex 301 was used in the following experiments.
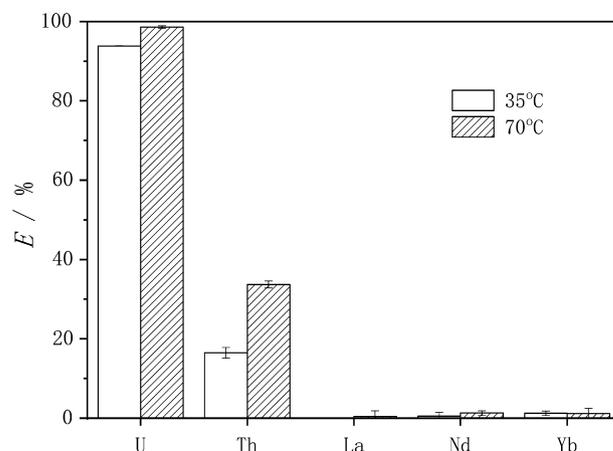

Fig. 2. Extraction efficiencies of different metal ions. (Conditions: 10 mmol L^{-1} TX-114, 1.0 mmol L^{-1} Cyanex 301, pH 3.0, 0.05 mmol L^{-1} metal ion, and 0.1 mol L^{-1} NaCl, phase separation temperature: 70 °C or 35 °C).

3.1.5. Effect of TX-114 concentration

TX-114 is the most widely used non-ionic surfactant in CPE experiments because its CPT (24 °C [43]) is close to room temperature. In the literature, 4 mmol L^{-1} or 0.2% (W/V) TX-114 are often used in the CPE procedure [14,16–18]. To get a suitable usage of TX-114, the effect of TX-114 concentration on the extraction efficiency was examined. In the range of 2.5–15 mmol L^{-1}, the extraction efficiency kept close to 99% (Fig. S3 in Supporting Information). However, when the TX-114 was less than 5 mmol L^{-1}, it was difficult to separate the two phases completely. This may be attributed to the high content of Cyanex 301 in the mixed micelles, which conferred to the TX-114 micelles a negative charge and made it more stable. Therefore, it is necessary to use sufficient TX-114 to decrease the ratio of Cyanex 301 in the mixed micelles and ensure the easy operation of the separation process. In the subsequent experiments, 10 mmol L^{-1} TX-114 was adopted.

3.2. Selectivity of the CPE process

Thorium and lanthanides often coexist with uranium. Moreover, the separation of UO_2^{2+}/Th^{4+} and UO_2^{2+}/Ln^{3+} is difficult. Thus, Th^{4+}, La^{3+}, Nd^{3+} and Yb^{3+} was selected as the competing ions to study the selectivity of the CPE system. As can be seen from Fig. 2, the extraction efficiency of UO_2^{2+} is nearly 100% at the optimized conditions, while that of Th^{4+} is about 30%. The selectivity coefficient (S) of UO_2^{2+}/Th^{4+} was 140, calculated by the following equations.

$$S_{U/Th} = \frac{D(U)}{D(Th)} \qquad (3)$$

$$D = \frac{C_i V_i - C_f V_f}{C_f V_f} \qquad (4)$$

where D is the distribution ratio. Also, it is noteworthy that La^{3+}, Nd^{3+} and Yb^{3+} could be hardly extracted. These results indicate that the optimized CPE process has a good selectivity towards UO_2^{2+}.

With respect to a CPE system with a relatively low molar ratio of Cyanex 301 and TX-114, e.g., the solution containing 1.0 mmol L^{-1} Cyanex 301 and 10 mmol L^{-1} TX-114, 35 °C was also a suitable phase separation temperature. As can be seen in Fig. 2, although the extraction efficiency towards UO_2^{2+} decreased a little in the presence of competing ions, the selectivity towards UO_2^{2+} increased to some extent.
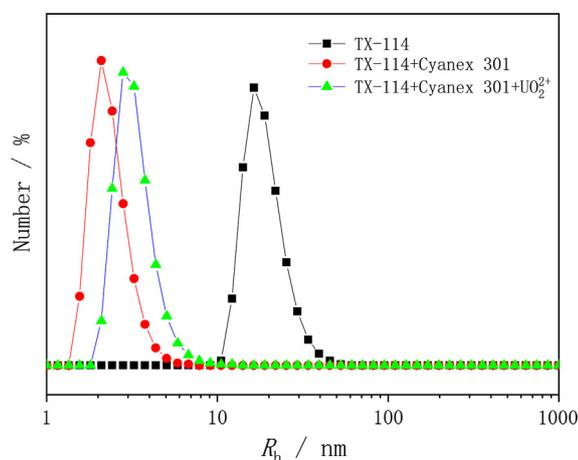
Fig. 3. DLS results of $10 \, mmol \, L^{-1}$ TX-114 aqueous solution with(out) $1.0 \, mmol \, L^{-1}$ Cyanex 301 and $1 \, mmol \, L^{-1}$ UO_2^{2+} (pH 3.0, 293.2 K).

3.3. Extraction mechanism

3.3.1. DLS and zeta potential measurements

In the CPE process, it is believed that Cyanex 301 is incorporated in the TX-114 micelle, where UO_2^{2+} is combined with Cyanex 301. These were confirmed by the results of DLS and zeta potential measurements at 293.2 K. The zeta potential of $10 \, mmol \, L^{-1}$ TX-114 aqueous solution (pH 3) was measured to be $0.30 \pm 5 \, mV$, nearly zero. Upon the addition of $1.0 \, mmol \, L^{-1}$ Cyanex 301, the zeta potential decreased to $-60 \pm 6 \, mV$, indicating that the Cyanex 301 anion was incorporated in the micelles and the negatively charged head group was on the surface. At the same time, the micelles size decreased greatly (Fig. 3), which may be attributed to the formation of ionic-nonionic mixed micelles that reduced the contribution of TX-114 [44,45].

When UO_2^{2+} was added to the mixed micelles of TX-114 and Cyanex 301, the zeta potential increased to $-9 \pm 4 \, mV$, and the size of the micelles also increased (Fig. 3). These results suggest that UO_2^{2+} is coordinated with Cyanex 301 and the surface charge was partially neutralized.

3.3.2. ITC study

To quantify the binding strength of metal ions to TX-114 micelles containing Cyanex 301, UO_2^{2+} (Th^{4+} or La^{3+}) aqueous solution was titrated into the micelles solution of Cyanex 301 and TX-114 in individual experiments using ITC (Figs. 4, and S4, S5 in Supporting Information). The enthalpy as a function of molar ratio of UO_2^{2+}/Cyanex 301 is shown in Fig. 4B, which was well fitted with MNIS model (Eq. (2)). The fitted and calculated thermodynamic parameters are listed in Table 2. The free energy change (ΔG) of the reactions of metal ions with the micelles are negative, indicating that the combinations of metal ions and micelles are spontaneous processes in 293.2 K. And the binding constant and the n values followed the order of $UO_2^{2+} > Th^{4+} > La^{3+}$, consistent with the result of the extraction selectivity (Fig. 2). All of the combinations of ions and micelles have positive changes in entropy and enthalpy, suggesting that the combinations are all entropically driven. Thus, it is believed that the dehydration of metal ions plays a dominant role in the interaction between ions and micelles, in accord with the result of binding of multivalent ions to modified pluronic micelles by Nispen et al. [36].

3.3.3. UV–vis spectrum study

In the CPE procedure, when the mixed micelles of TX-114 and Cyanex 301 was added with UO_2^{2+}, the solution turned yellow. In the UV–vis spectrum, there appears an obvious absorption peak at ca. 370 nm (Fig. 5A), suggesting the formation of the complex based on UO_2^{2+}. Furthermore, UV–vis spectra titration was used to determine
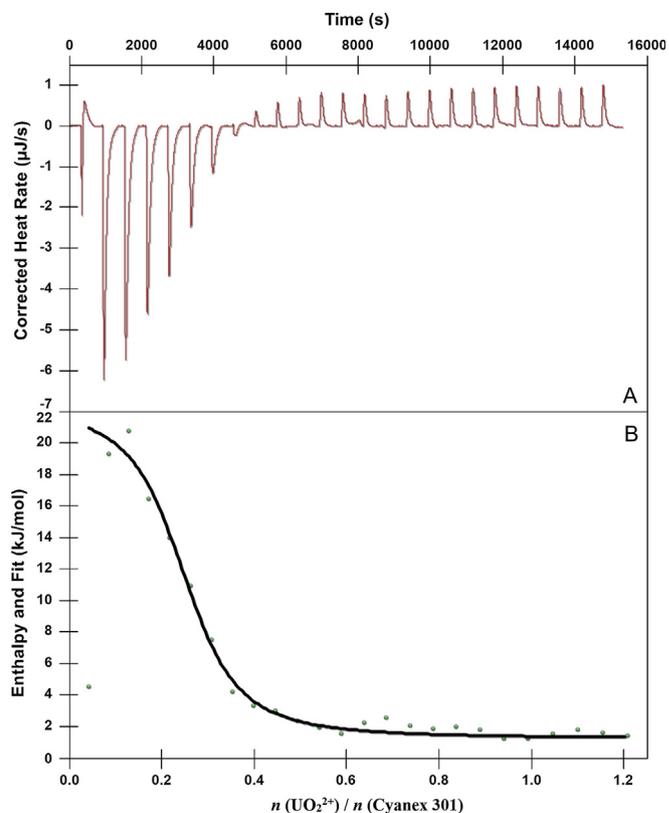

Fig. 4. (A) Real-time thermogram for micelle solution ($1.0 \, mmol \, L^{-1}$ Cyanex 301 and $10 \, mmol \, L^{-1}$ TX-114, pH 3.0) titration with $4.0 \, mmol \, L^{-1}$ UO_2^{2+} at 293.2 K. (B) Enthalpy as a function of molar ratio of UO_2^{2+}/Cyanex 301, fitted with MNIS model; symbols represent experimental data and line represents model prediction.

the stability constant of the UO_2^{2+}-Cyanex 301 complex in micelles (Fig. 5B). Because the solution containing $0.20 \, mmol \, L^{-1}$ UO_2^{2+} and $10 \, mmol \, L^{-1}$ TX-114 was a little turbid, and the molecular structure of TX-100 is similar to that of TX-114 (Scheme 1), TX-100 was used to replace TX-114. The best fit of the titration spectra is gotten by assuming that UO_2^{2+} and Cyanex 301 formed 1:2 complex (Scheme 2). And the stability constants β_1 and β_2 are determined to be 6.3×10^3 and 2.0×10^5, respectively. In order to investigate the influence of NaCl on the complexation between Cyanex 301 and UO_2^{2+}, the spectroscopic titration was also performed in the presence of $0.10 \, mol \, L^{-1}$ NaCl (Fig. 5C). Comparing to the spectra obtained in the absence of NaCl, it was found that the shape of the spectra obtained in the presence of NaCl was similar and the absorption peak still appeared at ca. 370 nm, which means that the addition of NaCl could not alter the coordination environment of UO_2^{2+}. In the presence of NaCl, the stability constants β_1 and β_2 of the UO_2^{2+}-Cyanex 301 complex in the micellar system were determined to be 5.9×10^3 and 1.0×10^7, respectively. The β_2 value is higher than that of UO_2^{2+}-Cyanex 301 complex in the absence of NaCl, which suggests that the ionic strength is able to increase the complexation strength of UO_2^{2+} and Cyanex 301 in micelles. The formation of a neutral complex in the micelle system lead to a high extraction efficiency. Since the stability constant is not large enough, quantitative extraction was only realized at the excess of Cyanex 301, consistent with the experimental result (Fig. 1D).

In order to examine the combination of Ln^{3+} and Cyanex 301 in micelles, Nd^{3+} was chosen as the representative since the spectrum of the Nd^{3+}-Cyanex 301 complex was well studied [46]. When Nd^{3+} was added to the mixed micelles of TX-100 and Cyanex 301, the position of the characteristic adsorption peaks of Nd^{3+} complex was not changed (Fig. S6 in Supporting Information), indicating that Nd^{3+} was still coordinated by water, but not directly coordinated with S atom from

Table 2
ITC data of micelle solution titrated with metal ions at 20 °C.

| Metal ion	ΔH/kJ mol^{-1}	K_a/M^{-1}	ΔG/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	n
UO_2^{2+}	21 ± 3	$(6.7 ± 0.2) \times 10^4$	−27.1 ± 0.1	163 ± 11	0.242 ± 0.017
Th^{4+}	58 ± 6	$(1.9 ± 0.1) \times 10^4$	−24.0 ± 0.1	280 ± 20	0.179 ± 0.003
La^{3+}	39 ± 1	$(9.3 ± 0.3) \times 10^3$	−22.3 ± 0.1	230 ± 4	0.122 ± 0.005
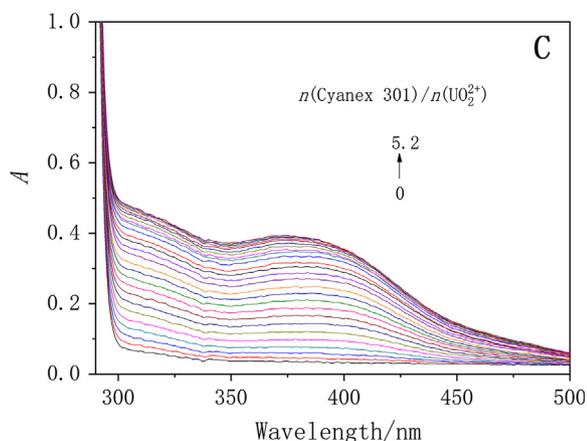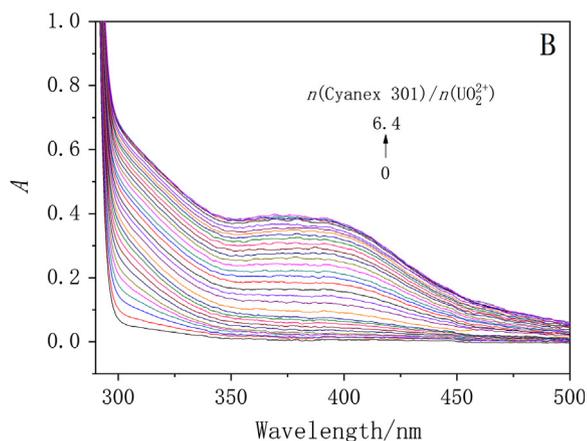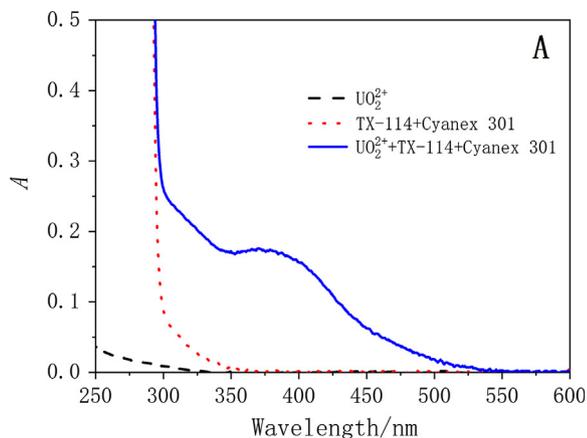
Fig. 5. (A) UV–vis spectra of 0.05 mmol L^{-1} aqueous solution of UO_2^{2+}, micelles solution containing 10 mmol L^{-1} TX-114 and 1.0 mmol L^{-1} Cyanex 301, and their mixture. (B) Spectroscopic titrations of UO_2^{2+}/TX-100 with Cyanex 301/TX-100 (293.2 K). Initial solution: $V = 2.00$ mL, $C_U/C_{TX-100}/C_H = 0.2/10/1.0$ mmol L^{-1}. Titrant: $C_{Cyanex\ 301}/C_{TX-100}/C_H = 2.0/10/1.0$ mmol L^{-1}. (C) Spectroscopic titrations of UO_2^{2+}/TX-100 with Cyanex 301/TX-100 in the presence of NaCl (293.2 K). Initial solution: $V = 2.00$ mL, $C_U/C_{TX-100}/C_H/C_{NaCl} = 0.2/10/1.0/100$ mmol L^{-1}. Titrant: $C_{Cyanex\ 301}/C_{TX-100}/C_H/C_{NaCl} = 2.0/10/1.0/100$ mmol L^{-1}.
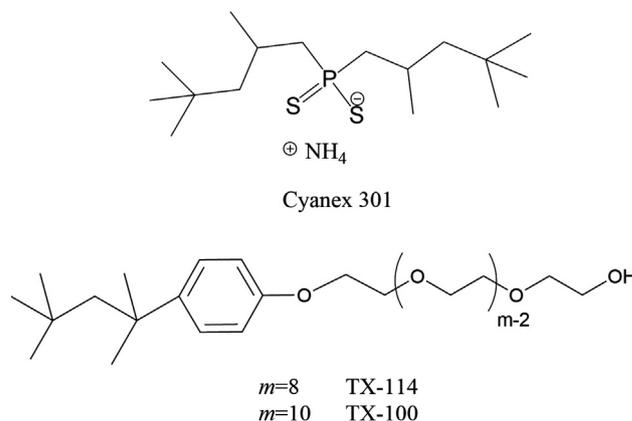
Scheme 1. Structures of Cyanex 301, TX-114 and TX-100.

$$UO_2^{2+} + A^- \longrightarrow UO_2A^+$$
$$UO_2A^+ + A^- \longrightarrow UO_2A_2$$
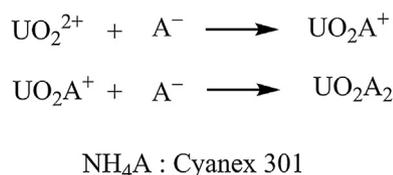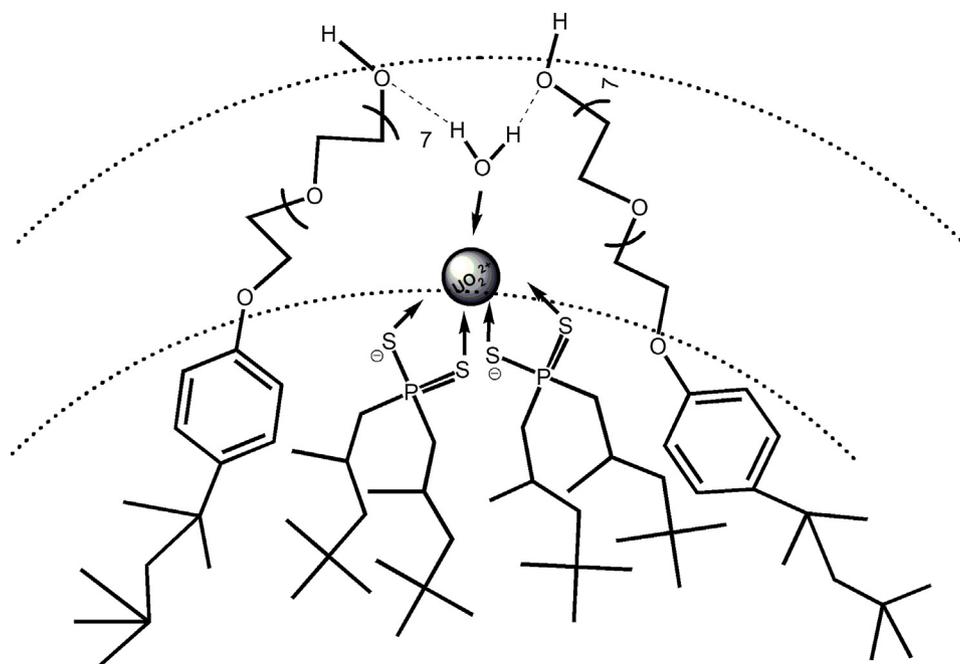
$$NH_4A : Cyanex\ 301$$

Scheme 2. Successive coordination steps of UO_2^{2+} by Cyanex 301.

Cyanex 301 [46]. In other words, Ln^{3+} could not combine with the micelles through coordination bond. Thus, it is not difficult to understand the poor extraction efficiency of lanthanide ions. Unfortunately, since Th^{4+} do not have absorption in the UV–vis spectrum, we could not get any coordination information by spectroscopic method.

Combining with the results of ITC analysis, it is believed that the combination of UO_2^{2+} with Cyanex 301 leads to the formation of neutral complex, which enters the micelles. Since the coordination number of UO_2^{2+} is often 5 or 6 in water, it is proposed that two Cyanex 301 molecules and one/two water molecules coordinate with UO_2^{2+}, which constructs a stable binding site for UO_2^{2+} in the interface of the micelle (Scheme 3). However, the hydrated lanthanide ions can only combine with the micelles on its surface through electrostatic interactions. As to Th^{4+}, the poor extraction efficiency and a smaller binding constant compared with UO_2^{2+} reflect that the complex of Th^{4+} and Cyanex 301 may not form in the micelles system, similar to lanthanide ions.

4. Conclusions

In this study, a CPE process based on TX-114 and Cyanex 301 mixed micelles solution is developed to selectively extract UO_2^{2+} in the presence of Th^{4+} and lanthanide ions. After optimization, quantitative extraction of UO_2^{2+} and a $S_{U/Th}$ value of 140 were realized. The thermodynamic parameters of the interaction between the related metal ions and the micelles were obtained by ITC, and the binding constant followed the order of $UO_2^{2+} > Th^{4+} > La^{3+}$, consistent with the result of extraction selectivity. In the absence of NaCl, the stability constants β_1 and β_2 of the UO_2^{2+}-Cyanex 301 complex in the micellar system were determined *via* UV–vis spectroscopic titration to be 6.3×10^3 and 2.0×10^5, respectively. In the presence of 0.10 mol L^{-1}

Scheme 3. Schematic representation of the combination of UO_2^{2+} with Cyanex 301 in the TX-114 micelles.

NaCl, the stability constants β_1 and β_2 were measured to be 5.9×10^3 and 1.0×10^7, separately. As far as we know, this is the first report about the measurement of stability constant of complex in micelles. It can be concluded that the combination of UO_2^{2+} and Cyanex 301 leads to the formation of a neutral complex, which enters the micelles and results in a high extraction efficiency. With respect to lanthanide ions and Th^{4+}, they could only combine with the micelles on the surface through electrostatic interactions, leading to a poor extraction efficiency. It is believed that the results reported herein will not only afford us a selective CPE process for the separation of UO_2^{2+} from Th^{4+} and lanthanide ions, but also contribute in a new way to investigating the coordination chemistry in micelle-mediated separation processes.

References

[1] J.S. Santos, L.S. Teixeira, W.N. dos Santos, V.A. Lemos, J.M. Godoy, S.L. Ferreira, Uranium determination using atomic spectrometric techniques: an overview, Anal. Chim. Acta 674 (2010) 143–156.

[2] E. Craft, A. Abu-Qare, M. Flaherty, M. Garofolo, H. Rincavage, M. Abou-Donia, Depleted and natural uranium: chemistry and toxicological effects, J. Toxicol. Env. Health-Pt B-Crit. Rev. 7 (2004) 297–317.

[3] J. Xiong, S. Hu, Y. Liu, J. Yu, H. Yu, L. Xie, J. Wen, X. Wang, Polypropylene modified with amidoxime/carboxyl groups in separating uranium(VI) from thorium (IV) in aqueous solutions, ACS Sustain. Chem. Eng. 5 (2017) 1924–1930.

[4] P. Samaddar, K. Sen, Cloud point extraction: A sustainable method of elemental preconcentration and speciation, J. Ind. Eng. Chem. 20 (2014) 1209–1219.

[5] K. Pytlakowska, V. Kozik, M. Dabioch, Complex-forming organic ligands in cloud-point extraction of metal ions: a review, Talanta 110 (2013) 202–228.

[6] I. Hagarová, Cloud point extraction utilizable for separation and preconcentration of (ultra)trace elements in biological fluids before their determination by spectrometric methods: a brief review, Chem. Pap. 71 (2016) 869–879.

[7] M. Bilal, T.G. Kazi, H.I. Afridi, M.B. Arain, J.A. Baig, M. Khan, N. Khan, Application of conventional and modified cloud point extraction for simultaneous enrichment of cadmium, lead and copper in lake water and fish muscles, J. Ind. Eng. Chem. 40 (2016) 137–144.

[8] V. Lemos, R. Dafranca, B. Moreira, Cloud point extraction for Co and Ni

[9] M. Hadj Youcef, T. Benabdallah, H. Ilikti, 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. Spectros. 51 (2006) 267–268.

[10] H. Reffas, T. Benabdallah, M. Hadj Youcef, A comparative study on the cloud point extraction behavior of copper(II) from sulphate medium by N, N'-bis(salicylidene) ethylenediamine using Triton X-100 and Tergitol 15-S-7 as non-ionic surfactants, Tenside Surfactants Deterg. 54 (2017) 179–186.

[11] M. Hadj Youcef, T. Benabdallah, H. Reffas, Cloud point extraction studies on recovery of nickel(II) from highly saline sulfate medium using salicylideneaniline mono-Schiff base chelating extractant, Sep. Purif. Technol. 149 (2015) 146–155.

[12] M.M. Hassanien, I.M.M. Kenawy, M.E. Khalifa, M.M. Elnagar, Mixed micelle-mediated extraction approach for matrix elimination and separation of some rare earth elements, Microchem. J. 127 (2016) 125–132.

[13] C. Labrecque, D. Larivière, Quantification of rare earth elements using cloud point extraction with diglycolamide and ICP-MS for environmental analysis, Anal. Methods 6 (2014) 9291–9298.

[14] A. Saha, S.B. Deb, A. Sarkar, M.K. Saxena, B.S. Tomar, Simultaneous pre-concentration of uranium and thorium in aqueous samples using cloud point extraction, RSC Adv. 6 (2016) 20109–20119.

[15] A. Favre-Reguillon, D. Murat, G. Cote, J. Foos, M. Draye, Temperature-induced surfactant-mediated pre-concentration of uranium assisted by complexation, J. Chem. Technol. Biotechnol. 81 (2006) 1872–1876.

[16] F. Shemirani, R.R. Kozani, M.R. Jamali, Y. Assadi, S.M.R. Milani, Micelle-mediated extraction for direct spectrophotometric determination of trace uranium(VI) in water samples, Sep. Sci. Technol. 40 (2005) 2527–2537.

[17] S. Shariati, Y. Yamini, M.K. Zanjani, Simultaneous preconcentration and determination of U(VI), Th(IV), Zr(IV) and Hf(IV) ions in aqueous samples using micelle-mediated extraction coupled to inductively coupled plasma-optical emission spectrometry, J. Hazard. Mater. 156 (2008) 583–590.

[18] M.B. Gholivand, M. Omidi, M. Khodadadian, Cloud point extraction and spectro-photometric determination of uranium(VI) in water samples after mixed micelle-mediated extraction using chromotrope 2R as complexing agent, Croat. Chem. Acta 85 (2012) 289–295.

[19] Z.F. Akl, Micelle-mediated preconcentration using cationic surfactants for the spectrophotometric determination of uranium in aqueous solutions, J. Radioanal. Nucl. Chem. 308 (2015) 693–700.

[20] C. Labrecque, S. Potvin, L. Whitty-Leveille, D. Lariviere, Cloud point extraction of uranium using H₂DEH[MDP] in acidic conditions, Talanta 107 (2013) 284–291.

[21] G. Verma, P. Paliwal, S. Kumar, V.K. Aswal, P.A. Hassan, Effect of di-(2-ethylhexyl) phosphoric acid on microstructure, cloud point and uranyl ion binding competence of Triton X-100 micelles, Colloid Surf. A-Physicochem. Eng. Asp. 468 (2015) 262–270.

[22] S. Gao, T. Sun, Q. Chen, X. Shen, Improvement of the cloud point extraction of uranyl ions by the addition of ionic liquids, J. Hazard. Mater. 263 (2013) 562–568.

[23] E. Bağda, E. Yabaş, N. Karakuş, Feasibility of tetracycline, a common antibiotic, as chelating agent for spectrophotometric determination of UO_2^{2+} after cloud point extraction, J. Radioanal. Nucl. Chem. 299 (2013) 1813–1820.

[24] A. Saha, T. Debnath, S. Neogy, H.N. Ghosh, M.K. Saxena, B.S. Tomar, Micellar extraction assisted fluorometric determination of ultratrace amount of uranium in aqueous samples by novel diglycolamide-capped quantum dot nanosensor, Sens.

Actuator B-Chem. 253 (2017) 592–602.

[25] A. Saha, K. Sanyal, N. Rawat, S.B. Deb, M.K. Saxena, B.S. Tomar, Selective micellar extraction of ultratrace levels of uranium in aqueous samples by task specific ionic liquid followed by its detection employing total reflection X-ray fluorescence spectrometry, Anal. Chem. 89 (2017) 10422–10430.

[26] M.E.F. Laespada, J.L.P. Pavon, B.M. Cordero, Micelle-mediated methodology for the preconcentration of uranium prior to its determination by flow injection, Analyst 118 (1993) 209–212.

[27] J. Li, G. Li, Q. Han, Determination of trace uranium by resonance fluorescence method coupled with photo-catalytic technology and dual cloud point extraction, Spectroc. Acta Pt. A-Molec. 169 (2016) 208–215.

[28] C. Labrecque, J.L. Lavergne, D. Larivière, Gross actinide preconcentration using phosphonate-based ligand and cloud point extraction, J. Radioanal. Nucl. Chem. 308 (2015) 527–537.

[29] C.D. Deng, Study on the selective thorium/uranium separation by supramolecular ordered assemble systemes, Master Thesis Peking University, Beijing, China, 2016.

[30] L.Y. Wang, M.S. Lee, Separation of Co(II) and Ni(II) from chloride leach solution of nickel laterite ore by solvent extraction with Cyanex 301, Int. J. Miner. Process. 166 (2017) 45–52.

[31] S.I. El-Dessouky, Mechanism of U(VI) extraction by Cyanex 301 in kerosene from nitrate medium, J. Radioanal. Nucl. Chem. 260 (2004) 613–617.

[32] J. Veliscek-Carolan, Separation of actinides from spent nuclear fuel: A review, J. Hazard. Mater. 318 (2016) 266–281.

[33] A. Saily, S.N. Tandon, Liquid–liquid extraction behavior of V(IV) using phosphinic acids as extractants, Fresenius J. Anal. Chem. 360 (1998) 266–270.

[34] Z.F. Akl, Sensitive quantification of uranium using cloud point extraction coupled with inductively coupled plasma-optical emission spectrometry, J. Radioanal. Nucl. Chem. 315 (2017) 21–28.

[35] C.D. Stalikas, Micelle-mediated extraction as a tool for separation and pre-concentration in metal analysis, Trac-Trends Anal. Chem. 21 (2002) 343–355.

[36] S.F.G.M. van Nispen, J.P.A. Custers, L.J.P. van den Broeke, J.T.F. Keurentjes, Characterization of the binding of multivalent ions to modified pluronic micelles by isothermal titration calorimetry and modified conductometry, Colloid Surf. A-Physicochem. Eng. Asp. 361 (2010) 38–44.

[37] C. Xu, G. Tian, S.J. Teat, L. Rao, Complexation of U(VI) with dipicolinic acid: thermodynamics and coordination modes, Inorg. Chem. 52 (2013) 2750–2756.

[38] Y. Zhu, J. Chen, R. Jiao, Extraction of Am(III) and Eu(III) from nitrate solution with purified Cyanex 301, Solvent Extr. Ion Exch. 14 (1996) 61–68.

[39] E. Freire, O.L. Mayorga, M. Straume, Isothermal titration, Anal. Chem. 62 (1990) 950A–959A.

[40] P. Gans, A. Sabatini, A. Vacca, Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs, Talanta 43 (1996) 1739–1753.

[41] M.A. Rub, F. Khan, D. Kumar, A.M. Asiri, Study of mixed micelles of promethazine hydrochloride (PMT) and nonionic surfactant (TX-100) mixtures at different temperatures and compositions, Tenside Surfactants Deterg. 52 (2015) 236–244.

[42] M. Sprynskyy, I. Kovalchuk, B. Buszewski, The separation of uranium ions by natural and modified diatomite from aqueous solution, J. Hazard. Mater. 181 (2010) 700–707.

[43] T. Sun, S. Gao, Q. Chen, X. Shen, Investigation on the interactions between hydrophobic anions of ionic liquids and Triton X-114 micelles in aqueous solutions, Colloid Surf. A-Physicochem. Eng. Asp. 456 (2014) 18–25.

[44] K. Thakkar, B. Bharatiya, D. Ray, V.K. Aswal, P. Bahadur, Cationic surfactants modulate aqueous micellization and wetting on PTFE by Triton X-100: Effect of alkyl chainlength, headgroup and counterion, J. Mol. Liq. 241 (2017) 136–143.

[45] K. Thakkar, B. Bharatiya, D.O. Shah, D. Ray, V.K. Aswal, P. Bahadur, Interaction of ionic liquid type cationic surfactants with Triton X-100 nonionic micelles, Colloid Surf. A-Physicochem. Eng. Asp. 484 (2015) 547–557.

[46] T. Sun, C. Xu, J. Chen, Formation of W/O microemulsions in the extraction of Nd (III) by bis(2,4,4-trimethylpentyl)dithiophosphinic acid and its effects on Nd(III) coordination, Dalton Trans. 45 (2016) 1078–1084.