Nonionic metal-chelating surfactants mediated solvent-free thermo-induced separation of uranyl†

Chantal Larpent,*[a] Sylvain Prévost,[ab] Laurence Berthon,[c] Thomas Zemb[b] and Fabienne Testard[b]

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Thermo-responsive metal-chelating surfactants permit the solvent-free, cloud point extraction of uranyl nitrate and afford a real molecular economy compared to conventional separation techniques.

Despite major progress in the field of separation techniques in recent decades, the removal of pollutants from aqueous media remains an important challenge and increasing environmental awareness has created a growing need for new solvent-free sustainable processes. In this context, considerable interest is devoted to stimuli-responsive systems based on polymers or surfactants which undergo a phase separation upon heating or addition of salts and thus provide environmentally benign alternatives to conventional liquid–liquid extractions.[1–3] Surfactant-based separation techniques that take advantage of the solubilization capabilities of supramolecular assemblies and do not require the use of organic solvents and extractants are still attracting widespread attention.[1,3,4] Among them, cloud point extraction (CPE), based on the temperature-dependent properties of nonionic surfactants, has been widely used for separation of various organic compounds as well as in the concentration steps of analytical methods.[1,3,4] Cloud point extraction technology is based on the separation of an aqueous micellar solution of a polyoxyethylene (POE) surfactant into a concentrated phase (coacervate), containing most of the surfactant, and a dilute aqueous phase when the temperature is raised above a given temperature referred to as the cloud point (CP).[1,3,4] The extraction relies on the micellar solubilization of the solute and hence requires large amounts of surfactant compared to solute, and applies to quite hydrophobic solutes. Owing to their solubility in water, separation and concentration of metal ions by CPE are most often performed in the presence of an additional chelating agent that forms a lipophilic metal complex and thus favors the partition in the micellar phase.[1,3–5] Consequently, according to green chemistry concepts, one of the main drawbacks of the CPE technique is its poor molecular efficiency in terms of the molar ratio of surfactant and chelating agent to substrate.

A possible approach to overcoming this drawback is to design special functional surfactants capable of recognizing the target. Considering the separation of metal ions, an outstanding issue in the field of environmental remediation, the design of metal-chelating thermo-responsive surfactants (MCTS), which combine metal binding affinity with temperature-dependent behaviour might afford a real molecular economy provided that the metallo-surfactant formed after complexation remains thermo-responsive. Functional surfactants have attracted a great deal of research attention. Among them various chelating surfactants have been described and used as catalysts or in conventional separation techniques.[6,7] On the other hand, polyoxyethylene substituted phosphine ligands have been used in thermo-regulated catalytic systems,[8] but, to our knowledge, there is no previously reported example of thermo-induced separation processes based on thermo-separating metal-chelating surfactants.

As an illustration of the molecular economy and the enhanced extraction efficiency brought by the use of functional surfactants, we report here on new MCTS specially designed for the solvent-free thermo-induced and salt-regulated separation of uranyl nitrate from aqueous solutions. The separation and concentration of uranium(VI) is indeed a topic of sustained interest in nuclear fuel processing, where the limitation of wastes is of prime importance, as well as in analytical science for the detection of traces of this element owing to its high toxicity.[9] In order to control simultaneously the surfactant properties and the binding affinity,[6] we designed and synthesized a series of MCTS, with a di-block molecular structure, by tethering nonionic alkylpolyoxyethylene surfactants (C_iE_j) with a uranyl chelating group (Fig. 1).

The driving force for the inverse temperature-dependent solubility of C_iE_j in water is the dehydration of the POE groups on heating. Consequently, the CPs of C_iE_j surfactants depend on their molecular structure with known relationships: the CP increases as the number of ethoxy units is increased and decreases with the length of the aliphatic tail.[10] The choice of the C_iE_j block in functional surfactants might therefore allow one to control the phase separation temperature. In this study, we compare MCTSs **1** derived from $C_{12}E_5$ and **2** derived from the more hydrophilic $C_{10}E_8$.[11]

Since 1,*n*-diamides (with $n = 3$ to 11, *e.g.* malonamides, uranyl ionophore®) are well-known ligands for the uranyl

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[a] *Institut Lavoisier, UMR-CNRS 8180, Université de Versailles-St-Quentin, 78035 Versailles, France. E-mail: larpent@chimie.uvsq.fr; Fax: +33 1 39 25 44 52; Tel: +33 1 39 25 44 13*
[b] *DSM/DRECAM/SCM/LIONS, CEA-Saclay, 91191 Gif/Yvette, France*
[c] *DEN/DRCP/SCPS/LCSE, CEA-ValRhô, BP17171, 30207 Bagnols-sur-Cèze, France*

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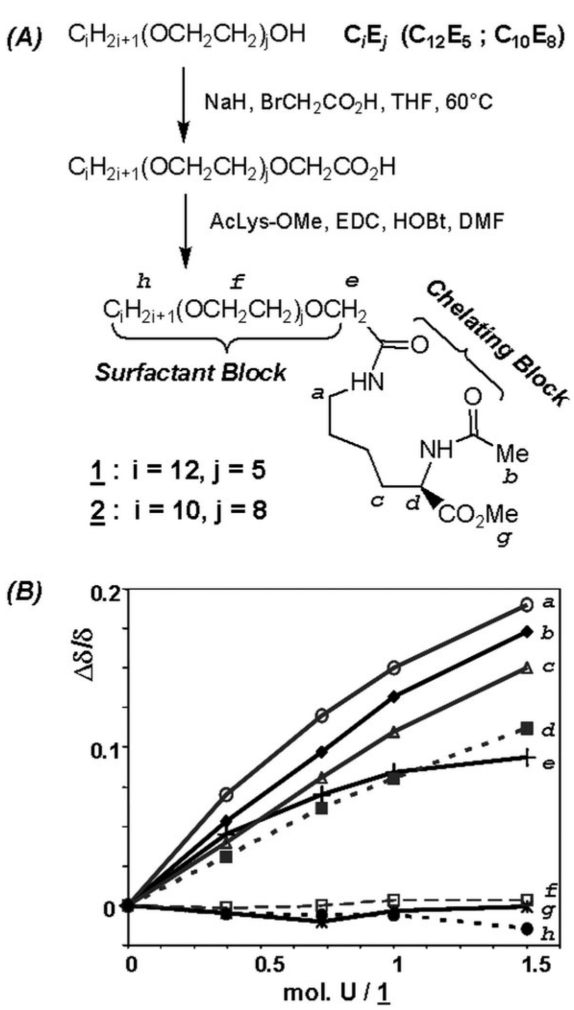

Fig. 1 (A) Structures and synthesis of MCTSs **1** and **2**. (B) ^{1}H NMR titration curve for **1** in $CDCl_3$ with increasing amounts of $UO_2(NO_3)_2$.

ion,[12–15] we choose to graft a diamide clip, derived from acetyllysine, to the tip of POE group in order to provide an affinity for the targeted ion. Lipophilic diamides have been used for the liquid–liquid extraction of U(VI) and the extraction yields were found to depend on the concentration of nitrate anions;[12] we therefore anticipated that cloud point extractions with our diamide-based thermo-responsive surfactants might be further regulated by the concentration of added salts thus offering a simple means to recover the surfactant.

Compounds **1** and **2** were easily prepared, in 72 and 77% yields, in two steps from $C_{12}E_5$ and $C_{10}E_8$ by alkylation with bromoacetic acid followed by coupling with *N*-acetyllysine methyl ester (Fig. 1A).

The interactions of MCTSs with uranyl nitrate were studied by NMR and mass spectrometry. Fig. 1B shows a typical titration curve based on the ^{1}H NMR shifts in $CDCl_3$ with increasing uranyl nitrate concentrations.[16] The protons close to the amide groups are the most shifted while protons of the C_iE_j unit are not significantly affected. These observations indicate that MCTSs coordinate to uranyl ion with the oxygen atoms of the two amide groups.[13] In water, similar variations of the chemical shifts are observed but only in the presence of an excess of nitrate anions suggesting that nitrates act as auxiliary ligands and shift the complexation equilibrium toward the formation of a neutral nitrato complex with two nitrate ions coordinated in a bidentate manner, as already observed with classical diamides.[13] ESI-MS spectra of 1 : 2 mixtures of MCTSs and uranyl nitrate in water display base peaks at *m*/*z* 459.5 and 511.5, respectively for **1** and **2**, which are assigned to the $[MCTS - UO_2]^{2+}$ ions, thus indicating that MCTSs form 1 : 1 complexes with uranyl at low uranium : surfactant ratios.[17]

MCTS **1** and **2** behave as classical nonionic surfactants and exhibit a reversible temperature-dependent behaviour with clouding and subsequent phase separation when a micellar solution is heated above its CP. As expected, their CPs (for 1 wt% solutions in water), 53 °C for **1** and 74 °C for **2**, increase with the polarity of the surfactant unit.[10] In the presence of alkali nitrates, the changes in clouding temperatures are comparable to those observed with classical C_iE_j:[1,18] The CPs of **1** and **2** are increased to 66 °C and 84 °C, respectively, in water + $LiNO_3$ 4 M and lowered to 20 °C and 26 °C, respectively, in water + $NaNO_3$ 4 M.

Interestingly, the clouding temperature of MCTS with a diblock molecular structure is controlled by the surfactant unit and can be further modulated by the addition of alkali nitrates.

Temperature-induced separation of uranyl nitrate from water without any added solvent is readily achieved with MCTSs **1** and **2** (Table 1). The CPE procedure, shown in Fig. 2, is remarkably simple and allows the concentration of uranyl in the coacervate, which does not exceed 5% of the overall volume. In agreement with the NMR analyses and as previously observed in liquid–liquid extractions,[12] the separation of uranyl is favoured in the presence of an excess of nitrate anions (Table 1, entries 6, 8, 9). Considering the decrease of CP towards ambient induced by sodium nitrate, $LiNO_3$ has been chosen as the nitrate source. Efficient separations, with up to 60–70% of U extracted in the concentrated phase and concentration ratio ([U] in the coacervate/[U] in the aqueous phase) ranging from about 30 to 85, are achieved in a single step in the presence of 4 M $LiNO_3$. MCTSs **1** and **2** are quite efficient even at low surfactant : uranyl ratio (4 : 1 to

Table 1 Thermo-regulated separations of uranyl nitrate

Entry	Surf.	R_{Ui}[a]	CP/°C	U_{ext} (%)	R_{Ue}[b]	R_{Uc}[b]
1	**2**	0.25	63	69	0.17	0.19
2	**2**	0.50	47	63	0.32	0.35
3	**2**	0.75	35	53	0.40	0.48
4	**2**	1	23	47	0.47	0.56
5	**1**	0.12	52	60	0.07	0.09
6	**1**	0.48	23	47	0.22	0.28
7	**1**	0.71	12	45	0.32	0.38
8	**1**	0.49[c]	53	0	0	0
9	**1**	0.49[d]	55	19	0.09	nd
10	$C_{12}E_5$	0.5	22	14	0.07	0.11
11	$C_{10}E_8$	0.5	82	14	0.07	0.13

[a] Unless otherwise stated [surfactant] = 0.04 M, [$LiNO_3$] = 4 M, [HNO_3] = 0.01 M, R_{Ui} = $UO_2(NO_3)_2$: surfactant molar ratio in the starting solution, separations were performed at T = CP + 10 °C. [b] R_{Ue} = mol U extracted per surfactant initially introduced and R_{Uc} = mol U per surfactant in the coacervate. [c] Without $LiNO_3$. [d] [$LiNO_3$] = 2 M.

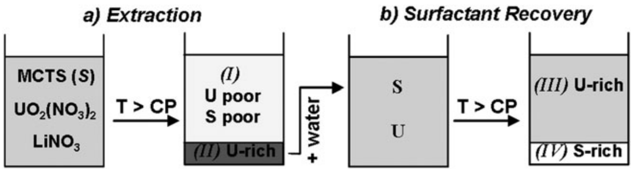

Fig. 2 Thermo-induced uranyl separation (a) and surfactant recovery (b). Typical example: (a) uranyl separation (entry 6, Table 1): a solution of **1** (S, 40 mM), $UO_2(NO_3)_2$ (U, 20 mM), HNO_3 (10 mM) and 4 M $LiNO_3$ separates above 23 °C into a dilute phase I (1.95 mL) and a concentrated deep yellow phase II (0.05 mL), U partition: 53% in I and 47% in II (concentration factor $[U]_{II}/[U]_0 \approx 20$), **1** partition: 7% in I and 93% in II. (b) Surfactant recovery: coacervate II is diluted in 1.95 mL water–HNO_3 (10 mM), where it separates above 52 °C into a dilute phase III and a concentrated phase IV, U partition: 99% in III and 1% in IV, **1** partition: 4% in III and 96% in IV.

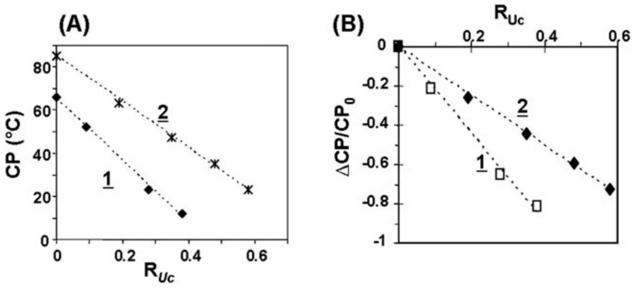

Fig. 3 Variations of CP in extraction experiments with surfactants **1** and **2**. (A): CP (°C) *versus* R_{Uc} (U : MCTS molar ratio in the coacervate). (B): Relative variation of CP [(CP during CPE–CP without U)/CP without U] *versus* R_{Uc}. **1** ($y = -2.22x$, $R^2 = 0.996$), **2** ($y = -1.25x$, $R^2 = 0.998$).

1 : 1; Table 1 entries 1–7) and permit the separation of up to 0.4–0.5 U-per-MCTS. Blank experiments with classical nonionic surfactants $C_{12}E_5$ and $C_{10}E_8$ confirm that the covalent linkage of the chelating moieties to the surfactant block improves the extraction efficiency (Table 1, entries 10–11).

Interestingly, MCTSs afford a real molecular economy compared to conventional extraction systems. For instance, in a classical liquid–liquid process, the extraction of uranyl was performed with a large excess of diamide extractant (about 300 to 1500 mol per U, the latter molar ratio leading to an almost quantitative extraction with a distribution coefficient of about 100)[12] and in previously reported cloud point extractions of uranyl nitrate, large excesses of surfactant (Triton X114, 0.25 to 2 wt%, *i.e.* about 100 to 1000 mol per U) and chelating agent (PAN or 8-HQ, 5 to 10 mol per U) were used.[5]

Moreover, profiting from the effect of the nitrate concentration on the complexation rate, back-extraction, which allows surfactant recovery, is readily achieved as shown in Fig. 2: dilution of the coacervate in water in the absence of additional nitrate salt followed by heating above the CP leads to a coacervate containing more than 90–95% of the surfactant initially introduced while U remains almost quantitatively in the diluted phase.

It is worth noting that significant decreases of the clouding temperatures are observed when the extraction yields increase. As shown in Fig. 3, for a given MCTS the decrease of the CP displays a reverse linear dependence on the uranium : surfactant molar ratio in the coacervate (R_{Uc}) *i.e.* on the molar fraction of uranyl complex. Remarkably, this figure reveals that the complexation yield can be easily deduced from the CP measurement.[19,20]

Clouding and subsequent phase separation of solutions of nonionic surfactants are known to involve a micelle growth, with a sphere to rod transition, driven by the reduction in headgroup area upon dehydration.[21] As already observed for mixtures of nonionic surfactants,[22,23] the variations of CP are consistent with the formation of mixed micelles containing free MCTS molecules and uranyl–surfactant complexes during extraction. A reduction of the area per surfactant molecule upon complexation, which induces the formation of larger aggregates, accounts for the observed linear decrease of the CP when the molar fraction of complex increases.[24,25] These observations may be explained by the formation of neutral nitrato uranyl–surfactant complexes with stoichiometries higher than 1 : 1, which might be favoured by the close proximity of the chelating groups at the micellar surface.[26] Accordingly, modifications of the morphology of aggregates formed by functional surfactants upon binding of metal ions have already been observed and micelle-to-vesicle transitions have been rationalised by the coordination of two polar headgroups to the metal.[27,28] Although further studies are required to determine the structure of the complexes formed during CPE, the appearance of 1 : 2 and 1 : 3 complex ions together with the predominant 1 : 1 complex ion in the ESI-MS spectra of the coacervates supports this hypothesis (the observed relative abundances are 100%, 90% and 25% for 1 : 1, 1 : 2 and 1 : 3 complexes, respectively).

It is noteworthy that the relative decrease of CP is steeper with compound **1**, derived from $C_{12}E_5$, than with **2**, derived from $C_{10}E_8$ (Fig. 3B). In the latter case, the bulky POE group imposes a larger area per molecule, consequently the curvature of the aggregates and hence the CP are less sensitive to the complexation yield. From an experimental point of view, MCTSs with large POE groups like **2** should be preferred because they offer a wider range of operating uranyl concentrations and temperatures: the clouding temperatures range from 23 °C to 63 °C for $UO_2(NO_3)_2$: surfactant ratios ranging from 1 : 1 to 1 : 4.

The functional surfactants reported here, which combine temperature-responsive behaviour with chelating properties, are useful tools for the solvent-free thermo-induced separation of uranyl associated with easy recovery of the surfactant and afford a real molecular economy. Their di-block structure permits an easy control of their solution properties, thereby allowing optimization of the operating temperature ranges by the proper choice of the surfactant unit. The building block strategy depicted here is expected to be quite general and should give access to libraries of functional surfactants with tunable metal binding affinities and modulable clouding temperature ranges. The design of thermo-responsive surfactants that bind transition metal ions and their applications for the removal of heavy metals as well as ligands in thermo-regulated phase transfer catalysis are currently under investigation.

Experimental

Synthesis of surfactants 1 and 2. Typical procedure for 2

A solution decyloxyoctaethylene glycol $C_{10}E_8$ (20.10 g, 39.4 mmol, high purity monodisperse obtained from Nikko) in 50 mL anhydrous THF was added under N_2 upon stirring to a suspension of NaH (60% in mineral oil, 5.50 g, 138.0 mmol) in 40 mL anhydrous THF. After 30 min, a solution of bromoacetic acid (8.30 g, 59.0 mmol) in 20 mL anhydrous THF was added dropwise over 0.5 h. After stirring for 12 h at 60 °C, the reaction mixture was quenched with 1 N HCl and THF was removed under vacuum. The aqueous phase was extracted with Et_2O and the organic phase was washed with 1 N HCl, brine and then dried over $MgSO_4$. The intermediate acid was isolated after removal of the solvent (22.40 g, 100%) as a yellow oil and used without further purification for the following step. 1-hydroxybenzotriazole HOBt (3.3 g, 24.3 mmol) and Ac-Lys-OMe (2.7 g, 14.4 mmol) were added under N_2 to a solution of intermediate acid (4 g, 7 mmol) in 25 mL dry DMF. After stirring for 15 min, EDC (3.4 g, 17.8 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After removal of DMF under reduced pressure, the residue was solubilized in CH_2Cl_2 and the organic phase was washed with 1 N HCl, brine and dried over $MgSO_4$. The crude product isolated after removal of the solvent was purified by column chromatography on silica gel using Et_2O–MeOH–i$PrNH_2$ (20 : 1 : 1) as the eluent to provide **2** (4.1 g, 77% from $C_{10}E_8$). R_f (AcOEt–MeOH 3 : 1) = 0.3. $[\alpha]_D$ + 4 (c = 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.16 (t, J = 6.5 Hz, 1H, NH_ε); 6.41 (d, J = 7.4 Hz, 1H, NH_α); 4.52 (dt, J = 7.4 Hz, J = 4.9 Hz, 1H, CH Lys); 3.97 (s, 2H, OCH_2CO); 3.72 (s, 3H, CO_2CH_3); 3.70–3.54 (m, 32H, OCH_2-CH_2O); 3.43 (t, J = 6.9 Hz, 2H, CH_2CH_2O); 3.28 (m, 2H, NCH_2); 2.02 (s, 3H, CH_3CO); 1.90–1.20 (m, 22H, CH_2); 0.87 (t, J = 6.9 Hz, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 172.93, 170.19, 170.08 ($C{=}O$); 71.53 (CH_2CH_2O); 70.97, 70.60, 70.57, 70.55, 70.51, 70.37, 70.18, 70.03 (OCH_2CH_2O, OCH_2CO); 52.27 (CH Lys); 52.09 (CO_2CH_3); 38.01 (NCH_2); 31.87, 31.49, 29.61, 29.58, 29.54, 29.28, 29.16, 26.06, 22.64, 22.31 (CH_2); 23.00 (CH_3CO); 14.07 (CH_2CH_3). IR ν (cm^{-1}): 3306 (NH), 2923, 2850 (C–H), 1745 (C=O ester), 1677 (C=O amide), 1109 (C–O–C); SM (ESI, CH_3CN–H_2O), m/z: 753.6 (MH^+, 72%); 775.6 (MNa^+, 100%); 791.6 (MK^+, 13%). Anal. Calcd. for $C_{37}H_{72}O_{13}N_2 \cdot 0.5\ H_2O$: C, 58.32; H, 9.66; N, 3.67; O, 28.35. Found: C, 58.15; H, 9.80; N, 3.43; O, 28.41%.

Surfactant **1** has been obtained from $C_{12}E_5$ using the same experimental procedure and was isolated with 72% yield after purification by column chromatography on silica gel using AcOEt–MeOH (6 : 1) as the eluent (experimental details and characteristics are given in the ESI†).

General procedure for CPE

The appropriate amount of uranyl nitrate was added to 2 mL of a solution of surfactant (0.04 mol L^{-1}), lithium nitrate (4 mol L^{-1}) and nitric acid (0.01 mol L^{-1}) in water. After homogenization, the cloud point (CP) was measured and the solution allowed to stand at T = CP + 10 °C in a thermostated bath until phase separation was obtained (1 to 4 h). The surfactant- and U-poor upper diluted phase was separated from the coacervate (highly viscous) and the concentrations of uranium and surfactant were measured respectively by X-ray fluorescence spectroscopy [30] and total organic carbon titration (DC-190 Rosemount Dohrmann carbon analyser). XRF analyses (11.8 to 14.8 keV) were performed with a X-MET 920 METOREX apparatus after dilution of the samples in 1 M nitric acid solution (reference solutions of U(VI) in nitric acid 1 M in the 23.6 to 2364 mg L^{-1} concentration range were used for calibration).

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28 An additional way of explaining the results is through consideration of the packing parameter, $p = v/a_o l_c$ (where l_c and v are the length and volume of the aliphatic chain and a_o the area occupied by a surfactant headgroup).[29] This factor is commonly used to predict the morphology of surfactant aggregates: the prediction of p is $p \leq 1/3$ for small spherical micelles, $1/3 < p \leq 1/2$ for cylindrical micelles and $1/2 < p \leq 1$ for vesicles or bilayers. The coordination of two surfactants to a same uranyl (*i.e.* formation of 1 : 2 complexes) will allow two separated headgroups to get close to each other: the average area per molecule (a_o) will therefore be reduced resulting in an increase of the value of p and, hence, in a micellar growth.

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