

New thermosensitive chelating surfactants for selective solvent-free extraction of uranyl nitrate

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Abstract – Functional surfactants were synthesised by grafting a chelating group (amino-acid residue) to the tip of a polyethoxylated nonionic surfactant chain (C_iE_j : $C_iH_{2i+1}(OCH_2CH_2)_jOH$) or in a branched position. C_iE_j nonionic surfactants are known to be thermoreversible and to exhibit a clouding phenomenon associated to phase separation of micelles. The functional surfactants retain both surface-active properties, characteristic thermoreversible behaviour and have efficient complexing properties toward uranyl. In the presence of uranyl nitrate, small micelles are formed at ambient temperature and the demixing leads to a separation of the target ion trapped by the functional surfactant (cloud point extraction). Those surfactants are more efficient than mixture of classical C_iE_j and complexing agent solubilized in the micelles. This reveals a synergistic effect of the covalent bond between the chelating group and the nonionic surfactant C_iE_j . This paper presents a systematic study of the extraction and aggregation properties and the influence of the nature of the ions.

INTRODUCTION

With the increasing demand of environmentally friendly systems, aqueous phase separation method is a direction for solvent free system [1]. Cloud Point Extraction (CPE) [2] relies upon the ability of surfactants to dehydrate while temperature is increased, leading to a phase separation; thus, no other solvent is required, and the process is reversible – just lowering the temperature, promising efficient desorption capacities. Yet CPE usually requires large amount of surfactant and chelant, and yields a two aqueous phase system: a surfactant-concentrated aqueous phase with the trapped compound (referred as the demixed phase) and a surfactant-diluted aqueous phase more or less free of this compound. Hence a limitation of CPE is often the concentration of chelant in the washed phase, and/or water proportion in the separated phase. To improve extraction, a possibility is to link covalently the chelating group to the surfactant [3]. Following this strategy, we synthesised new thermoreversible chelating surfactants [4, 5] by adding a chelating group, protected lysine, as a pendant (branched molecule) or to the polar extremity (linear molecule) of nonionic C_iE_j surfactants (Fig. 1). Synthesis steps lead to molecules presenting a diamide clamp mimicking the commercial uranyl ionophore [6]. Their capacities as extractant have been studied in correlation with their self-assembling properties [4]. They outperformed

classical CPE systems based on thermoreversible surfactants plus complexing molecules dissolved in micelles [2]. The separated phase retains small quantities of water and the diluted aqueous phase contains small quantities of surfactant (less than 10% of initial quantity).

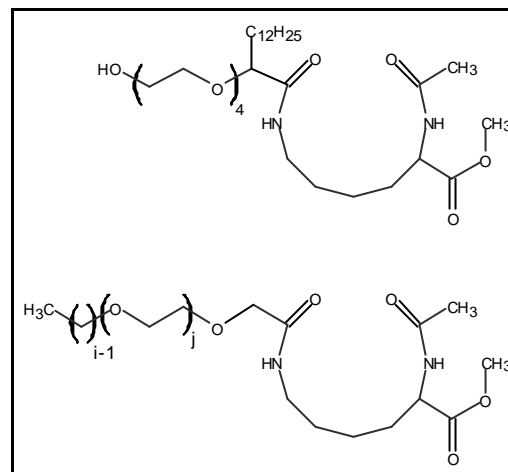


Figure 1: Structures of functionalsurfactants: branched ($C_{12}LE_4$, top) and linear ($C_{12}E_5L$, $i=12$, $j=5$; $C_{10}E_8L$, $i=10$, $j=8$; bottom).

MATERIALS AND METHOD

Materials

The functional surfactants were synthesized as described previously [4, 5]. Polyoxyethylene

ethers (C_iE_j) were supplied by NIKKO Chemicals. Lithium nitrate and uranyl nitrate hexahydrate were purchased from FLUKA. All commercial products were used without any further purification.

Determination of Surface Tension at the Air-Water Interface

The critical micelle concentration (CMC) and area per head group (σ) were determined by surface tension measurements at the air-water interface using the so-called Du-Nouy ring method.

Determination of Cloud Point

The cloud point of functional surfactant aqueous solutions was determined visually for different weight concentrations. Solutions were filled in thin tubes and gradually heated up in a temperature-controlled water bath. At the cloud point, the solution becomes turbid and finally separates into two distinct phases.

SAXS Experiments

Small-Angle X-ray Scattering experiments were performed over a large q -range ($0.015 \text{ \AA}^{-1} - 0.42 \text{ \AA}^{-1}$) using a high sensitivity SAXS camera with a rotating anode [7].

SANS Experiments

Small-Angle Neutron Scattering experiments were performed on the D22-beam line at the Institut Laue Langevin in Grenoble (France): two configurations were used ($\lambda = 6 \text{ \AA}$, $D = 10 \text{ m}$ or 2 m collimation, 11.2 m) to cover a q -range from 5×10^{-3} to 0.5 \AA^{-1} and with a typical acquisition time of 15 to 30 min for each configuration.

Extraction Experiments

A stock solution containing 4 mol/L lithium nitrate and 0.01 mol/L nitric acid was prepared. 2 mL samples consisting of the surfactant (0.02 mol/L) and 0.02 mol/L uranyl nitrate were prepared by dissolving appropriate amounts of the starting materials in the stock solution. After mixing, uranium concentration and pH were measured.

For the cloud point extraction, the sample solution was kept in a thermostated bath. The temperature was increased until cloud point

apparition. The thermostated bath was regulated 10°C upper the cloud point temperature.

After decantation, the 2 phases were separated. The uranium and surfactant concentrations were measured in the aqueous phase.

RESULTS AND DISCUSSION

Surface-Active Properties

Table I summarises the values of CMC and area per head group for the functional surfactants and the precursor C_iE_j . The CMC and hence the energy of micelle formation are not much modified by the presence of the chelating group on the C_iE_j .

TABLE I. CMC and area per head group at 25°C in pure water.

Compounds	CMC (mol/L)	σ (\AA^2)
$C_{12}E_4$ [8]	6.4×10^{-5}	46
$C_{12}E_5$	9.5×10^{-5}	51 ± 2
$C_{10}E_8$ [8]	1.0×10^{-3}	70
$C_{12}LE_4$	$9.3 \times 10^{-5} \pm 10^{-6}$	78 ± 5
$C_{12}E_5L$	$9.6 \times 10^{-5} \pm 10^{-6}$	81 ± 2
$C_{10}E_8L$	$6.4 \times 10^{-4} \pm 5 \times 10^{-5}$	77 ± 5

The area per head group at the air-water interface is increased significantly by comparison to the corresponding C_iE_j . This implies that the lysine group is part of the polar head group and seems to impose the area per head group at the air-water interface.

Cloud Point in Binary Phase Diagram

A lower consolute boundary is present in the binary water/functional surfactant phase diagram. When grafting the chelating group as a pendant group on $C_{12}E_4$ or to the extremity of $C_{12}E_5$, the cloud point rises. This increase corresponds to a temperature jump resulting from respectively the addition of 2 to 3 ethylene oxide group for $C_{12}LE_4$ and 1 ethylene oxide group for $C_{12}E_5L$. The acetyl lysine increases the hydrophilicity of the surfactant.

TABLE II. Cloud point of surfactants in water

Compounds	Weight composition	Cloud point
$C_{12}E_4$	1% w/w	6°C
$C_{12}E_5$	1% w/w	30°C
$C_{10}E_8$	1% w/w	84°C
$C_{12}LE_4$	1% w/w	61°C
$C_{12}E_5L$	1% w/w	52°C
$C_{10}E_8L$	1% w/w	68°C

Inversely, the cloud point $C_{10}E_8L$ derivative is lower than the cloud point of $C_{10}E_8$ as shown in Table II. Therefore the influence of the acetyl lysine depends on the length of the ethoxy group part in the C_iE_j precursor.

Uranyl Extraction

Table III gives the results of the cloud point extractions. The new functional surfactants have efficient complexing properties toward uranyl and are more efficient than the mixtures of the corresponding nonionic surfactants C_iE_j and the acetyl lysine solubilised in the micelles. This reveals the synergistic effect obtained by the covalent link between the two groups.

TABLE III. Extraction of uranyl nitrate from 0.01 mol/L HNO_3 and 4 mol/L $LiNO_3$.

Compounds	[C] mmol/L	$[UO_2^{2+}]_0$ mmol/L	UO_2^{2+} extracted
$C_{12}E_5$	40	19	13%
$C_{12}E_5$ + lysine	40/40	20	20%
$C_{12}E_5L$	41	19	47%
$C_{10}E_8L$	43	19	63%
$C_{12}E_4L$	42	20	45%

As demonstrated in classical liquid/liquid extraction [9], the higher the $LiNO_3$ concentration, the higher the extraction efficiency.

NMR, ESI-MS and SLRT studies are in progress to characterise the complex. Preliminary ESI-MS results indicates the presence of 1/2 or 1/1 complexes in the concentrated phase after cloud point separation.

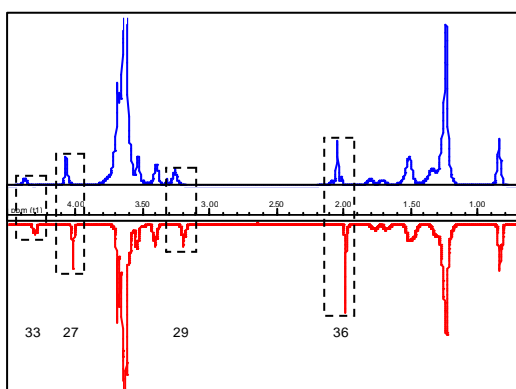


Figure 2: 1H NMR spectra of 0.08 mol/L $C_{10}E_8L$ in heavy water with 0.01 mol/L DNO_3 and 4 mol/L $LiNO_3$, without uranyl (top), and with 0.04 mol/L uranyl (bottom). See Fig. 3 for number of proton atom.

Moreover, NMR analyses of the aqueous solution before separation indicate that the diamide residue coordinates to uranyl. In ^{13}C NMR, the signals of the amide carbonyl are altered. 1H NMR spectra have shown that protons closed to the diamide group are the most shifted (Fig. 2). These first results reveal that uranyl is complexed by the diamide as shown in Fig. 3. Magnetic anisotropy of uranyl ion causes protons near the plane perpendicular to the axial O-U-O bond to exhibit down-field shifts [10]; lysine-protons around amides are the most affected, highlighting the role of the diamide in this complexation.

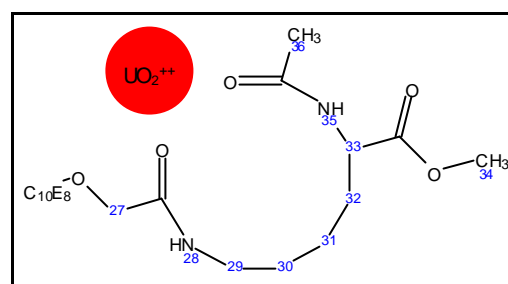


Figure 3: Amino-acid part of the $C_{10}E_8L$ with numbered protons; ^{13}C and 1H NMR indicate that uranyl is trapped by the diamide function.

The effect of salts on the cloud point of classical C_iE_j water solution is well documented [11]. Data reported in Table IV show that the cloud point of the functional surfactant is modified by the presence of recognised or unrecognised salt. ΔT_C is the cloud point shift compared to the value in pure water.

TABLE IV. Effect of recognised and non-recognised salts on the cloud point.

Compound	$[UO_2^{2+}]$	$[LiNO_3]$	ΔT_C
$C_{12}E_5$ 4% w/w	0 mol/L	4 mol/L	+5°C
$C_{12}E_5$ 1% w/w	0.2 mol/L	0 mol/L	+7°C
$C_{12}E_5$ 1% w/w	0.2 mol/L	4 mol/L	-28°C
$C_{12}E_5L$ 3% w/w	0 mol/L	4 mol/L	+12°C
$C_{12}E_5L$ 1% w/w	0.2 mol/L	0 mol/L	-1°C
$C_{12}E_5L$ 5.5% w/w	0.04 mol/L	4 mol/L	-42°C

The addition of $LiNO_3$ induces a classical salting-in effect by increasing the cloud point. If uranyl nitrate is added to the solution no variation in the cloud point is observed. This is concomitant to no extraction of uranyl. When both $LiNO_3$ and uranyl nitrate are added, a large decrease in the cloud point is observed (salting-out) with a large increase in uranyl extraction as shown in Fig. 4.

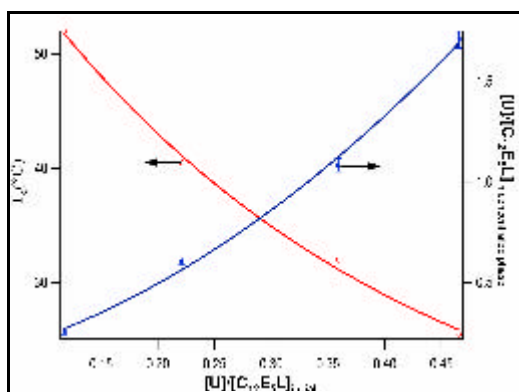


Figure 4: Cloud point variation and $[U]/[C_{12}E_5L]$ in the concentrated phase versus $[U]/[C_{12}E_5L]$ initial ratio. Initial solution: 0.04 mol/L $C_{12}E_5L$, 4 mol/L $LiNO_3$, 0.01 mol/L HNO_3 .

Specific Effect

This correlation between extraction and decrease of the cloud point was used to determine the selectivity of uranyl extraction. Table V gives the obtained decrease in cloud point in the presence of different ions. Clearly uranyl has a specific effect on the cloud point. Now, competitive ions extractions are to be studied to understand the specificity of the uranyl effect on the cloud point.

TABLE V. Shifts in cloud point when different salt are added to (1% w/w $C_{10}E_8L$, 4 mol/L $LiNO_3$, 0.01 mol/L HNO_3). Salts are present at a concentration of about 0.3 mol/L for cations (about 25 times molecular concentration).

Salt	T_C	ΔT_C
Na^+	67°C	-27°C
La^{3+}	53°C	-41°C
Nd^{3+}	53°C	-41°C
UO_2^{2+}	<20°C	>74°C
Eu^{3+}	62°C	-32°C
Gd^{3+}	50°C	-44°C
Er^{3+}	53°C	-41°C

Aggregation Properties

The effect of recognised and unrecognised salt on the aggregation properties were also studied by SAXS and SANS measurements [12]. At 20°C, addition of 4 mol/L $LiNO_3$ to the 0.04 mol/L $C_{12}E_5L$ solution decreases the aggregation number (from 68 to 58) and corresponds to an increase in the cloud point (47°C to 63°C). The opposite effect is observed upon addition of both $LiNO_3$ and $UO_2(NO_3)_2$ which induces an increase in aggregation number

($N=105$) and a large decrease in the cloud point ($T_C=37^\circ C$). The strongest microstructural effect of the presence of uranyl nitrate is to induce a sphere-to-short cylinder (ellipsoid) transition. Mixed micelles are present in the solution containing free surfactant monomers and uranyl/surfactant complexes.

CONCLUSION

Functional surfactants retain both the surface-active properties and the characteristic thermoreversible behaviour. These new functional surfactants give complexes with uranyl nitrate and are more efficient than mixtures of classical nonionic surfactants and acetyllysine ligand. This reveals the synergistic effect obtained by the covalent linkage of chelating group to a surfactant. Thermosensitive metal-chelating surfactants hold most promise for the development of new solvent free extraction processes.

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