Oleylethoxycarboxylate – An efficient surfactant for copper extraction and surfactant recycling via micellar enhanced ultrafiltration

Michael Schwarze [a,*], Leonardo Chiappisi [b], Sylvain Prévost [b,c], Michael Gradzielski [b]

[a] Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 124, Sekr. TC8, D-10623 Berlin, Germany
[b] Technische Universität Berlin, Stranski Laboratorium für Physikalische Chemie und Theoretische Chemie, Institut für Chemie, Straße des 17. Juni 124, Sekr. TC7, D-10623 Berlin, Germany
[c] Helmholtz-Zentrum Berlin, Lise-Meitner-Campus, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

ABSTRACT

The nonaoxyethylene oleylether carboxylic acid Akypo RO90 VG, a surfactant with ionic character at high pH and non-ionic character at low pH, has been investigated with respect to copper removal from aqueous streams via micellar enhanced ultrafiltration (MEUF) with subsequent copper and RO90 separation using the method of cloud point extraction (CPE). Almost quantitative Cu^{2+} removal is obtained in MEUF and more than 90% Cu^{2+} is separated from RO90 in CPE. The investigation of Cu^{2+}/RO90 complexes with small-angle neutron scattering (SANS) shows almost no structural change of RO90 micelles in the presence of Cu^{2+}. These results show the importance of the surfactant head group for optimizing the specific interaction with the ion to be extracted. This optimization and the ability to recycle the surfactant by a temperature variation and using the cloud point phenomenon is an elegant approach to achieve efficient metal ion extraction.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Micellar-enhanced ultrafiltration (MEUF) has become an efficient tool for the separation of ions [1], dyes [2,3] or organic molecules [4,5] from aqueous streams. Above the critical micelle concentration (cmc), surfactant monomers aggregate into micelles that exhibit specific interactions with dissolved matter (solute), e.g. ions bound to ionic micelles with opposite charge or non-polar compounds are solubilized. A more complex procedure consists in the use of surfactants complexing the solute, which often requires the chemical modification of the surfactant headgroup [6,7]. After binding the solute, micelles and thereby the solute can be separated from water by filtration using an appropriate ultrafiltration membrane. Most of the performed MEUF studies deal with the removal of heavy metal cations and the anionic surfactant sodium dodecylsulfate (SDS) is mainly used for this purpose with more than 90% ion removal reported for, e.g. Cd^{2+} [8], Cu^{2+}, Pb^{2+} [9] and Zn^{2+} [9,10]. The major disadvantage of using ionic surfactants is the high cmc. This means that not only a higher surfactant concentration is needed to form micelles but also the surfactant will be present in the purified stream at higher concentrations. As shown by different groups, one approach to significantly reduce

the cmc is the use of mixed-micellar solutions in MEUF [11–14]. Nevertheless, very low cmc values are obtained only for non-ionic surfactants that in general show no strong affinity to cations. Although there are several examples showing metal ion extraction with non-ionic surfactants via cloud point extraction [15,16], in MEUF so far mostly simple ionic surfactants have been employed for the purpose of ion extraction [1]. In our study we extended this concept of having an ionic head group that interacts strongly with the ion to be extracted by supplementing it with a hydrophilic moiety, here EO groups, that on one side allows for an additional attractive interaction (like a flexible crown ether) and on the other side imparts temperature sensitivity to the surfactant. Nonaoxyethylene oleylether carboxylic acid, distributed by Kao Chemicals Europe under the trade name AKYPO® RO90 VG, shortly RO90, is a surfactant with a very low cmc that depending on the pH has the properties of non-ionic and ionic surfactants. Being a commercial surfactant it is also available in large quantities, as for instance required for potential larger scale applications. At low pH it behaves like a non-ionic surfactant, while at higher pH, after dissociation of the carboxylic acid group, it gains the properties of an ionic surfactant however keeping a rather low cmc. This means that here we improve upon the classical approach with anionic surfactants by having a surfactant with both pH and temperature dependencies and a substantially lower cmc, all just with having one appropriately built surfactant.

* Corresponding author. Fax: +49 30 314 79552.
  E-mail address: ms@chem.tu-berlin.de (M. Schwarze).

In this contribution we investigate RO90 as an alternative surfactant to SDS for the removal of copper ions from water. We study the aggregates formed by copper and RO90 by small-angle neutron scattering (SANS) and test their performance in MEUF. Furthermore, we investigate surfactant recycling from the concentrated retentate by cloud point separation at low pH, where the surfactant is non-ionic. The proposed mechanism for copper removal and surfactant recycling is shown in Fig. 1.

2. Materials and methods

2.1. Materials

The surfactants used in the experiments were sodium dodecylsulfate (SDS, AppliChem, 99.5% purity, Mw = 288.38 g mol^{-1}). RO90, a technical surfactant produced by Kao Chemicals under the treade name AKYPO® RO90 VG, was used without further purification. According to the producer its molecular weight is 711 g mol^{-1}, the hydrophobic part of the surfactant is given by a 1:1 mixture of C$_{16}$ and C$_{18:1}$ aliphatic chains, the hydrophilic by an average of nine ethylenoxide units terminated by a carboxymethyl group. A representative chemical structure is shown in Fig. 2. For the calculations densities of 0.85, 0.81 and 1.19 g cm^{-3} for the oleic alcohol, the cetyl alcohol and the oligoethylenoxide moieties and carboxylic group, respectively, were used. The volumes of the hydrophobic (v_c) and hydrophilic (v_s) parts of RO90 and the scattering length densities were calculated accordingly and are summarized in Table 1. Samples were prepared using double distilled water and D$_2$O from Eurisotop (99.85% D) for the small-angle neutron scattering experiments.

As copper source copper (II) sulfate (CuSO$_4$·5H$_2$O, Sigma-Aldrich, 99% purity, Mw = 249.69 g mol^{-1} or CuSO$_4$, Sigma-Aldrich, 99% purity, Mw = 159.61 g mol^{-1}) was used. Sodium hydroxide (NaOH) from Sigma Aldrich or hydrochloric acid (HCl) from Roth was used to adjust the pH value.

2.2. Micellar enhanced ultrafiltration

Micellar enhanced ultrafiltration was carried out in a stirred filtration cell (model GN10-400 from Berghof Germany) having a maximum volume uptake of 400 mL. For the filtration experiments hydrophilic membranes made of cellulose (PLCC, Millipore, Germany) and having a molecular weight cut-off (MWCO) of 5 kDa were used. A contact angle of water on the membrane of 18 ± 2° was determined using an OCA 20 instrument (Dataphysics, Germany). This low value indicates the hydrophilic character of the membrane. Before filtration the membranes were soaked in propan-2-ol/water solution (v/v = 1/1) for about 20 h and then shaken in distilled water twice for 30 min. For a typical filtration experiment the cell was charged with 200 mL feed solution and then filtered at room temperature (about 22 °C) at a pressure of 0.1 MPa set with nitrogen. To reduce concentration polarization the solution was stirred at 250 min^{-1}. Samples were collected over time and filtration was carried out until a volume concentration factor (VCF) of about 2 was reached. The VCF is calculated as follows
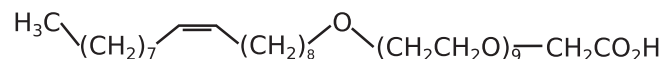
Fig. 2. Representative chemical structure of RO90 (here shown for the case of an oleyl rest; similarly probable one would find a cetyl moiety here).

Table 1
Physiochemical properties of RO90 and its hydrophylic and lipophylic moieties. Densities are given in g/cm^3, molecular weight in g/mol, volumes in nm^3, SLDs in 10^{-5} nm^{-2}.

	Density	Mw	Volume	SLD
Hydrophobic	0.83	254.5	0.51	−1.66
Hydrophilic	1.19	455	0.63	9.63
Total	1.06	709.5	1.14	4.61

$$VCF = \frac{V_{t=0}}{V_t} \quad (1)$$

where $V_{t=0}$ and V_t are the volumes of the retentate at the beginning and after a certain time t, respectively. Copper removal (R_{Cu}) was calculated from the copper concentrations in permeate (c_P) and retentate (c_R)

$$R_{Cu} = 1 - \frac{c_P}{c_R} \quad (2)$$

where c_R was obtained from the mass balance

$$c_R = \frac{V_F \cdot c_F - V_P \cdot c_P}{V_F - V_P} \quad (3)$$

with V_F, V_P, and c_F being the feed volume, the permeate volume, and the feed copper concentration, respectively.

2.3. Small-angle neutron scattering

Small-angle neutron scattering (SANS) experiments were carried out on the V4 instrument at the Helmholtz-Zentrum Berlin, Berlin, Germany [17]. Samples were prepared in D$_2$O and contained in quartz cuvettes of 2 mm neutron pathway, thermalized at 25 °C. Measurements were performed at three configurations, with sample-to-detector distances of 1, 6 (wavelength λ = 0.455 nm, fwhm 10%) and 15.76 m (λ = 1.02 nm, fwhm 10%) and respective collimation lengths of 2, 8 and 16 m, thus covering a q-range of 0.03–6 nm^{-1}, where q is the magnitude of the scattering vector ($q = 4\pi/\lambda \sin(\theta/2)$, θ being the scattering angle). Detector offset and neutron wavelength were determined using silver behenate [18]. Solid angle variation and pixel efficiencies were accounted for using H$_2$O 1 mm as a reference for data at 1 m, and neglected at larger distances. Data reduction was performed with BerSANS [19], taking into account the ambient background with the data obtained with cadmium at the sample position, sample transmission and thickness, subtracting the scattering of a 2 mm thick D$_2$O sample as solvent background (thereby the incoherent background from the hydrogenated material remains), and normalizing by the flux evaluated from the attenuated direct beam. Finally, the 2D detector image was radially averaged. Fits were performed in
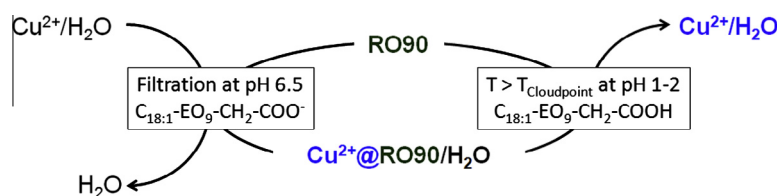
Fig. 1. Scheme for copper removal and subsequent copper/surfactant separation with RO90 surfactant.