



Adsorption and filtration behaviour of non-ionic surfactants during reverse micellar-enhanced ultrafiltration

L.A.T. Nguyen^{a,b}, M. Minding^b, M. Schwarze^b, A. Drews^{c,*}, R. Schomäcker^b, M. Kraume^a

^a TU Berlin, Chair of Chemical Engineering, FH 6.1, Fraunhoferstr. 33-36, 10587 Berlin, Germany

^b TU Berlin, Department of Chemistry, TC 8, Straße des 17. Juni 124, 10623 Berlin, Germany

^c HTW Berlin, School of Life Science Engineering, FB 2, Wilhelminenhofstr, 75A, 12459 Berlin, Germany

ARTICLE INFO

Article history:

Received 5 August 2012

Received in revised form

8 January 2013

Accepted 9 January 2013

Available online 18 January 2013

Keywords:

Ultrafiltration

Reverse micelles

Surfactant

Adsorption

ABSTRACT

Micellar-enhanced ultrafiltration is an established method for the separation of oil-in-water micelles from aqueous streams, e.g., in wastewater treatment and catalytic reaction processes. However, its counterpart, the ultrafiltration (UF) of reverse micelles, known as water-in-oil-micelles, has been rarely researched until now. Our study shows that UF of non-ionic reverse micelles using the ternary system 1-dodecene/water/Marlophen NP5 is not technically feasible. The effects of hydrophobic and hydrophilic membrane properties as well as the variation of surfactant concentration on the filtration behaviour were investigated. Two regions could be distinguished in terms of filtration behaviour when surfactant concentration was increased: (a) below the critical micelle concentration (cmc) flux declined sharply, and (b) above the cmc it increased. Below the cmc, the adsorption of surfactants onto the membrane surface seems to be irreversible when oil (long-chain olefin) is the continuous phase. Above the cmc, the reverse micelle formation leads to a high flux recovery. However, due to surface diffusion, retention of micelles was negligible in all cases.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Micellar enhanced ultrafiltration (MEUF) is an established method to separate dissolved low molecular weight substances from aqueous streams [1,2]. The basic principle of this method is to embed these substances in micelles which form at surfactant concentrations above a critical value, i.e., the critical micelle concentration (cmc). These can then be retained by ultrafiltration (UF) membranes. Two types of MEUF can be differentiated depending on the continuous medium of the feed solution: UF of normal micelles from an aqueous solution (o/w-MEUF) and UF of reverse micelles from an organic solution (w/o-MEUF). These ternary mixtures of water, oil and surfactant, called microemulsions, are thermodynamically stable, optically transparent and macroscopically homogeneous [3]. The micelles can fix target substances like reactants and catalysts, as well as organic micropollutants. Preferentially, the compounds are dissolved in the hydrophobic interior of the normal micelles or in the hydrophilic interior of the reverse micelles. In contrast to the normal micelles, reverse micelles are surfactant aggregates in non-polar solvents where the hydrophilic head groups of the amphiphilic molecules are oriented into the core of the spherical aggregates [4]. Reverse

micellar solutions are used, e.g., in biotechnology because the “water pool” of the reverse micelles can serve as a host for hydrophilic enzymes. In this way, they act as a microreactor for substrates which are preferentially soluble in non-polar media [5].

For separating normal micelles from aqueous solutions, o/w-MEUF has been shown to be an efficient technique to remove ions, salts and micropollutants from wastewater [1,6–8] as well as to recover catalysts from process water [2,9]. In comparison to o/w-MEUF, the knowledge on UF of reverse micelles is very rudimentary until now. The separation principle of w/o-MEUF is illustrated in Fig. 1. Most of the published studies on w/o-MEUF have focused on systems with ionic surfactants like AOT (sodium diethylhexyl sulfosuccinate) [10–12] and TTAB (tetradecyltrimethylammonium bromide) [13] in organic solvents like iso-octane, cyclohexane and a mixture of heptanes/octanol. In these studies, surfactant retention of more than 90% was achieved. Because the water content of the AOT-system can be varied over a wide range and its phase behaviour with water and several oils has been studied intensively [3], AOT has been most widely applied for reverse micellar solutions [5]. To implement a continuous enzymatic reaction with a simultaneous UF of catalysts, most of the authors applied ceramic membranes (MWCO 10–15 kDa) for ionic surfactants [10,11,13], while Orlich and Schomäcker used polymeric membranes (polyamide, MWCO 10–20 kDa) with the non-ionic surfactant Marlipal O 13/60

* Corresponding author. Tel.: +49 30 501 93309; fax: +49 30 501 92125.
E-mail address: anja.drews@htw-berlin.de (A. Drews).

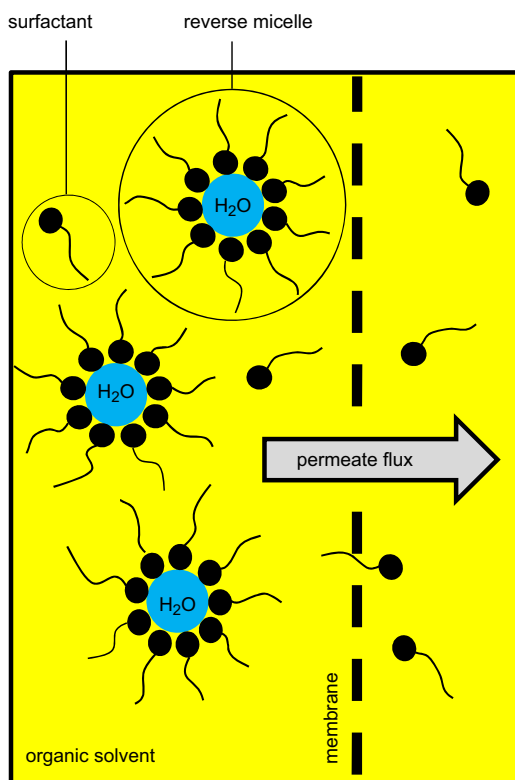


Fig. 1. Separation principle of w/o-MEUF (UF of reverse micelles).

(hexaethoxylene-iso-tridecanol) [14,15]. Without implementing the upstream reaction, Schomäcker et al. investigated the w/o-MEUF, utilising the ionic surfactant AOT [12] as well as the non-ionic Igepal CA520 (pentaethyleneglycolmonoisonylphenylether) [16] using the same polyamide membrane.

For the hydroformylation of 1-dodecene in micellar systems, non-ionic surfactants turned out to yield good conversion and selectivity [17]. In this process, the rhodium catalyst is embedded in the micelles in order to be recycled after the reaction [18,19]. A variety of non-ionic surfactants with different ethoxylation degrees is available. This enables optimal adjustment of the desired phase behaviour at the reaction temperature. However, as outlined above, little is known about the filtration behaviour of non-ionic surfactant w/o-micelles with long-chain olefins as the continuous phase. Therefore, in this study, we investigated the UF of reverse micelles in the ternary system 1-dodecene/water/Marlophen NP5 with a focus on the effect of the surfactant concentration as well as on the influence of using hydrophobic or hydrophilic membranes.

2. Experimental

2.1. Chemicals

Marlophen NP5, a technical grade non-ionic surfactant manufactured by Sasol Germany GmbH, was used in this study. Marlophen NP5 is an ethoxylated nonylphenol alcohol (Fig. 2). Its molecules are polydisperse with an average ethoxylation degree n of 5. Hence, this technical surfactant is easily soluble in oil at room temperature. The molecular weight of Marlophen NP5 is 441 g/mol, the density is 1.03 g/mL and the viscosity at 20 °C is 340 mPa s [20].

For the purpose of this study, 1-dodecene in synthesis quality was purchased from Merck Darmstadt KGaA. This non-polar

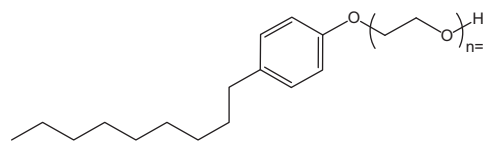


Fig. 2. Chemical structure of Marlophen NP5.

Table 1
Contact angles of the membranes used in the study.

Membrane	Contact angle (°)
PTFE	63.7
PA	56.0
PES	53.0
PAN	42.7
TiO ₂	30.3

solvent has a density ρ_s of 0.76 g/mL, and a molecular weight of 168.33 g/mol. Its moisture was measured by a Karl Fischer titrator [21] and we found the water content to be 0.0048 wt%. The acetonitrile (HPLC grade) used for the UV/vis-measurement (see Section 2.7) was purchased from Carl Roth GmbH+Co. KG. In all experiments, Milli-Q ultrapure water was used, and all chemicals were applied without further purification.

All solutions used in the study were prepared by weight. The surfactant mass fraction γ is given as:

$$\gamma = \frac{m_{\text{surfactant}}}{m_{\text{surfactant}} + m_{\text{oil}} + m_{\text{water}}} \quad (1)$$

with m_i the used mass of the respective compounds.

2.2. Membrane types

Three hydrophobic flat sheet membranes with the same nominal molecular weight cut-off MWCO of 10 kDa were used: Polytetrafluoroethylene (PTFE, Alfa Laval Nordic A/S), polyethersulfone (PES, Microdyn Nadir GmbH) and polyamide (PA, Berghof GmbH & Co. KG). Two hydrophilic membranes were also tested: titanium dioxide (TiO₂, Fraunhofer IKTS) with a nominal pore size of 5 nm and a thickness of 1 mm, and polyacrylonitrile (PAN, PolyAN GmbH) with a MWCO of 10 kDa. The membrane pore sizes or MWCO, respectively, were selected based on the measured reverse micelle sizes of 6–8 nm (see Section 2.5).

The hydrophilic and hydrophobic properties of the tested membranes were determined by optical contact angle measurements based on the static sessile drop method. Prior to the measurement, every membrane had already been rinsed with deionized water and then dried. The overview of the measured values is given in Table 1. Hence, the hydrophilicity decreases in the following order: TiO₂, PAN, PES, PA and PTFE.

2.3. Experimental set-up

The UF experiments were carried out using a batch stirred cell obtained from Schleicher and Schuell (SC 75) with a working volume of 75 mL and an effective membrane area A_{membrane} of $1.39 \times 10^{-3} \text{ m}^2$. This solvent-resistant test cell was made of stainless steel and borosilicate glass. The set-up is shown schematically in Fig. 3. The stirrer speed in the test cell was set to 200 min^{-1} . All experiments were carried out at 20 °C and a nitrogen pressure Δp of 3 bar.

An attempt to pretreat the membranes (shaking in and pre-filtration with alcoholic solutions) was carried out but proved to be inapplicable to the w/o-MEUF of 1-dodecene/water/Marlophen

Download English Version:

<https://daneshyari.com/en/article/634478>

Download Persian Version:

<https://daneshyari.com/article/634478>

[Daneshyari.com](https://daneshyari.com)