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Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

## Product recovery in surfactant-based separation processes: Pervaporation of toluene from concentrated surfactant solutions

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### ARTICLE INFO

#### Article history:

Received 6 September 2012

Received in revised form

2 May 2013

Accepted 3 May 2013

Available online 10 May 2013

#### Keywords:

Surfactants

Cloud point extraction

Recovery

Membrane

Pervaporation

### ABSTRACT

Aqueous micellar two-phase systems have been proposed for the cloud point extraction (CPE) of hazardous compounds or high valued products from aqueous solutions. The efficiency of the CPE strongly depends on the reuse of surfactant as well as the product recovery from the coacervate phase. In this work the membrane process pervaporation was successfully applied to remove contaminants from concentrated surfactant solutions. Experimental results show that a polyoctylmethylsiloxane membrane is the most suitable membrane to separate toluene from a 20 wt% Triton X-114 solution. Furthermore, it is demonstrated that trans-membrane fluxes decrease with increasing surfactant concentration. In case of toluene no correlation between concentration and depletion rate was observed. However, it was observed, that the viscosity of the solution is highly influenced by toluene concentration and thus, effects the efficiency of the pervaporation process. To improve the pervaporation performance the influence of temperature and volumetric flow rate on the depletion rate was investigated. The toluene depletion from surfactant-rich solution increases from 30.2% to 55.1% after 200 min by optimising these parameters. The presented results show that the product recovery after the cloud point extraction can successfully be fulfilled by pervaporation. Compared to alternative separation methods no loss of surfactant or excessive foaming was observed in any of the experiments.

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### 1. Introduction

Increasing surfactant concentration in an aqueous solution above a certain concentration, the so called critical micelle formation concentration (cmc) leads to the formation of aggregates, referred to as micelles [1]. The hydrophilic head group is directed towards the aqueous bulk phase and the hydrophobic tail towards the centre of the aggregates [2]. The hydrophobic core region of the micelle allows the solubilisation of lipophilic substances and therefore increases the solubility of hydrophobic substances in aqueous solutions significantly. Depending on the hydrophobicity of the substance, it is localised between the core of the micelle and the interface to the aqueous bulk phase [3].

Aqueous solutions of non-ionic surfactants split into two phases if the temperature is increased above a certain value. Above the so called cloud point temperature (CPT) two phases coexist: an aqueous phase and a surfactant-rich phase, often referred to as coacervate phase [4]. The aqueous phase contains surfactant concentrations near the cmc, while the coacervate

phase is a surfactant rich phase. Organic solutes are solubilized in the core of the micelle, hence, they are significantly enriched in the coacervate phase.

The cloud point extraction (CPE) uses the concentration of hydrophobic substances in the core regions of the micelles and the phase separation caused by temperature increases as separation processes. As a result of the cloud point extraction a low volume, high concentrated phase containing nearly the whole target compound is observed. The process can be realised as continuous or batch [5]. There are a wide range of applications for the CPE, e.g. the extraction of biomaterials [6], preconcentration of metal ions [7], wastewater treatment [5] and extraction for chemical analysis [8]. The CPE has significant advantages compared to other separation processes due to the low energy consumption [6], the environmentally friendly nature of many non-ionic surfactants [9] as well as their biodegradability [10]. Especially the volume reduction of the concentrated stream is a huge advantage for post-treatment. But the efficiency of CPE strongly depends on the reuse of the surfactant as well as the product recovery from the coacervate phase [11]. Therefore, many investigations concerning the recovery of surfactants from contaminated micellar solutions are reported in literature [12]. Different unit operations were studied, like air stripping [13], vacuum stripping [10], and pervaporation. Compared to vacuum and air stripping the pervaporation

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process is not affected by foaming, thus, it seems to be a promising technique for the recovery of surfactants [14]. In addition the surfactant is completely retained by the dense membrane used for pervaporation, the permeate is free of surfactant [15].

Pervaporation is a membrane based separation process; the separation is based on the interactions of the single components with the membrane polymer [16]. The driving force for the mass transport is the difference in the chemical potential of the compounds between feed and permeate site of the membrane [17]. The mass transport mechanism usually is described by the extended solution-diffusion model [18]. However, several studies [15,19] for aqueous surfactant solutions showed that in the presence of surfactants additional phenomena are observed which affect the mass transport. Hence, the extended solution-diffusion model cannot be applied in the presence of surfactants. Besides, with increasing surfactant concentration the viscosity increases, and thus, the influence of the feed side boundary layer increases [15]. Since the feed side boundary layer poses an additional transport resistance, it influences the permeation flux essentially [20]. In addition, in aqueous micellar solutions, the solute is enriched in the micelles. Thus, the solution contains less solute in the aqueous phase which results in a reduced direct transfer to the membrane surface [19]. However, Gittel et al. [19] showed that the solute transported in micelles to the membrane surface is not negligible. Therefore, for the description of the mass transfer of the solute to the membrane surface both mechanisms must be taken into account, the transport of the solute in the aqueous solution and the transport of the solute in the micelles. Furthermore, surfactants increase the transport resistance by sorption on the membrane surface. Hartwig et al. [19] showed, that depending on the surfactant concentration, the membrane is covered with up to 200 monolayers.

Previously, the pervaporation has been investigated for aqueous solutions with low surfactant concentrations ( $w_{\text{surfactant}} \ll 2$  wt %) [9,14,21–23]. However, in CPE processes surfactant concentrations in the coacervate phase are at least one order of magnitude higher. Therefore, the present study aims to evaluate the purification of concentrated surfactant solutions by pervaporation. First, the composition of the coacervate phase was determined for the system Triton X-114/water/toluene by a novel method based on a temperature controlled centrifuge [24]. Different membranes were compared according to their separation efficiency of toluene from concentrated surfactant solutions. Further, optimised process parameters including the influence of the temperature as well as the flow rate were investigated, and analysed by means of viscosity measurements.

## 2. Experimental section

### 2.1. Materials

The non-ionic surfactant Triton X-114 (TX-114) from Sigma-Aldrich in laboratory grade was used for all experiments. Toluene with a purity of  $\geq 99.9\%$  from Merck was chosen as model contaminant. For analytical purposes acetonitrile from Merck with a purity of  $\geq 99.9\%$  was used. For pervaporation experiments composite membranes with different polymers and active separation layer thicknesses were tested, see Table 1. The membranes were multilayer composite membranes manufactured by the Helmholtz-Zentrum Geesthacht. The composite membranes were produced in two steps. In the first step the microporous support layer was prepared. Therefore a solution, containing 13 wt% polyacrylonitrile (PAN) solution in a high boiling organic solvent was cast on a polyester non-woven and immersed in a water bath by a casting machine for membrane formation by phase inversion.

**Table 1**

Overview of tested composite membranes for toluene depletion from surfactant rich solutions. Composition of different polymer isooctane solutions with different additives.

Membrane	Support layer	Separation layer	Separation layer thickness ( $\mu\text{m}$ )
25 wt% POMS	Polyacrylonitrile	Polyoctylmethylsiloxane	5.5
12 wt% PDMS	Polyacrylonitrile	Polydimethylsiloxane	16.0
10 wt% PDMS	Polyacrylonitrile	Polydimethylsiloxane	8.0
10 wt% PDMS, crosslinked	Polyacrylonitrile	Polydimethylsiloxane	8.0

More detailed information on the PAN membrane is given by Scharnagl et al. [25]. In a second step the support layer was coated with solutions of different polymers solved in isooctane with different additives by means of a coating machine. The polymer contents and membrane thicknesses are shown in Table 1. Since the membranes are also commercially applied for gas permeation applications no additional information regarding membrane formulation can be given. The dense separation layer was formed by evaporation of the volatile solvent from the polymer solution. For the POMS and PDMS layers, thermally induced, catalysed crosslinking took place also during the solvent evaporation stage. One 10% PDMS membrane was additionally radiation crosslinked in subsequent preparation step. This membrane was included into the study in order to investigate whether this additional crosslinking step improves separation performance. The separation layer thickness was determined by scanning electron microscopy.

### 2.2. Determination of the ternary LLE: Triton X-114/water/toluene

In order to determine the coacervate phase composition, the ternary liquid–liquid equilibria for the system toluene/TX-114/water at 40 °C were measured. Aqueous solutions containing 5 wt% TX-114 and toluene concentrations between 0.0 wt% and 0.9 wt% were prepared. After stirring for at least 5 min samples were filled in graduated 10 ml centrifuge vials. While heating the centrifuge (Hettich Rotina 420R) the samples were preheated in a water bath for 60 min and shaken in regular intervals to avoid early phase separation. Subsequently, samples were centrifuged for 45 min at 3000 rpm. After centrifugation, the glasses were kept in a water bath to avoid cooling, samples from each phase were taken and analysed. All compositions were measured three times, the deviation from the mean value is calculated according to the *t*-distribution.

### 2.3. Pervaporation experiments

A schematic diagram of the pervaporation equipment is shown in Fig. 1. A double-walled glass vessel (2 l) was used as feed tank. The temperature of the feed solution was controlled by a thermostat (Julabo, Type FP 35). The feed solution was introduced in the membrane test cell or circulated in the bypass, controlled by a valve. A sketch of the membrane test cell with a membrane area of 100 cm<sup>2</sup> is shown in Fig. 2. The test cell has a diameter of 130 mm with a central feed inlet and a permeate outlet at the outer circumference. Hence a radial flow pattern in established. In order to keep the cross flow velocity nearly constant, a curvature is machined into the feed side part of the test cell. Starting a pervaporation experiment, the feed solution was filled in the feed tank and circulated in the bypass until process conditions were reached. Subsequently, the concentrated surfactant solutions was introduced in the centre of the test cell and discharged at an annular gap at the outer circumference. The retentate was returned in the feed tank through an immersion tube, which

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