



Retention of surfactants by organic solvent nanofiltration and influences on organic solvent flux



Daniel Zedel^{a,b}, Anja Drews^{a,*}, Matthias Kraume^b

^aHTW Berlin, Chair of Process Engineering in Life Science Engineering, Dept. of Eng. II, Wilhelminenhofstraße 75A, 12459 Berlin, Germany

^bTU Berlin, Chair of Chemical and Process Engineering, Fraunhoferstraße 33-36, 10587 Berlin, Germany

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ABSTRACT

For the first time, the non-ionic surfactant Marlipal 24/70 was removed from 1-dodecene using organic solvent nanofiltration. Fluxes of up to $40 \text{ Lm}^{-2} \text{ h}^{-1}$ and retentions of more than 90% were achieved. The flux increase with increasing pressure was non-linear, whilst the retention increase appeared to be almost linear over the observed range. Both effects could be attributed to membrane swelling and compaction which influence the morphology of the membrane. Retention decreased with increasing temperature whilst the flux increased. It could be shown that the temperature influence on the pure solvent flux might be due to a decrease in solvent viscosity, additional to the increased membrane swelling at higher temperatures, which strongly influences the retention of surfactant solutions (retention is reduced). Higher surfactant concentrations led to lower fluxes but to substantially higher retentions due to a decreased membrane swelling degree, surfactant aggregation into micelles, or increased adsorption onto the membrane. The characteristic membrane behaviour seen in this study can be coherently explained but additional effects have been carefully considered. Additionally, the experimental data were compiled to allow, firstly, predictions of the number of batch filtration steps needed to achieve a certain surfactant concentration in the permeate and, secondly, the determination of the characteristic membrane performance.

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1. Introduction

Surfactants, most well known for their application in washing processes, are also used in cosmetics, the pharmaceutical, mining and food industry, in paper recycling and in oil production [1]. In addition, surfactants can be utilised as mediators in various chemical reactions, where they later have to be removed from the reaction product in order to achieve high product qualities. When organic compounds are the reactants and an aqueous catalyst solution is used, surfactants can be added as solubilisers to overcome the miscibility gap by creating a microemulsion [2]. Some of the potential surfactant mediated reactions are presented in Dwars et al. [2] and include chemical reduction and oxidation reactions and C–C coupling reactions. The hydroformylation of the higher alkenes 1-octene [3] and 1-dodecene [4–6] can serve as example reactions for the refinement of long-chain biobased renewable raw materials. Whilst the solubilisation speeds up the reaction, it makes the phase separation and product purification more difficult. Additional process steps in comparison to just using a catalyst in an aqueous phase

need to be implemented in order to achieve the desired product quality, especially the surfactant needs to be removed.

Membrane processes, for example reverse osmosis (RO) and nanofiltration (NF) are used for separation in aqueous systems in a growing number of applications as an energy-saving and gentle alternative to traditional unit operations in chemical engineering. A transition into non-aqueous applications offers the same advantages (energy-saving, thus increasing the economical viability of existing processes) in this field [7]. Since the 1980s, major oil companies and chemical companies have filed patents for the use of polymeric membranes to separate molecules from organic solutions [8]. This fairly recent industrial application of organic solvent nanofiltration (OSN, also named solvent resistant nanofiltration SRNF or organophilic nanofiltration ONF) as a means of solvent separation has an enormous potential rendering separation down to a molecular level possible. Such industrial implementations include food, catalytic, petrochemical and pharmaceutical applications, with the largest currently running plant in the solvent recovery and lube oil dewaxing in the petrochemical industry, handling $11,500 \text{ m}^3 \text{ d}^{-1}$ of feed [9–11]. There are two basic membrane types typically in use for OSN, mainly polymeric and ceramic membranes. Thin film composite membranes (TFC) and integrally skinned asymmetric membranes are amongst the most often used. Polymeric

* Corresponding author.

E-mail address: Anja.Drews@htw-berlin.de (A. Drews).

URL: <http://www.htw-berlin.de> (A. Drews).

Nomenclature

Abbreviations

cmc	critical micelle concentration
CP	concentration polarisation
FESEM	field emission scanning electron microscopy
MWCO	molecular weight cut-off
NF	nanofiltration
ONF	organophilic nanofiltration
OSN	organic solvent nanofiltration
PAN	polyacrylonitrile
PDMS	polydimethylsiloxane
PEG	polyethylene glycol
PFM	pore flow model
PI	polyimide
PMHS	polymethylhydrogensiloxane
RO	reverse osmosis
SDM	solution diffusion model
SEM	scanning electron microscopy
SRNF	solvent resistant nanofiltration
TFC	thin film composite

Constants

b	arbitrary constant
R	gas constant
k_b	Boltzmann constant

Symbols

δ	momentum boundary layer thickness in m
δ_c	concentration boundary layer thickness in feed stream in m
δ_F	concentration boundary layer thickness in feed stream in m
μ	dynamic viscosity in mPa s
σ	surface tension in mN m ⁻¹
ρ	density in kg m ⁻³ or g mL ⁻¹
ρ_F	density in feed stream in kg m ⁻³ or g mL ⁻¹
A	surface area in m ²

A_{eff}	effective surface area in m ²
A_{mem}	membrane surface area in m ²
d_{pore}	pore diameter in m
D	diffusion coefficient in m ² s ⁻¹
D_{ij}	diffusion coefficient of Marlipal 24/70 in 1-dodecene in m ² s ⁻¹
E_{μ}	activation energy for the viscosity in kcal mol ⁻¹ or kJ mol ⁻¹
E_p	activation energy for the permeation rate in kcal mol ⁻¹ or kJ mol ⁻¹
J	flux in L m ⁻² h ⁻¹
J_p	permeate flux in L m ⁻² h ⁻¹
k_F	mass transfer coefficient in feed stream in m s ⁻¹
\dot{m}	mass flow rate in g s ⁻¹
m	mass in g
m_{solvent}	solvent mass in g
$m_{\text{surfactant}}$	surfactant mass in g
M	molecular weight in Da
$\Delta\pi$	osmotic pressure difference in bar
Δp	pressure difference in bar
P	permeance in L m ⁻² h ⁻¹ bar ⁻¹
R_0	hydrodynamic radius in m
R^2	coefficient of determination
R	retention
R°	micellar retention
R_{tot}	overall retention
T	temperature in °C or K
t	time in s
V	volume in m ³ or mL
V_{max}	maximum volume in m ³ or mL
\bar{w}_p	accumulative mass fraction in permeate in wt.%
w	mass fraction in wt.%
$w_{\text{Dod.}}$	mass fraction of 1-dodecene in wt.%
w_F	mass fraction in feed in wt.%
$w_{\text{M24/70}}$	mass fraction of Marlipal 24/70 in wt.%
w_p	mass fraction in permeate in wt.%
w_R	mass fraction in retentate in wt.%

membranes with polydimethylsiloxane (PDMS) and polyimide (PI) are some of the more widely used materials for the active layer and polyacrylonitrile (PAN) for the support structure (ultrafiltration layer) [8,9]. Like in aqueous nanofiltration, transport processes in organic solvent nanofiltration are mainly described by two different models, the solution diffusion model (SDM) and the pore flow model (PFM). Both models are used with satisfactory results in many cases [12,13]. In some, however, hybrid models and alterations to existing models (for example solution diffusion with imperfections model [14,15]) have proven to be adequate.

In this work, the separation of surfactants from organic solvents with organic solvent nanofiltration was systematically tested for the first time, to our knowledge, to prove its feasibility and to map the typical membrane operation range. In the literature, organic solvent nanofiltration was used with different types of membranes, solvents and solutes of different molecular weight (some of which are presented in Section 2). Different classes of solvents were tested (for example different alcohols and alkanes, though no alkenes) as well as solutes (salts, long chain alkanes, catalysts). Due to this variety of combinations, at the current stage filtration behaviour at, e.g., similar molecular weights of solute and solvent, is difficult to predict. Using dense polymer membranes is promising because of the difference in molecular weight of 1-dodecene as the solvent and Marlipal 24/70 as the surfactant (see Table 1), which amongst others can be used in the hydro-

formylation of 1-dodecene, as mentioned by Haumann et al. [4]. In order to separate the product of the hydroformylation from the aqueous catalyst phase, a liquid–liquid separator (decanter) is employed [6]. This leaves small amounts of surfactant in the product phase in the decanter [16]. In this work only the organic phase (here a binary mixture of 1-dodecene and Marlipal 24/70) is considered. In order to evaluate the process efficiency, the main membrane filtration characteristics permeance and retention were analysed in a high pressure dead end filtration test cell at different operating conditions (stirrer speed, transmembrane pressure difference, temperature) and feed compositions.

2. State of the art

To our knowledge, so far no experiments have been done to specifically remove surfactants from organic solvents. Additionally, alkenes have not yet been used as solvents for systematic analyses of membrane performance, using PDMS-based membranes for organic solvent nanofiltration.

2.1. Influences on flux

In dead end test cells, a linear pure solvent flux increase at increasing transmembrane pressure difference was found by some groups [7,17–19], a non-linear increase by others [19,20]. For the

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