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## SURFACTANT SEPARATION IN PRESSURE-DRIVEN MEMBRANE PROCESSES

The separation and transport properties of polymer membranes were tested for surfactant solutions in the concentration range of 0.1–3.0 CMC. It was found that the critical micelle concentration was a crucial parameter determining the effectiveness of ultrafiltration process. With an increase in surfactant concentration the retention coefficients and hydraulic performance decreased, with a rise of above the CMC value. Permeation tests on the nanofiltration membranes enabled efficient removal of surfactant on a level of above 90%. In contrast to ultrafiltration membranes, the effectiveness of nanofiltration ones was stable irrespective of surfactant concentration in model solution.

### 1. INTRODUCTION

Pressure-driven membrane processes, i.e., microfiltration, ultrafiltration, nanofiltration and reverse osmosis, are widely used in the environmental area, mainly in water and wastewater treatment. A financial attractiveness of membrane processes results not only from low energy consumption and low capital costs, but also from the new possibilities of recovering and utilizing very diluted valuable components. This enables recycling of the streams in industrial plants and leads to the lowering of the concentration of pollutants being discharged to the environment [1].

Surfactants, which are surface-active amphiphilic agents containing both hydrophilic and hydrophobic components, are classified into four groups, depending on the charge of the hydrophilic moiety: anionic, cationic, nonionic or zwitterionic. Surfactants of low concentration are present in monomeric form of both non-polar and polar solvents. At a higher concentration (critical micelle concentration (CMC)), they form regular aggregates (micelles), and then monomers and micelles reach an equilibrium [2], [3]. The CMC value greatly depends on the polarity of solvent, structural characteristics of a surfactant molecule, temperature and ionic strength of the solution

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[4]–[7]. When surfactant molecules aggregate in aqueous solutions, micelles are formed, withdrawing the hydrophobic groups from the water. The hydrophilic groups in the micelle are orientated towards the water, whilst the hydrophobic groups are repelled toward the interior of the micelle structure.

Based on this knowledge it may be inferred that the membrane processes such as ultrafiltration are highly suitable for the recovery of surfactants with critical micelle concentrations. If the surfactant concentration is as low as that of monomer, then nanofiltration has been suggested as an effective removal process.

## 2. EXPERIMENTAL

Experiments were carried out on surfactant solutions prepared from distilled water and powdered surfactant. Sodium dodecylbenzenesulfonate (SDBS) was purchased from Sigma and used as such without further purification. The active content was about 80% by wt. and the molecular weight amounts to 348.48 Da. The concentration of SDBS in model solutions ranged from 0.1 CMC to 3.0 CMC. Its critical micelle concentration (CMC) was determined via surface tension measurements and amounted to 800 ppm (figure 1).

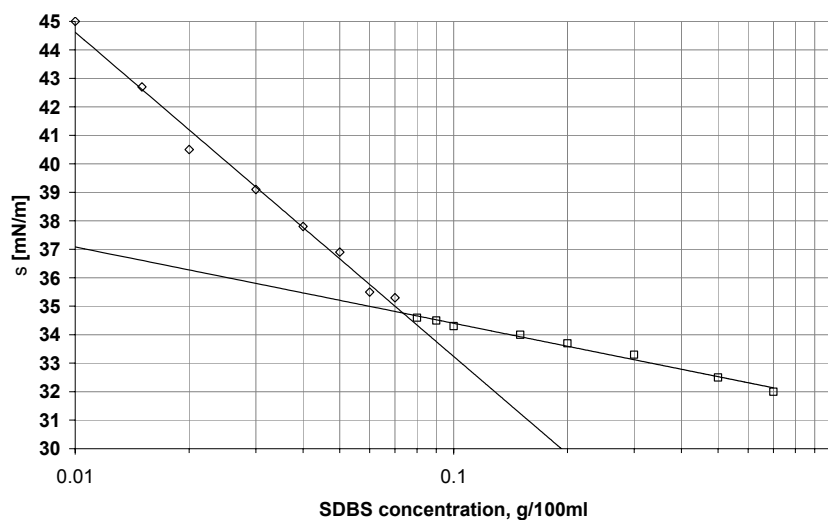


Fig. 1. Solution surface tension vs SDBS concentration (22 °C)

The permeation tests were carried out with the use of commercial nanofiltration and ultrafiltration membranes. The main properties of the polymers are shown in tables 1–3.

Table 1

Characteristics of Nadir<sup>®</sup> membranes [8]

Membrane material	Properties	pH range	Max. temperature, °C
Polyethersulfone	hydrophilic, high chemical stability	0–14	95
Cellulose	extremely hydrophilic, highly solvent-resistant	1–11	55

Table 2

Nadir<sup>®</sup> nanofiltration membranes [8]

Membrane type	Membrane material	Na <sub>2</sub> SO <sub>4</sub> retention (%)	Pure water flux (dm <sup>3</sup> /m <sup>2</sup> h) <sup>1)</sup>	Pure water flux (dm <sup>3</sup> /m <sup>2</sup> h) <sup>2)</sup>
NP010	polyethersulfone	25–40	>200	22
NP030	polyethersulfone	80–95	>400	4.5

<sup>1)</sup> Test conditions: 40 bar, 20 °C, stirred cell: 700 RPM.

<sup>2)</sup> Determined by the author. Test conditions: 3 bar, 22 °C, stirred cell: 300 RPM.

Table 3

Nadir<sup>®</sup> ultrafiltration membranes [8]

Membrane type	Membrane material	Cut-off (kDa)	Pure water flux (dm <sup>3</sup> /m <sup>2</sup> h) <sup>1)</sup>	Pure water flux (dm <sup>3</sup> /m <sup>2</sup> h) <sup>2)</sup>
UP005	polyethersulfone	5	>30	41
UP010	polyethersulfone	10	>150	265
UP030	polyethersulfone	30	>100	345
UC005	cellulose	5	>25	45
UC010	cellulose	10	>40	82
UC030	cellulose	30	>300	1244

<sup>1)</sup> Test conditions: 3 bar, 20 °C, stirred cell: 700 RPM.

<sup>2)</sup> Determined by the author. Test conditions: 3 bar, 22 °C, stirred cell: 300 RPM.

Flat sheet membranes were tested in a laboratory set-up, whose main part was an Amicon 8400 cell with the total volume of  $0.350 \times 10^{-3} \text{ m}^3$  and a working area of the membrane of  $4.54 \times 10^{-3} \text{ m}^2$ . In order to maintain a stable concentration of the substances in the feed solution, the permeate was recirculated to a filtration cell (figure 2). The filtration experiments were carried out at the transmembrane pressures range of 0.5–3 bar.

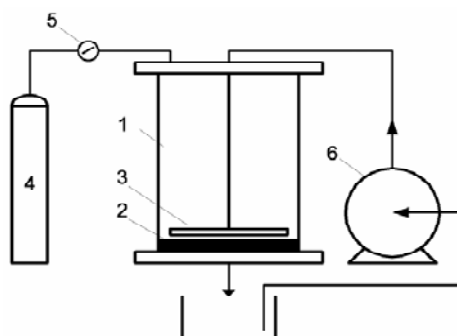


Fig. 2. Laboratory set-up:

1 – filtration cell, 2 – membrane, 3 – stirrer, 4 – gas cylinder, 5 – reducer, 6 – recirculation pump

During the experiments the following measurements and calculations were done:

- Permeate volume flux ( $J$ ):

$$J = \frac{V}{t \cdot A}, \quad \text{dm}^3/\text{m}^2\text{h},$$

where  $V$  is the permeate volume ( $\text{dm}^3$ ),  $t$  stands for the time (hour), and  $A$  denotes the working area of the membrane ( $\text{m}^2$ ).

- Normalized flux which was determined as the ratio of the permeate volume flux ( $J$ ) after time  $t$  to the initial distilled water flux ( $J_{\text{H}_2\text{O}}$ ).
- Retention coefficient of anionic surfactant ( $R$ ):

$$R = \frac{c_f - c_p}{c_f} \cdot 100, \quad \%,$$

where  $c_f$  and  $c_p$  are the surfactant concentration in the feed and permeate, respectively.

- The anionic surfactant concentration was measured spectrophotometrically at a 222 nm wavelength using UV-MINI-1240 spectrophotometer (Shimadzu) and  $1.0 \times 10^{-2}$  m quartz cuvettes.

### 3. RESULTS AND DISCUSSION

Transport and separation properties of ultrafiltration membranes during permeation tests are presented in figure 3. It was observed for both polymers that with an increase in the surfactant concentration the removal efficiency of SDBS systematically decreased. When the surfactant concentration was increased up to the CMC value, the improvement in membrane selectivity was observed. At the same time, the polyethersulfone membranes were characterized by far higher retention coefficients than the cellulose ones.

This can be exemplified by the SDBS retention coefficient reaching 32–87% and 19–73% for UP010 membrane and UC010 membrane, respectively.

Comparing the separation properties of the membranes with different cut-off values, it can be inferred that the greater the molecular weight cut-off of the membranes (the more spongy the structure and the larger the pore size), the less effective the SDBS separation from the water solutions, especially in the concentration range below the CMC value. For the surfactant concentrations above the CMC value, the drop in surfactant retention with the increase in cut-off value was less pronounced and did not exceed 5%.

Permeation tests on the nanofiltration membranes (figure 4) enabled the efficient removal of anionic surfactant on a level of above 90%. The values of retention coefficient (in contrast to ultrafiltration tests) were stable irrespective of surfactant concentration in model solution. More dense structure of nanofiltration polymer ensured effective separation of both surfactant monomers and micelles.

Based on the results obtained, it also should be stressed that during filtration the permeability of the membranes deteriorated in comparison with the flux of distilled water (figures 3 and 4). As in the case of separation properties, the increase in the surfactant concentration in range below the CMC value resulted in worsening the membranes permeability. When the surfactant concentration was increased up to the CMC value, the membrane permeability improved slightly. As a result of further increase in surfactant concentration, the drop in the hydraulic performance of the membranes was observed again.

It was also observed that the deterioration in permeate volume flux (in comparison with the distilled water) was more pronounced for less hydrophilic membranes (i.e., made of polyethersulfone) and for greater cut-off values. The increase in the cut-off value of the membranes (thereby the pore diameter) made the surfactant deposition within the pores of the polymer easier.

Table 4

Wetting angles of the membranes

Membrane type	Contact angle of the brand-new membrane (°)	Contact angle of the membrane after filtration test (°)
UP005	85.0	56.1
UC005	18.5	27.5

On the basis of data presented in table 4, it can be inferred that the changes in wetting angles of membranes take place on account of the inherent tendency of surfactant molecules to accumulate at the interface. In view of the amphiphilic nature of the surfactant molecules, they are obviously deposited at the membrane surface, with their hydrophilic parts, being negatively charged, oriented toward the solution phase. As a result of the location of surfactant monomers, the polyethersulfone membranes become more hydrophilic. The brand-new cellulose membranes despite their extreme

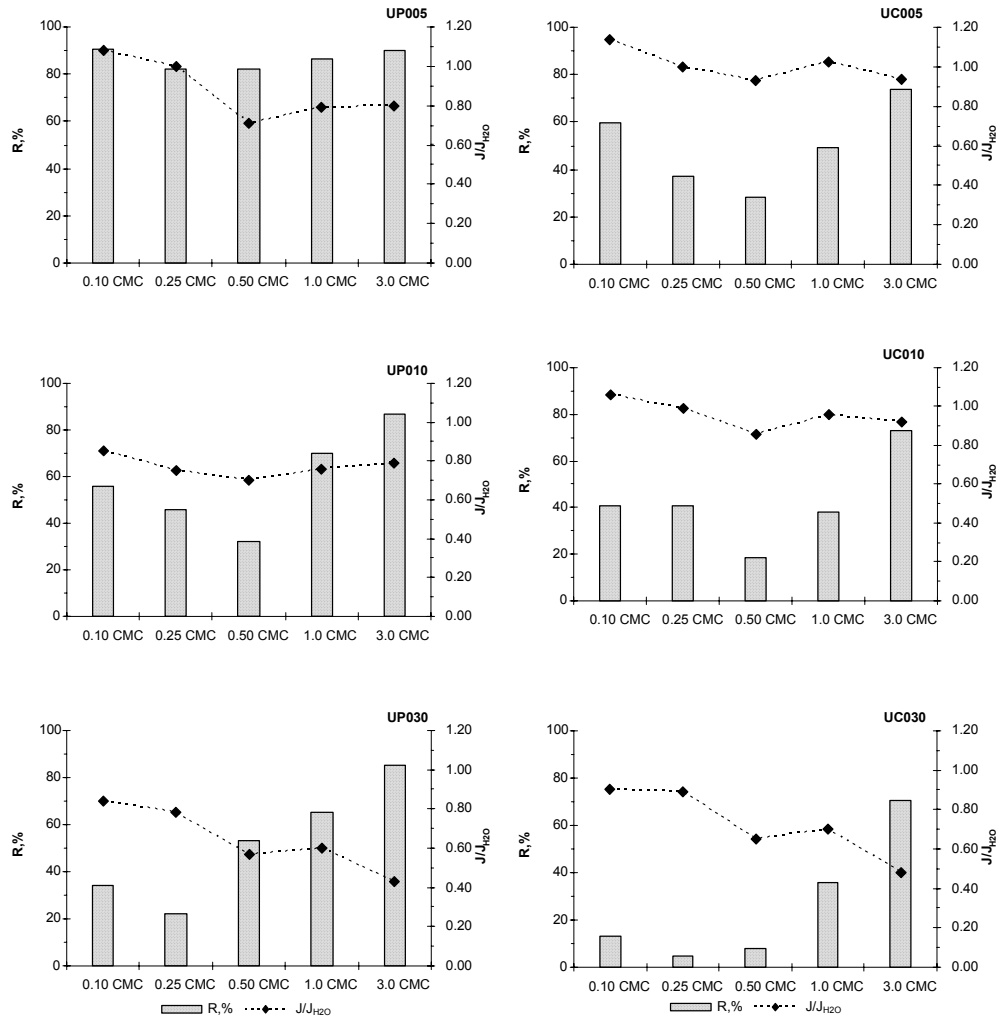


Fig. 3. Retention coefficient and normalized flux vs surfactant concentration during ultrafiltration process

hydrophilicity were also susceptible to surfactant adsorption causing polymer hydrophobisation.

The transport and separation properties of membranes during permeation of surfactant solutions can be attributed to several phenomena, such as sieving mechanism, concentration polarization, membrane fouling and interactions between surfactant and membrane.

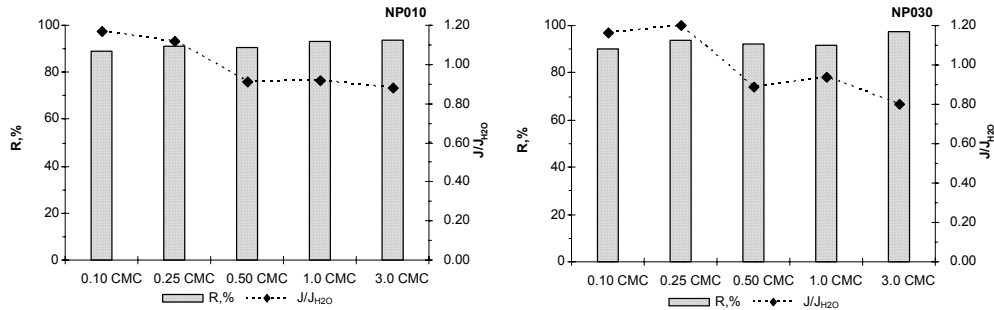


Fig. 4. Retention coefficient and normalized flux vs surfactant concentration during nanofiltration process

For surfactant concentration far below the CMC value, the high surfactant retention was mainly connected with monomer adsorption on the membrane surface and within the pores. Then the monomer competition for the hydrophobic spots on the membrane is not strong and probably the monomers “lie” horizontally along the surface [9]. At higher concentration a closed-packed layer of surfactant on the membrane surface and the interior of the pores is probably formed, resulting in the decline of the permeate volume flux. According to MIZOGUCHI et al. [10] at the surfactant concentration below the CMC value the membrane pore blocking can also be caused by the pre-micelles formed in the concentration polarization layer.

For the concentration close to the CMC value, as a result of the micelle creation, the separation increased and simultaneously the improvement in transport properties took place. Taking into account the radius of the SDBS micelle (22 Å) [9] and its average molecular weight (which is about 50 times greater than the molecular weight of SDBS molecule [11]), a conclusion can be drawn that the sieving mechanism is predominant during the surfactant separation by polymer membranes, especially in the concentration range above the critical micelle concentration.

Because the micelle surface is hydrophilic, it has a greater affinity with the solvent than with the polymer membranes. At the same time, the electrostatic repulsion between negatively charged micelles results in a less compact polarization layer and thereby the solvent transport was facilitated [3].

#### 4. SUMMARY

The experimental investigation revealed that the critical micelle concentration was a crucial parameter determining both transport and separation properties of ultrafiltration membranes. The increase in surfactant concentration resulted in the decrease of the retention coefficients and the hydraulic performance, with a rise above the CMC value. It was also inferred that the deterioration in permeate volume flux (in compari-

son with the flux of distilled water) was more pronounced for less hydrophilic membranes, as well as for membranes with greater cut-off values.

The permeation tests on the nanofiltration membranes enabled the efficient removal of both surfactant monomers ( $C < \text{CMC}$ ) and surfactant micelles ( $C > \text{CMC}$ ). In contrast to ultrafiltration membranes, the effectiveness of nanofiltration ones was stable irrespective of surfactant concentration in model solution.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] KOLTUNIEWICZ A., NOWORYTA A., *Method of yield evaluation for pressure-driven membrane processes*, The Chemical Engineering Journal, 1995, 58, 175–182.
- [2] MULLIGAN C.N., YONG R.N., GIBBS B.F., *Surfactant-enhanced remediation of contaminated soil: a review*, Engineering Geology, 2001, 60, 371–380.
- [3] FERNANDEZ E., BENITO J.M., PAZOS C., COCA J., *Ceramic membrane ultrafiltration of anionic and nonionic surfactant solutions*, Journal of Membrane Science, 2005, 246, 1–6.
- [4] BENITO I., GARCIA M.A., SAZ J.M., MARINA M.L., *Spectrophotometric and conductometric determination of the critical micellar concentration of sodium dodecyl sulfate and cetyltrimethylammonium bromide micellar systems modified by alcohols and salts*, Colloid and Surfaces A: Physicochemical and Engineering Aspects, 1997, 125, 221–224.
- [5] KO S., SCHLAUTMANANDE M.A., CARRAWAY R., *Effects of solution chemistry on the partitioning of phenanthrene to sorbed surfactants*, Environmental Science & Technology, 1998, 32, 3542–3548.
- [6] SHIAO Y., CHHABRA V., PATIST A., FREE M.L., HUIBERSS P.D.T., GREGORY A., PATEL S., SHAH D.O., *Chain length compatibility effects in mixed surfactant systems for technological application*, Advances in Colloid and Interface Science, 1998, 74, 1–29.
- [7] FUGUET E., RAFOLS C., ROSES M., BOSCH E., *Critical micelle concentration of surfactants in aqueous buffered and unbuffered systems*, Analytica Chimica Acta, 2005, 548, 95–100.
- [8] The catalogue of Nadir<sup>®</sup> membranes.
- [9] JÖNSSON A.S., JÖNSSON B., *The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes*, Journal of Membrane Science, 1991, 56, 49–76.
- [10] MIZOGUCHI K., FUKUI K., YANAGISHITA H., NAKANE T., NAKATA T., *Ultrafiltration behavior of a new type of non-ionic surfactant around the CMC*, Journal of Membrane Science, 2002, 208, 285–288.
- [11] KUMAR S., SHARMA D., KABIRUD D., *Small-angle neutron scattering studies on sodium dodecylbenzenesulfonate-tetra-n-butylammonium bromide system*, Journal of Surfactants and Detergents, 2006, 9, 77–82.

#### SEPARACJA SURFAKTANTÓW W CIŚNIENIOWYCH PROCESACH MEMBRANOWYCH

Zbadano właściwości separacyjne i transportowe membran polimerowych w stosunku do roztworów surfaktantu w zakresie stężeń 0,1–3,0 CMC. Stwierdzono, że istotnym parametrem decydującym o skuteczności separacji substancji powierzchniowo czynnych (SPC) w procesie ultrafiltracji jest krytyczne



stężenie micelizacji. Zaobserwowano, że początkowo współczynnik retencji SPC oraz hydrauliczna wydajność membran w przypadku wszystkich testowanych polimerów zmniejszają się wraz ze wzrostem stężenia składnika w roztworze, a następnie – powyżej wartości CMC – ponownie rosną.

Membrany nanofiltrycyjne zapewniały dużą skuteczność separacji SPC z roztworów wodnych (powyżej 90%) i w przeciwieństwie do membran ultrafiltracyjnych uzyskiwane współczynniki retencji były stabilne w całym zakresie badanych stężeń.