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Dead-end and cross-flow ultrafiltration of ionic and non-ionic surfactants

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ABSTRACT

Different molecular weight cut-offs (MWCO = 2–30 kDa) flat sheet membranes and hollow fibre modules were applied for filtration of surfactant aqueous solutions (Triton QS-44, CTAB and Triton X-100). The experiments were performed in a stirred cell (dead-end regime) and in a semi-pilot membrane installation (cross-flow regime). The effect of the process conditions (transmembrane pressure and cross-flow velocity) and the interaction between the membranes' polymer and surfactants under a wide range of concentrations on ultrafiltration effectiveness was evaluated. The results demonstrated that the highest retention coefficient of anionic and cationic surfactants was obtained with the hydrophobic membranes; however, hydrophilic membranes were characterised by distinctly higher retention of the non-ionic surfactant. It was proved that with a good adjustment it is possible to determine, with the help of a linear dependence, the concentration of a surfactant in the permeate depending on the concentration in the feed solution.

Keywords: Membrane; Ultrafiltration; Ionic and non-ionic surfactant; Surfactant leakage

1. Introduction

Surfactants are considered as some of the most versatile products of the chemical industry. They are the basic constituents of a variety of chemical products such as detergents, paints, dyestuffs, cosmetics, pharmaceuticals, pesticides, fibres, plastics, etc. [1]. As a consequence of the increasing consumption of surfactants and their impact on the environment, they should be removed in the following cases [2]: (i) cleaning-in-place (CIP) rinsing waters in detergent production plants [3–5]; (ii) detergent wastewater [6–8]; and (iii) surfactant-aided processes such as micellar-enhanced ultrafiltration (MEUF) [9–12].

Integration of the membrane processes with traditional technologies or designing new production cycles based on membrane techniques allows the intensification of the production processes and reasonable water–sewage management that is non-threatening to the natural environment [13–16].

One of the most crucial parameters determining the effectiveness of surfactant separation by means of pressure-driven membranes is the critical micelle concentration (CMC) and the size of the created micelle. Microfiltration (MF) and ultrafiltration (UF) have been suggested as a means of recovery of surfactants with CMCs. If the surfactant concentration is low, that is, monomer concentration ($c < \text{CMC}$), then nanofiltration (NF) has been suggested as an effective removal process.

Archer et al. [17] studied the NF of model solutions containing an anionic surfactant (sodium lauryl-ether-sulphate) below its CMC value. Because of the high values obtained for the permeate flux and rejection (maximum of 97.8% and 67.8 L/m^{2}h for BQ

01 membrane), the authors recommend the process in environmental areas. Moreover, the results showed that the separation depends greatly on the properties of the surfactant and the electrostatic interactions between the membrane and the ionic species in the aqueous solution.

Wendler et al. [18] studied the mechanisms in NF of aqueous solutions of different anionic surfactants and their mixtures with the presence of NCl. High retention in the range of 95 up to 99.9% referring to the feed concentration is found to be dependent on the solvent flux. The addition of the salt worsened the permeate quality as a result of lower solvent flux and of mass transfer due to the electrical potential.

Cornelis et al. [19] revealed that NF is feasible to reduce water usage in industrial processes involving non-ionic surfactants when a proper membrane is selected. According to the authors, the flux was controlled by three mechanisms: the narrowing of membrane pores through adsorption of monomers when the molecular weight cut-off (MWCO) is comparable to or larger than the monomer size, causing flux decline; an improved wettability of the membrane surface through adsorption of monomers on hydrophobic groups, causing flux to increase above pure water flux; and a decreased wettability through adsorption of monomers on hydrophilic groups, causing flux decline. The non-ionic surfactant concentration, MWCO and the membrane's hydrophilicity determine which mechanism is dominant.

Kaya et al. [20] tested NF of anionic (LABS and SLES) and non-ionic (NPE) surfactants using three different flat sheet membranes (NF PES10, N 30F and XN 45). The rejection of surfactants and flux decline took place due to the adsorption of surfactants on both surface and pore walls. The highest rejections for anionic surfactants amounted to 97–98% using NF PES10 and N 30F. The lowest non-ionic rejection was determined using NF PES10, which achieved about 46% at the end of the process time of 240 min, while most of it was ensured at about 93% using XN 45.

Low-pressure membrane processes (i.e. MF and UF) are regarded as effective for the separation of surfactant micelle from water solutions. Therefore, much attention in the literature is paid to MEUF due to the ability of surfactants to form micelles into which the pollutants are solubilised. With a properly designed hybrid system (selection of a surfactant, its concentration and ionic character, membrane material and its cut-off values), the micelles together with the solubilisant (micropollutant) remain in retentate. Permeate, on the other hand, consists of surfactant monomers and non-solubilised molecules of separated contaminants.

Since Scamehorn et al. [21,22] proposed the MEUF process for separation of small molecular compounds, the main stream of research has addressed the application of this method in sewage treatment. The research concentrates mainly on the achievement of highly effective separation of the compounds by optimising the process parameters (pressure difference, membrane MWCO, molar ratios of surfactants to solute, kind of surfactant and additives, pH and ionic strength) and omits issues connected with the leakage of the surfactants' monomers to the permeate. On the other hand, the application of the MEUF method without effective recovery of the surfactants is uneconomic and environmentally unacceptable due to the high load of pollution entering the waste stream. Taking into account the economic and ecological aspect of the MEUF method applied, it is crucial to strive for the selection of process conditions that ensure a high retention of the separated compounds as well as the surfactants used.

Fernandez et al. [23] reported ultrafiltration of anionic (SDS) and non-ionic (Tergitol NP-9) surfactants using a ZrO_2 tubular membrane. Above the CMC value, the retention coefficient amounted to 70 and 30% for SDS and Tergitol NP-9, respectively. Higher SDS retentions were achieved probably due to the pre-sieving effect of the electrostatic repulsion between negatively charged SDS micelles in the polarisation layer.

Goers et al. [3] stated that CMC is an important parameter for the design of the separation plant, because micelles are rejected by the UF micelle and therefore the permeate concentration is in the range of CMC or higher. The retention coefficient of micelle achieved on PES5 kDa membrane ranged between 50% (nonionic APG) and 99.7% (nonionic ET5). The authors pointed out that the solubility of the surfactants at a higher concentration significantly influenced the performance of the process. For a surfactant with poor solubility (ET5), a gel polarisation layer formed on the membrane surface which was the limiting factor of the membrane's permeability.

On the other hand, Jönsson et al. [24] reported higher surfactant separation below CMC than expected. The high retention may be due not only to the restriction pores as a result of adsorption, but also to the existence of micelle far below the theoretical CMC.

Also, our previous studies confirm the high efficiency of UF membranes in the concentration range below CMC [25,26].

The objective of the present research was the critical assessment of the effectiveness of the low-pressure ultrafiltration process in the removal of various types of surfactants (anionic, cationic and non-ionic) from aqueous solution far below and above CMC. Taking into account mainly the ecological aspect, the effect of surfactant leakage to the permeate side during ultrafiltration was evaluated. The concentrations of surfactants selected for the purpose of the research in the field of the concentrations below the CMC match the values registered in the sewage originating from the production of cleaning materials and also in washing wastewater. However, within the range of concentrations above the CMC, they correspond with the typical values for the MEUF process.

The impact of the ionic character of surfactants, the membrane polymer material and the cut-off values of the membrane on the transport and separation properties of membranes in the dead-end system was analysed. For the purpose of the filtration performed in the cross-flow system, the impact of process parameters (transmembrane pressure and cross-flow velocity at the membrane surface) on the permeate flux of ultrafiltration modules and their susceptibility to fouling was additionally analysed.

2. Materials

2.1. Model solutions

Model solutions of surfactants characterised in Table 1 were applied in the research. The CMCs of surfactants were determined on the basis of the measurements of the surface tension of solutions. The research was conducted using the du Noüy ring method, with the help of a semi-automatic Lauda tensiometer at a temperature of 22°C.

The solutions applied in the research and corresponding pH values are presented in Table 2. The concentrations of surfactants in aqueous solutions were determined using the potentiometric titration method on the apparatus 785 DMP Titrino.

2.2. Membranes and modules

In the research in the dead-end system, flat sheet membranes produced by Microdyn-Nadir®, thoroughly characterised in Table 3, were used. The membranes are formed on a highly porous polypropylene substrate, which significantly enhances their mechanical durability.

The research determining the transport and separation properties of flat sheet membranes was carried out with the use of the installation whose scheme is presented in Fig. 1. The ultrafiltration cell Amicon 8400 constituted the basic element of the installation. The surface of the membranes tested amounted to $4.53 \times 10^{-3}\,\mathrm{m}^2$, whereas the total capacity of the filtration cell equalled 350 mL. In order to obtain a constant concentration of a substance in the feed solution, the permeate was re-circulated to the cell. Additionally, the installation was thermostated, which ensured the maintenance of a constant solution temperature.

Tests in the cross-flow system were performed on the hollow fibre Koch/Romicon® modules (Table 4), which were erected in a large laboratory installation (Fig. 2).

The following were the main elements of the filtration installation: the membrane module, a pump enabling circulation of the solution in the system, a 10 L capacity feed tank and thermostated water circulation. Ultrafiltration of the solutions of surfactants in the flow system was examined at a temperature of 20°C within the range of transmembrane pressures of 0.25–4 bar and the cross-flow velocity at the membrane surface in the range of 1–4 m/s.

In order to restore the primary transport properties of the membranes and modules, 0.1 N sodium hydroxide solution was used as a cleaning agent. Afterwards, the membranes were rinsed in de-ionized water until a flux value was obtained that varied by a maximum of 5% of the initial flux value.

Table 1
Characteristics of surfactants

Surfactant	Triton QS-44	CTAB	Triton X-100
Type	Anionic	Cationic	Non-ionic
Chemical description	Polyether phosphate ester (free acid form)	Cetyltrimethylammonium bromide	Polyethylene glycol tert-octylphenyl ether
Purity	80%	>98%	>99%
Supplier	Sigma	Sigma	Fluka
CMC (mg/L)	250[a] (22°C)	335[a] (22°C)	165[a] (22 °C)
Aggregation number	–	170	100–155
Diameter of the micelle (nm)	–	3.5 [24]	8.5 [25]

[a] Determined by the author.

Table 2
The pH of the feed solutions

C_f/C_{CMC}	Triton QS-44	CTAB	Triton X-100
0.1	3.81	5.52	5.91
0.5	3.68	5.79	5.77
1	3.40	5.90	5.58
3	3.01	6.03	5.53
5	2.83	6.03	5.44
10	2.62	6.12	5.38

For the experiments, the surfactant retention was calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (1)$$

where C_f and C_p are the surfactant concentration in the feed and permeate, respectively.

The ultrafiltration performance was evaluated using permeate flux (J) and relative flux (RF) during filtration time:

$$J = \frac{1}{A}\frac{dV}{dt} \qquad (2)$$

$$\mathrm{RF} = \frac{J}{J_w} \qquad (3)$$

where V is the collected volume of the permeate (m^3), A denotes the membrane area (m^2), t is time of sample collection and J_w is the membrane flux for pure (deionized) water.

3. Results

3.1. Permeate flux of membranes and modules

Filtration of water deionized on flat sheet membranes and modules was performed within the range of transmembrane pressures of 0.25–3 bar and 0.25–4 bar, respectively. The rectilinear relations obtained between the transmembrane pressure and the flux of water allowed us to determine the resistance of the membranes based on the equation:

$$R_m = \frac{\Delta P}{\mu_w J_w}$$

where R_m is the hydraulic resistance of the membrane (m^{-1}), ΔP is the transmembrane pressure, μ_w is the dynamic viscosity of the deionized water (Pa s) and J_w is the permeate flux of the deionized water ($m^3\ m^{-2}\ s^{-1}$).

With an increase in the cut-off membranes, a decrease in the resistance of the active layer was noticed, due to the larger diameter of pores (Tables 3 and 4).

3.2. Flat sheet membranes

Separation and transport properties of flat sheet membranes in relation to the model solutions of surfactants are presented in Figs. 3–5. The research was conducted in an extended range of concentrations (0.1–10 CMC) in order to compare the impact of surfactants and membranes within the interval of the concentrations below and above the CMC.

Analysis of the removal of ionic and non-ionic surfactants on the flat sheet ultrafiltration membranes demonstrated that the cut-off value of membranes in connection with their surface charge and hydrophilic/hydrophobic character determines the effectiveness of the process.

3.2.1. Ultrafiltration of Triton QS-44

A distinct deterioration of the Triton QS-44 retention together with an increase in the membranes' cut-off values was observed for both polymer materials, especially within the range of the concentrations below CMC (Fig. 3). On the other hand, for concentrations above the CMC value, the decrease of the retention together with the increase of the membranes' cut-off values were less visible due to the size of the nascent micelles. For example, with an increase in the cut-off values from 5 to 30 kDa, the decrease of Triton QS-44 separation amounted to: 29% (UP membrane) and 40% (UC membrane) for a concentration of 0.5 CMC, and 9% (UP) and 16% (UC) for a concentration of 10 CMC. The following was also observed: an initial

Table 3
Characteristics of Nadir® ultrafiltration membranes

Membrane type	Cut-off (kDa)	R_m ($\times 10^{12}\,m^{-1}$)	Pure water flux[a] ($10^{-6}\,m^3\,m^{-2}\,s^{-1}$)	Properties	Contact angle of the brand-new membrane[b]	pH range	Max. temperature (°C)
UP005	5	22.3	13.333	Hydrophilic polyethersulfone membranes with high chemical stability	85.0	0–14	95
UP010	10	5.6	53.056				
UP030	30	2.7	109.167				
UC005	5	25.1	11.667	Extremely hydrophilic cellulose membranes, highly solvent-resistant	18.5	1–11	55
UC010	10	14.3	21.667				
UC030	30	1.1	254.444				

[a] Determined by the author. Test conditions: 3 bar, 22°C, stirred cell: 300 RPM.
[b] Determined by the author using UP005 and UC005.

Table 4
Characteristics of ultrafiltration modules

Parameter	Module type	
	Koch/Romicon® PM2	Koch/Romicon® PM5
Cut-off (kDa)	2	5
Membrane polymer	Polysulfone	
Membrane area (m^2)	0.09	
Module length (mm)	457	
Module diameter (mm)	25.4	
Number of capillaries	66	
Internal capillary diameter (mm)	1.1	
Pure water flux[a] ($10^{-6}\,m^3\,m^{-2}\,s^{-1}$)	18.611	68.611
R_m ($10^{12}\,m^{-1}$)	11.1	4.1

[a] Determined by the author. Test conditions: 3 bar, 22°C, CFV = 3 m/s.

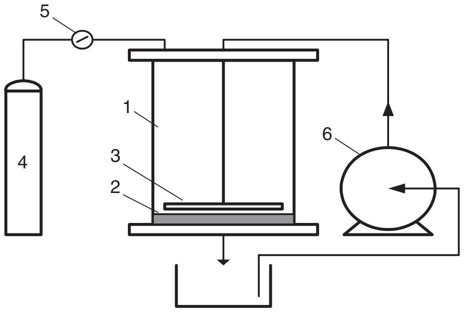

Fig. 1. Laboratory set-up for testing flat-sheet membranes: (1) ultrafiltration cell, (2) membrane, (3) stirrer, (4) gas cylinder (N_2), (5) reducer, (6) pump.

decrease in the effectiveness of the separation together with an increase in concentration of the surfactant in the feed solution, and then above CMC—its repeated systematic growth. On the basis of the results obtained, it was estimated that the value of the retention was stabilizing after reaching a concentration in the feed solution at a level of 5 CMC.

On the other hand, while analysing the membranes' transport properties it can be seen that the increase of the Triton QS-44 concentration within the range of concentrations below the CMC resulted in a reduction of the permeate flux of the membranes (Fig. 3). When the surfactant's concentration reached the value of the CMC, the permeability of the membranes increased insignificantly. A greater decrease of the permeate flux in relation to the stream of distilled water together with an increase in the cut-off values of membranes and their hydrophobic character were also declared. For example, the RF with the cut-off value of 30 kDa for the concentration of 5 CMC amounted to approx. 36 and 76% for the UP and UC series membrane, respectively.

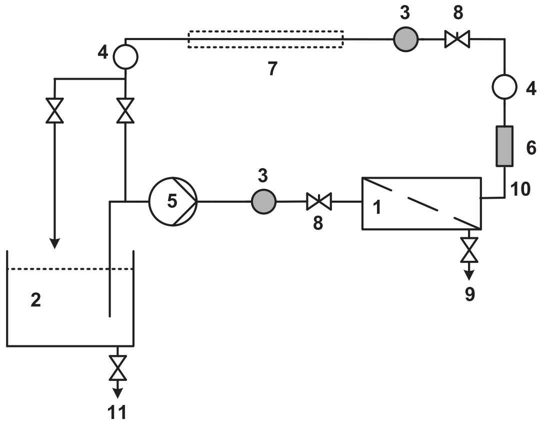

Fig. 2. Schematic diagram of the membrane installation (1) membrane module, (2) feeding tank, (3) manometer, (4) thermometer, (5) pump, (6) rotameter, (7) cooler, (8) pressure regulation valve, (9) permeate, (10) retentate, (11) drain valve.

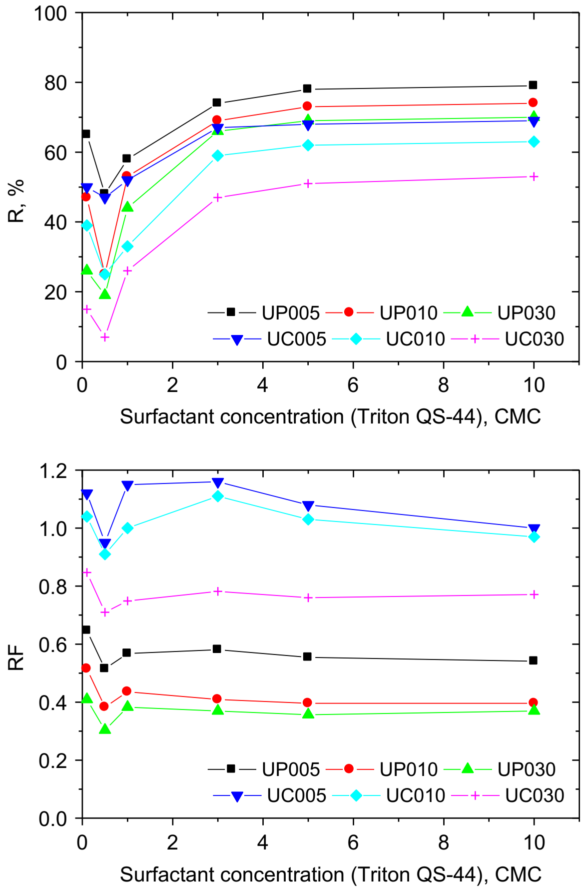

Fig. 3. Triton QS-44 retention and RF as a function of surfactant concentration.

Reduction of the permeate flux in relation to the distilled water in the ultrafiltration process was probably a consequence of the adsorption of the Triton QS-44 monomers in the membrane's pores and on its surface. This process is most probably the effect of the same interactions that determine the aggregation of surfactants into micelles, i.e. the compromise between the lack of contact of the hydrophobic chain with water and the strong affinity of hydrophilic heads and water.

Apart from the hydrophobic interactions, it is also necessary to consider the participation of electrostatic interactions between Triton QS-44 and membranes in the adsorption process. According to the literature data, membranes possess an insignificant negative charge resulting from the contact with the examined solutions (Table 2) (the membranes from cellulose derivatives have a minor negative charge within the range of pH = 3–7 [27], whereas for modified

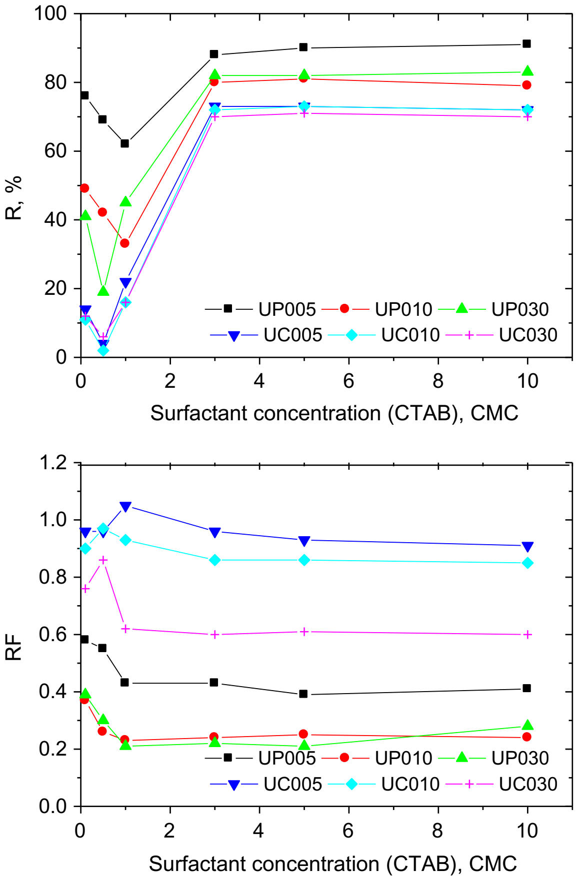

Fig. 4. CTAB retention and RF as a function of surfactant concentration.

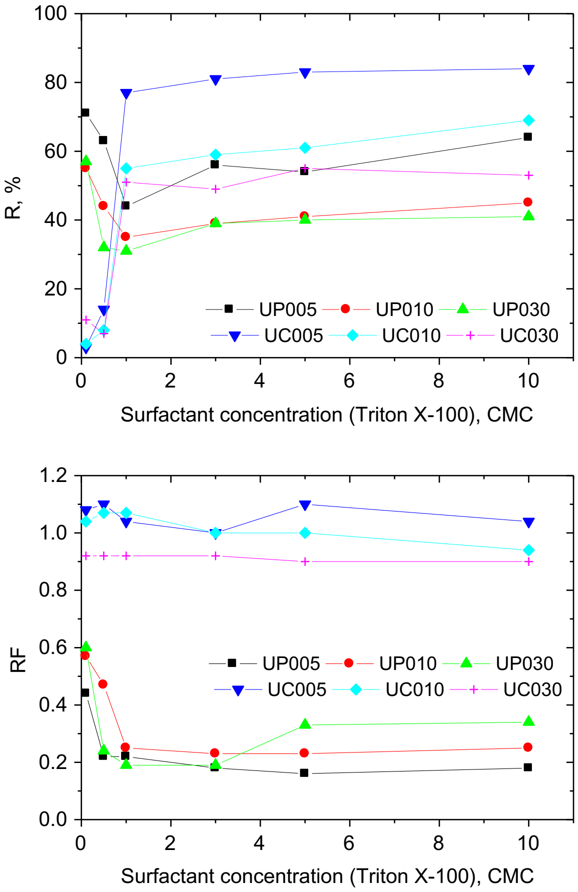

Fig. 5. Triton X-100 retention and RF as a function of surfactant concentration.

polyethersulphone membranes it is at pH > 3.0 [28]). It is assumed that the charge density may determine the conformation of monomers inside the pores. In the case of membranes endowed with a large negative charge, an increase in the distance between the membrane wall and the head endowed with the charge probably occurs as a result of the electrostatic repulsion. That is when the pores are filled to a greater extent and, thus, a significant reduction of their diameter occurs.

A larger decrease of the permeate flux together with an increase in the Triton QS-44 concentration in the solution (within the range below the CMC) and the membrane's cut-off values are most probably the result of a greater number of "free" monomers and their easier access to large pores. For concentrations within the range of the CMC values, as a result of the formation of micelles, an increase in the permeate flux of membranes was observed. Considering that the micelles' surface is hydrophilic, it demonstrates a larger affinity to the solution than to the polymer material of the membrane. Simultaneously, electrostatic interactions between the micelles endowed with a negative charge result in a loosening of the structure of the polarisation layer and, thus, easier transport of the solvent occurs.

The effectiveness of the surfactants' separation in the ultrafiltration process is probably caused not only by the pores' decrease due to the monomers' adsorption, but also by the creation of micelles in the polarisation layer of the membrane with the increased concentration in relation to the feed solution below the CMC value and in the total volume of the solution above the CMC.

3.2.2. Ultrafiltration of CTAB

The transport and separation properties of ultrafiltration membranes in relation to the CTAB solutions are presented in Fig. 4. In the case of the CTAB separation, a similar tendency to that of the Triton QS-44 was observed. A decrease in CTAB retention within the range of concentrations below the CMC occurred. Afterwards, a significant increase of the separation within the range above the CMC took place. Moreover, the polyethersulphone membranes, for which there was a significant decrease of the retention and relative permeability of membranes together with an increase in the membranes' cut-off, were characterised by a higher degree of CTAB retention. On the other hand, hydrophilic membranes, despite considerable differences in the sizes of pores, were characterised by a very close separation and were significantly less susceptible to blocking than the hydrophobic membranes.

Schwarze et al. [29] also reported higher CTAB retention for hydrophobic membranes than for hydrophilic ones. Moreover, it was pointed out that for polyethersulphone membranes with cut-offs of 5 and 10 kDa, the retention of CTAB micelles amounted to 100%. This means that the concentration of CTAB in the permeate should be not higher than CMC.

The results obtained confirm partially the above data. The concentration of CTAB in permeate does not exceed CMC for polyethersulphone membrane with a cut-off of 5 kDa. However, for polyethersulphone membranes with higher cut-off values (10 and 30 kDa) and CTAB concentration in the feed equal to 10 CMC, the CTAB concentration in the permeate was ca. 2 CMC.

For the CTAB solutions, in comparison to Triton QS-44 solutions, the following was observed: a greater susceptibility to blocking of membranes expressed by a lesser relative permeability and higher retention of surfactants due to a decrease in the pores' diameter, resulting from the adsorption. As the literature indicates, electrostatic affinity between a membrane and cationic surfactant is even stronger than the hydrophobic interactions [30]. Most probably, the hydrophilic heads endowed with a positive charge are located in direct contact with the membrane endowed with a negative charge. Hydrophobic chains, however, remain in contact with the hydrophobic chains of a different molecule of the surfactant, forming the so-called hemicelles.

3.2.3. Ultrafiltration of Triton X-100

Ultrafiltration of the solutions of a non-ionic surfactant showed slightly different tendencies from the cases of anionic and cationic surfactants (Fig. 5). Cellulose membranes demonstrated a systematic growth of the surfactant's retention coefficient together with an increase in its concentration in the feed solution. Within the range of concentrations above the CMC, cellulose membranes were characterised by distinctly higher retention than polyethersulphone membranes.

For example, the Triton X-100 separation from the solution with concentrations of 0.5 and 5 CMC amounted to 44 and 41% for the UP010 membrane, and 8 and 61% for the UC10 membrane, respectively. Cellulose membranes, due to their hydrophilicity, were blocked on a small scale, which correlated with the stable permeate flux within the entire range of concentrations and the insignificant degree of separation of the surfactant in solutions with concentrations below the CMC value.

On the other hand, hydrophobic membranes were characterised by a rapid fall in the membranes' permeability, together with an increase in the surfactant's concentration in the permeate. Due to the hydrophobic interactions and intensive Triton X-100 adsorption on the surface and in the pores of the membrane, a strong separation of Triton X-100 from the monomeric solution was observed, compared to the membranes made of regenerated cellulose. However, separation of Triton X-100 from micellar solutions on the UP series membranes was surprisingly low. Taking into account the diameter of the nascent micelles (8.5 nm) and their mass at a level of approx. 80 kDa (Table 1) and the cut-off of the membranes applied, it was reasonable to expect the separation of this compound to be significantly more effective. This phenomenon may possibly be explained by the permeation of elongated micelles or creeping of the surfactant's monomers adsorbed in the membrane pores [29,31].

Literature reports confirm the results obtained [24,29]. Schwarze et al. [29] also obtained a higher separation of non-ionic surfactant from water solutions in the range of 0–40 g/L with the use of hydrophilic membranes. The authors stated that for a high surfactant concentration in the feed solutions (i.e. 40 g/L), it is possible that high retentions are reached as a result of a gel layer at the membrane surface.

According to Byhlin et al. [32], the hydrophobic membrane showed a flux reduction already at concentrations below the CMC, whereas no flux reduction was observed for a hydrophilic membrane with the same nominal MWCO.

3.3. Ultrafiltration modules

Evaluation of the effectiveness of the separation of surfactants from aqueous solutions in the cross-flow system was the next stage of the research. Two capillary ultrafiltration modules with similar cut-off values, i.e. 2 and 5 kDa, were used in the tests. Their detailed characteristics are illustrated in Table 4.

The research performed indicated that the capillary ultrafiltration models used were characterised by a minor decrease of the permeate flux during filtration (Fig. 6). Additionally, they were less susceptible to blocking by the surfactant molecules (compared to the UP005 flat sheet membrane with the most similar properties) due to more effective control of the polarisation layer. Average values of the permeate flux decrease on the UP005 flat sheet membrane and capillary ultrafiltration modules are compiled in Table 5. The capillary modules used were characterised by similar values of the relative permeability, whereas the PM2 module was slightly less susceptible to blocking than the PM5 module, due to smaller pore diame-

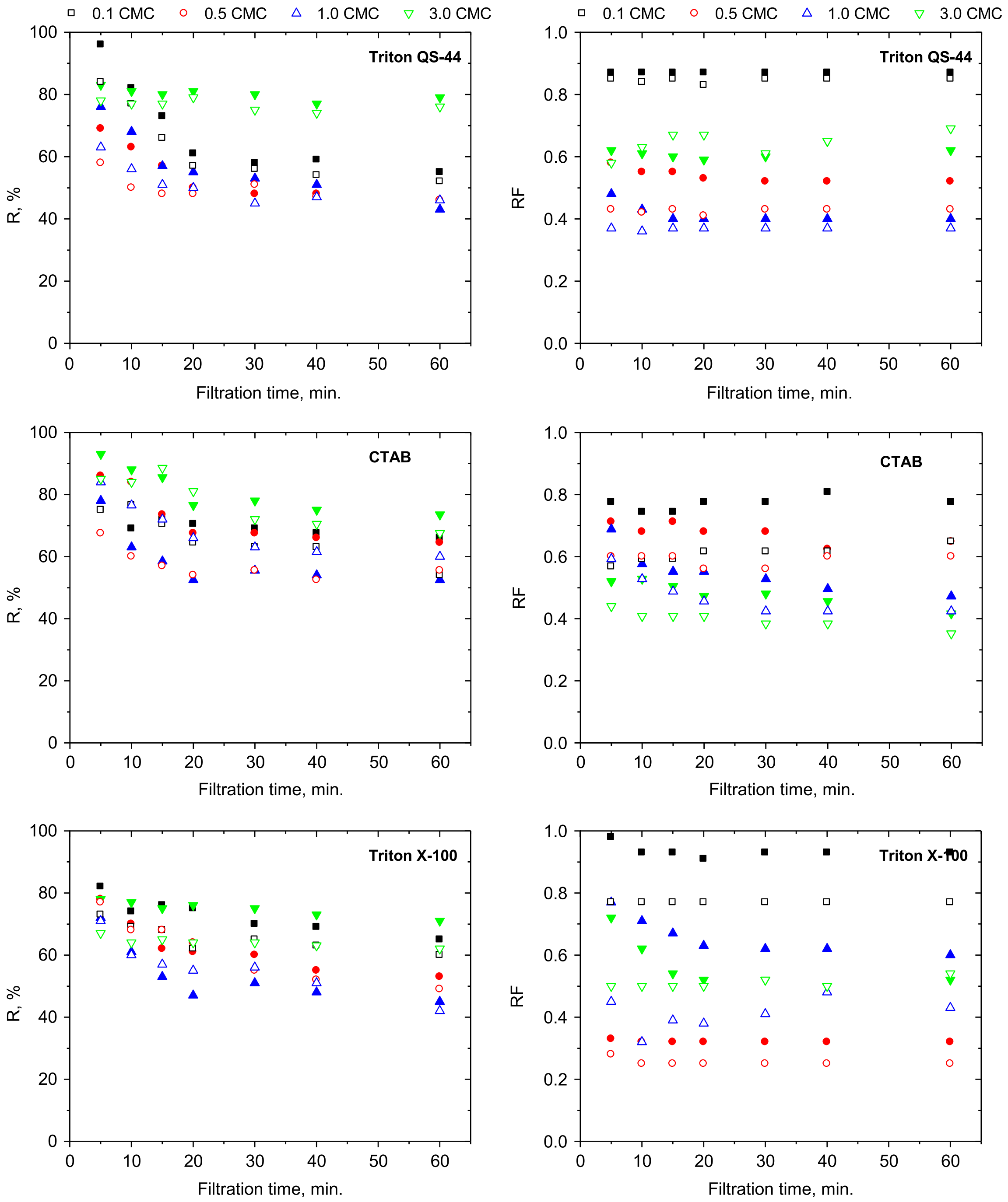

Fig. 6. Triton QS-44, CTAB and Triton X-100 retention and RF as a function of surfactant concentration (PM2—solid symbols; PM5—open symbols).

Table 5
The average values of RF for UP005 flat membrane and capillary modules (PM2 and PM5)

C_f/C_{CMC}	UP005			PM2			PM5		
	Triton QS-44	CTAB	Triton X-100	Triton QS-44	CTAB	Triton X-100	Triton QS-44	CTAB	Triton X-100
0.1	0.65	0.58	0.44	0.77	0.69	0.83	0.75	0.54	0.69
0.5	0.51	0.55	0.22	0.53	0.65	0.34	0.44	0.58	0.29
1	0.57	0.43	0.22	0.49	0.61	0.70	0.45	0.54	0.48
3	0.58	0.43	0.18	0.91	0.80	0.87	0.94	0.72	0.82

Table 6
Triton QS-44, CTAB and Triton X-100 retention and RF as a function of transmembrane pressure (PM5, surf. conc.: 0.5 CMC, CFV = 2.5 m/s, $T = 60$ min)

Parameter	Surfactant	Transmembrane pressure (bar)				Linear approximation
		1	2	3	4	
R (%)	Triton QS-44	41	42	39	35	$y = -2.1x + 44.5$; $R^2 = 0.88$
	CTAB	46	38	36	39	$y = -2.3x + 45.5$; $R^2 = 0.68$
	Triton X-100	45	44	42	36	$y = -2.9x + 49$; $R^2 = 0.93$
RF	Triton QS-44	0.51	0.44	0.43	0.35	$y = -0.049x + 0.555$; $R^2 = 0.97$
	CTAB	0.83	0.81	0.71	0.69	$y = -0.052x + 0.89$; $R^2 = 0.96$
	Triton X-100	0.32	0.31	0.25	0.22	$y = -0.036x + 0.365$; $R^2 = 0.97$

Table 7
Triton QS-44, CTAB and Triton X-100 retention and RF as a function of cross-flow velocity (PM5, surf. conc.: 0.5 CMC, TMP = 1.5 bar, T = 60 min)

Parameter	Surfactant	Cross-flow velocity, m/s				Linear approximation
		1	2	3	4	
R (%)	Triton QS-44	37	40	41	43	$y = 1.9x + 35.5$; $R^2 = 0.98$
	CTAB	33	37	38	40	$y = 2.2 + 31.5$; $R^2 = 0.96$
	Triton X-100	31	35	37	38	$y = 2.3 + 29.5$; $R^2 = 0.95$
RF	Triton QS-44	0.42	0.43	0.43	0.48	$y = 0.018x + 0.396$; $R^2 = 0.86$
	CTAB	0.61	0.66	0.72	0.83	$y = 0.72x + 0.525$; $R^2 = 0.98$
	Triton X-100	0.25	0.29	0.31	0.32	$y = 0.023x + 0.235$; $R^2 = 0.96$

ters. Simultaneously, a minor decrease in the surfactants' retention occurred for both modules during the membrane filtration.

Further into the experiment, the impact of the process parameters (transmembrane pressure and cross-flow velocity at the membrane's surface) on the efficiency of the ultrafiltration process is determined (Tables 6 and 7). Tests were conducted for the module with a cut-off of 5 kDa and a concentration of surfactants at the level of 0.5 CMC.

Together with the increase of the driving force of the process, a distinct increment of the permeate flux of the module occurred. As a result of the increased permeate flux, the polarisation layer effect at the surface of the membrane was highlighted more and thus a greater decrease of the RF of membranes with an increase in the transmembrane pressure were recorded. The increased concentration of component in the polarisation layer of the membrane caused more intensive transport of the component through the membrane's active layer, which resulted in the growth of the concentration of surfactants in the permeate.

On the other hand, the increase of the cross-flow velocity at the surface of the membrane caused improved retention of the surfactants and a decrease of the intensity of the membranes' blocking. Improvement of the transport and separation properties together with an increase in the cross-flow velocity was obtained through more effective control of the polarisation layer thickness as a result of an increment of the shear forces in the membrane channels.

3.4. Leakage of the surfactant to the permeate side

The leakage of surfactants to the permeate for the experiments performed is compiled in Fig. 7, while the results of a linear approximation for the presented relations are illustrated in Table 8. The results demonstrated that with good adjustment it is possible to determine, with the help of a linear dependence, the concentration of a surfactant in the permeate depending on the concentration in the feed solution.

4. Summary

The research performed allowed us to formulate the following conclusions:

(1) The cut-off value of membranes, in direct connection with their surface charge and hydrophilic/hydrophobic character, determines the effectiveness of the surfactants' separation on the membranes.

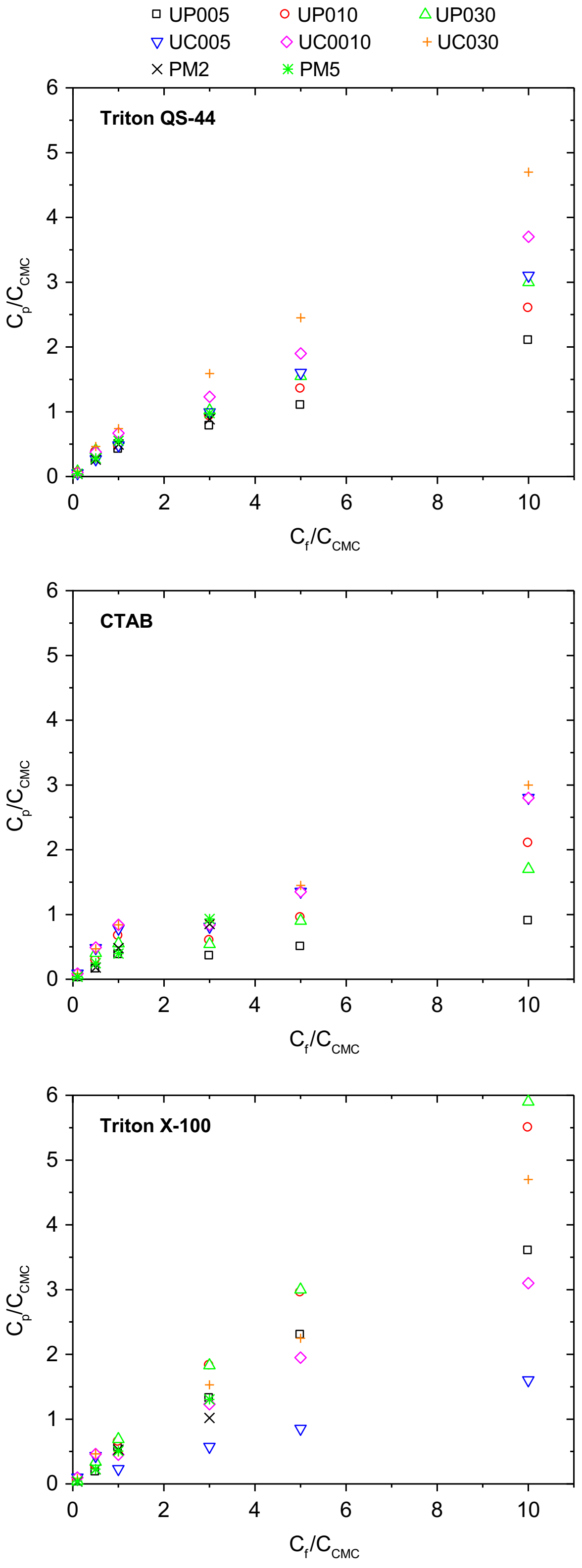

Fig. 7. Triton QS-44, CTAB and Triton X-100 concentration in the permeate as a function of surfactant concentration in the feed solution.

Table 8
Results of linear approximation ($y = ax$) of the relationship $C_p/C_{CMC} = a(C_f/C_{CMC})$

Membrane	Triton QS-44		CTAB		Triton X-100	
	a	R^2	*a*	R^2	*a*	R^2
UP005	0.22	0.97	0.10	0.78	0.39	0.97
UP010	0.27	0.97	0.21	0.90	0.56	1.00
UP030	0.31	0.97	0.18	0.84	0.59	1.00
UC005	0.31	0.99	0.28	0.92	0.17	0.91
UC010	0.38	0.98	0.28	0.90	0.33	0.96
UC030	0.48	0.99	0.30	0.92	0.47	0.99
PM2	0.32	0.88	0.31	0.91	0.36	0.94
PM5	0.35	0.88	0.32	0.97	0.44	0.99

(2) More effective Triton QS-44 and CTAB separation across the entire range of concentrations was obtained on the hydrophobic membranes created from polyethersulphone, which were also characterised by a greater susceptibility to blocking due to the adsorption of monomers. On the other hand, for Triton X-100 within the range of concentrations above the CMC, cellulose membranes were characterised by distinctly higher retention. They were blocked to a smaller extent due to their hydrophilicity, which correlated with the stable permeate flux and the insignificant degree of separation of the surfactant from solutions with concentrations below the CMC value.

(3) Hydrophilic/hydrophobic properties of membranes and the interaction between the membrane and separated surfactant may have a greater impact on the effectiveness of the process than just the sieve effect. The least effective separation, of the nonionic surfactant Triton X-100, forming micelles with the largest number of aggregations and largest diameter, confirms this thesis. For example, the values of the retention of surfactants from the solutions with a concentration of 5 CMC amounted for Triton QS-44, CTAB and Triton X-100 respectively, to: 73, 81 and 41% (for the UP010 membrane) and 62, 73 and 61% (for the UC010 membrane).

(4) Capillary polysulphone modules operating in conditions of long-term membrane filtration were characterised by an insignificant decrease of the permeate flux. Additionally, they were less susceptible to blocking by the surfactant molecules compared to the flat sheet membranes, due to more effective control of the polarisation layer as a result of a tangential flow of the solution in the cross-flow filtration.

(5) With increased transmembrane pressure, the polarisation layer effect at the surface of the membrane was highlighted more, which resulted in a decrease of the relative permeability and an increased concentration of the surfactants in the permeate. On the other hand, an increase of the cross-flow velocity at the surface of the membrane caused the improvement of transport and separation properties of membranes through more effective control of the thickness of the polarisation layer.

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