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THE SEPARATION PROPERTIES OF POLYETHERSULPHONE AND POLYSULPHONE ULTRAFILTRATION MEMBRANES USING SODIUM DODECYL SULPHATE (SDS) SOLUTIONS WITH THE ADDITION OF SODIUM SULPHATE

The experimental objectives assessed in this case scenario were to investigate the transport and separations properties of polyethersulphone (PES) and polysulphone (PS) ultrafiltration membranes under the following prescribed conditions:

- addition of sodium sulphate (Na_2SO_4) to sodium dodecyl sulphate (SDS) salt solutions,
- change of pH level of SDS solutions.

Experiments were carried out in a laboratory ultrafiltration cell at pressures of 0.10, 0.15 and 0.20 MPa. The concentration of SDS in model solutions amounted to 100 mg/dm^3, whereas Na_2SO_4 concentration ranged from 0.2 to 2.5 g/dm^3. As sodium sulphate was added to the SDS solution, the retention properties of the membranes deteriorated. No discernible effect on the retention coefficient of the membranes was found as the sodium sulphate dosage was increased. The best separation effect was observed for solutions with a pH equal to 7.0.

1. INTRODUCTION

The use of surfactants for industrial purposes and in many consumer products such as soaps and detergents has resulted in their worldwide consumption of approximately 10.4 million tonnes per annum [1]. One of the main consequences of this level of production is the increase in the pollutant levels of wastewaters produced in plants manufacturing toiletries and detergents during the washing processes [2]. The polluting loads of this wastewater are mainly due to the residual products in a reactor, which have to be washed away in order to use the same facility for the manufacture of other

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products. The extreme diversity of raw materials and production schemes employed in the toiletry and detergent industries is reflected in the variety and complexity of this type of wastewater. A direct result of this production is the necessity of the manufacturer to assess the effluent characteristics of their wastewaters and consequently to define pollution control methods.

Surfactants are amphiphilic compounds that contain a hydrophobic portion, which effectively repels water molecules, and a hydrophilic portion that attracts the water solution. They are principally surface acting agents that when used in low concentrations can greatly reduce the surface tension of water. They reduce the free energy of the system by replacing the bulk molecules of higher energy at a water–liquid interface. The presence of these molecules on the surface effectively lowers surface and interfacial tension.

Surfactant monomers can form spheroid or lamellar structures with organic pseudophase interiors [3]. The minimum concentration at which this occurs is called the *critical micellar concentration* (cmc). At higher concentrations than cmc, monomers and micelles coexist in equilibrium. Salinity, hydrocarbon chain length and surfactant type will influence the concentration.

The high and varied polluting load of the detergent wastewater can cause significant environmental problems. Prior to its discharge into the environment an efficient treatment process must be applied. Due to its complexity, detergent wastewater is very difficult to treat. Membrane processes, such as ultrafiltration, have been suggested as a means of recovery of surfactants with critical micellar concentrations. If the surfactant concentration is low, that is, monomer concentration ($c < cmc$), then nanofiltration has been suggested as an effective removal process.

The research objective described in this paper was to continue experimental procedures previously published [4]. In the first stage of experimental procedures, five Intersep Nadir ultrafiltration membranes, made of regenerated cellulose (C), cellulose acetate (CA), polyamide (PA), polysulphone (PS) and polyethersulphone (PES) were used. The type of membrane materials influenced the efficiency of sodium dodecyl sulphate (SDS) separation. A decrease of separation and transport properties of these membranes with increasing SDS concentration was observed. The best separation effect was achieved for the polyethersulphone (PES) and polysulphone (PS) membranes, it was therefore decided that further analysis be carried out on these materials.

Sodium sulphate (Na_2SO_4) was chosen as a SDS additive because it is one of the inorganic builders present in many laundry detergents (the table) [5]. Builders are added to keep the product homogeneous under varying storage conditions and to provide desirable dispensing characteristics. Additionally a mixture of 60% of sodium sulphate and 40% of SDS provides a higher decrease of surface tension and interfacial tensions than 100% SDS [6]. The presence of SDS in detergents prevents the accumulation of dirt molecules on the surface of the clothes fibre during the washing process.

Table

Typical compositions of detergents for consumer laundry products [5]

	Europe		U.S.A	
	Powders with P	Powders without P	Liquids phosphate	Powders with P
Anionics	5–10	5–10	10–15	5–10
Nonionics	2–10	0–10	10–15	2–10
Builders	10–35	20–25	0–5	25–35
Bleachers	10–25	20–25	–	–
Activators	0–5	0–2	–	–
Polymers	1–2	1–2	0–3	1–2
Brighteners	<0.3	<0.3	<0.3	<0.3
Silicate	2–6	2–6	<0.3	2–6
Silicones	<1	<1	<1	–

2. MATERIAL AND METHODS

The laboratory set-up was composed of an Amicon 8400 ultrafiltration cell with a total volume of 350 cm^3 and diameter of 76 mm. In all experiments being carried out, sodium sulphate (Na_2SO_4) was added to the SDS solution at the pressures of 0.10, 0.15 and 0.20 MPa and pH levels of 5, 7, 9 and 11. The concentration of SDS in model solutions amounted to 100 mg/dm^3. The pH levels of feed solutions were changed by the addition of hydrochloric acid (HCl) and sodium hydroxide (NaOH).

Two types of Intersep Nadir ultrafiltration membranes, i.e. polysulphone (PS) and polyethersulphone (PES), were used in this study. The molecular weight cut-off (MWCO) of the membranes investigated amounted to 4, 10 and 30 kDa. The concentration of SDS in the feed and the permeate were determined by means of colour reactions using the indicator Rhodamine G6 and spectrophotometrically at a wavelength (λ) of 565 nm. The efficiency of the ultrafiltration process was estimated based on the classical coefficient:

$$R = \frac{C_f - C_p}{C_f} \cdot 100\%,$$

where C_f is concentration of SDS in the feed solution and C_p is concentration of SDS in the permeate.

3. RESULTS AND DISCUSSION

The objective of the experimental research was to evaluate the removal of sodium dodecyl sulphate (SDS) in the presence of sodium sulphate from water solutions by ultrafiltration. The retention properties of the two membrane materials tested at the MWCO of 30 kDa are illustrated in figure 1. The polyethersulphone (PES) and polysulphone (PS) membranes allowed the separation of SDS amounting to 39.3% and 33.7%, respectively. With the addition of sodium sulphate a dramatic decrease in retention of SDS of approximately 26–34% for the PES30 membrane and 17-26% for the PS30 membrane was observed.

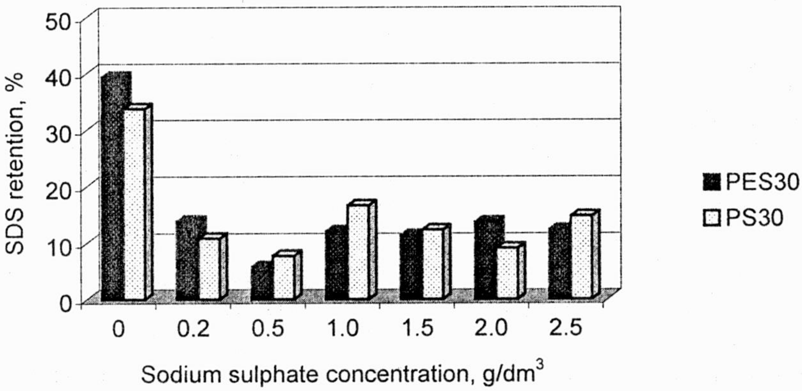

Fig. 1. The influence of sodium sulphate concentration on SDS retention by PES30 and PS30 kDa membranes (pH = 7, ΔP = 0.10 MPa)

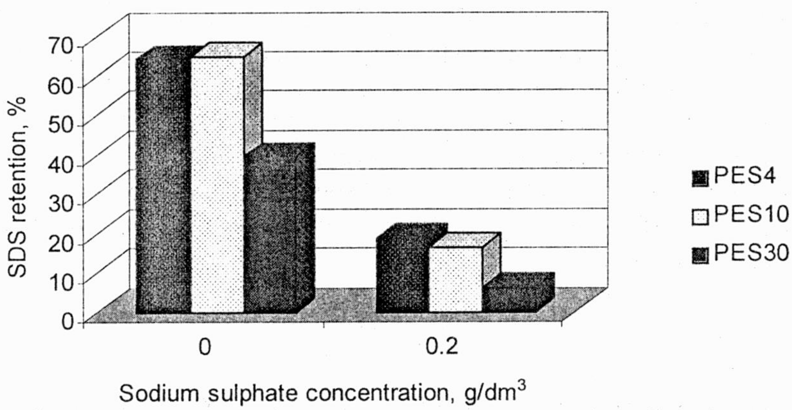

Fig. 2. Retention characteristics of SDS vs. sodium sulphate concentration and cut-off of PES membranes (pH = 7, ΔP = 0.10 MPa)

As the SDS concentration in the feed solution was lower than the critical micelle concentration (cmc for SDS = 2.2 g/dm^3), the solution was monomeric in character, but there is a very high probability that the concentration in polarisation layer is higher than cmc concentrations and therefore micelles are formed. The average molecular weight for SDS micelles is about 50 times greater than the molecular weight for SDS molecules. This implies that the average molecular weight of SDS micelles is about 14000 g/mol [7], and explains why PES4 and PES10 membranes achieve the same retention of SDS (figure 2) of about 64%. For the PES30 membrane, the separation effect was lower by about 25%.

With the addition of sodium sulphate a dramatic decrease in retention of SDS was observed. This was probably due to a 'salting out' effect whereby in certain sodium concentrations the ions started destabilizing the micelles. Apparently, beyond a critical concentration, the sodium ions also started disrupting the micellar packing resulting in less stable micelles [8]. There was no discernible effect on the retention coefficient of the membranes with the increase in the amount of the sodium sulphate added to the SDS solution. Only a small reduction of volume flux was observed with an increase in the concentration of sodium sulphate (figure 3). Similar tendency was noticed for higher pressures.

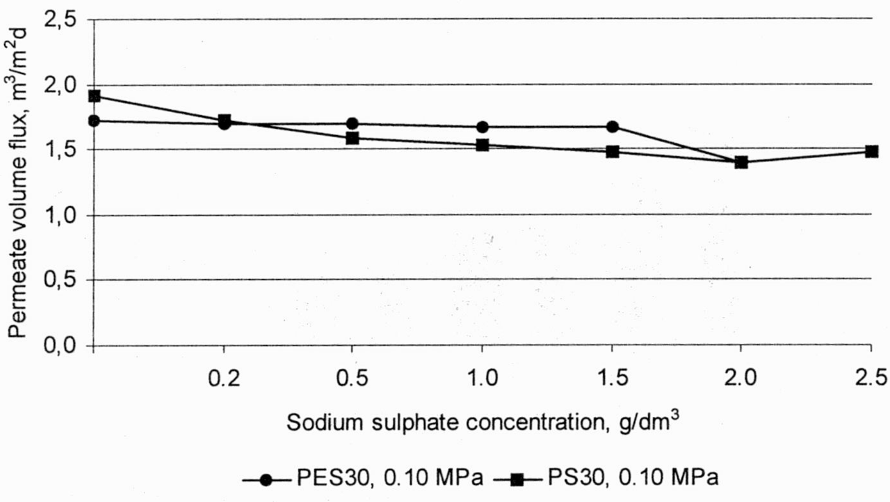

Fig. 3. Transport properties of PES30 and PS30 kDa membranes vs. sodium sulphate concentration (pH = 7, ΔP = 0.10 MPa)

The effects of an increase in pressure on the separation efficiency for the PS30 and PES30 membranes were evaluated and it became evident that they produced only a small reduction in the retention as the pressure was increased (figures 4 and 5).

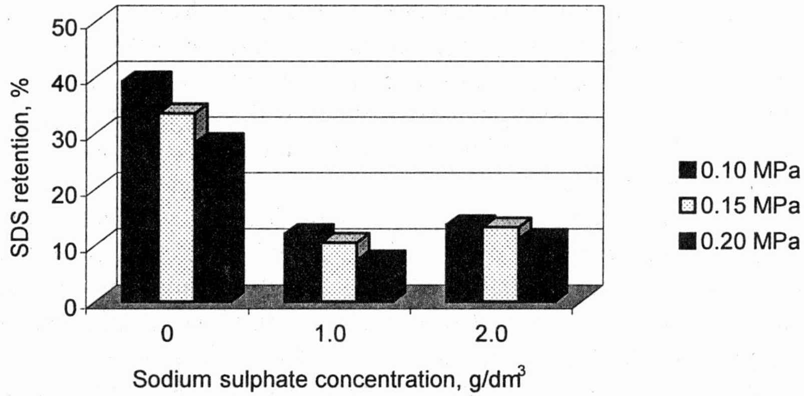

Fig. 4. The influence of sodium sulphate concentration and pressure on SDS retention by PES30 kDa membrane (pH = 7)

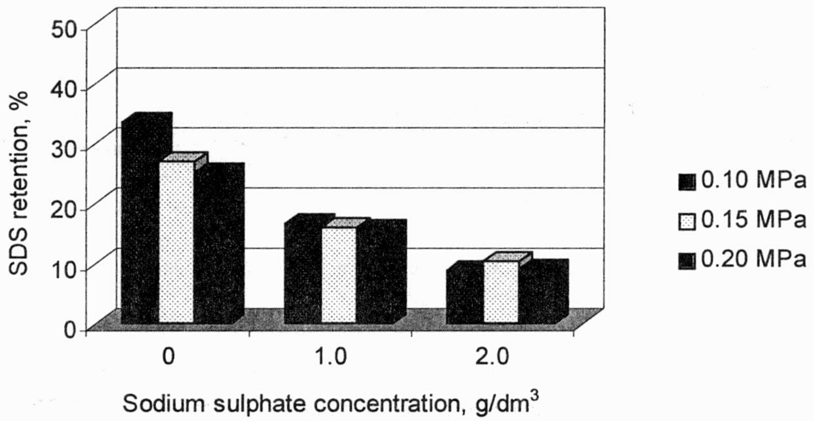

Fig. 5. The influence of sodium sulphate concentration and pressure on SDS retention by PS30 kDa membrane (pH = 7)

Further analysis was carried out to establish the effect of pH levels on the separation properties of the membranes tested (figure 6). The best separation effect was achieved for pH = 7.0. As the pH level was increased to 9.0 and 11.0, or decreased to pH = 5.0, the separation effect was lower due to the probability of higher concentration of sodium and hydrogen ions from NaOH and HCl, respectively. The presence of Na^+ and H^+ ions results in the probability of destabilizing the micelle concentrations.

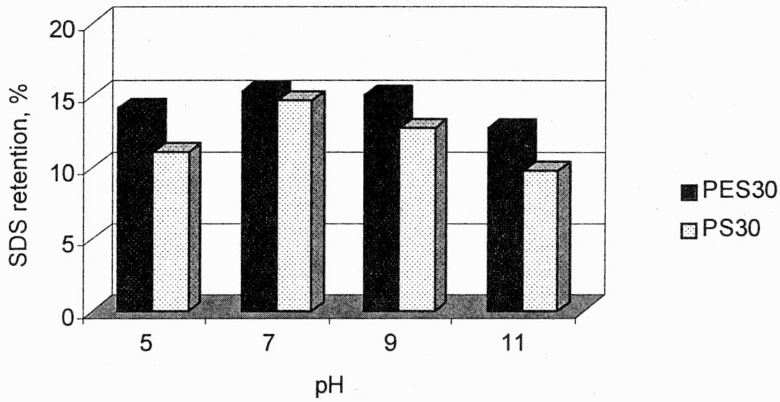

Fig. 6. The influence of pH on SDS retention by PES30 and PS30 kDa membranes at 2.5 g/dm^3 of sodium sulphate (ΔP = 0.10 MPa)

4. CONCLUSIONS

The objective of the experimental research was to assess the separation properties of various UF membranes. The selected membrane materials utilised in the experimental procedure were subjected to just one anionic surfactant, SDS.

Based on the experimental investigation the following conclusions can be deduced:

- A decrease in retention of SDS for the polyethersulphone (PES) and polysulphone (PS) membranes with addition of sodium sulphate was observed.
- No discernible effect on the retention coefficient of the membranes was produced as the sodium sulphate dosage was increased.
- As the pressure was increased a small reduction in the retention of the membranes was noted.
- The best separation effect was observed for pH equal to 7.0.

REFERENCES

[1] PRATS D., RUIZ F., VAZQUEZ B., RODRIGUEZ-PASTOR M., *Removal of anionic and nonionic surfactants in a wastewater treatment plant with anaerobic digestion. A comparative study*, Water Research, 1997, Vol. 31, No. 8, pp. 1925–1930.

[2] PAPADOPOULOS A., SAVVIDES C., LOIZIDIS M., HARALAMBOUS K.J., LOIZIDOU M., *An assessment of the quality and treatment of detergent wastewater*, Water Science Technology, 1997, Vol. 36, No. 2–3, pp. 377–381.

[3] MULLIGAN C.N., YONG R.N., GIBBS B.F., *Surfactant-enhanced remediation of contaminated soil: a review*, Engineering Geology, 2001, Vol. 60, pp. 371–380.

[4] KOWALSKA I., KABSCH-KORBUTOWICZ M., MAJEWSKA-NOWAK K., BOR F.L., *An assessment of ultrafiltration membrane materials in sodium dodecyl sulphate removal from water solutions*, Environmental Protection Engineering, 2001, Vol. 27, No. 3–4, pp. 19–25.
[5] *The handbook of environmental chemistry, Detergents*, 1992, Volume editor: N.T. de Oude.
[6] ANASTASIU S., JELESCU E., *Środki powierzchniowo czynne*, Wydawnictwo Naukowo-Techniczne, Warszawa, 1973.
[7] ZIELIŃSKI R., *Surfaktanty. Towaroznawcze i ekologiczne aspekty ich stosowania*, Wydawnictwo Akademii Ekonomicznej w Poznaniu, Poznań, 2000.
[8] PATIS A., HUIBERS P.D.T., DENEKA B., SHAH D.O., *Effect of tetraalkylammonium chlorides on foaming properties of sodium dodecyl sulfate solutions*, Langmuir, 1998, Vol. 14, pp. 4471–4474.

WŁAŚCIWOŚCI SEPARACYJNE POLIETEROSULFONOWYCH I POLISULFONOWYCH MEMBRAN ULTRAFILTRACYJNYCH W ODNIESIENIU DO SOLI SODOWEJ SIARCZANU DODECYLU W OBECNOŚCI SIARCZANU SODU

Przedstawiono właściwości separacyjne i transportowe ultrafiltracyjnych membran z polieterosulfonu i polisulfonu w odniesieniu do roztworu soli sodowej siarczanu dodecylu (SDS) o stężeniu 100 mg/dm^3 w obecności siarczanu sodu w ilości 0.2–2.5 g/dm^3. Badania prowadzono w komorze ultrafiltracyjnej przy ciśnieniu 0.10, 0.15 i 0.20 MPa i dla różnych odczynów analizowanych roztworów. Zaobserwowano obniżenie efektu separacji dla najmniejszej ze stosowanych dawek siarczanu sodu, natomiast dalsze zwiększenie dawki siarczanu nie wpływało w istotny sposób na efekt separacji. Najlepszy efekt separacji uzyskano dla obojętnego odczynu roztworu.