

# Surfactant removal from water solutions by means of ultrafiltration and ion-exchange

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Received 20 December 2006; accepted 3 January 2007

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## Abstract

The aim of the study was to compare the removal efficiency of anionic surfactant (belonging to alkylbenzenesulfonate family) from water solutions by means of ultrafiltration and ion-exchange. During the first stage of the experiments, the influence of surfactant type and its concentration, membrane cut-off and polymer material on ultrafiltration performance was evaluated. The next stage of the study was focused on effectiveness of ion-exchange using MIEX resin as a method of surfactant removal from water solutions. The effect of pollutant concentration, resin dose, mixing time, pH of the solution and mineral salt presence was assessed.

It was noticed that the ultrafiltration separation of surfactant was significantly influenced by membrane material. The best separation characteristics were achieved by polysulfone and polyethersulfone membranes. The PES5 and PS5 ones allowed lower the surfactant concentration to be achieved ranging from 71 to 91% and from 55 to 81% for 5 kDa and 10 kDa. High surfactant retention was obtained at lower concentrations. With the increase in surfactant concentration the retention values decreased with a slight increase in CMC value.

From the experimental investigation, the magnetic ion-exchange resin was found to be very effective in anionic surfactant removal in a wide range of concentrations. As well as the ion-exchange process was shown to be insensitive to the pH value of the solution and the mineral salt presence.

*Keywords:* Surfactant; Ultrafiltration; Membrane; Ion-exchange; MIEX

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## 1. Introduction

Increased water consumption for both industrial and domestic purposes has led to a shortage of good quality surface and groundwater resources and to an increase in the costs of water and

wastewater treatment. As a consequence of this shortage it would be prudent for any rational water management authority to secure the purest water sources for direct human consumption and to encourage the reuse of processed water for industrial applications [1].

*Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.*

Environmental risks associated with detergent manufacture, its use and disposal are of great concern due to the relative toxicity of detergent products and its core ingredients (surfactants) on aquatic life. According to McWilliams et al. [2] a factor that has to be considered in the environmental assessment of surfactants (apart from the intrinsic toxicity of the surfactant) is that of the potential synergistic effects (among other things) on migration, dispersion, bioavailability of otherwise low-toxicity chemical compounds in a formulation. Most surfactants are susceptible to biodegradation and other reactive breakdowns, which may lead to metabolites with significantly different chemical properties. However Cserhati et al. [3], according to published data, indicate that the role of surfactants in the environment is ambiguous. They can cause serious environmental pollution with increased toxicity in living organisms; whilst on the other hand, they can promote removal of inorganic and organic pollutants from the environment.

Due to the diversity of surfactants and their physico-chemical properties it is difficult to develop a single and an effective treatment method of detergent wastewater. From among techniques which were studied in this research area [4–17] can be listed biodegradation, coagulation, foaming, oxidation, adsorption, ion-exchange and membrane processes.

Numerous reports indicate that membrane technology is emerging as one of the leading contenders in the recovery of water and concentrated products from the rinsing waters used in the batch production of surfactants and detergents or as a polishing step before the effluents are discharged [18,19]. Micro- and 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, ( $c < c_{mc}$ ) then nanofiltration has been suggested as an effective removal process. The discharge of the treated detergent effluents by means of low-pressure membrane

processes to the environment can not always be possible and additional treatment process must be applied. Therefore the ion exchange processes would seem to be very effective solution to this problem.

In recent years considerable attention has been focused on the application of magnetic ion exchange resin (MIEX) for water and wastewater treatment. The ion exchange resin beads contain a magnetized component within their structure, which results in the forming of rapidly settling agglomerates. The very small resin bead size provides a high surface area allowing effective exchange kinetics of select ions [20].

The aim of the study was to compare the removal efficiencies of anionic surfactant (belonging to alkylbenzenesulfonate family) from water solutions by means of ultrafiltration and ion-exchange. During the first stage of the experiments, the influence of surfactant type and its concentration, membrane cut-off and polymer material on ultrafiltration performance was evaluated. The next stage of the study was focused on the effectiveness of ion-exchange using MIEX resin as a method of surfactant removal from water solutions. The effect of pollutant concentration, resin dose, mixing time, pH of the solution and mineral salt presence was assessed.

## 2. Materials and methods

### 2.1. Solutions

Marlon AS3 (mixture of alkylbenzenesulfonic acids, alkyl chain lengths from 10 to 13 carbon atoms) was obtained from Sasol Germany GmbH. The active content was above 96.5% by wt. The CMC value was determined by measuring the solution conductivity at temperature of 25°C and amounted to 580 mg/L. The aqueous solutions were prepared with distilled water and the concentration of surfactant ranged from 15 to 600 mg/L and from 15 to 300 mg/L during UF and ion-exchange experiments, respectively. All analyses were carried out at 25°C.

The alkylbenzenesulfonates are used in textile processing, as wetting, dispersing and cleaning agents. They are also important emulsifiers in industrial processes, in polymerization and in the formulation of crop protection agents. More than 80% of LAS production is used in laundry detergents, cleaners and in virtually all product types in the household sector.

The surfactant concentration in the feed and the permeate was determined by means of colour reaction using the indicator Rhodamine G6 and spectrophotometric measurements of the absorbance at a wavelength 565 nm.

## 2.2. Ultrafiltration process

In the study Microdyn-Nadir GmbH membranes made of polyethersulfone (PES), polysulfone (PS), regenerated cellulose (C), cellulose acetate (CA) and polyamide (PA) with molecular weight cut-off equal to 5 and 10 kDa were used. Ultrafiltration was conducted using a laboratory set-up [21], which the main part was an Amicon 8400 UF cell. The effective surface area of the membrane was  $4.54 \times 10^{-3} \text{ m}^2$  and the volume of  $350 \times 10^{-6} \text{ m}^3$ . Prior to first cycle, the UF membranes were treated with distilled water at 0.20 MPa until a constant volume flux was established (Table 1).

Table 1  
Distilled water flux of the membranes investigated

Membrane material	Distilled water flux, L/m <sup>2</sup> d (transmembrane pressure = 0.20 MPa)	
	5 kDa	10 kDa
Polyethersulfone (PES)	646	1726
Polysulfone (PS)	193	2175
Regenerated cellulose (C)	781	1211
Acetate Cellulose (CA)	819	847
Polyamide (PA)	1798	2423

In order to maintain a stable concentration of the substances in the feed solution, the permeate was recirculated to an UF cell. The ultrafiltration experiments were carried out at the following transmembrane pressures: 0.10, 0.15 and 0.20 MPa.

During the experiments the normalized flux was determined — as the ratio of the permeate flux ( $J$ ) to the initial distilled water flux  $J_0$ .

## 2.3. MIEX process

The ion-exchange experiments with MIEX resin (Orica Watercare) were carried out using a Velp Scientifica JLT4 jar tester. One litre samples of the solution were put into beakers, and the following amounts of resin were added: 2.5, 5, 10, 15 and 20 mL/L. The content in the beakers was well mixed with speed of 150 rpm. After an allotted time of mixing (5, 10, 20, 40 and 60 min), the samples of the solution were taken for measurements of surfactant concentration. During the kinetic studies the influence of either pH or ionic strength was evaluated. The pH of the tested solutions ranged from 5 to 11, adjustment was via the addition of 0.1 M NaOH or HCl. The concentration of mineral salt (sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>) amounted to 0.2, 0.5, 1.0 and 1.5 g/L.

## 3. Results and discussion

Fig. 1 presents the retention coefficient and normalized flux vs. surfactant concentration during ultrafiltration process. As can be seen, the highest Marlon AS3 separation was noticed for very low surfactant concentration in the feed. When the concentration increased the removal efficiency systematically decreased. However for surfactant concentration above the CMC value (580 mg/L) the improvement in membranes selectivity was observed. The highest retention coefficient was achieved by polyethersulfone and polysulfone membranes, and amounted to 71–91% and 55–81% for 5 kDa and 10 kDa, respectively. Alternatively, polyamide membranes

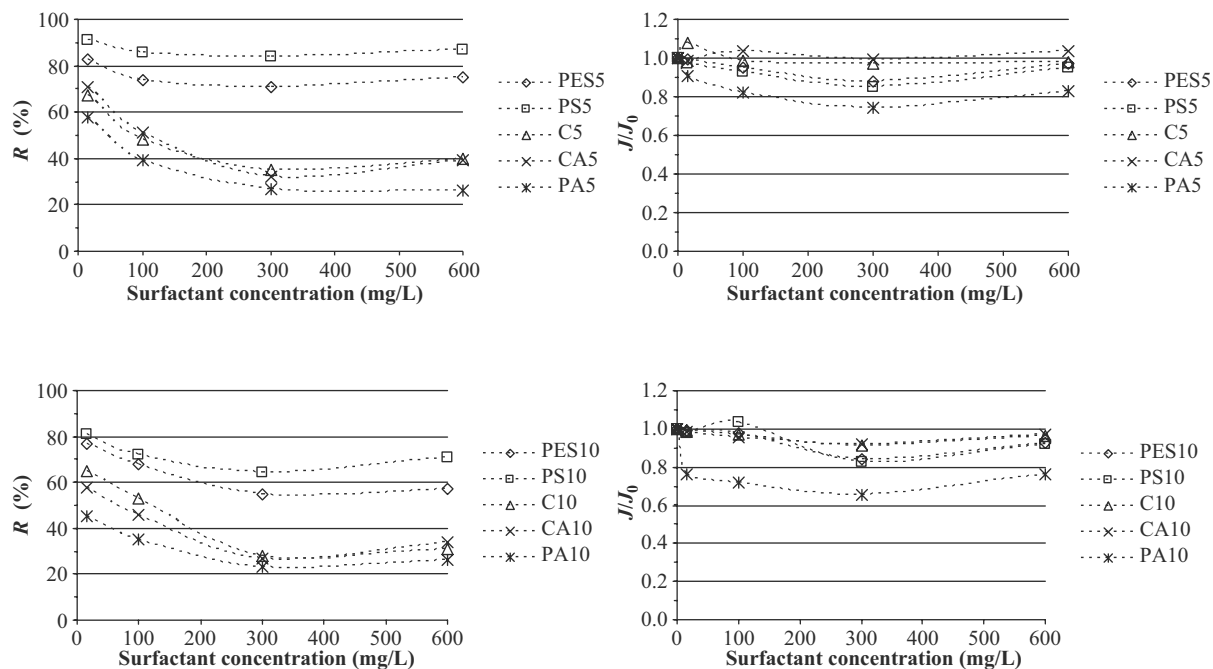


Fig. 1. Retention coefficient and normalized flux vs. surfactant concentration during ultrafiltration process (transmembrane pressure = 0.20 MPa).

exhibited the worst separation properties — 26–58% and 23–45% for 5 kDa and 10 kDa, respectively. It should also be noted that the retention coefficient achieved for regenerated cellulose and acetate cellulose membranes (for each cut-off tested) was very similar due to hydrophilic–hydrophobic properties of the polymers. The membranes selectivity amounted to 32–71% and 27–65% for 5 kDa and 10 kDa membranes, correspondingly.

It should be noted from the results that the increase in surfactant concentration resulted in worsening membranes permeability. When the surfactant concentration was increased up to CMC value, the membrane permeability improved slightly. The results obtained for model solutions indicate that C and CA membranes were characterized by very good operational stability. The permeate volume flux of 5 kDa membranes remained on a invariable level, while for 10 kDa

membranes, due to the less compact polymer structure, the drop in permeability did not exceed 10% (in comparison to the distilled water). The highest deterioration in permeate volume flux was exhibited by the polyamide membranes whose characteristics showed more hydrophobic properties and more spongy structure of polymer than C and CA ones.

Transport and separation properties of membranes during ultrafiltration of surfactant solutions can be attributed to several phenomena, such as concentration polarization, membrane fouling and interactions between surfactant and membrane. For low concentration (far below CMC) the high surfactant retention could be mainly attributed to monomer adsorption on the membrane surface and within the pores. According to Jönsson et al. [22] the monomer competition to the hydrophobic spots on the membrane is low and probably the monomers “lie” horizontally along the surface.

At higher concentration a closed-packed layer of surfactant on the membrane surface and interior of the pores is probably formed resulting in decline of the permeate flux. According to Mizoguchi et al. [23] for surfactant concentration below the CMC the membrane pore blocking can be also caused by the pre-micelles formed in the concentration polarization layer.

For concentration close to CMC value, as a result of the micelles creation, the separation slightly increased and simultaneously the improvement in transport properties was noted. Because the micelle surface is hydrophilic, it has a greater affinity to the solvent than to the UF membranes. At the same time the electrostatic repulsion between negatively charged micelles results in the less compact polarization layer and thereby the solvent transport was facilitated [17].

Kinetic profiles of surfactant removal by MIEX resin are presented in Fig. 2. It should be noted that with an increase in MIEX resin dose the separation efficiency of anionic surfactant

increased. Exemplary for a concentration of 300 mg Marlon AS3/L, the increase of MIEX dose in the range from 2.5 to 20 mL/L improved the removal efficiency from 18 to 83% and from 61 to 92% for 5 and 40 min of mixing, respectively.

For all applied resin doses most of the exchange took place within the first 30 min; whilst a plateau of surfactant separation was attained at a faster rate for lower surfactant concentration in solution and for higher amounts of resin used. Although the best separation efficiency occurred for the highest MIEX dose, the amount of 10 mL MIEX resin and 20 min of mixing was regarded as the optimal parameters for the further tests.

It should be noted (see Fig. 2) that the magnetic ion-exchange resin was found to be very effective in anionic surfactant removal in a wide range of concentrations. At the same time the ion-exchange process was insensitive to the pH value of the solution and the mineral salt presence (Fig. 3).

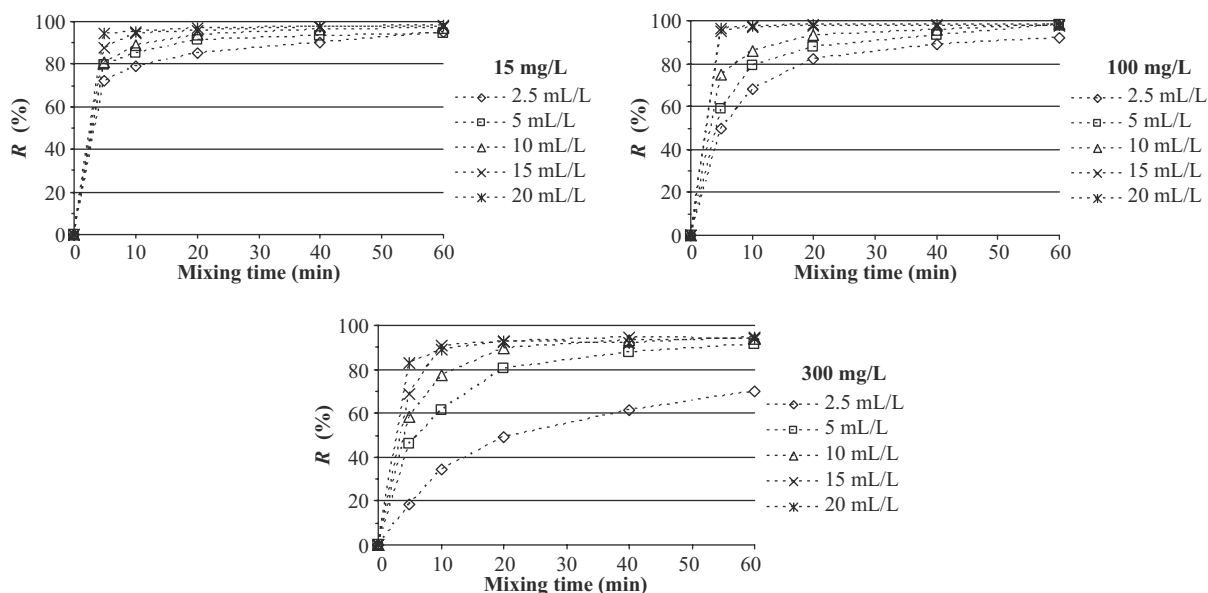


Fig. 2. The influence of MIEX dose and mixing time on separation efficiency of anionic surfactant during ion-exchange process.

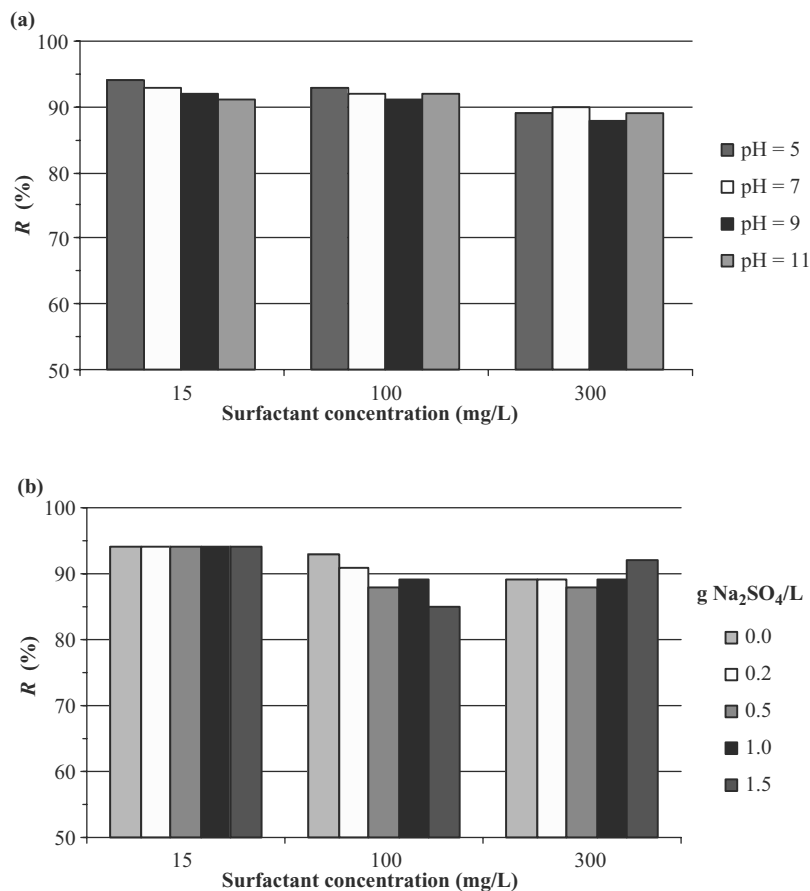


Fig. 3. The influence of solution pH (a) and mineral salt dosage (b) on separation efficiency of anionic surfactant during ion-exchange process (MIEX dose = 10 mL/L, mixing time = 20 min).

#### 4. Conclusions

The experimental investigation demonstrated that the ultrafiltration separation of surfactant was significantly influenced by membrane material. The best separation characteristics were achieved by polysulfone and polyethersulfone membranes. High surfactant retention was obtained at low concentrations. With the increase in surfactant concentration the retention values decreased and again slightly increased above CMC value.

The experimental process showed that the magnetic ion-exchange resin was found to be very effective in anionic surfactant removal. The high

separation efficiency of anionic surfactant from model solutions in a wide range of concentrations was observed. At the same time the ion-exchange process was insensitive to the pH value of the solution and the mineral salt presence.

From the results obtained it can be confirmed that the ion-exchange (with MIEX resin) can be effectively applied as an additional post-treatment process to remove the residual amounts of surfactants after ultrafiltration treatment in order to meet more stringent legislative requirements in the discharge detergent wastewater to the sewage system or to environment.

## Acknowledgements

The work was partly supported by the Polish Ministry of Education and Science, Grant # 3 T09D 025 26. Author would like to thank ORICA for providing the MIEX resin.

## References

- [1] A. Rozzi, F. Malpei, L. Bonomo and R. Bianchi, Textile wastewater reuse in northern Italy (COMO), *Water Sci. Technol.*, 39 (1999) 121–128.
- [2] P. McWilliams and G. Payne, Bioaccumulation potential of surfactants: a review, Presented at Chemistry in the Oil Industry VII, Royal Society of Chemistry & EOSCA, Manchester, November 2001.
- [3] T. Cserhati, E. Forgacs and G. Oros, Biological activity and environmental impact of anionic surfactants, *Environ. International*, 28 (2002) 337–348.
- [4] V. Mezzanotte, E. Bolzacchini, M. Orlandi, A. Rozzi and S. Rullo, Anaerobic removal of linear alcohol ethoxylates, *Bioresource Technol.*, 82 (2002) 151–156.
- [5] T.W. Federle and N.R. Itrich, Fate of free and linear alcohol-ethoxylate-derived fatty alcohols in activated sludge, *Ecotoxicol. Environ. Saf.*, 64 (2006) 30–41.
- [6] A.H. Mahvi and B. Maleki, Removal of anionic surfactants in detergent wastewater by chemical coagulation, *Pakistan J. Biol. Sci.*, 7 (2004) 2222–2226.
- [7] S. Boonyasuwat, S. Chavadej, P. Malakul and J.F. Scamehorn, Anionic and cationic surfactant recovery from water using a multistage foam fractionator, *Chem. Eng. J.*, 93 (2003) 241–252.
- [8] L. Gu, B. Wang, H. Ma and W. Kong, Catalytic oxidation of anionic surfactants by electrochemical oxidation with  $\text{CuO-Co}_2\text{O}_3\text{-PO}_4^{3-}$  modified kaolin, *J. Hazard. Mater. B*, 137 (2006) 842–848.
- [9] I. Arslan-Alaton and E. Erdinc, Effect of photochemical treatment on the biocompatibility of a commercial nonionic surfactant used in the textile industry, *Water Res.*, 40 (2006) 3409–3418.
- [10] J. Sanz, J.I. Lombrana, A.M. De Luis, M. Ortueta and F. Varona, Microwave and Fenton's reagent oxidation of wastewater, *Environ. Chem. Lett.*, 1 (2003) 45–50.
- [11] W. Kong, B. Wang, H. Ma and L. Gu, Electrochemical treatment of anionic surfactants in synthetic wastewater with three-dimensional electrodes, *J. Hazard. Mater. B*, 137 (2006) 1532–1537.
- [12] S. Hua Wu and Phillip Pendleton, Adsorption of anionic surfactant by activated carbon: effect of surface chemistry, ionic strength, and hydrophobicity, *J. Colloid Interf. Sci.*, 243 (2001) 306–315.
- [13] P. Das Purakayastha, Anjali Pal and M. Bandyopadhyay, Adsorbent selection for anionic surfactant removal from water, *Ind. J. Chem. Technol.*, 12 (2005) 281–284.
- [14] H. Cheng and D.A. Sabatini, Simultaneous uptake of anionic surfactants and micellar-solubilized contaminants using anion-exchange resins, *Water Res.*, 36 (2002) 2062–2076.
- [15] C.A. Basara, A. Karagunduzb, A. Cakicic and B. Keskinlerb, Removal of surfactants by powdered activated carbon and microfiltration, *Water Res.*, 38 (2004) 2117–2124.
- [16] A.C. Archer, A.M. Mendes and R.A.R. Boaventura, Separation of an anionic surfactant by nanofiltration, *Environ. Sci. Technol.*, 33 (1999) 2758–2764.
- [17] E. Fernandez, J.M. Benito, C. Pazos and J. Coca, Ceramic membranes ultrafiltration of anionic and nonionic surfactant solutions, *J. Membr. Sci.*, 246 (2005) 1–6.
- [18] B. Goers, E. Hintzsche, J. Schneider and G. Wozny, Reduction of water consumption and wastewater in detergent production, *Henkel-Referate*, 34 (1998) 43–49.
- [19] M. Simonic, I. Petrinic and S. Sostar-Turk, Treatment of the laundry wastewater by using the membrane technology, *Tekstilec*, 47 (2004) 167–174.
- [20] [www.miexresin.com](http://www.miexresin.com)
- [21] K. Majewska-Nowak, I. Kowalska and M. Kabsch-Korbutowicz, Ultrafiltration of SDS solutions using polymeric membranes, *Desalination*, 184 (2005) 415–422.
- [22] A.S. Jönsson and B. Jönsson, The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes, *J. Membr. Sci.*, 56 (1991) 49–76.
- [23] K. Mizoguchi, K. Fukui, H. Yanagishita, T. Nakane and T. Nakata, Ultrafiltration behavior of a new type of non-ionic surfactant around the CMC, *J. Membr. Sci.*, 208 (2002) 285–288.