Fouling behaviour of a reverse osmosis membrane by three types of surfactants

Naoyuki Kishimoto and Honami Kimura

ABSTRACT

The fouling behaviour of a reverse osmosis (RO) membrane by three types of surfactants and a countermeasure to the fouling were studied. The filtration experiments showed that the permeability during filtration depended on the surfactant concentration and the charge of surfactant. Higher surfactant concentration deteriorated the permeability due to the concentration polarization. A negatively charged anionic surfactant, sodium lauryl sulfate (SLS), had less influence on the permeability than cationic and non-ionic surfactants. As the RO membrane used in this research had a hydrophilic and negatively charged membrane surface, adsorption of the anionic surfactant was prevented by the electrostatic force between the membrane surface and the hydrophilic group of the surfactant. To control the fouling by the cationic and non-ionic surfactants, addition of SLS to the surfactant solution was tested. Consequently, the addition of excess SLS changed the surface charge of aggregates into more negative value and the permeability during filtration was successfully improved. Furthermore, the drop in pure water permeability after filtration was not observed by the addition of excess SLS. Thus, the modification of charge of solutes to the same sign of the membrane surface charge was thought to be useful to control a membrane fouling by surfactants.

Key words | fouling, permeability, reverse osmosis, surfactant, zeta potential

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INTRODUCTION

Reverse osmosis (RO) can separate almost all solutes from a water stream. In general, it is also an energy-saving technology as it does not involve phase change of water. Therefore, the application of RO for water reclamation is increasing. Although various RO membranes have been developed with enhanced fouling resistance, fouling is still a big problem for applying RO to practical processes and leads to deterioration of RO plant performance both in terms of production rate and treated water quality. Therefore, many researchers have made efforts to control the fouling.

Many factors affect fouling behaviour of RO membrane, for example, membrane surface roughness (Elimelech et al. 1997), membrane surface hydrophilicity (Xu & Drewes 2006), membrane surface charge (Wilbert et al. 1998; Jiraratananon et al. 2000; Yoem et al. 2000; Ozaki et al. 2001; Sagle et al. 2009), cross flow velocity

and concentration polarization (Koyuncu 2002). Among these factors, much attention has been paid to membrane surface hydrophilicity and membrane surface charge in terms of development of fouling-resistant RO membranes. To control surface hydrophilicity and surface charge, a RO membrane coated with a polymer or a surfactant has been suggested. Wilbert et al. (1998) modified RO membranes with several non-ionic surfactants. As a result, a non-ionic surfactant with hydrophilic–lipophilic balance of 13.5 was found to be effective in decreasing the cost of purifying water with a cellulose acetate membrane, but was ineffective with a polyamide RO membrane. Coating a polyamide RO membrane with polyether-polyamide polymer was successful in enhancing fouling resistance, but pure water flux of the modified RO membrane decreased (Louie et al. 2006). Sagle et al. (2009) investigated desalination properties and fouling resistance of poly(ethylene

glycol) coated RO membranes. It was observed that a cationic surfactant in wastewater caused a stronger decline in water flux than an anionic surfactant because of the negative surface charge of the membrane. Thus, the effect of modification of RO membrane surface on fouling appears to depend on the nature of foulants as Louie et al. (2006) pointed out.

Surfactants are widely used in various industries, such as the textile industry, and are often detected in domestic and industrial wastewater. Observed concentrations include 3.7–31.8 mg L^{-1} (Holt et al. 1995) and 0.2–22 mg L^{-1} (Takeuchi et al. 2005) in domestic wastewater, and 10–2,000 mg L^{-1} in industrial wastewater (Gonzalez-Gil et al. 2002). Although some surfactants have been suggested as coating material, surfactants are also a major cause of RO membrane fouling (Srisukphun et al. 2009, 2010). Therefore, fouling behaviour of a RO membrane by three types of surfactants, an anionic, a cationic and a non-ionic surfactant, and a countermeasure to fouling by surfactants were studied in this research.

MATERIALS AND METHODS

Materials

Surfactants used in this study were as follows: sodium lauryl sulfate (SLS, syn. sodium dodecyl sulfate) as an anionic surfactant, cetyltrimethylammonium bromide (CTAB) as a cationic surfactant and polyoxyethylene-p-isooctylphenol (Triton X-100) as a non-ionic surfactant. These surfactants were dissolved in pure water and used in a series of experimental runs. Table 1 summarizes the composition of raw water used in each run. Total surfactant concentration of each test solution ranged from 60 to 1,900 mg L^{-1}, which is in the range of typical concentrations in industrial wastewater (Gonzalez-Gil et al. 2002). A polyamide thin-film composite RO membrane (TW30-1812-36, Dow Chemical, USA) was used for all experiments. This membrane is categorized as a low-pressure RO membrane with a maximum trans-membrane pressure (TMP) of 1,000 kPa. The effective membrane surface area was 0.29 m^2 and stabilized salt rejection was more than 96% according to the product information bulletin.

Table 1 | Composition of raw water

| | Surfactant concentration (mM) | | | |
Run no.	CTAB	SLS	Triton X-100	Appearance of solution
1	0.18	–	–	Transparent
2	–	0.21	–	Transparent
3	–	–	0.093	Transparent
4	1.8	–	–	Transparent
5	–	2.1	–	Transparent
6	–	–	0.93	Transparent
7	2.0	4.0	–	Turbid
8	2.0	2.0	–	Turbid
9	4.0	2.0	–	Turbid
10	–	1.8	0.93	Transparent

Experimental procedure

Figure 1 shows an experimental setup, which is composed of a membrane module, a pump (CDP6800, Aquatec, USA), a regulator (R91W-2AK-NLN, Norgren, UK), a pressure gauge (PG-35, Copal Electronics, Japan), a flow meter (RK1710, Kofloc, Japan), a reservoir tank and a magnetic stirrer (CT-1A, Pasolina, Japan). The reservoir tank stored 5 L of surfactant solution, which was pumped up to the membrane module. Both permeate and retentate were returned to the reservoir tank. Permeate flux was monitored with the flow meter. The TMP was controlled between 36 and 629 kPa with the regulator. The TMP applied was much lower than
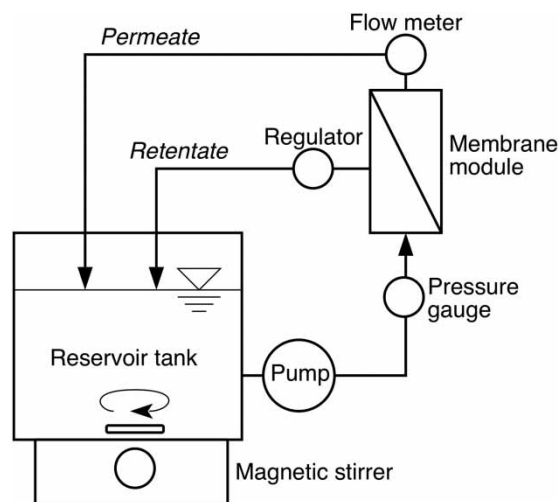

Figure 1 | Experimental setup.

that in a conventional RO system, which typically ranges from 1.0 to 1.5 MPa for brackish water and 5.5 to 6.5 MPa for seawater (Fritzmann et al. 2007). However, Rozzi et al. (1999) used a TMP of 400 kPa for pretreated secondary textile effluents and Drewes et al. (2003) used a TMP of 50 kPa for pretreated domestic wastewater. Thus, the TMP applied was not an extraordinary condition.

The experimental procedure was as follows. Before filtration of a surfactant solution, pure water was filtered for more than 60 min and pure water fluxes were recorded at several TMPs. As the pure water flux was proportional to the TMP, permeability of pure water was evaluated as the slope of a regression line between the pure water flux and the TMP. Then, a surfactant solution was filtered for 6–10 h. Permeability during the filtration of the surfactant solution was evaluated as permeate flux divided by TMP. After the filtration was finished, the surfactant solution was drained and the membrane module was flushed with 5 L of pure water to remove residual surfactants. Finally, the reservoir tank was refilled with 5 L of fresh pure water and permeability of pure water was measured again. During filtration of a surfactant solution, the permeate and the solution in the reservoir tank were periodically sampled and total organic carbon (TOC) and surfactant concentrations were analyzed with a TOC analyzer (TOC-V, Shimadzu, Japan) and colorimetric kits (Nanocolor Test

0–32 for SLS, Nanocolor Test 0–34 for CTAB and Nanocolor Test 0–47 for Triton X-100, Macherey-Nagel, Germany). The membrane module was renewed at every experiment. Many aggregates were observed in mixtures at runs 7–9. Zeta potential of the aggregates was analyzed with a zeta potential analyzer (ZC-2000, Microtec, Japan). Zeta potential of 30 aggregates was measured. Then, the average and the standard deviation were estimated. The discriminate value of the zeta potential analyzer was set at 16.

RESULTS AND DISCUSSION

Permeability of RO membrane to surfactant solutions

In all cases, surfactants were not detected in the permeate (detection limit: 0.57 μM for CTAB, 0.59 μM for SLS and 0.46 μM for Triton X-100). Therefore, rejection rate of the membrane used was estimated to be more than 99%.

Figure 2 shows the permeability changes during filtration of surfactant solutions. The permeability dropped instantaneously at the beginning of filtration except when filtering 0.21 mM of SLS solution. Furthermore, higher surfactant concentration resulted in more severe deterioration of the permeability. Srisukphun et al. (2010) reported that increasing concentrations of surfactant
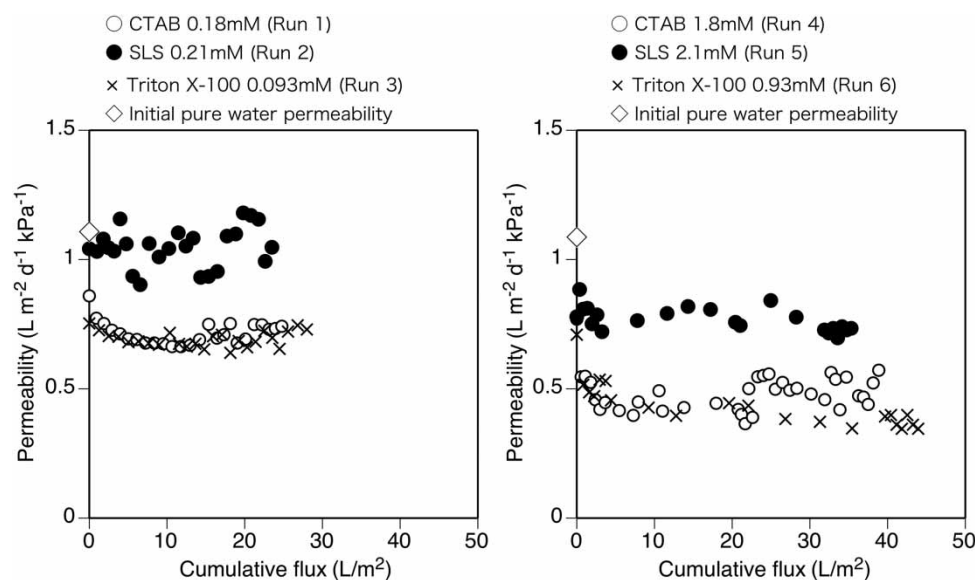

Figure 2 | Change in permeability during filtration of a surfactant solution (Runs 1–6).

promoted RO membrane fouling when the surfactant concentration was less than critical micelle concentration (CMC), and the fouling was the most severe around the CMC. The CMC for CTAB, for SLS and for Triton X-100 was 0.87 mM (Furst *et al.* 1996), 7.3 mM (Sarkar & Poddar 2000) and 0.28 mM (Saiyad *et al.* 1998), respectively. The SLS concentration used in this study was less than the CMC and the high concentration solutions of CTAB and Triton X-100 were around the CMC. Therefore, our observations accorded with the result of Srisukphun *et al.* (2010). Figure 3 summarizes the pure water permeability before and after filtration. The pure water permeability was not changed when using 0.21 mM of SLS solution or 0.093 mM of Triton X-100 solution, whereas the pure water permeability decreased after filtration in other cases. When the deterioration of permeability is caused by concentration polarization, pure water permeability is not changed before and after filtration. But when the permeability drop is caused by adsorption of foulant on the membrane, pure water permeability drops after filtration. Therefore, the permeability drop using 0.21 mM of SLS or 0.093 mM of Triton X-100 was caused by the concentration polarization. In other cases, deterioration of pure water permeability was observed, but the pure water permeability after filtration was higher than the permeability during filtration. This
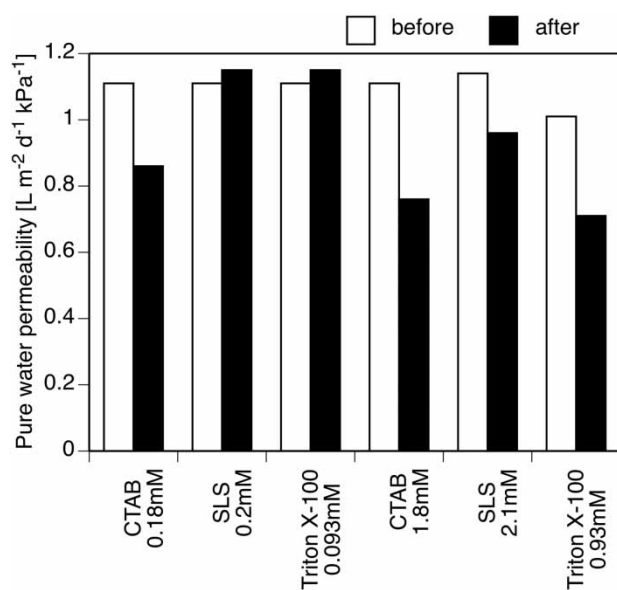
means that both the concentration polarization and the adsorption of a foulant (surfactant) contributed to the deterioration of permeability during filtration.

Among three types of surfactant, the permeability deterioration by CTAB was the most severe of the three and the deterioration by SLS was the least. Adsorption of a foulant on membrane is generally influenced by interactions between a foulant and membrane surface properties, especially membrane surface hydrophilicity and membrane surface charge. In this study, a low-pressure RO membrane made of polyamide was used and its surface was hydrophilic and negatively charged (Wilbert *et al.* 1998). Therefore, adsorption behaviour of surfactants is thought to be as follows (Kondoh 2001): a hydrophilic group of a surfactant is firstly adsorbed on the membrane surface. Then a hydrophobic group of a free surfactant is associated with the hydrophobic group of the surfactant adsorbed on the membrane surface. The former process is also influenced by the membrane surface charge and the charge of the hydrophilic group. As shown in Figure 2, the deterioration of permeability by SLS was less than other surfactants. This means that the negatively charged hydrophilic group of SLS was difficult to adsorb on the negatively charged membrane and the positively charged surfactant, CTAB, was easy to adsorb. This observation is consistent with a previous report in which a permeate flux of a positively charged RO membrane deteriorated after the adsorption of an anionic surfactant (Yoem *et al.* 2000). Figure 3 also demonstrates that the electrostatic force between the membrane and the surfactant affects desorption of surfactants from the membrane surface. When a surfactant has opposite charge to a membrane surface, it is difficult to desorb.

Fouling control

As previously mentioned, the electrostatic interaction between the membrane surface and surfactants is one of the key factors to control fouling by surfactants. Accordingly, a modification of the charge of CTAB by addition of SLS was observed through runs 7–9.

Figure 4 shows changes in permeability at each run. Although an initial drop in permeability was almost the same in all runs, the subsequent in permeability depended on the molar ratio of SLS to CTAB (R_{AC}). The higher R_{AC}
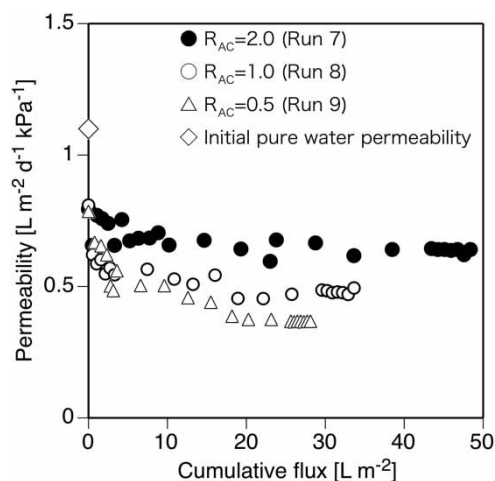

Figure 3 | Pure water permeability before and after filtration of a surfactant solution (Runs 1–6).

Figure 4 │ Change in permeability during filtration of a mixture of CTAB and SLS (Runs 7–9).

Figure 5 │ Pure water permeability before and after filtration of a mixture of CTAB and SLS (Runs 7–9).

resulted in less decrease in permeability. Zeta potential of aggregates in the mixture of SLS and CTAB is summarized in Table 2. The zeta potential increased with the decrease in R_{AC}. A negative zeta potential was observed only at run 7 ($R_{AC} = 2.0$), when the permeability during filtration was the highest of the three. Figure 5 shows pure water permeability before and after filtration. The pure water permeability after filtration did not decrease after run 7, but did so after runs 8 and 9. Thus, it was concluded that the addition of the excess anionic surfactant to the cationic surfactant solution successfully decreased the zeta potential of aggregates and prevented adsorption of aggregates on the membrane surface. The mechanism of the decrease in zeta potential of aggregates was thought to be as follows: hydrophilic groups of the anionic surfactants and the cationic surfactants electrostatically attracted each other and formed an aggregate, whose surface was covered with the hydrophobic groups of the surfactants. Then, hydrophobic groups of free surfactants associated with the hydrophobic

surface of the aggregate. Although every free surfactant can associate with the surface of the aggregate, the associated anionic surfactant was more abundant than the associated cationic surfactant under the anionic-surfactant-rich environment. Consequently, the aggregate surface was negatively charged.

Finally, effectiveness of addition of excess SLS to Triton X-100 solution was checked at run 10. As shown in Figure 6,
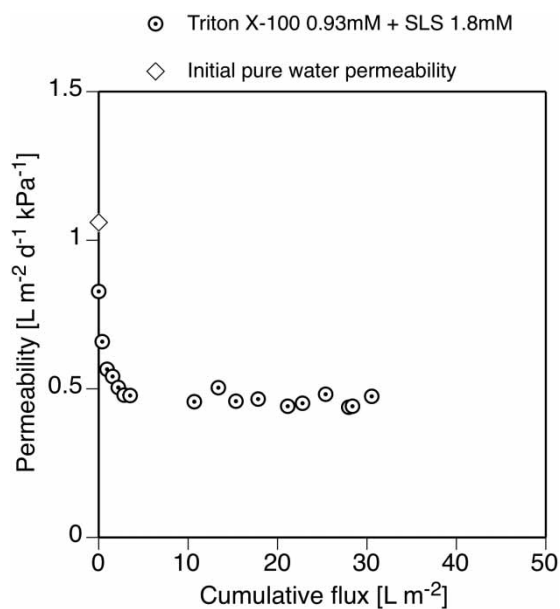
Table 2 │ Zeta potential of aggregates in mixtures of SLS and CTAB. The value of zeta potential means (average) ±(standard deviation)

| Run no. | Concentration (mM) | | R_{AC} | Zeta potential (mV) |
	SLS	CTAB		
7	4.0	2.0	2.0	−41.7 ± 4.2
8	2.0	2.0	1.0	42.6 ± 3.7
9	2.0	4.0	0.5	53.2 ± 23.0

Figure 6 │ Change in permeability during filtration of a mixture of Triton X-100 and SLS (Run 10).

the permeability in the case of addition of excess SLS (run 10) was slightly higher than that in the case of single addition of Triton X-100 (run 6 in Figure 2). The pure water permeability before and after filtration at run 10 was 1.06 and 1.04 L m^{-2} d^{-1} kPa^{-1}, respectively, whereas the pure water permeability after filtration at run 6 decreased from 1.01 to 0.71 L m^{-2} d^{-1} kPa^{-1}. Thus, the addition of excess SLS is also effective to decrease the adsorption of non-ionic surfactant, Triton X-100, on the RO membrane surface and to improve the permeability.

CONCLUSION

The fouling behaviour of a RO membrane by three types of surfactants and a countermeasure to the fouling were experimentally investigated in this research.

The polyamide thin-film composite RO membrane can reject three types of surfactants, CTAB as a cationic surfactant, SLS as an anionic surfactant and Triton X-100 as a non-ionic surfactant. The observed rejection rates were more than 99%.

The permeability during filtration depended on the surfactant concentration and the charge of surfactant. Higher surfactant concentration deteriorated permeability due to concentration polarization. A negatively charged anionic surfactant, SLS, had less influence on the permeability than cationic and non-ionic surfactants. As the RO membrane used in this research had a hydrophilic and negatively charged membrane surface, adsorption of the anionic surfactant was prevented by the electrostatic force between the membrane surface and the hydrophilic group of the surfactant.

To control fouling by the cationic and non-ionic surfactants, addition of the anionic surfactant, SLS, to the surfactant solution was tested. Consequently, the addition of excess SLS changed the surface charge of aggregates into more negative values and the permeability during filtration was improved. Furthermore, the drop in pure water permeability after filtration was not observed after the addition of excess SLS. Thus, the modification of charge of solutes to the same sign of the membrane surface charge was considered to be useful to control membrane fouling by surfactants.

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