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# A new class of draw solutions for minimizing reverse salt flux to improve forward osmosis desalination

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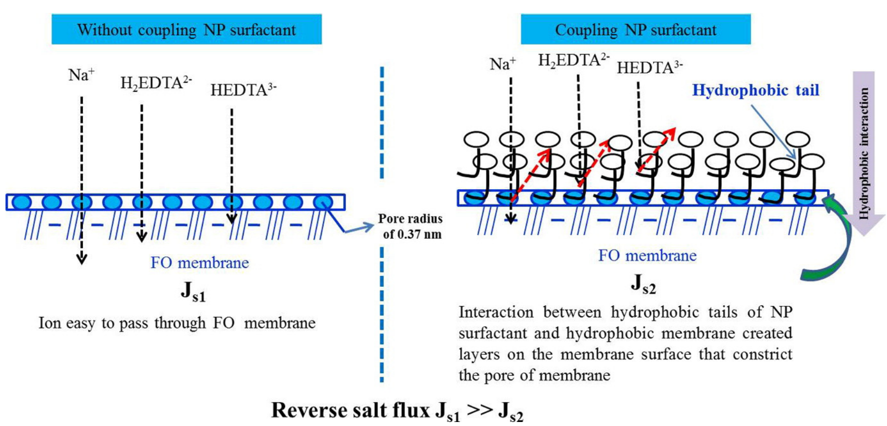
## HIGHLIGHTS

- NP surfactant coupled with highly charged EDTA could minimize salt leakage.
- Reverse salt flux of the novel DS was 3 times lower than that of EDTA-2Na only.
- Interaction between tails of NP with FO membrane constricted membrane pore.
- Approximately 95% recovery of draw solute achieved by using NF-TS80 membrane

## GRAPHICAL ABSTRACT

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## ABSTRACT

The applications of forward osmosis (FO) have been hindered because of the lack of an optimal draw solution. The reverse salt flux from the draw solution not only reduces the water flux but also increases the cost of draw solute replenishment. Therefore, in this study, Tergitol NP7 and NP9 with a long straight carbon chain and low critical micelle concentration (CMC) were coupled with highly charged ethylenediaminetetraacetic acid (EDTA) as an innovative draw solution to minimize reverse salt diffusion in FO for the first time. The results showed that the lowest reverse salt flux of 0.067 GMH was observed when 0.1 M EDTA-2Na coupled with 15 mM NP7 was used as a draw solution and deionized water was used as a feed solution in FO mode (active layer facing with the feed solution). This is due to the hydrophobic interaction between the tails of NP7 and the FO membrane, thus creating layers on the membrane surface and constricting the FO membrane pores. Moreover, 1 M EDTA-2Na coupled with 15 mM NP7 is promising as an optimal draw solution for brackish water and sea water desalination. Average water fluxes of 7.68, 6.78, and 5.95 LMH were achieved when brackish water was used as a feed solution (5, 10, and 20 g/L NaCl), and an average water flux of 3.81 LMH was achieved when sea

*Abbreviations:* FO, forward osmosis; DS, draw solution; FS, feed solution; CMC, critical micelle concentration; EDTA, ethylenediaminetetraacetic acid; LMH, $L/m^2h$; GMH, $g/m^2h$; NF, nanofiltration; RO, reverse osmosis; NP, nonylphenol ethoxylates; TOC, total organic carbon; TDS, total dissolved solid.

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water was used as a feed solution (35 g/L NaCl). The diluted draw solution was recovered using a nanofiltration (NF-TS80) membrane with a high efficiency of 95% because of the high charge and large size of the draw solution.


## 1. Introduction

Forward osmosis (FO) is a valuable technology with a low operating cost and is used for wastewater treatment (Achilli et al., 2009b), brackish water and seawater desalination (McCutcheon et al., 2006), food processing (Garcia-Castello et al., 2009; Petrotos and Lazarides, 2001), and power generation (Achilli et al., 2009a; Seppala and Lampinen, 1999). In FO, the energy required to transport water across the membrane is negligible because of the absence of hydraulic pressure. Typically, selecting a semipermeable membrane and a suitable draw solution are crucial for attaining high FO system performance (Ge et al., 2013). Recently, considerable efforts have focused on developing a novel draw solution to meet the following requirements: (1) high water flux; (2) low reverse salt diffusion; and (3) easy recovery of the diluted draw solution (Chekli et al., 2012; Ge et al., 2013). However, the high salt leakage and high energy consumption involved in recovering the diluted draw solution are major challenges that restrict the development of FO.

During the last few years, most studies have investigated the used of inorganic salts as draw solutions due to their low cost and high osmotic pressure potential, which creates a high water flux (Achilli et al., 2010; Alnaizy et al., 2013). However, the low charge and small hydrated radius of monovalent and divalent ions in the draw solution can result in a high reverse flux of salts, such as 0.6 M NaCl ($J_s = 7.2$ GMH), 0.6 M $NH_4HCO_3$ ($J_s = 18.2$ GMH), or 0.5 M $MgCl_2$ ($J_s = 5.6$ GMH), when deionized (DI) water was used as the feed solution (Kiriukhin and Collins, 2002). In addition, recovering these draw solutions requires a high amount of energy as the pressure-driven reverse osmosis (RO) membrane is still required to recover water from the salts (Zhao et al., 2012) or the standard of the water obtained is not close to that of drinking water. This is caused by the leakage of a high amount of ammonium bicarbonate into water (Ge et al., 2013). To overcome these disadvantages of inorganic salts, magnetic nanoparticles (MNPs) were synthesized and used as a smart draw solution, and no reverse salt flux occurred. However, particle agglomeration was observed during recycling through a magnetic separator, and the FO performance deteriorated accordingly (Ge et al., 2011; Ling et al., 2010). Moreover, the synthesis of MNPs is complicated and difficult.

Furthermore, other materials have been used for FO, such as the polyelectrolyte of polyacrylic acid sodium salts (Ge et al., 2012), 2-methylimidazole-based organic compounds (Yen et al., 2010), switchable polarity solvents (Stone et al., 2013), ferric and cobaltous hydro acid complexes (Ge et al., 2014), dimethyl ether solutions (Sato et al., 2014), and poly (sodium 4-styrenesulfonate) (Tian et al., 2015). These draw solutions showed justifiable water flux. Nevertheless, high reverse salt flux and relatively energy-intensive regeneration make them impractical in FO desalination. Therefore, identifying novel draw solutes with characteristics of high water flux, low reverse salt flux, and easy recovery is necessary.

Among the currently used draw solutions, ethylenediaminetetraacetic acid (EDTA-2Na) not only has a high water flux and low reverse salt diffusion but also can be recovered relatively easily by using a nanofiltration (NF-TS80) membrane, as demonstrated in our previous study (Hau et al., 2014; Nguyen et al., 2015). To increase efficiency with minimal salt leakage, nonylphenol ethoxylates (Tergitol NP7 and NP9) combined with EDTA-2Na are selected as the proposed draw solution. The benefits of using Tergitol NP7 and NP9 instead of the other surfactants are these NPs have an expanded structure of long straight carbon chain to enhance the recovery because of steric effect, and low CMC creating layers on the membrane surface at lower concentration to constrict the membrane pores and minimize reverse salt diffusion. Moreover, the coupling of the surfactant with EDTA-2Na formed the large size of particles in the draw solution, thus it was easily recovered using the NF membrane (Gadelha et al., 2014). The high molecular weight of the coupled EDTA-2Na and surfactant also limit the problem on the environmental and human compatibility due to their high removal by small pore sized FO and NF membranes.

To our best knowledge, any use of draw solution based on coupling NP7 and NP9 with EDTA-2Na for FO performance has not been published up to now. Therefore, the effect of coupling NP7 and NP9 nonionic surfactants with EDTA-2Na on the reverse salt flux and water flux were investigated under the following conditions: (1) various surfactant concentrations; (2) various EDTA-2Na concentrations; (3) desalination; and (4) recovery of the diluted draw solution by using the NF membrane.

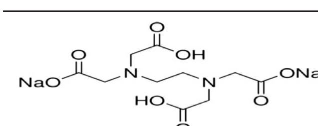
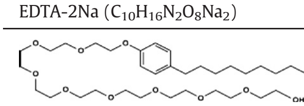
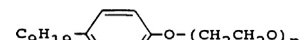
## 2. Materials and method

### 2.1. Materials

A thin-film composite membrane was supplied by Hydration Technology Innovations (Albany, Oregon, USA). The FO membrane is relatively hydrophobic with a measured contact angle of approximately 70° and thickness of less than 50 μm (Cartinella et al., 2006). Moreover, it has a negative charge with a mean pore radius of 0.37 nm (Tiraferri et al., 2011). Laboratory-grade EDTA-2Na (purity of 99.0%) was purchased from Sigma-Aldrich Corporation, Germany. Nonylphenol ethoxylate surfactants, Tergitol NP7 and NP9, were supplied by the Dow Chemical Company, Midland (Albany, Oregon, USA). The average molecular weight is 600 g/mol, the molecular formula is $C_{15}H_{24}O(C_2H_4O)_x$, and the CMCs of NP7 and NP9 at 25 °C are 39 and 60 mg/L, respectively (Muherei et al., 2009). EDTA-2Na coupled with the surfactants was controlled at pH 8 before FO tests (Hau et al., 2014). In FO experiments, DI water, brackish water (5 g/L, 10 g/L, and 20 g/L NaCl), and seawater (35 g/L NaCl) were used as the feed solution. The NF membrane NF-TS80 was used to recover the draw solution (EDTA-2Na combined with anonionic surfactant).

The structures of EDTA-2Na and nonylphenol ethoxylate surfactants are provided in Table 1. The formation of a highly charged species of EDTA that could generate a high water flux with minimal reverse salt diffusion depends on the pH. In addition, the carboxyl group of EDTA-2Na complexes easily with $Na^+$ ions can be attributed to the reduction in reverse salt diffusion. The nonylphenol ethoxylate surfactants NP7 and NP9, which have long and straight carbon chains, can be coupled with EDTA-2Na to maintain minimal reverse transport. Furthermore, this combination could increase the size of particles in the draw

**Table 1**
Structures of EDTA-2Na and nonylphenol ethoxylate surfactant.

| | |
|---|---|
|  EDTA-2Na ($C_{10}H_{16}N_2O_8Na_2$) | |
|  Structure of nonylphenol ethoxylate surfactant |  Formula of nonylphenol ethoxylate surfactant |