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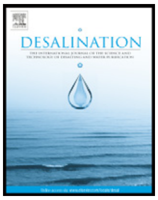

Assessment of micellar solutions as draw solutions for forward osmosis

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HIGHLIGHTS

- Micellar solutions were tested as draw solutions (DS) in Forward osmosis.
- Three cationic and two anionic surfactants were studied.
- The water fluxes in flat-sheet and hollow fibre membranes were measured.
- The DS showed more stable fluxes and 3–300 times less reverse transport than brine.
- 50–95% recovery of draw solute achieved by UF and Krafft point temperature swing.

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ABSTRACT

In this paper, the viability of using micellar draw solutions (DS) for Forward Osmosis (FO) is presented for the first time. Above the critical micelle concentration (CMC) and the Krafft temperature (Tk), the monomers in a surfactant solution aggregate to form micelles, resulting in a relatively constant osmotic pressure above the CMC. These properties can be useful for a FO system in order to maintain a constant water flux and to enable draw solution regeneration at low energy. Three cationic and two anionic surfactants were studied at different concentrations as potential draw solutions for FO applications. Both flat sheet and hollow fiber FO membranes were used in the study. The study revealed that the micellar solutions generated more stable flux compared to other inorganic DS; the hypothesis of a constant flux above the CMC was valid only for concentrations slightly above the CMC, and micellar solutions behaved similar to inorganic solutes at concentrations significantly higher than the CMC. It was shown that external concentration polarization (ECP) does not have a significant effect in micellar solutions just above the CMC. Furthermore, all surfactants demonstrated between 3 and 300 times less reverse transport compared to NaCl at similar concentrations. Finally, the surfactant solute could be regenerated with recoveries as high as between 95% and 99%. It was thus verified that micellar solutions are an attractive DS for application to Forward Osmosis and potentially in the forward osmosis membrane bioreactor (FO-MBR).

1. Introduction

Forward osmosis (FO) is a technique that is driven by natural osmotic pressure difference across a semi-permeable membrane. It extracts clean water from a lower solute concentration feed stream (wastewater or saline water) to a higher solute concentration draw solution (DS). The absence of an external hydraulic pressure in FO reduces the energy requirement, and contributes to a lower fouling propensity, thus implying lower operational costs [1–3]. However, for the commercial application of FO, several aspects of the technique await substantial further investigation. One such aspect is the identification of an appropriate draw solute which is capable of generating sufficiently high osmotic pressure, with minimum reverse transport across the membrane and low toxicity to the biomass when used in the forward osmosis membrane bioreactor (FOMBR) system. Moreover, the draw solute recovery method should incur a low energy cost.

Generally, inorganic solutes such as NaCl, $MgCl_2$ and K_2SO_4 are used as draw solutions in FO systems, and recovered by reverse osmosis (RO)

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[4,5]. The major issue of inorganic draw solutes is that of their small size, which encourages the reverse draw solute diffusion to the feed solution. This diffusion may pose problems, such as toxicity to the feed and an enhancement of the osmotic pressure on the feed side which causes a flux decline. Recently, researchers have investigated several innovative DS, such as water soluble mixtures of ammonia and carbon dioxide, magnetic nano-particles, dendrimers, polyelectrolytes, polymer hydrogels, and hydroacid complexes, among others [6–12]. The ammonia and carbon dioxide mixture (ammonium bicarbonate) is good in generating high water fluxes but it was found to be toxic for the microbial specie if used in the forward osmosis membrane bioreactor (FO-MBR), and presented a lower recovery of ammonia [13,14]. Similarly, an agglomeration problem was observed for magnetic nanoparticles during the regeneration stage. Polymer hydrogels such as PNIPAM [Poly- (N-isopropyl acrylamide)] demonstrated easy regeneration of the draw solute, but produced insufficient water fluxes [10]. In principle, using small molecular weight electrolytes and solutes may not be economical and practical because of the challenge of achieving low-energy recovery, and because of the problem of salt leakage due to reverse diffusion of the DS across the membrane and its associated toxicity [15,16].

In this paper, the application of surfactant/micellar solutions as draw solutes was evaluated. Surfactants are blends of organic, amphiphilic molecules, which present dual structural units: a hydrophilic group (polar group, the head) and a hydrophobic group (long hydrocarbon chain, the tail) [17]. Surfactants are classified according to the presence/absence of formally charged groups in the hydrophilic head. The major types are: (i) anionic, (ii) cationic, (iii) nonionic, and (iv) zwitterionic (in which the head carries both negative and positive charges). Micelles arise spontaneously in solution as a result of the reversible colloidal aggregation of surfactant monomers, at concentrations above the critical micelle concentration (CMC) and the Krafft temperature (Tk). As the monomers are amphiphilic, it becomes energetically beneficial, above the CMC, for the monomers to aggregate and minimize the free energy of the system [18]. Micellar systems have found a wide application in industries as diverse as petroleum, food, chemicals and biotechnology [19].

Micellar masses comprising 50–100 associated monomers typically range from a few hundred up to several thousand Daltons. Above a certain temperature, the solubility of a surfactant increases dramatically in the concentration region above the critical micelle concentration (CMC), due to the crossing of the phase boundary between a saturated micellar solution and a hydrated crystalline surfactant [20]. This temperature is known as the Krafft temperature (Tk). Micelle-monomer equilibrium in aqueous solution plays an important role in generating a relatively constant osmotic pressure, independent of concentration [21,22]. This arises as a result of the fact that the concentration of the surfactant monomer phase, and hence the solute chemical potential (or Gibbs Free Energy), is constrained to remain relatively constant in order to maintain thermodynamic equilibrium with the micellar phase; this monomer concentration corresponds to the CMC. This rather unique micellar property of generating constant osmotic pressure above the CMC can be of potential use for a more stable operation of FO systems. It should be noted, however, that far above the CMC, changes in the micellar phase lead to subsequent increases in the solute chemical potential, and hence the osmotic pressure, so that such a stable operation would no longer apply.

In the current study, five different surfactants were considered as potential draw solutes at concentrations either near or very much above the CMC. The effectiveness of the micellar solutions to generate relatively high water flux, the regeneration potential through ultrafiltration and the Krafft temperature method, and solute reverse transport were measured. Apart from the criterion of commercial availability and affordability, we made this choice of surfactants to provide a range of surfactant types (anionic, cationic, long and short chain, straight and branched chain, etc.). These then provided a range of CMC values, Krafft temperatures, and other properties.

2. Basis of water flux modeling in the FO process

Current membranes used in FO systems are characterized by their asymmetric configuration, which comprises of a thin rejection (active) layer and a porous support layer (Fig. 1). As the water flows through the semi-permeable membrane, concentration polarization of the solute arises. This phenomenon is responsible for a reduction of the effective osmotic potential and hence the driving force. Concentration polarization can arise externally to the membrane, known as called external concentration polarization (ECP). Due to the asymmetry of the membrane, concentration polarization also occurs within the membrane structure, known as internal concentration polarization (ICP).

When the active layer faces the draw solution (AL-facing-DS), and the porous layer faces the feed, this configuration results in concentrative ICP on the feed side and dilutive ECP on the draw side. Likewise, when the active layer faces the feed solution (AL-facing-FS), it results in dilutive ICP on the draw side and concentrative ECP on the feed side. External concentration polarization can be minimized by sufficient cross-flow and stirring; however, ICP still plays a significant role in lowering the effective osmotic pressure difference. This effect was first considered in the work by Lee et al. [23] and later emphasized by Loeb et al. [24], and can be described as follows (see also [7]):

We assume that the active layer faces the DS and that the ECP is well controlled, so that $C_{draw,bulk} = C_{draw,AL}$. We also assume that the osmotic pressure is proportional to its concentration (this assumption is not strictly true above the CMC, as the proportionality constant changes. However, we delay such considerations to later work). Also, for FO, no hydraulic pressure is applied, so that:

$$J_w = AH_o\left(C_{draw} - C_{support}\right). \tag{1}$$

Here, A is the water permeability coefficient of the membrane, Ho is the proportionality coefficient relating solute concentration to osmotic pressure (see also Eq. (9)), and $(C_{draw} - C_{support})$ is the solute concentration difference across the active layer.

An ideal membrane would only allow water to flow; however, solute diffusion may also occur. The reverse solute flux in the dense layer is given by:

$$J_s = B\left(C_{draw} - C_{support}\right), \tag{2}$$

where B is the solute permeability coefficient, C_{draw} is the concentration of the draw solution at the external membrane surface, and $C_{support}$ is the concentration of the feed solution at the support-membrane interface.

In the porous layer of the membrane, the solute flow consists of two parts: (i) Diffusive, due to diffusion down the salt concentration gradient and (ii) Convective, due to the bulk flow of water through the membrane.

Therefore, at steady-state, the solute flux by convection-diffusion is given by:

$$J_w C(x) - D_{eff}\nabla C + J_s = 0, \tag{3}$$

where, C is the solute concentration as a function of the co-ordinate *x* (distance from membrane-solution interface in the porous support layer) and D is the solute diffusion coefficient.

The mass transfer coefficient within the porous support layer is defined as [25]:

$$K = \frac{D}{S} \text{ where structural parameter } S = \frac{l\tau}{\epsilon} \tag{4}$$

Therefore, inserting (1) and (2) in (3), and solving:

$$J_w = K\ln\left[\frac{AH_oC_{draw} - J_w + B}{AH_oC_{feed} + B}\right], \quad \textbf{\textit{AL facing DS}} \tag{5}$$