EDTA: a synthetic draw solute for forward osmosis
Kerusha Lutchmiah, Jan W. Post, Luuk C. Rietveld and Emile R. Cornelissen

ABSTRACT

The draw solution is the driving force of the forward osmosis (FO) process; however, the solute loss of the draw solute to the feed side is a general, financial limitation for most applications. The anthropogenic amino acid ethylenediaminetetraacetic acid (EDTA) was investigated as a draw solution for FO. At concentrations of approximately 1.0 osmol/kg, EDTA demonstrated comparable water fluxes ($J_v = 5.29$ L/m² h) to the commonly used salt, NaCl ($J_v = 4.86$ L/m² h), and both produced better water fluxes than glucose ($J_v = 3.46$ L/m² h). EDTA showed the lowest solute loss with $J_s$ (reverse solute loss or solute leakage) = 0.54 g/m² h. The molecular weight, degree of ionisation and charge of EDTA played a major role in this efficiency and EDTA was therefore well rejected by the membrane, showing a low $J_s/J_v$ ratio of 0.10 g/L. Owing to the low solute loss of EDTA and its resistance to biodegradation, this compound has the potential to be used as a draw solute for FO during long periods without requiring much replenishment.

Key words | draw solution, EDTA, forward osmosis, reverse solute leakage

INTRODUCTION

Membrane processes have many advantages compared to conventional treatment processes, which include lowering costs and energy consumption, and/or attaining higher qualities of the required product. Forward osmosis (FO) is a relatively new process within the field of membrane technology and is seen as an energy-efficient process. Unlike most membrane processes, FO is not hydraulically driven. It is osmotically driven and therefore depends on the strength of the driving force, i.e. the draw solution.

A draw solution can in fact be produced from any solute creating an osmotic pressure higher than the feed solution, yet finding the ideal draw solution for each application is challenging due to the characteristics required: (i) high osmotic pressures; (ii) easy recovery; (iii) membrane compatibility; (iv) zero toxicity; and (v) low reverse solute loss (Chung et al. 2012; Zhao et al. 2012). The issue of solute loss is a general problem for most applications and regards the loss of draw solutes through the membrane towards the feed. This is a substantial limitation, both financial and operational, and also influences the efficiency of the FO process. Many diverse draw solutes have been investigated over the years in an attempt to overcome this limitation. This includes various organic and inorganic-based substances (Achilli et al. 2010; Chung et al. 2012; Zhao et al. 2012). Organic compounds tend to have larger molecular structures than inorganic salts for example, and therefore leak less through the membrane, but biological degradation of these substances is an issue, adding additional replenishment costs to long-term studies (Lutchmiah et al. 2014a, b).

Ethylenediaminetetraacetic acid (EDTA) is an anthropogenic polyamino carboxylic acid and chelating agent, which is widely used to dissolve limescale, owing to its formation of soluble complexes with cations in solution (Campos et al. 1996; Zhen et al. 2012). EDTA has a molecular weight of 292.24 g/mol and is therefore not expected to leak much through the FO membrane when compared to lower molecular weight compounds. Furthermore, EDTA is not readily biodegradable (Dow 2006). For this reason it could be suitable for long-term studies without requiring continuous replenishment.

To the best of the authors’ knowledge, EDTA as a draw solute has only been presented a few times before: in an FO set-up employing a reverse osmosis membrane (Ma et al. 2012) and in another instance using FO membranes (Wang...
In both cases the exact operational conditions and analyses could not be established. This paper aims to investigate the performance of the synthetic amino acid EDTA as a possible draw solution in FO applications, using an FO membrane and based on molecular and colligative properties.

**MATERIALS AND METHODS**

**Feed and draw solutions**

Deionised water (Milli-Q, Millipore) was used as the feed solution and solvent in all cases. The following solutes were tested as draw solutions in the FO U-tube system: (1) NaCl (J.T. Baker, The Netherlands): 0.53 mol/kg; (2) EDTA, buffered to pH = 10 with NaOH (Sigma-Aldrich, Germany): 0.76 mol/kg; (3) glucose (Sigma-Aldrich, Germany): 1.54 mol/kg. The osmolality of the solutions was determined by cryoscopic osmometry (Gonotec Osmomat 050) with each solution achieving values of approximately 1 ± 0.2 osmol/kg. These values were converted to osmotic pressure via the factor 24.5 density of the solute x 1.013 bar as per Wilson & Stewart (2013) to achieve osmotic pressures (π) between 23 and 33 bar (Figure 1). Solute leakages of all compounds were considered in time. The characteristics of the above-mentioned compounds can be found in Table 1.

**Membrane material**

A cellulose triacetate (CTA) FO-type membrane was used (‘Expedition’ type or ‘HydroWell’, Hydration Technology Innovations (HTI), Albany, OR, USA). The FO membrane is highly hydrophilic and has a thickness <50 μm (McCutchion et al. 2006). It comprises an active, dense selective layer and a porous support layer (SL) consisting of an embedded polyester mesh which provides the mechanical support. The asymmetric membrane was used in only one of the two possible orientations, namely the active layer facing the feed side.

**Experimental set-up**

FO experiments were carried out in a laboratory-scale U-tube set-up similar to that mentioned in previous work (Lutchmiah et al. 2014a, b). The membrane (active area: 124 cm²) was placed in a membrane holder. A constant mixing rate of 375 L/h was applied to both the feed and draw side to maintain homogeneity by using magnetically driven centrifugal pumps (Verder, V-MD15). The pump outlet was placed perpendicular to the membrane surface to diminish external concentration polarisation. The

Table 1  Characteristics of the compounds used as draw solutes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
<th>Solubility* (g/L) at 20 °C</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>58.44</td>
<td>359</td>
<td>Na⁺ Cl⁻</td>
</tr>
<tr>
<td>EDTA</td>
<td>C₁₀H₁₆N₂O₈</td>
<td>292.24</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>NaOH</td>
<td>39.99</td>
<td>1,100</td>
<td>Na⁺ OH⁻</td>
</tr>
<tr>
<td>Glucose</td>
<td>C₆H₁₂O₆</td>
<td>180.15</td>
<td>1,330</td>
<td></td>
</tr>
</tbody>
</table>

*Values taken from Sigma-Aldrich (2012).
water flux ($J_w$ in L/m² h) was determined by the volume increase on the draw side via a measuring tube. Dilution of the draw solution in time, due to solute migration towards the feed side, was also taken into account. The reverse solute flux ($J_s$ in g/m² h) towards the feed side was determined by means of total organic carbon (TOC), conductivity and chemical oxygen demand via kits: LC 500: 0–150 ± 0.8 mg/L O₂ and LCK 514: 100–2,000 ± 3.5 mg/L O₂ (Hach Lange, Germany). All experiments were performed for 7 h.

**Total organic carbon analysis**

The TOC analysis was done by sparging, i.e. analysing non-purgeable organic carbon, using the TOC-VCPH analyser (Shimadzu). Sample preservation, by means of acid addition (2 M HCl), was carried out to maintain sample integrity by reducing the rate of microbiological growth, which otherwise may cause contamination or degradation of the organics.

**Membrane surface characterisation**

Zeta potential was used to quantify the magnitude of the electrical charge at the surface of a virgin FO CTA membrane. The zeta potential of a virgin HTI FO membrane sample was determined in duplicate (10 mm × 20 mm) in a SurPASS Electrokinetic Analyzer (Anton Paar, Graz, Austria) with Adjustable Gap Cell as measuring cell. The membrane pieces were mounted opposite each other in a measuring cell at a distance of 100 μm. The background electrolyte solution was 0.001 mmol/L KCl solution. pH adjustment was performed within the range 3.5–8.5 with 0.05 M HCl and 0.05 NaOH.

**The solute permeability coefficient**

The solute permeability coefficient ($B$) values of NaCl and EDTA (pH 10) were experimentally determined in a cross-flow reverse osmosis set-up as described by Tang et al. (2010). These values were furthermore compared to optimised values for $B$ from a modelled fit using a water permeability coefficient ($A$) value of $1.28 \times 10^{-12}$ m/s Pa, which was determined via the same method and was found to be consistent with previous work (Phillip et al. 2010), and a membrane structure parameter ($S$) value of 552 μm. More details regarding the model used to optimise the values can be found in Lutchmiah et al. (2014a, b).

**RESULTS AND DISCUSSION**

**Reference experiments**

A 0.53 mol/kg NaCl solution was used to characterise each new membrane coupon before and after an experimental series. The water flux ($J_w$) and the solute leakage ($J_s$) were determined from these experiments (Figure 1). An average of $4.86 \pm 0.33$ L/m² h ($n = 10$) was found for the water flux and $3.26 \pm 0.50$ g/m² h for the salt flux. The $J_s/J_w$ ratio (0.67 ± 0.08 g/L) was used as the reference. These results are consistent with previous research (Cornelissen et al. 2008; Lutchmiah et al. 2011).

**Flux performance**

Figure 1 shows the flux comparisons between NaCl ($\pi = 23$ bar), EDTA ($\pi = 29$ bar) and glucose ($\pi = 53$ bar). Here EDTA shows the highest water fluxes (5.29 L/m² h) and lowest solute leakage (0.54 g/m² h). It is probable that the higher initial osmotic pressure of EDTA (than NaCl) is the cause for the higher water flux; however, glucose, which at this concentration produces the highest osmotic pressure of all the compounds studied, ranks the lowest (3.46 L/m² h).

With regard to the respective $J_s/J_w$ ratios (Figure 1), EDTA (0.10 g/L) was also found to be lower than the other compounds, with glucose showing a $J_s/J_w$ ratio of 2.13 g/L. Solute leakage of EDTA was further investigated (Figure 2) at various concentrations and compared to NaCl.

From Figure 2 it can be seen that the fluxes for both compounds increase with an increase in $\pi$, but the solute leakage of EDTA changes only slightly (0.27–0.54 g/m² h). The NaCl leakage (Lutchmiah et al. 2011) is approximately 10-fold higher (2.54–5.67 g/m² h). The increasing water flux with a consistently low $J_s/J_w$ ratio of 0.10 ± 0.01 g/L.
(Figure 3) makes the use of EDTA as a draw solution advantageous. Figure 3 also shows the trend in the \( J_s/J_v \) ratio for NaCl with an increase in \( \pi \). In this case the NaCl ratio decreases slightly from 6 to 46 bar and then increases again slightly thereafter; however, the values remain between 0.50 and 0.59 g/L. Higher concentrations should be tested with EDTA too, but the low solubility of the amino acid tends to be an issue.

According to Equation (1), \( J_s \) is derived from the \( B \) value and the concentration difference of the solute (\( \Delta c \)). This indicates that an increase in \( J_s \) will occur due to the increase in \( \Delta c \). The increase in the concentration and therefore osmotic pressure also explains the behaviour of the solute leakage observed in Figure 2.

\[
J_s = B \Delta c
\]

(1)

\( J_s \) is also influenced by the \( B \) value (Equation (1)). \( B \) represents the solute transport through the membrane; a low \( B \) value results in a lower solute flux.

The determined and optimised \( B \) values (i.e. values fitting with the respective \( A \) and \( S \) values mentioned previously) for NaCl and EDTA can be found in Table 2. The values for NaCl are similar to those found in the literature (Phillip et al. 2010; Yong et al. 2012). According to both the determined and optimised values, EDTA shows a lower \( B \) value than NaCl and can therefore explain the lower solute leakage in general. However the optimised \( B \) value for EDTA shows a lower value (\( 2.29 \times 10^{-8} \) m/s) than that determined (\( 4.08 \times 10^{-8} \) m/s). This difference could be a cause of the set-up itself or due to the interaction with the membrane at higher pressures. A slight difference was also observed for NaCl. Moreover, the variation could be related to the solute properties.

The \( B \) value is influenced by the diffusion coefficient (\( D \)) of the solute via Equation (2) derived from Fick’s law of diffusion

\[
B = \frac{D \phi}{\Delta t}
\]

(2)

where \( \phi \) denotes the partition coefficient (amount of substance per unit volume) and \( \Delta t \) the membrane thickness. From Equation (2) it can be observed that \( B \) increases proportionally with an increase in \( D \); however, the increase in \( D \) is dependent on \( \phi \) due to the change in concentration. The \( B \) and \( D \) values can be found in Table 2.

Furthermore, the higher degree of ionisation of EDTA would result in a larger hydration layer around the ions, increasing its effective mass and decreasing the diffusion coefficient (Furukawa et al. 2007). As such, a fully ionised EDTA molecule should have a lower \( D \) value than that stipulated in Table 2. By decreasing \( D \) in the model by 10, 20 and 50%, predicted \( J_s \) values decreased as well. Due to this decrease, the predicted values using the optimised fit for \( B \) were no longer coherent with the experimental \( J_s \) data. \( B \) was therefore re-optimised, i.e. increased to fit the experimental values. In this way the difference between the determined and optimised \( B \) values is reduced.

### Influence of molecular and membrane properties

#### Molecular weight

Although Figure 4 does not show a specific trend between the water flux and the molecular weight, it does show a decrease in solute leakage with the molecular weight increase. This illustrates that the size of the molecule plays a significant role in the leakage of the solute through the membrane. Thus the larger the molecular weight and the higher the degree of ionisation, the more slowly the solute diffuses through the membrane, i.e. lowering the solute loss, as is the case with EDTA.

![Figure 3](https://iwaponline.com/wst/article-pdf/70/10/1677/470028/1677.pdf)
Membrane surface charge

In Figure 5 it can be seen that the zeta potential was found to be negative over a wide pH range (pH 3–9) for all pieces of the CTA membrane, on both the active layer (AL1 and AL2) and SL. The isoelectric point, i.e. the pH value where the zeta potential = 0 mV, lies at pH 4.1 and drops with an increase in pH. When in contact with EDTA (buffered to pH 10) the membrane charge becomes negative, and EDTA, which is already a negatively charged compound, is repulsed according to Coulomb’s law (Laud 1987). The negatively charged EDTA molecule should therefore be repulsed by the support or active layer of the membrane, theoretically lowering the solute flux in comparison to the uncharged solutes, i.e. NaCl and glucose. This behaviour has been confirmed by the above-mentioned experiments.

The pH effect

The recommended operating pH for CTA membranes lies between pH 3 and 8. Above or below this pH range hydrolysis of the CTA may occur (Vos et al. 1966). This could possibly result in inconsistent FO performance (Ge et al. 2012) and/or a decline in rejection, i.e. an increase in solute leakage. Substantial changes in membrane performance when using EDTA, however, were not observed during these short-term experiments, considering that $J_s$ was consistently low. Long-term experiments may provide more insight into the extent of acetylation (hydrolysis) with greater exposure to a pH 10 draw solution and the long-term stability of CTA membranes at higher pHs. Furthermore, new generation thin-film composite (TFC) membranes for FO, which can be operated at broader pH ranges, i.e. 2–12 (Lutchmiah et al. 2014a, b), may be more practical in this type of pH range.

CONCLUSIONS

In this study, EDTA was tested as a draw solution for use in FO applications. Various factors affecting the water and solute flux performance in FO systems were evaluated. Based on experimental investigations, the main findings of this study are summarised:

- EDTA showed comparable water fluxes to NaCl, but higher fluxes than glucose: 5.29, 4.86 and 3.46 L/m²h, respectively.
- Increasing concentrations of EDTA showed consistently low $J_w/J_s$ ratios of 0.10 g/L, demonstrating that the size, degree of ionisation and ultimately the diffusion coefficient of a molecule is important in reducing solute flux.
- Zeta potential measurements confirmed the negative charge of the FO membrane. This allows the negative EDTA molecule to be rejected by the membrane and may also explain the reason for the low solute fluxes.

EDTA is not readily biodegradable, which is advantageous in applications where the draw solution is required for long periods without much replenishment. However at the pH employed in this study degradation of the CTA membrane may occur. In such cases membranes with a broader pH range, e.g. TFC membranes, would be more practical during long-term experiments. The FO product water together with EDTA could be beneficial when applied directly to processes requiring the removal of heavy metals, i.e. during the cleaning of membrane installations.
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REFERENCES


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