EDTA: a synthetic draw solute for forward osmosis

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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/m^2 h) to the commonly used salt, NaCl (J_v = 4.86 L/m^2 h), and both produced better water fluxes than glucose (J_v = 3.46 L/m^2 h). EDTA showed the lowest solute loss with J_s (reverse solute loss or solute leakage) = 0.54 g/m^2 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

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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.
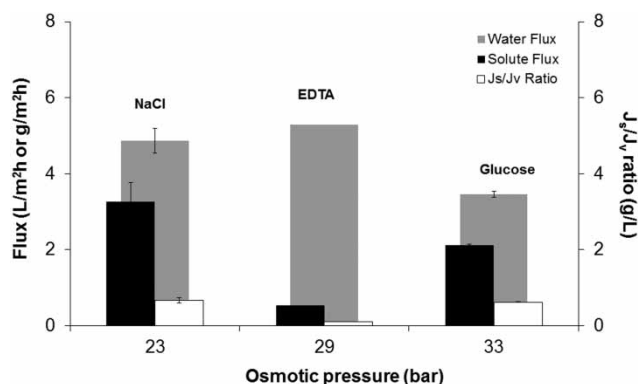
To the best of the authors' knowledge, EDTA as a draw solute has only been presented a few times before: in an FO set-up employing a reverse osmosis membrane (Ma *et al.* 2012) and in another instance using FO membranes (Wang

et al. 2013). 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.
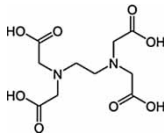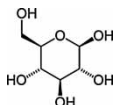
MATERIALS AND METHODS

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 030) 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*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 (McCutcheon *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 cm^2) 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

Figure 1 | The efficiency (water flux, solute flux and J_s/J_v ratios) of NaCl, EDTA and glucose used as FO draw solutions at $\pi = 23$, 29 and 33 bar, respectively.

Table 1 | Characteristics of the compounds used as draw solutes

Compound	Molecular formula	Molecular weight (g/mol)	Solubility[a] (g/L) at 20 °C	Chemical structure
Sodium chloride	NaCl	58.44	359	Na$^+$ Cl$^-$
EDTA	$C_{10}H_{16}N_2O_8$	292.24	146	
NaOH	NaOH	39.99	1,100	Na$^+$ OH$^-$
Glucose	$C_6H_{12}O_6$	180.15	1,330	

[a]Values taken from Sigma-Aldrich (2012).

water flux (J_v in L/m^2 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/m^2 h) towards the feed side was determined by means of total organic carbon (TOC), conductivity and chemical oxygen demand via kits: LCl 500: 0–150 ± 0.8 mg/L O$_2$ and LCK 514: 100–2,000 ± 3.5 mg/L O$_2$ (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-V$_{CPH}$ 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 1.28×10^{-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 532 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_v) and the solute leakage (J_s) were determined from these experiments (Figure 1). An average of 4.86 ± 0.33 L/m^2 h ($n = 10$) was found for the water flux and 3.26 ± 0.50 g/m^2 h for the salt flux. The J_s/J_v 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 ($\pi = 33$ bar). Here EDTA shows the highest water fluxes (5.29 L/m^2 h) and lowest solute leakage (0.54 g/m^2 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/m^2 h). With regard to the respective J_s/J_v 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_v 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 π, but the solute leakage of EDTA changes only slightly (0.27–0.54 g/m^2 h). The NaCl leakage (Lutchmiah *et al.* 2011) is approximately 10-fold higher (2.54–5.67 g/m^2 h). The increasing water flux with a consistently low J_s/J_v ratio of 0.10 ± 0.01 g/L
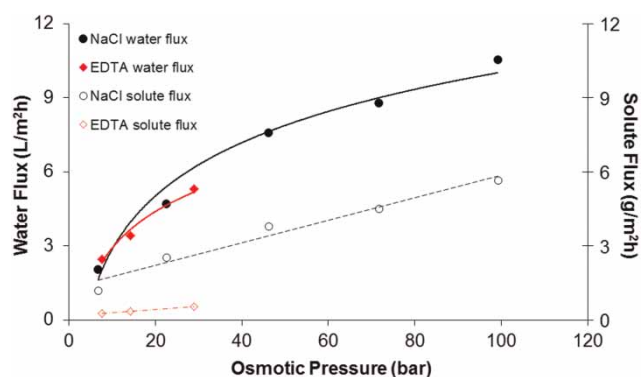

Figure 2 │ The influence of NaCl and EDTA fluxes at increased osmotic pressures ($\pi = 6$–110 bar).

(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 π. 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 (Δc). This indicates that an increase in J_s will occur due to the increase in Δc. The increase in the concentration and therefore osmotic pressure also explains the behaviour of the solute leakage observed in Figure 2

$$J_s = B.\Delta c \tag{1}$$

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
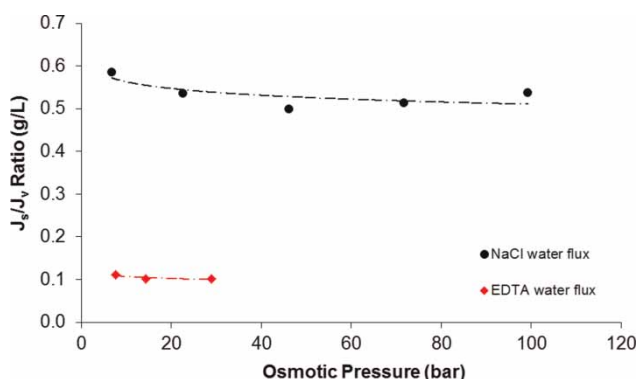

Figure 3 | J_s/J_v ratios for NaCl and EDTA at varied osmotic pressures (bar).

Table 2 | The solute permeability coefficient (B) and diffusion coefficient (D) of the draw solutes

Compound	B determined ($\times 10^{-8}$ m/s)	B optimised fit ($\times 10^{-8}$ m/s)	D ($\times 10^{-9}$ m²/s)
NaCl	4.12 ± 0.4	5.41	1.23 (Lobo & Quaresma 1989)
EDTA	4.08 ± 1.6	2.29	0.60 (Fredd & Fogler 1998)
Glucose			0.52 (Washburn 1929)

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 (2.29×10^{-8} m/s) than that determined (4.08×10^{-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

$$B = \frac{D\phi}{\Delta t} \tag{2}$$

where ϕ denotes the partition coefficient (amount of substance per unit volume) and Δt 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 ϕ 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.
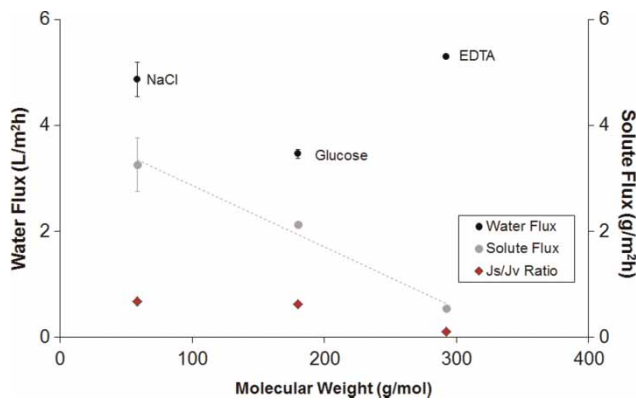
Figure 4 │ The effect of molecular weight on the water flux and solute leakage.

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.
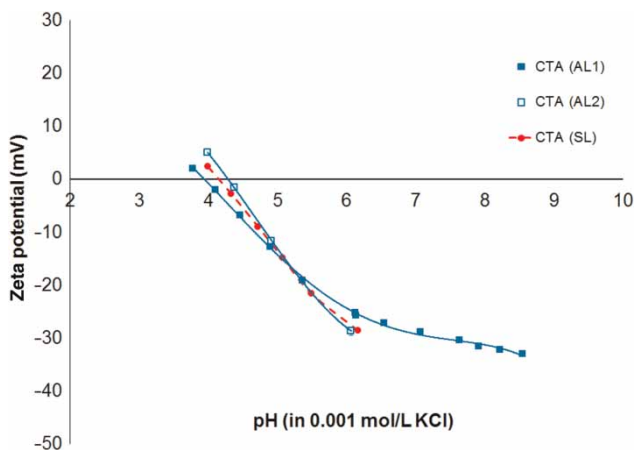
Figure 5 │ Measured zeta potential for the active and support layers of virgin FO CTA membranes.

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/m² h, respectively.
- Increasing concentrations of EDTA showed consistently low J_s/J_v 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.

ACKNOWLEDGEMENTS

REFERENCES

Achilli, A., Cath, T. Y. & Childress, A. E. 2010 Selection of inorganic-based draw solutions for forward osmosis applications. *Journal of Membrane Science* **364** (1–2), 233–241.

Campos, C. A., Rojas, A. M. & Gerschenson, L. N. 1996 Studies of the effect of ethylene diamine tetraacetic acid (EDTA) on sorbic acid degradation. *Food Research International* **29** (3–4), 259–264.

Chung, T.-S., Li, X., Ong, R. C., Ge, Q., Wang, H. & Han, G. 2012 Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications. *Current Opinion in Chemical Engineering* **1** (3), 246–257.

Cornelissen, E. R., Harmsen, D., de Korte, K. F., Ruiken, C. J., Qin, J. J., Oo, H. & Wessels, L. P. 2008 Membrane fouling and process performance of forward osmosis membranes on activated sludge. *Journal of Membrane Science* **319** (1–2), 158–168.

Dow 2006 Product safety assessment (PSA): salts of ethylenediaminetetraacetic acid (EDTA). http://www.dow.com/productsafety/finder/edta.htm.

Fredd, C. N. & Fogler, H. S. 1998 Alternative stimulation fluids and their impact on carbonate acidizing. *Society of Petroleum Engineers Journal* **3** (1), 34–41.

Furukawa, K., Takahashi, Y. & Sato, H. 2007 Effect of the formation of EDTA complexes on the diffusion of metal ions in water. *Geochimica et Cosmochimica Acta* **71** (18), 4416–4424.

Ge, Q., Su, J., Amy, G. L. & Chung, T.-S. 2012 Exploration of polyelectrolytes as draw solutes in forward osmosis processes. *Water Research* **46** (4), 1318–1326.

Laud, B. B. 1987 *Electromagnetics*. New Age International Publishers, New Delhi, India.

Lobo, V. M. M. & Quaresma, J. L. 1989 *Handbook of Electrolyte Solutions, Part A*. Elsevier, Amsterdam, The Netherlands.

Lutchmiah, K., Cornelissen, E. R., Harmsen, D. J. H., Post, J. W., Lampi, K., Ramaekers, H., Rietveld, L. C. & Roest, K. 2011 Water recovery from sewage using forward osmosis. *Water Science and Technology* **64** (7), 1443–1449.

Lutchmiah, K., Lauber, L., Roest, K., Harmsen, D. J. H., Post, J. W., Rietveld, L. C., van Lier, J. B. & Cornelissen, E. R. 2014a Zwitterions as alternative draw solutions in forward osmosis for application in wastewater reclamation. *Journal of Membrane Science* **460**, 82–90.

Lutchmiah, K., Verliefde, A. R. D., Roest, K., Rietveld, L. C. & Cornelissen, E. R. 2014b Forward osmosis for application in wastewater treatment: A review. *Water Research* **58**, 179–197.

Ma, Y., Liu, A., Chen, D., Li, G., He, T. & Li, X. 2012 Draw agent in forward osmosis based on EDTA. *Journal of Nanjing University of Technology (Natural Science Edition)* **34** (3), 79–83.

McCutcheon, J. R., McGinnis, R. L. & Elimelech, M. 2006 Desalination by ammonia-carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance. *Journal of Membrane Science* **278** (1–2), 114–123.

Phillip, W. A., Yong, J. S. & Elimelech, M. 2010 Reverse draw solute permeation in forward osmosis: Modeling and experiments. *Environmental Science and Technology* **44** (13), 5170–5176.

Sigma-Aldrich 2012 MSDS database. http://www.sigmaaldrich.com/.

Tang, C. Y., She, Q., Lay, W. C. L., Wang, R. & Fane, A. G. 2010 Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration. *Journal of Membrane Science* **354** (1–2), 123–133.

Vos, K. D., Burris, F. O. & Riley, R. L. 1966 Kinetic study of hydrolysis of cellulose acetate in pH range of 2–10. *Journal of Applied Polymer Science* **10** (5), 825–832.

Wang, H., Li, X., He, T., Wang, Z., Zhao, B., Song, J., Yin, Y., Zeng, C. & Lin, X. 2013 The use of EDA and EDTA as organic draw solutes in forward osmosis. *Membrane Science and Technology* **33** (6), 87–91.

Washburn, E. W. 1929 *International Critical Tables*. McGraw-Hill, New York.

Wilson, A. D. & Stewart, F. F. 2013 Deriving osmotic pressures of draw solutes used in osmotically driven membrane processes. *Journal of Membrane Science* **431**, 205–211.

Yong, J. S., Phillip, W. A. & Elimelech, M. 2012 Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes. *Journal of Membrane Science* **392–393**, 9–17.

Zhao, S., Zou, L., Tang, C. Y. & Mulcahy, D. 2012 Recent developments in forward osmosis: Opportunities and challenges. *Journal of Membrane Science* **396**, 1–21.

Zhen, H.-B., Xu, Q., Hu, Y.-Y. & Cheng, J.-H. 2012 Characteristics of heavy metals capturing agent dithiocarbamate (DTC) for treatment of ethylene diamine tetraacetic acid–Cu (EDTA–Cu) contaminated wastewater. *Chemical Engineering Journal* **209**, 547–557.