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Development of Switchable Polarity Solvent Draw Solutes

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The art of selecting a draw solute is balancing a range of desirable non-orthogonal properties of which a number of property combinations correlate inversely. Our work with switchable polarity solvents is a microcosm of the wider efforts to explore and develop solutes for forward osmosis processes. The experimental and theoretical process of selecting what is currently our best draw solute candidate will be presented. This includes particularity in selecting our draw solute such as our SPS screening, SPS quantitative structure activity relationship (QSAR), and the entropic driver for SPS function. This work opens into the broader role of entropic sensitivity in thermally driven draw solutes and the development of theory relevant to osmotic processes. We will also present operational data for SPS draw solutions in terms of FO performance metrics, draw-product water separation process and experimental data, draw solution regeneration data, and process energy model.

INTRODUCTION

Forward osmosis (FO) has the potential to reduce water treatment lifecycle costs and address specific water treatment needs in three ways. First, FO may reduce pretreatment costs, which can be greater than the “core” process energy costs in many applications. Second, FO can treat higher concentrations than RO and obtain higher volume recoveries; this means handling (and treating) less feed water and producing a smaller volume of concentrated brine than RO. Third, FO, with temperature responsive draw solutes or use of thermal recovery techniques such as membrane distillation, may shift energy use from electricity to more cost effective thermal energy. Unless FO serves exclusively as a pretreatment for RO or another osmotic filtration, all draw solutes must 1) have a readily generated high osmotic concentration state to treat high concentrations feeds and/or 2) the draw should be regenerated thermally.

Draw solutes are often divided into two categories. First are conventional solutes which are concentrated through conventional means of dewatering a solution containing dissolved solids such as RO or one of the many forms of distillation. The second group is stimuli-responsive draw solutes sometimes referred to as unconventional draw solutes or next-generation draw solutes. Stimuli-responsive draw solutes separate from water by any means or combination of means that can be devised. As mentioned above if the process is to be more efficient than the separation must be achieved by means that are more affordable than hydraulic pressure. For the purposes of water treatment the only form of energy that can be delivered to solution, more efficiently than hydraulic pressure is heat.

There are many reviews that have substantial sections to address draw solutes. Common to all these reviews is a list of desirable characteristics for draw solutes which usually includes a high osmotic concentration (thermodynamic driving force), favourable mass transport properties (low viscosity, high diffusivity, good solution mixing, membrane specific interactions, water flux), low to no reverse solute flux of the draw solute into the feed, an effective means of recovery, nontoxicity, and low cost. These requirements are often addressed qualitatively however with limited effort many of these requirements can be described in quantitative terms.

DISCUSSION

Quantities methods of discussing draw solute properties are listed and in some cases introduced in Table 1.

Table 1. Essential Quantitative Draw Solute Properties (units are not comprehensive)

Property	Symbol	Units
Maximum Available Osmotic Pressure	π_{HI}	Bar, Osm
Entropic Sensitivity	$\Delta\Pi/\Delta T$	ΔBar/ΔK
Minimum Stimuli-Driven Osmotic Concentration	π_{SPO}	Bar, Osm
Carrying Capacity	$\Delta V/V_{HI}$ or $K_{\Delta V}$	L/L or L/mol
Osmotic Density	ρ_{π}	Bar/Kg
Osmotic Cost	$\rho_{\pi c}$	Bar/USD
Solute Cycle Rate	τ	cycle/hr
Solute Lifetime	λ	hrs/life
Water Flux	J_w	L/(m^2hr)
Membrane Permeability – Reverse Solute Flux	J_s	mol/(m^2/hr)

By using the units in Table 1 it becomes possible to compare a range of operational conditions and draw solute properties. In terms of developing SPS draw solutes our team initial investigated dimethylcyclohexylamine (DMCHA)[1,2] which has very good maximum available osmotic pressure, carrying capacity, osmotic density, osmotic cost, and water flux but had poor minimum stimuli-driven osmotic concertation (MSDOC), less than desirable entropic sensitivity and problematic material compatibility properties. To solve the material compatibility property it was desirable to move to a draw solute with a higher molecular mass than DMCHA which would be less chemically aggressive. A high molecular mass was also expected to have a lower MSDOC as well as a better entropic sensitivity. However these improvements are non-orthogonal with maximum available osmotic pressure, osmotic density, and water flux. In attempt to find a material that balanced the desirable proprieties our group studied a range of tertiary amines with the potential to be SPS draws solutes. The resulting information was used to develop quantitative structural activity relationship (QSAR) model for SPS function.[3,4] The QSAR suggested that 1-cyclohexylpiperidine (CHP) would be a promising draw solute for which we have since reported a range of property and flux data.[5,6] The CHP being a higher molecular mass than DMCHA addressed material compatibility issues as well as issues with entropic density and MSDOC but retained very reasonable maximum available osmotic pressure, carrying capacity, osmotic density, and water flux. CHP is not currently mass produced but can be expected to be mass produced at a reasonable osmotic cost. Being attentive to quantitative properties is fundamental to commercializing SPSs as draw solutes.

Using these quantitative draw solute properties and related value we developed an ASPEN based SPS FO process model to estimate energy and cost requirements.[7] This sort of model is extremely useful during the integration, scale-up, and optimization of a FO process. However, a full model is not required for many analyses or comparisons of draw solutes. For example, in Figure 1 the fraction of water that can be recovered is determined from the initial (or maximum available) osmotic pressure and final osmotic pressure. While most researchers have a conceptual understanding of this relationship Figure 1 quantifies in a way that is unambiguous and requires performance metrics be discussed in very concrete terms.

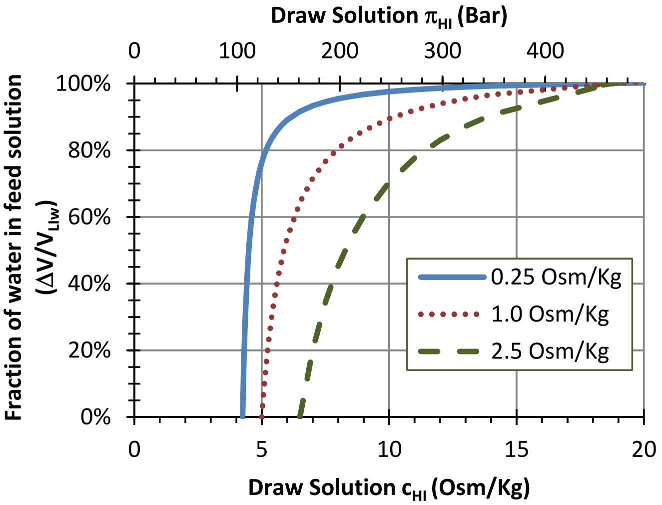

Figure 1. The fraction of available water in a feed solution which can be removed by a draw solution of a given osmotic pressure (assuming a 100 bar of excess osmotic pressure). Solid line "brackish water" 0.25 Osm/Kg (assuming 9,000 ppm TDS), dotted line "saline water" 1.0 Osm/Kg (assuming 35,000 ppm TDS), and dashed line "brine" 2.5 Osm/Kg (assuming 90,000 ppm TDS).

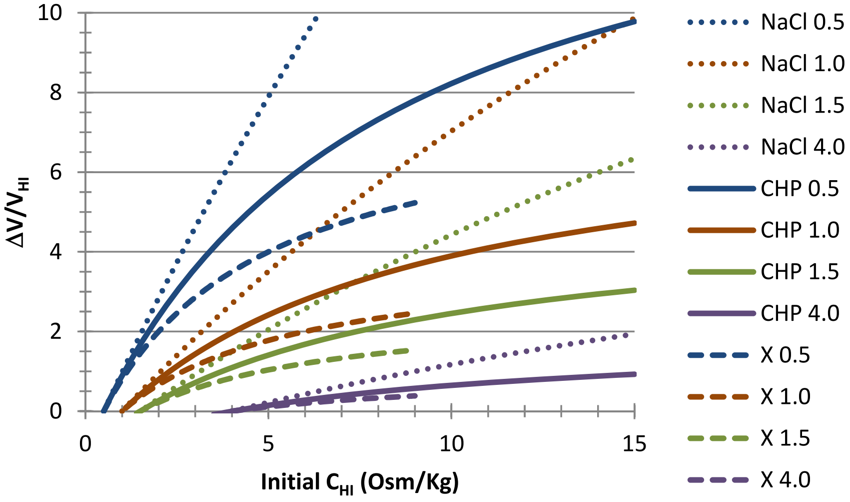

Figure 2. The dependence of carrying capacity ($\Delta V/V_{HI}$) on the initial draw concentration (Osm/Kg) is provided for a range of final draw concentrations (blue 0.5 Osm/Kg, red 1.0 Osm/Kg, and green 1.5 Osm/Kg) and the draw solutes osmotic density (dotted lines NaCl ρ_{π} = 35.8 Osm/Kg$_{solute}$, solid lines CHP ρ_{π} = 7.6 Osm/Kg$_{solute}$, and dashed lines X ρ_{π} = 4.0 Osm/Kgsolute). Solute X has been limited to 9 Osm/Kg which corresponds to 75wt%.

The use of these sorts of quantitative models allows draw solutes to be directly compared in a variety of ways. In Figure 2 the carrying capacity of three draw solutes with different osmotic densities is compared based on their initial (or maximum available) osmotic pressure and their final osmotic pressure. Membrane kinetics informs the required osmotic pressure driving force for a process/system and thus the final concentration of the draw solution. When this is combined with the initial draw solution concentration is possible to establish the carrying capacity of the solution. The carrying capacity defines the volume of "working" fluid which needs to be cycled per unit product. The effects of carrying capacity cascades through an entire integrated FO process influencing both the capital and operational cost of the system. The carrying capacity has a similar importance to membrane flux, two non-orthogonal processes which must be balanced.

CONCLUSION

By introducing meaningful metrics to evaluate draw solutes it will allow draw solutes to be evaluated early in the development cycle. This will prevent the pursuit of draw solutes that are not cost effective to commercialize. In addition properties that are measured can be improved. The improvement can be in the form of selecting a better draw solute or a matter of balancing the energy use and scale of interrelated components in an integrated system. For example, FO membrane water flux which is determined by the osmotic pressure differences between the feed and draw solution must be balanced against the solution carrying capacity which depends largely on the final concentration of the draw solution.

NOMENCLATURE

c = cost
$C_{subscript}$ = molality
DMCHA = *N,N*-dimethylcyclohexylamine
FO = forward osmosis
J_w = water flux
J_s = reverse draw solute flux
$K_{\Delta V}$ = mole ratio carrying capacity
mol = moles
mol/Kg = molality
MSDOC = minimum stimuli-driven osmotic concentration
Osm/Kg = osmolality
RO = reverse osmosis
$V_{subscript}$ = solution volume
ΔV = Water transfer from feed to draw
$\Delta V/V_{HI}$ = volumetric carrying capacity
$\Delta V/V_{LIw}$ = fraction of water in feed solution

Greek symbols
Π, $\pi_{subscript}$ = osmotic pressure
λ = lifetime
τ = cycle time
ρ = mass density
ρ_{π} = osmotic density
$\rho_{\pi c}$ = osmotic cost density

Subscripts
HI = draw solution input
HO = draw solution FO module output
SPO = draw solution stimuli-process output
LI = feed solution input
LO = feed solution output
p = pressure
s = solute
w = water

REFERENCES

(1) Stone, M. L.; Rae, C.; Stewart, F. F.; Wilson, A. D. Switchable Polarity Solvents as Draw Solutes for Forward Osmosis. *Desalination* **2013**, *312*, 124–129.
(2) Reimund, K. K.; Coscia, B. J.; Arena, J. T.; Wilson, A. D.; McCutcheon, J. R. Characterization and Membrane Stability Study for the Switchable Polarity Solvent N,N-

Dimethylcyclohexylamine as a Draw Solute in Forward Osmosis. *Journal of Membrane Science* **2015**, (Submitted).

(3) Wilson, A. D.; Stewart, F. F. Structure–function Study of Tertiary Amines as Switchable Polarity Solvents. *RSC Adv.* **2014**, *4* (22), 11039–11049.

(4) McNally, J. S.; Noll, B.; Orme, C. J.; Wilson, A. D. Density Functional Theory Analysis of the Impact of Steric Interaction on the Function of Switchable Polarity Solvents. *J. Phys. Chem. B* **2015**, *119* (22), 6766–6775.

(5) Wilson, A. D.; Orme, C. J. Concentration Dependent Speciation and Mass Transport Properties of Switchable Polarity Solvents. *RSC Adv.* **2015**, *5* (10), 7740–7751.

(6) Orme, C. J.; Wilson, A. D. 1-Cyclohexylpiperidine as a Thermolytic Draw Solute for Osmotically Driven Membrane Processes. *Desalination* **2015**, *371*, 126–133.

(7) Wendt, D. S.; Orme, C. J.; Mines, G. L.; Wilson, A. D. Energy Requirements of the Switchable Polarity Solvent Forward Osmosis (SPS-FO) Water Purification Process. *Desalination* **2015**, *374*, 81–91.