Use of Switchable Solvents as Forward Osmosis Draw Solutes

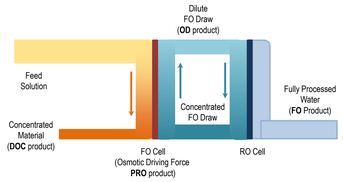
Aaron D. Wilson, Ph.D.
Frederick F. Stewart, Ph.D.
Mark L. Stone, Ph.D.
aaron.wilson@inl.gov
2013

Water Purification/Desalination Methods

- Established
  - Reverse osmosis (RO)
    - Membrane fouling
    - Requires pressures greater than 50 atm of pressure applied to a membrane
    - Recovers only 35-50% water from sea water
  - Distillation
    - Mature
    - Energy intensive.
- An alternative
  - Forward osmosis (FO)
    - Reduced fouling vs RO
    - Higher water recovery and reduced waste stream volume vs RO
    - Lower energy requirements than distillation

Desalination of Seawater; American Water Works Association, 2011.

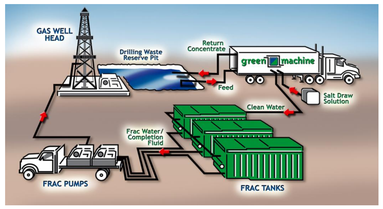
Osmotically Driven Membrane Process



- Pure water is moved from a feed solution across a porous membrane to a draw solution driven by the high osmotic pressure of the draw solutions.
- FO with Conventional draw solutes ensures a homogenized feed solution for an RO finishing step which otherwise suffer from debilitating fouling.
- Standing challenges in FO:
  - An unconventional draw solute that can be removed by means other than RO while retaining significant osmotic pressure.
  - A FO membrane that is more robust than cellulose tri-acetate (CTA). (many solution being pursued and delivered)

Cath, T. Y.; Childress, A. E.; Elimelech, M. Forward osmosis: Principles, applications, and recent developments. *Journal of Membrane Science* **2006**, *281*, 70–87.

Forward Osmosis Applications



HTI and Emerald Surf Sciences

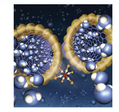
Forward osmosis desalination plant *Modern Water* at Al Khaluf, Oman.

1) Draw solute is incorporated into the product .
- Emergencies energy drink production.
- Water for evaporative cooling.
- Frac completion fluid /recovery fluid.

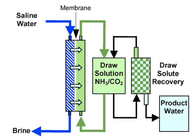
2) Draw solution must be removed through reverse osmosis.
- Desalination.
- Low-temperature food products concentration.
- Landfill/Mining Lechate.

Industrial Leaders in FO

- *Hydration Technology Innovations (HTI)*
  - Established cellulose triacetate (CTA) membrane supplier , currently developing and releasing more robust membranes.
  - Smalll plant FO systems to energy drink pouches
- *OASYS Water*
  - Commercialization of recently developed polyamide thin film composite membranes
  - Unconventional ammonium carbonate FO draw system
- *Modern Water*
  - FO systems and plants
  - 2nd Plant - a 200 cubic meter per day FO desalination facility at Al Najdah, Oman completed September 2012.
- *Porifera*
  - Membrane developer
  - Conventional FO-RO system for the US Army which is more cost effective than RO.
- *Fuji Film*
  - Unconventional draw system
  - Membranes

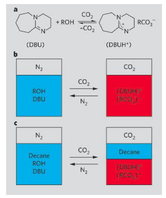


FornaG.; Holt, J. K.; Stadermann, M.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. Ion Exclusion by Sub-2-Nm Carbon Nanotube Pores. *PNAS* **2008**, *105*, 17250–17255.siero, F.; Park, H.

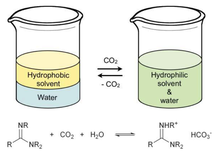


McCutcheon, J. R.; McGinnis, R. L.; Elimelech, M. A novel ammonia--carbon dioxide forward (direct) osmosis desalination process. *Desalination* **2005**, *174*, 1–11.

Brief History of Switchable Materials

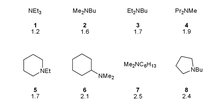


Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. Green chemistry: Reversible nonpolar-to-polar solvent. *Nature* **2005**, *436*, 1102.



Jessop, P. G.; Phan, L.; Carrier, A.; Robinson, S.; Durr, C. J.; Harjani, J. R. A solvent having switchable hydrophilicity. *Green Chem.* **2010**, *12*, 809-814.

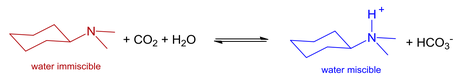
- Switchable polarity solvents (SPSs) are not limited to exotic guanadines and amidines but inlcude tertiary amines simple enough for production on a massive scale. ($logK_{OW}$ listed)



Jessop, P. G.; Kozycz, L.; Rahami, Z. G.; Schoenmakers, D.; Boyd, A. R.; Wechsler, D.; Holland, A. M. Tertiary amine solvents having switchable hydrophilicity. *Green Chem.* **2011**, *13*, 619–623.

SPS as Next Generation FO Draw Solutes

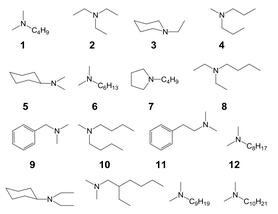
- High concentration in polar form.
- Can be mechanically separated once switched to non-polar form.



N,N-dimethylcyclohexylamine
- Commodity scale polyurethane polymerization catalyst.
- $62.40 per Liter from Aldrich
- ~$1.0 per Kg at the ton scale.

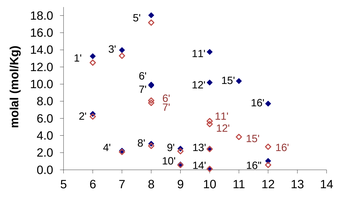
N,N-dimethylcyclohexylammonium bicarbonate
- A concentration derived form 1:1 (v:v) amine:water solution forms 7.6 mol/Kg or 59wt% at 25 C with 1 atm CO_2 which extrapolates to 13.2 Osm/Kg
- It has since been demonstrated that 2:1 (v:v) amine:water solution forms a solution which has a total solute concentration of 35.2 mol/Kg and 760 atm of osmotic pressure.

Maximum Concentration of SPS



- Comprehensive structure function screening

(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) Wilson, A. D.; Stewart, F. F. Deriving osmotic pressures of draw solutes used in osmotically driven membrane processes. *Journal of Membrane Science* **2013**, *431*, 205–211.
(3) Wilson, A. D.; Stewart, F. F. Structure-Function Study of Tertiary Amines as Switchable Polarity Solvents. *manuscript in preparation* **2013**.

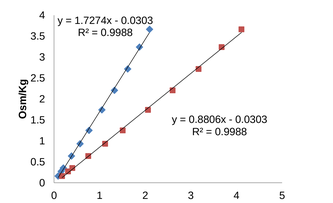


Carbon:Nitrogen Ratio

(filled blue diamonds) maximum amine concentration
(open red diamonds) maximum carbonic acid concentration.

- Two forms of SPS with different ratios of amine to carbonic acid.
- Study indicates how additional switchable materials can be designed.

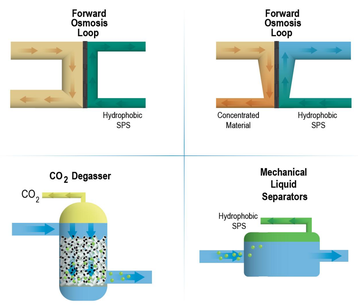
Freezing Point Osmometry



Freezing point osmometry dimethylcyclohexylammonium bicarbonate solution based on amine concentration (blue diamonds) and total solute concentration (red squares).

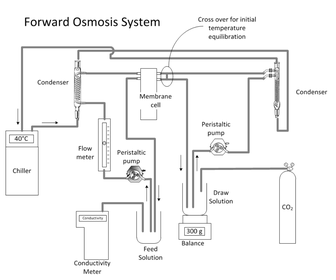
- The maximum solubility of NaCl is 6.14 mol/Kg with a 13.8 Osm/Kg.
- The maximum total solute concentration of a dimethylcyclohexylammonium bicarbonate solution is 35.2 mol/Kg or 31.0 Osm/Kg which should extract water from a fully saturated brine solution resulting in the precipitation of NaCl.

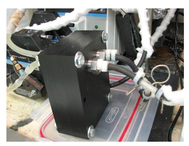
SPS as FO Draw Solute



- Instead of putting membranes under high pressures (50 atm) the solutions are exposed to carbon dioxide pressures that differ by as little as 1 atm.

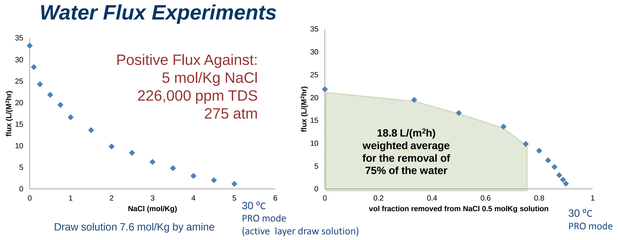
Experimental Set-Up





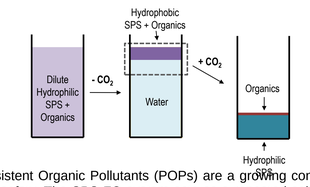
HTI cartridge FO membrane: cellulose triacetate embedded about a polyester screen mesh

Water Flux Experiments



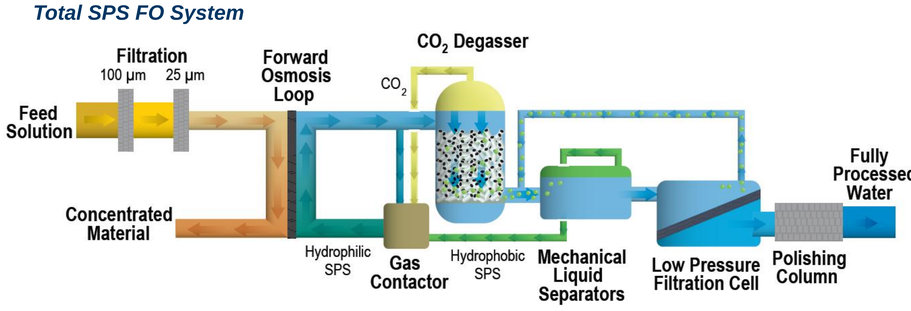
- NaCl at 0.5 mol/Kg is considered a reasonable model for 35 salinity sea water ~3.5 wt%.
- Our system has a 18.8 L/(m^2h) weighted average for the removal of 75% of the water.
- Compares favorably with the 14-20 L/(M^2hr) used in commercial Sea Water RO for the removal of less than 60% of the water.

Removal of Trace Organics



- Persistent Organic Pollutants (POPs) are a growing concern to health and safety. The SPS FO system acts as a repeated solvent extraction process which can concentrate organics for convenient disposal.
- Toluene (water solubility 0.47 g/L, $logK_{OW}$= 2.69) favors the organic phase (1,200 µg/ml) over the aqueous phase (110 µg/ml). The majority of POPs have a higher $logK_{OW}$ (3.0-8.2) which would favor the organic phase more dramatically.

Total SPS FO System



Low and Constant Pressure RO Finishing

- Phase separation of solute avoids "solution polarization", the increase in feeds solution concentration with the removal of water.
- Expected to require substantially lower pressures than conventional RO.
- Demonstrated on a 4 L scale >95% was purified with existing sea water RO technology (Polyamide Thin-Film Composite Membrane) 99.65% rejection of dimethylcyclohexylamine.

Energy Cost of Ammonia-CO_2 vs. SPS FO

	Ammonia-CO_2 kJ/mol	SPS FO kJ/mol
Carbamate decomposition $NR_3CO_2NH_2 \rightarrow NH_3 + CO_{2(g)}$	72.3(X*) X = 0.1-0.8	0
Bicarbonate decomposition $NR_3H_2CO_3 \rightarrow NR_{3(aq)} + CO_{2(g)} + H_2O$	64.3(1-X) 1-X = 0.9-0.2	~64.3
NH_3 heat of dissolution	30.5(1+X)	~0
Total	98.7 to 125.6	~64.3

*X is the stoichiometric excess of NH_3 used to maintain solute solubility.

- The SPS FO system will phase separate from water without bring the solution to near reflux.**

**HANCOCK, N. *Engineered Osmosis for Energy Efficient Separations: Optimizing Waste Heat Utilization FINAL SCIENTIFIC REPORT DOE F 241.3 DE-EE0003467*; 2013.

Conclusion

- Switchable polarity solvents are draw solutes that allows an entirely new FO process for the purification of water and concentration of solutions.
  - The SPS FO system is expected to save costs because its driven by heat rather than electricity. Heat is at least 1/10th the cost of electricity.
- The SPS FO system demonstrated substantial osmotic pressures and FO flux.
  - This osmotic pressure allows for greater concentration of the feed solution reducing the waste volume compared to RO and conventional FO systems.
- The material compatibility remains the greatest challenge but can be solved by:
  - designing and selecting materials/membranes stable to dimethylcyclohexylamine.
  - or designing a better SPS based on our structure function study.

Acknowledgements

- LDRD
- Royalty Fund