

# Supporting Information

## Membrane-less and Non-evaporative Desalination of Hypersaline Brines by Temperature Swing Solvent Extraction

Chanhee Boo,<sup>†</sup> Robert K. Winton,<sup>†</sup> Kelly M. Conway,<sup>†</sup> and Ngai Yin Yip<sup>\*,†,‡</sup>

<sup>†</sup> Department of Earth and Environmental Engineering, Columbia University, New York, New York 10027-6623, United States

<sup>‡</sup> Columbia Water Center, Columbia University, New York, New York 10027-6623, United States

(\* E-mail: [n.y.yip@columbia.edu](mailto:n.y.yip@columbia.edu))

Number of Pages: 9  
Number of Tables: 1  
Number of Figures: 5

## MATERIALS AND METHODS

**Materials and Chemicals.** Diisopropylamine (DIPA,  $\geq 99.5\%$ ), *N,N*-dimethylcyclohexylamine (DMCHA, 99%), and triethylamine (TEA, 99%) from Sigma-Aldrich (St. Louis, MO) and *N*-ethylcyclohexylamine (ECHA, 99%) from Fisher Scientific (Pittsburgh, PA) were used as received. Hypersaline brines were prepared by dissolving sodium chloride (ACS reagent grade NaCl, J. T. Baker, Phillipsburg, NJ) in deionized (DI) water obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA). Oil red O (Sigma-Aldrich) and methylene blue (Acros Organics) dyes were dissolved in TEA and DI water, respectively, to yield 1.2 w/w% solutions. To enhance visual differentiation of the layers and facilitate decantation during TSSE experiments, a few drops of the oil red O and methylene blue dye solutions were dosed to the solvent and aqueous phases, respectively. Reverse osmosis (RO) membrane, SW30 XLE, used for post-treatment solvent removal experiments was acquired from Dow Filmtec (Midland, MI).

**Characterization of Salt Concentration and Solvent Residues.** Salt (NaCl) concentration in the product water and final solvent were analyzed by first evaporating the samples to remove all water and solvent. The salt residue was then redissolved in a known volume of DI water and measured using a calibrated conductivity meter (Orion Star A121, ThermoFisher Scientific, Waltham, MA). Total organic carbon (TOC) in the product water and dewatered raffinate were evaluated using a TOC analyzer (QbD1200, Hach, Loveland, CO) to determine the solvent concentrations. To avoid possible contamination by the dye, the aqueous phase was not stained for solvent concentration measurements.

**Analysis of Water Content in Solvent.** Water content in the solvent was evaluated by volumetric method using a Karl Fischer titrator (870 KF Titrino plus, Metrohm, Herisau, Switzerland). pH of the analyte was adjusted to 5-7 using salicylic acid to prevent side reactions during titration. Sum of the measured water content in solvent at  $T_H$  and the amount of product water yields the water content in solvent at  $T_L$ . As only average water content values measured at  $T_H$  were used for the calculation, data presented in Figure 2B of the main manuscript are without standard deviations.

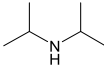
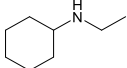
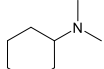
**Determination of Osmotic Pressure.** The osmotic pressures,  $\pi$ , of 1.0 and 4.0 M NaCl solutions (i.e., saline feedwaters) were determined using OLI Stream Analyzer (OLI System, Inc. Morris Plains, NJ). The product water contains trace amounts of salt (NaCl) and solvent. Because

of the relatively low concentrations, we assume the osmotic pressures of the salt and solvent, calculated using the van't Hoff relation, to be additive. That is,  $\pi = RT\sum \nu C$ , where  $C$  is the molar concentration of NaCl or residual solvent,  $R$  is the gas constant, and  $T$  is the absolute temperature. The numbers of species,  $\nu$ , each solute molecule dissociates into are 2 and 1, for NaCl and amine, respectively.

**Solvent Removal with Dead-end RO.** Removal of DIPA and DMCHA by RO was evaluated using a dead-end filtration setup with a custom-built membrane cell. Feed water containing 10 g/L of DIPA or DMCHA in DI water was filtered through the RO membrane, with effective area of 5.07 cm<sup>2</sup>, at an applied hydraulic pressure of 13.8 bar. TOC of the collected permeate was analyzed to determine the solvent removal.

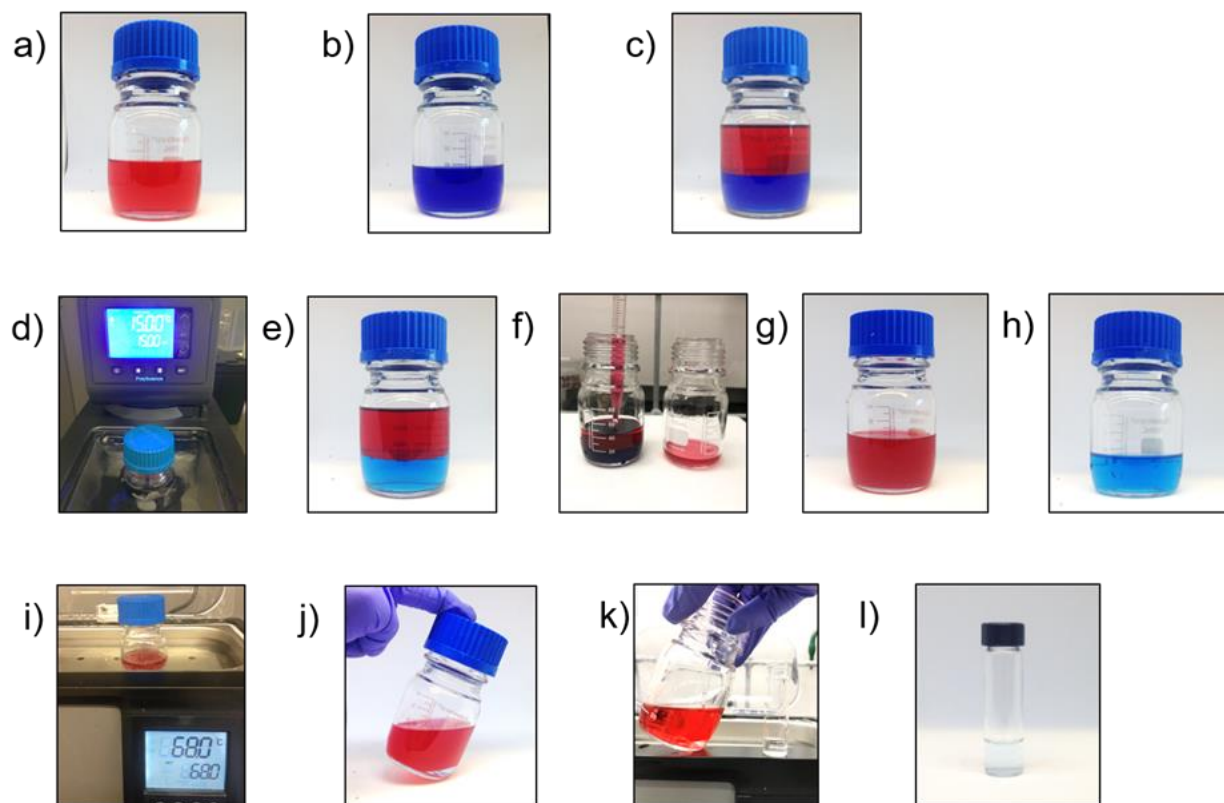
**Assessment of Energy Consumption.** Specific energy requirement, defined as the energy required to yield a cubic meter of product water, to desalinate 1.5 M NaCl brine in a continuous TSSE process (as depicted in Figure 3A) with DIPA at 50% recovery was evaluated. Interpolating the experimental  $n_{\text{water}}/n_{\text{solvent}}$  values for 1.0, 2.0, and 3.0 M feed concentration in Figure 1A, the amount of solvent to produce 1 m<sup>3</sup> product water is determined to be  $\approx 9.9 \times 10^3$  kg (note that the solvent is recycled in the TSSE desalination process). The heat energy required to raise the temperature of the water-in-solvent extract from  $T_L = 15$  °C to  $T_H = 68$  °C is calculated with specific heat capacity data (0.62 and 1.16 Whkg<sup>-1</sup>K<sup>-1</sup> for water and DIPA, respectively), assuming additivity and neglecting non-ideal effects of the mixture. The energy input to drive TSSE desalination is then determined by assuming the thermal recovery efficiency to be in the range of 80-90%, i.e., temperature difference across the heat exchanger of Figure 3A is 10.6 to 5.3 °C (20 and 10% of  $T_H - T_L$ , respectively).

**Table S1.** Chemical structure and properties of DIPA, ECHA, and DMCHA.

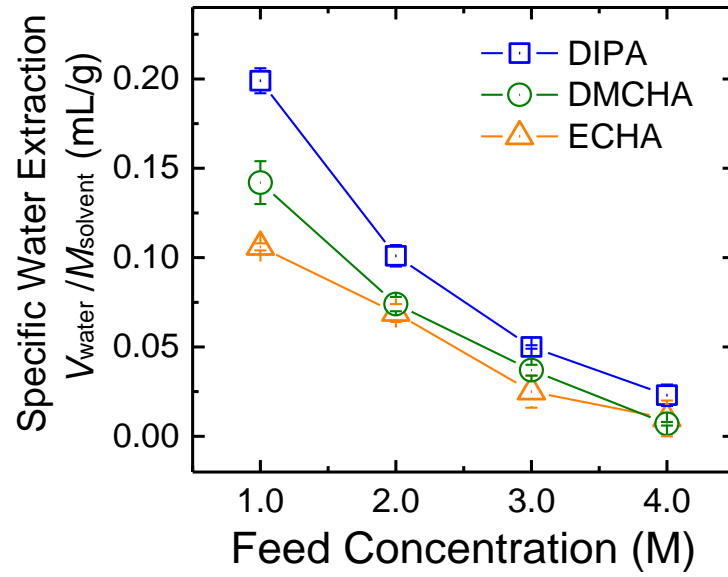
Amine Solvent	chemical structure	amine notes	molecular weight <sup>1</sup> (g/mol)	density <sup>1</sup> (g/ml)	p <i>K</i> <sub>a</sub> <sup>1</sup>	boiling temperature <sup>1</sup> (°C)	water content <sup>2</sup> (wt %)
Diisopropylamine (DIPA)	 (C <sub>6</sub> H <sub>15</sub> N)	Secondary 6C	101.19	0.710	11.05	84	0.53
<i>N</i> -ethylcyclohexylamine (ECHA)	 (C <sub>8</sub> H <sub>17</sub> N)	Secondary 8C	127.23	0.844	11.15	164	0.24
<i>N,N</i> -dimethylcyclohexylamine (DMCHA)	 (C <sub>8</sub> H <sub>17</sub> N)	Tertiary 8C	127.23	0.850	10.16	160	0.31

<sup>1</sup>From CRC Handbook of Chemistry and Physics.

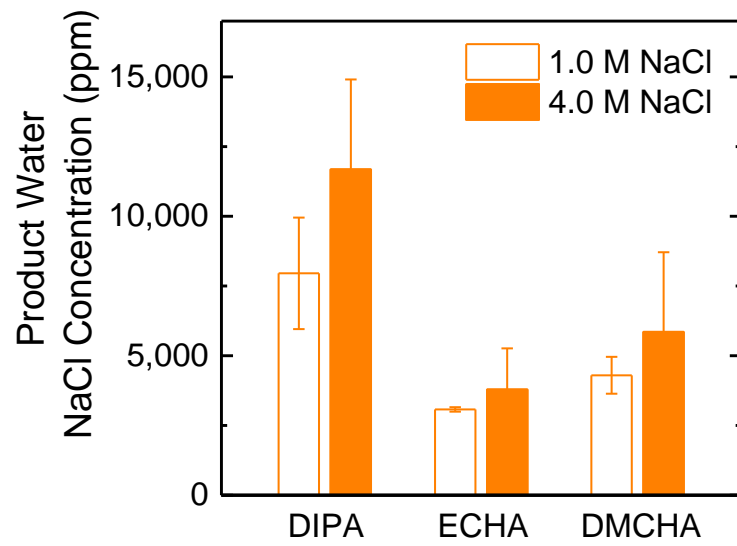
<sup>2</sup>Water content of as-received solvent measured using Karl Fischer titration.



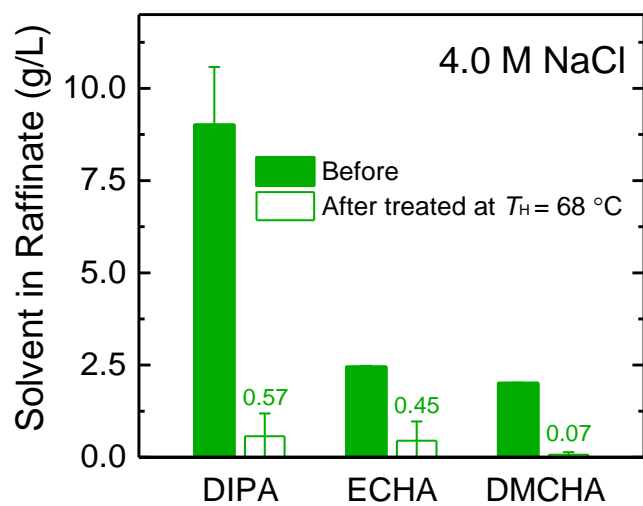
**Figure S1.** Pictures of the TSSE experiment steps. a) solvent, b) brine, c) a biphasic mixture immediately after mixing of solvent and brine, d) biphasic mixture in a temperature bath at  $T_L = 15\text{ }^\circ\text{C}$ , e) biphasic mixture after equilibrated at  $T_L = 15\text{ }^\circ\text{C}$  for 1 h, f) transferring water-in-solvent extract to another media bottle, g) water-in-solvent extract, h) dewatered raffinate, i) water-in-solvent extract in a temperature bath at  $T_H = 68\text{ }^\circ\text{C}$ , j) product water at bottom of solvent, k) extracting product water, and l) final product water.



**Figure S2.** Product water volume extracted per solvent weight as a function of brine (NaCl) concentration. Data and error bars are mean and standard deviation, respectively, from triplicate experiments.

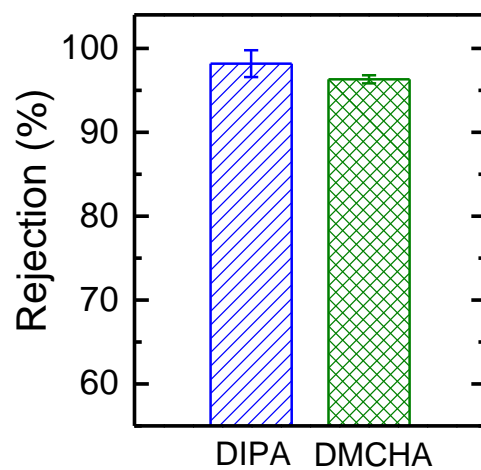


**Figure S3.** Residual salt concentration in product water for TSSE desalination of 1.0 and 4.0 M NaCl brines. Data and error bars are mean and standard deviation, respectively, from triplicate experiments.



**Figure S4.** Residual solvent concentration in the dewatered raffinate after TSSE desalination of 4.0 M NaCl (solid columns, indicated as Before). The raffinate was then warmed up to  $T_H = 68^\circ\text{C}$  to induce demixing of residual solvent from the aqueous phase (empty columns). Data and error bars are mean and standard deviation, respectively, from duplicate experiments.





**Figure S5.** Rejection of DIPA and DMCHA (10 g/L in DI water as feed) by RO membrane measured in a dead-end filtration setup at a hydraulic pressure of 13.8 bar. Data and error bars are mean and standard deviation, respectively, from triplicate experiments.