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

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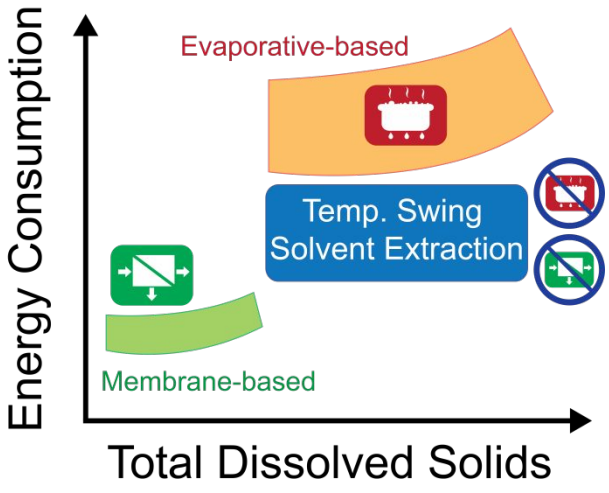
ABSTRACT

Hypersaline brines are of growing environmental importance, but are technologically-underserved by present desalination methods. Temperature swing solvent extraction (TSSE) is a radically different desalination technology that is *membrane-less* and *not* based on *evaporative phase-change*. TSSE utilizes low-temperature heat and a low-polarity solvent with temperature-dependent water solubility for the selective extraction of water over salt from saline feeds. This study demonstrates TSSE desalination of high-salinity brines simulated by NaCl solutions with three amine solvents: diisopropylamine (DIPA), *N*-ethylcyclohexylamine (ECHA), and *N,N*-dimethylcyclohexylamine (DMCHA). We show that TSSE can desalinate brines with salinities as high as ≈234,000 ppm total dissolved solids (i.e., 4.0 M NaCl) and achieve salt removals up to 98.4%. Among the solvents, DIPA exhibited the highest water extraction efficiency, whereas ECHA and DMCHA produced water with the lowest salt content and solvent residues, respectively. Lastly, high water recovery >50% was demonstrated for TSSE desalination of 1.5 M NaCl brine using DIPA in semi-batch experiments with multiple extraction cycles. This study underscores the unique capabilities of TSSE for the desalination of hypersaline brines.

TOC Art



INTRODUCTION

Hypersaline brines are of growing environmental concern.[1, 2] Prominent examples of such high-salinity brines include produced water from the oil and gas industry,[3, 4] waste streams of minimum/zero liquid discharge operations,[5] inland desalination concentrate,[6, 7] landfill leachate,[8] and flue gas desulfurization wastewater.[9] Very high total dissolved solids (TDS) >60,000 ppm pose considerable technical challenges in treatment.[10] Reverse osmosis (RO) is the most energy-efficient and cost-effective technique for desalinating seawater.[11] However, because osmotic pressure scales with TDS concentration, exceedingly high operating pressures needed to overcome the osmotic pressure of hypersaline brines preclude the application of RO.[12, 13] Evaporation-based thermal methods, e.g., multiple effect distillation, thermal brine concentrator, and crystallizer, are the prevailing processes to desalinate or dewater highly concentrated brines.[5, 14, 15] These processes achieve separation by phase-change(s) between liquid and vapor water.[16, 17] However, because the enthalpy of vaporization for water is huge (≈630 kWh/m^3) and the energy efficiency of evaporative phase-change methods is thermodynamically constrained,[18, 19] these processes inherently require intensive thermal energy input,[20] even though the quality of energy is lower (heat as opposed to electricity for RO).[21] Therefore, there is a pressing need to develop energy-efficient technologies for the more sustainable desalination of environmentally-relevant hypersaline streams.

Solvent extraction is a separation method widely employed for chemical engineering processes.[22, 23] The technique is a relatively inexpensive, simple, and effective separation for a wide range of industries, including production of fine organic compounds,[24, 25] purification of natural products,[26] and extraction of valuable metal complexes.[27] Solvent extraction can be an alternative desalination approach that is radically different from conventional methods because it is membrane-less and not based on evaporative phase-change. Application of solvent extraction for desalination was first explored using amine solvents in the 1950s,[28] but the effort was limited to desalting brackish water of relatively low salinity (<10,000 ppm TDS).[29] More recently, the technique was investigated for desalination of seawater simulated by 3.5 w/w% NaCl solution with decanoic acid as the solvent.[30]

In this study, we demonstrate temperature swing solvent extraction (TSSE) desalination of high-salinity brines using three amine solvents. The performance metrics of water extraction, salt removal, product water quality, and osmotic pressure reduction were evaluated and the most

suitable solvent for specific performance objectives were identified. Attainable water recovery for desalination of high-salinity brines was further assessed in semi-batch TSSE experiments with multiple extraction cycles. The implications of TSSE as an alternative membrane-less and non-evaporative technique for hypersaline desalination are discussed.

TEMPERATURE SWING SOLVENT EXTRACTION

Working Principles of TSSE Desalination. TSSE employs a low-polarity solvent with temperature-dependent water solubility,[28] and the working principles are depicted in Figure 1. Firstly, saline feedwater is combined with the solvent (step I), with both at temperature T_L. Due to the low polarity of the solvent, the two liquids are immiscible and a biphasic mixture is formed. However, some water from the aqueous phase partitions into the solvent phase because of hydrophilic moieties on the solvent chemical structure. That is, the solvent extracts water from the saline feedwater, leaving a concentrated raffinate, whereas ionic salt species do not favor partitioning into the low-polarity solvent. The dewatered concentrate is physically separated (step II), and the water-in-solvent extract is brought to temperature T_H, with moderate ΔT of ≈20-60 °C. Because the solubility of water in the solvent decreases with increasing temperatures, the temperature swing from $T_L \rightarrow T_H$ causes water to demix from the solvent to form a biphasic aqueous-solvent mixture (step III). The product water, containing trace amount of salt, is easily decanted from the solvent as the two liquids are immiscible and the regenerated solvent is cycled back for reuse after returning to temperature T_L (step IV).

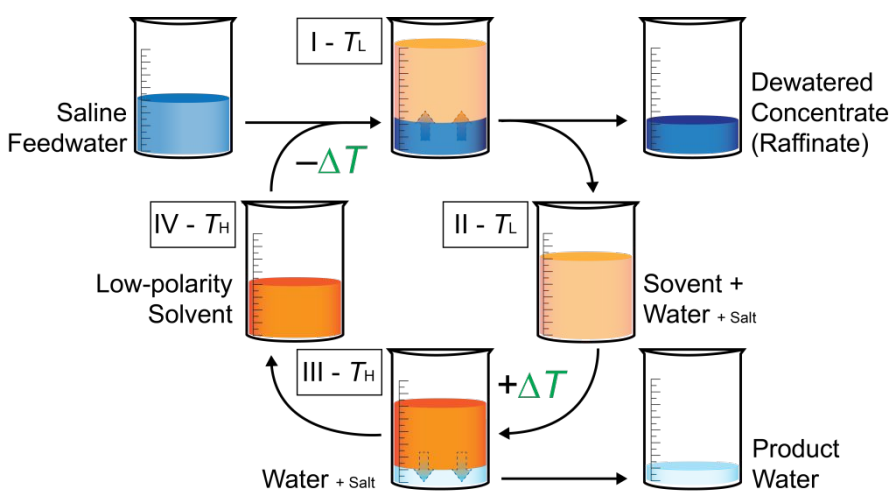


Figure 1. Schematic illustrating the working principles of temperature swing solvent extraction. A low-polarity solvent that is immiscible with aqueous solutions and exhibits temperature-dependent water solubility is used to extract water from the saline feed. A moderate temperature swing of ≈20-60 °C depresses the solubility of water in the solvent, thus driving separation to yield product water and a dewatered concentrate (raffinate).

To dissolve water while being immiscible with the aqueous phase, the solvent should possess hydrophilic moieties in a mainly hydrophobic chemical structure. Amines, for instance, have a nitrogen atom with a lone pair of electrons that can form hydrogen bond with water molecules.[31] Alkyl groups adjacent to the nitrogen atom further increase the dipole moment of the amine molecule by inductive effect, thus increasing the affinity for water molecules.[28] Solubility of water in the solvent should also be highly sensitive to temperature in the operating range. At higher temperatures, free rotation of the alkyl groups on amines increases.[32] Hence, the effect of steric hindrance is amplified and less water molecules are associated with the N atom, resulting in a decrease in water solubility of the amine solvent.[28] This study employed one tertiary and two secondary amines for the desalination of hypersaline brines, but other appropriate solvents can also be used for TSSE.

MATERIALS AND METHODS

Detailed description of the materials and methods are found in the Supporting Information and briefly presented here.

Temperature Swing Solvent Extraction Desalination Experiments. Diisopropylamine (DIPA), *N*-ethylcyclohexylamine (ECHA), and *N,N*-dimethylcyclohexylamine (DMCHA) were evaluated for TSSE desalination of hypersaline brines simulated with 1.0 to 4.0 M aqueous NaCl solutions. Chemical structure and properties of the solvents are summarized in Table S1 of the Supporting Information. First, 40 g of amine solvent and 40 mL of NaCl brine were combined in a glass media bottle and gently mixed. After equilibrating the biphasic mixture at T_L = 15 °C for 1 h, the water-in-solvent extract (i.e., light phase of biphasic mixture in step I of Figure 1) was carefully transferred to another media bottle using a glass pipette. The extract was placed in a high temperature bath at T_H = 68 °C for 1 h to drive phase separation, yielding the aqueous product water (heavy phase in step III of Figure 1). The product water was carefully separated using a glass

pipette and weighed to determine the water extraction efficiency, defined as the mole ratio of product water to solvent used. Pictures of the TSSE experiment are shown in Figure S1 of the Supporting Information. Composition of the product water, final solvent, and concentrated raffinate were further analyzed (details in the Supporting Information). For semi-batch TSSE experiments to evaluate total water recovery, 40 g of solvent was continually reused in multiple cycles for stepwise water extraction from a 1.5 M NaCl brine sample of 40 mL initial volume, such that the raffinate was progressively concentrated over the extraction cycles.

RESULTS AND DISCUSSION

TSSE can Desalinate Ultrahigh Salinity Brines. TSSE desalination of hypersaline brines was evaluated using NaCl solution with concentrations ranging from 1.0 to 4.0 M, which correspond to TDS of ≈58,500-234,000 ppm. Water extraction efficiencies of DIPA, ECHA, and DMCHA are presented in Figure 2A. DIPA exhibited the highest water extraction efficiency over the entire salinity range investigated, followed by DMCHA and ECHA. For every mole of DIPA, DMCHA, and ECHA, approximately 1.13, 1.00, and 0.75 moles of water were extracted, respectively, from 1.0 M NaCl brine. Water extraction efficiency monotonically decreased with increasing NaCl concentration because partitioning of water molecules into the solvent (step I of Figure 1) is reduced for brines with higher chemical potentials, i.e., higher salinities (or, equivalently, more saline feeds have lower water potential).[33, 34] Critically, the three amine solvents investigated produced water even from 4.0 M NaCl with TDS concentration >6× seawater, demonstrating the promise of TSSE for ultrahigh-salinity desalination. Product water volume extracted per solvent weight across the salinity range for the three amines are provided in Figure S2 of Supporting Information.

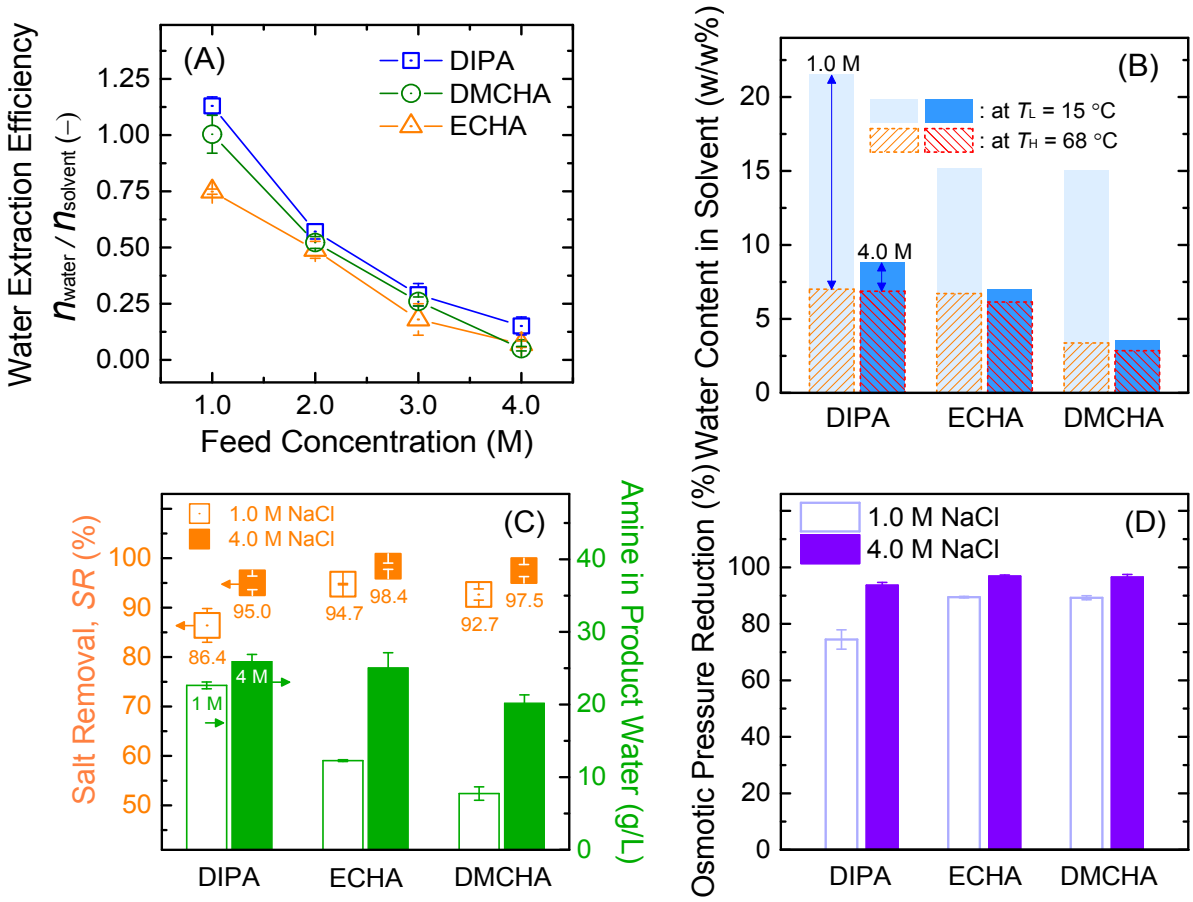


Figure 2. (A) Water extraction efficiency of DIPA, DMCHA, and ECHA as a function of brine (NaCl) concentration, expressed as the mole ratio of product water to solvent. (B) Water content in solvents during TSSE desalination. The difference in water content in amine at low and high temperatures (solid and diagonal patterned columns, respectively) corresponds to the amount of product water. (C) Salt removal and residual solvent concentrations in the product water (symbols, left vertical axis and columns, right vertical axis, respectively) for desalination of 1.0 M and 4.0 M NaCl brines. (D) Osmotic pressure reduction of product water relative to saline feed for 1.0 and 4.0 M NaCl by TSSE desalination with DIPA, ECHA, and DMCHA. For all plots, data and error bars are mean and standard deviation, respectively, from triplicate experiments.

Water extraction efficiency is determined by the sensitivity of water solubility to temperature change, a key thermophysical property of solvents for TSSE desalination. Water content in all three solvents decreased with temperature increase from T_L = 15 °C to T_H = 68 °C during TSSE desalination of both 1.0 and 4.0 M brines (Figure 2B). Hence, product water demixes from the oversaturated solvent until the water content reaches the lowered solubility limit (step III of Figure 1). DIPA exhibited a more significant change in water solubility from the temperature swing

148 (indicated by blue arrow) than the other two amine solvents, which explains the highest water
149 extraction efficiency performance (Figure 2A). For 1.0 M NaCl, water contents in ECHA and
150 DMCHA were comparable at T_L (light blue column in Figure 2B), but DMCHA retained a much
151 smaller amount of water than ECHA at T_H (orange diagonal patterned column). The greater change
152 in water solubility with ΔT yielded a higher water extraction efficiency for DMCHA than ECHA
153 in TSSE desalination of 1.0 M NaCl (Figure 2A). For different saline feed concentrations, water
154 content of each solvent at T_H was comparable (orange and red diagonal patterned columns),
155 suggesting that the oversaturated solvent released water until it reached the same water solubility
156 (or water content) at T_H, although the solvent has extracted different amounts of water from the
157 1.0 and 4.0 M brines at T_L.

158 **Greater Salt Removal is Achieved for Higher Salinities.** Product water quality of
159 TSSE desalination was evaluated for salt (NaCl) removal and residual solvent concentration
160 (Figure 2C). Salt removal, *SR*, is defined as the percentage of NaCl removed from the product
161 water relative to the saline feedwater, i.e., $SR = 1 - C_p/C_f$, where C is concentration and subscripts
162 P and F denote product and feed, respectively). High salt removals >90% were achieved with all
163 solvents for 1.0 and 4.0 M brines (orange symbols, left vertical axis), with the exception of DIPA
164 exhibiting SR = 86.4% for 1.0 M NaCl. In particular, ECHA showed the highest salt removal of
165 94.7% and 98.4% among the solvents assessed for TSSE desalination of 1.0 and 4.0 M NaCl
166 brines, respectively. Salt removal was higher for 4.0 M NaCl brine compared to 1.0 M with all
167 amines. The enhanced salt removal at higher NaCl concentration highlights that TSSE is especially
168 favorable for ultrahigh salinities. Product water salt concentrations are shown in Figure S3 of the
169 Supporting Information. No salts were detected to have accumulated in the final solvent, i.e., after
170 low temperature demixing (step IV of Figure 1), signifying the recyclability of the amine solvents.

171 Residual solvent concentrations in the product water for TSSE desalination of 1.0 and 4.0 M
172 NaCl brines are presented in Figure 2C (green columns, right vertical axis). For all amines, residual
173 solvent concentrations in the product water desalinated from 1.0 M NaCl are lower compared to
174 4.0 M (empty and solid columns, respectively). Among the solvents evaluated, DMCHA yielded
175 product water with the lowest amine residues for both 1.0 and 4.0 M NaCl brines. Although the
176 amine residues would render the product water unsuitable for potable use, the output stream may
177 be employed for other fit-for-purpose applications, such as internal reuse of TSSE-treated

178 hydraulic fracturing water from shale gas production. Alternatively, the trace solvent content can
179 be effectively removed by an optional post-treatment, such as reverse osmosis, to yield higher
180 product water quality (results and discussion later). Solvent concentrations in the dewatered
181 raffinate are much lower than in the product water: 9.0, 2.5, and 2.0 g/L for DIPA, ECHA, and
182 DMCHA, respectively, for 4.0 M NaCl desalination (Figure S4). This is because partitioning of
183 solvent into aqueous phases with significantly higher salinity is thermodynamically less favorable.
184 The residual solvent can further be removed from the raffinate and recovered for reuse by warming
185 the raffinate to T_H, inducing the solvent to demix from the aqueous solution. After this phase
186 separation at 68 °C, residual solvent in the raffinates are substantially lowered to 0.57, 0.45 and
187 0.07 g/L for DIPA, ECHA, and DMCHA, respectively (Figure S4). The consistently low solvent
188 concentrations in product water and dewatered raffinate across the salinity range underline the
189 suitability of DMCHA for TSSE where minimal solvent loss is a specific performance objective.

190 **Osmotic Pressure of Hypersaline Brine is Significantly Reduced.** Salt
191 concentration in the product water is drastically reduced compared to the hypersaline feed, but the
192 residual solvent is an additional impurity (Figure 2C). A more inclusive parameter that accounts
193 for both salt and solvent contributions is the product water osmotic pressure (π). Osmotic pressure
194 reduction of the product water relative to the hypersaline feed, $1 - \pi_p/\pi_f$, is shown in Figure 2D for
195 TSSE desalination of 1.0 and 4.0 M NaCl brines (details on osmotic pressure analysis are in the
196 Supporting Information).

197 DIPA, ECHA, and DMCHA achieved 74.5, 89.5, and 89.2% osmotic pressure reductions,
198 respectively, for 1.0 M NaCl brine, whereas higher osmotic pressure reductions of 93.7, 96.9, and
199 96.6% are observed for the product water from 4.0 M NaCl desalination. The trends of osmotic
200 pressure reduction are similar to salt removal for the three amine solvents and different salinities,
201 albeit slightly lower (comparing Figures 2D and orange square symbols of 2C), the difference
202 being the effect of undesired solvent residues in product water. Thus, the amine residues only
203 marginally influenced the TSSE desalination performance metric of osmotic pressure reduction.
204 Osmotic pressure of the initial 4.0 M NaCl feed is 258 bar, considerably beyond the operating
205 range of conventional RO; product water osmotic pressures after TSSE desalination were
206 substantially lowered to ≈16.3, 8.0, and 8.9 bar with DIPA, ECHA, and DMCHA, respectively,
207 below seawater osmotic pressure of ≈25 bar. With the reduced osmotic pressures, the product

water can be further polished using RO or other post-treatment with significantly lower energy demand.

High Water Recovery of Hypersaline Brines by TSSE. TSSE desalination can be readily scaled-up. Figure 3A depicts a process flow diagram of a conceptual TSSE desalination facility operated as a continuous process. Saline feedwater is the heavy phase and enters the liquid-liquid extraction column towards the top. Solvent, the light phase, is introduced near the bottom of the column to obtain countercurrent flow. The solvent extracts water from the saline stream at temperature T_L and the denser aqueous concentrate exits the column at the bottom as the raffinate. The less dense water-in-solvent extract leaves the column from the top and is channeled to the heat exchanger. Heat transfer across the exchanger, between the hot regenerated solvent on the other side and the extract stream. The water-in-solvent extract is further heated up to T_H by a thermal energy input. The warmed extract is then directed to the decanting separator, where gravity-aided demixing separates the extract into a biphasic mixture to yield product water and regenerated solvent. After exchanging heat with the incoming extract, the recovered solvent is cycled back to the extraction column for reuse. The product water can be further polished in a post-treatment step to meet specific water quality requirements.

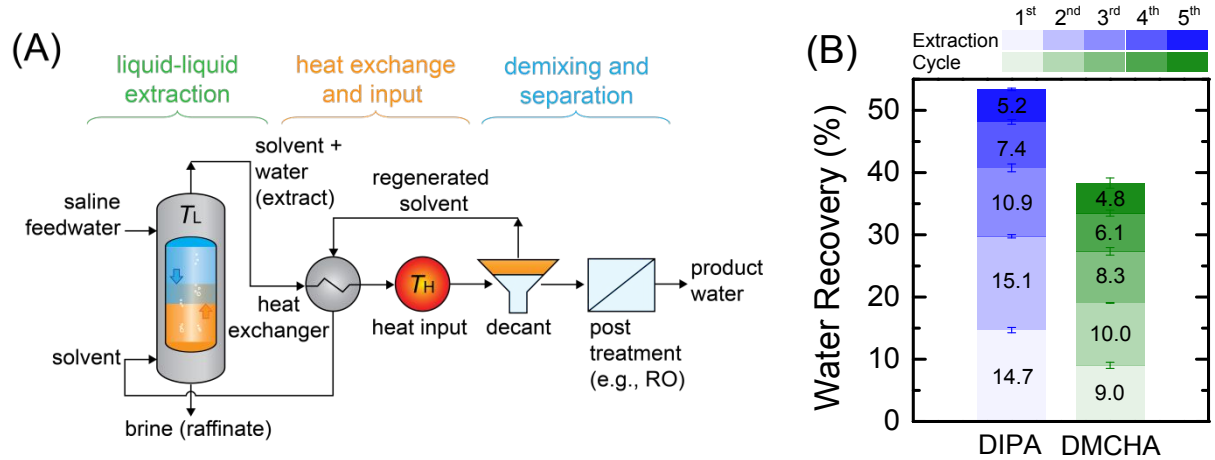


Figure 3. (A) Process flow diagram of a continuous TSSE desalination process. (B) Water recovery achieved by TSSE desalination of 1.5 M NaCl brine with DIPA and DMCHA in semi-batch experiments with multiple (five) extraction cycles. The solvent is reused for the next cycle without being replenished, and the concentrated raffinate at the end of a cycle is the feed for the next extraction. Water recovery of each extraction cycle is denoted in the column segments.

229 Continuous operation of TSSE desalination was simulated by semi-batch experiments with
230 multiple extraction cycles, using DIPA or DMCHA as the solvent and 1.5 M NaCl as the feed
231 brine. The dewatered raffinate and regenerated solvents were reused for subsequent extraction
232 cycles to evaluate the total water recovery of continuous TSSE desalination, defined as portion of
233 initial feed volume desalinated to product water. Overall, water recovery decreased with each
234 sequential extraction cycles for both DIPA and DMCHA as the raffinate is progressively
235 concentrated (Figure 3B). The slightly higher water recovery of the second extraction cycle
236 compared to the first is an artefact of the experimental procedure (initial solvents of the pure amine
237 have very low water content, Table S1). After five TSSE cycles, DIPA and DMCHA achieved
238 53.4% and 38.3% water recoveries, respectively, in desalination of 1.5 M NaCl brine. A basic
239 analysis estimates the energy consumption of continuous TSSE desalination of 1.5 M NaCl with
240 DIPA at 50% water recovery to be between 39 and 77 kWh per cubic meter of product water, with
241 heat exchanger efficiency of 90 and 80%, respectively (calculation details in Supporting
242 Information). The semi-batch experiments demonstrate that high water recoveries are achievable
243 in TSSE desalination of hypersaline brines, and further validate the recyclability of solvents for
244 multiple extraction cycles.

245 The effectiveness of RO post-treatment (as depicted in Figure 3A) to remove the residual
246 solvents from the product water was evaluated (Figure S5 of Supporting Information). DIPA and
247 DMCHA with relatively large molecular weights (101.2 and 127.2, respectively) were effectively
248 removed by the RO membrane, with rejections over 98 and 96%, respectively. The RO post-
249 treatment utilized a relatively low hydraulic pressure of 13.8 bar as osmotic pressure of the product
250 water from TSSE desalination is minimal, representing a low energy cost for the post-treatment
251 separation. Furthermore, higher rejections will be achieved for crossflow RO modules in actual
252 operation, compared to the dead-end filtration employed in this study.

253 IMPLICATIONS FOR HYPERSALINE DESALINTION

254 This study demonstrates that temperature swing solvent extraction is uniquely suited for the
255 desalination of hypersaline brines, a segment of intensifying environmental importance but not
256 accessible by RO and handicapped by intrinsically poor energy efficiencies of evaporative
257 methods. The technology is not restricted by feed solution properties, unlike membrane-based RO

with hydraulic/osmotic pressure limitation. Because TSSE does not require phase-change of water, the penalizing energy cost associated with enthalpy of vaporization is inventively sidestepped and significantly higher energy efficiencies are attainable. As only moderate temperatures are needed (<70 °C in this study), the heat input can be supplied by low-grade thermal sources such as industrial waste heat, shallow-well geothermal, and low-concentration solar collectors, further enhancing the sustainability of TSSE. The solvent is at the core of TSSE. This study shows that specific performance objectives can be achieved by rational solvent selection, specifically, DIPA for high water extraction efficiency, ECHA for high salt removal, and DMCHA for low solvent loss. Other solvents with different chemical structures and properties can yield better performances to further expand the prospects of TSSE for energy-efficiency and cost-effective desalination of high-salinity brines.

ASSOCIATED CONTENT

Details on materials and chemicals, characterization of salt concentration and solvents residues, analysis of water content in solvent, determination of osmotic pressure, solvent removal with dead-end RO, and assessment of energy consumption. Chemical structure and properties of amine solvents (Table S1). Pictures of the TSSE experiment steps (Figure S1). Product water volume extracted per solvent weight (Figure S2). Residual salt concentration in product water (Figure S3). Residual amine concentration in concentrated raffinate (Figure S4). Rejection of DIPA and DMCHA by RO membrane in a dead-end setup (Figure S5).

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