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Phase equilibria insights into amine-water-NaCl interactions in liquid-liquid biphasic systems for temperature swing solvent extraction desalination

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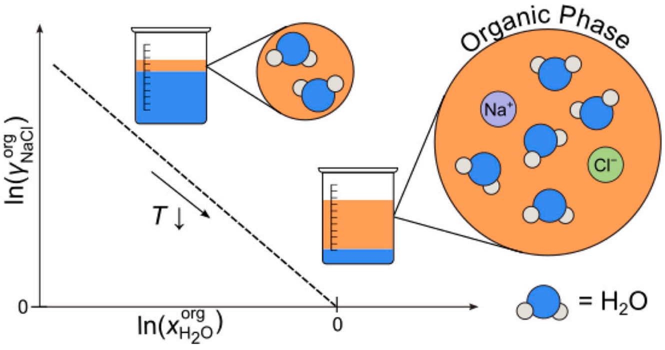
HIGHLIGHTS

- Effect of temperature on equilibrium partitioning in TSSE is studied.
- A tradeoff between productivity and selectivity is observed.
- Transport of Na^+ and Cl^- ions into the solvent phase is equimolar.
- Salt activity is strongly correlated with water content of organic phase.
- Ion interactions with water are more important than with amine in the organic phase.

GRAPHICAL ABSTRACT



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ABSTRACT

This study sheds light on the fundamental phenomena governing temperature swing solvent extraction (TSSE) desalination by investigating the influence of temperature on the equilibrium partitioning of water, salt, and solvent. The distribution of components across a range of temperatures and feed salinities typical to TSSE hypersaline desalination was examined for two amine solvents. A tradeoff between selectivity and productivity is established, providing a novel framework to assess TSSE performance. Salt was shown to be a key determinant in equilibrium partitioning by diminishing the ability of the solvent to extract water at lowered temperatures and salting-out amines from the aqueous phase. Na^+ and Cl^- ions consistently partition into the solvent phase in equimolar ratios. Analysis further reveals a linear correlation between the natural logarithms of salt activity coefficients and water contents of the organic phase. The two collaborating results suggest that water-ion interactions are more important than amine-ion interactions in the organic phase, resolving a critical gap in the understanding of salt transport. The findings of this study can provide important insights for the informed development of temperature swing solvent extraction for hypersaline desalination.

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1. Introduction

Hypersaline streams, such as oil and gas produced water, inland desalination concentrate, and landfill leachate, can damage ecosystems and pollute water sources if discharged into the environment [1,2]. Due to their very high salt concentrations and co-presence of other contaminants, proper management of these streams is generally mandated by state and federal regulations [3–5]. Desalination is becoming an increasingly attractive treatment option [6–9]. Dewatering hypersaline streams reduces their volume, facilitating subsequent disposal, and simultaneously produces remediated water for reuse, including fit-for-purpose applications [9,10]. However, established technologies for seawater and brackish water desalination are ill-suited to handle high-salinity streams. The very high hydraulic pressures required to overcome the osmotic pressure associated with high salt contents exceed the tolerance of conventional reverse osmosis membrane modules. Additionally, sparingly soluble minerals almost always present in hypersaline streams cause mineral scaling that deteriorates the performance of membrane-based processes [11,12]. Evaporative technologies of brine concentrators and brine crystallizers are the existing methods to desalinate hypersaline brines. But the techniques are very energy-intensive due to the high vaporization enthalpy of water and low Carnot-like energy efficiencies [9,13].

Temperature swing solvent extraction (TSSE) is a membrane-less and non-evaporative approach to hypersaline desalination that utilizes switchable solvents with thermally-responsive polarity [14–17]. In TSSE, the saline feed and solvent are combined to form a biphasic mixture. During the extraction step, the solvent is in its more hydrophilic state and, as such, draws water from the aqueous feed stream into the solvent phase. Due to the low dielectric constant environment of the solvent, salt ions are rejected and remain in the aqueous phase [16,18–20]. The water-laden solvent phase is then decanted from the dewatered aqueous phase and brought to the disengagement temperature. The application of this external thermal stimulus triggers the thermoresponsive solvent to switch to its more hydrophobic state, thereby lowering the solubility limit of water. Consequently, the previously extracted water de-mixes, or disengages, from the solvent, yielding a desalinated product stream. The product water is physically separated, and the regenerated solvent is recycled back to the process. Because TSSE is both membrane-less and non-evaporative, the approach avoids many of the limitations faced by traditional high-salinity desalination technologies [9,14–16,21].

Although TSSE was first explored for brackish and seawater desalination in the 1950s and 1960s [14,22–24], recent research has focused on its potential for hypersaline desalination [16,17,21,25,26]. Experimental studies have demonstrated desalination capabilities for a range of solvent classes, including amines, aliphatic acids, and ionic liquids [16,25,26]. As TSSE is a nascent hypersaline desalination technology, most studies focus on proof-of-concept demonstrations; in-depth fundamental understanding of the principal phenomena governing the process is still lacking. Molecular dynamic simulations have begun to offer insight into the transport of solvent and water molecules but have, so far, fallen short in accurately predicting the fate of salt [27,28]. Experimental investigations indicate that salt significantly influences partitioning behavior during extraction and disengagement [29,30], but its mechanistic role is unclear. Although phase equilibria for brackish and seawater desalination [29,30] and extractive crystallization [31–33] applications have been assessed, further studies are needed to deepen understanding of the underlying principles governing the transport of solvent, water, and salt molecules in biphasic systems and the interactions between the three primary components at salinities and temperatures pertinent to hypersaline TSSE desalination.

In this study, we investigate the influence of temperature, the key operating parameter in TSSE desalination, on the equilibrium partitioning of water, salt, and solvent. Two amine solvents with distinct molecular structures and thermochemical properties, *N*,*N*-dimethylcyclohexylamine and diisopropylamine, were equilibrated with aqueous solutions of different salinities and across a range of temperatures representative of hypersaline TSSE desalination. Water and salt contents of the organic phase as well as the solvent content of the aqueous phase were carefully evaluated. A productivity-selectivity tradeoff in solvent extraction desalination is established, and factors influencing the temperature sensitivity of solvent loss to the aqueous phase are assessed. Key similarities and differences in performance between the two solvents are highlighted and the underlying mechanisms are discussed. By evaluating the transport of sodium and chloride ions and investigating the activity coefficients of salt in the organic phase, we seek to shed light on the mechanisms driving salt rejection. Implications of these findings for TSSE operation and solvent design for amines and other solvent classes are discussed. This work aims to advance fundamental understanding of the principal phenomena governing TSSE, thus providing a basis for informed development of the technology for hypersaline desalination.

2. Materials and methods

2.1. Materials and chemicals

N,*N*-dimethylcyclohexylamine (DMCHA, 99 %) and diisopropylamine (DIPA, >99.5 %) from Sigma Aldrich (St. Louis, MO) were used as received. Molecular structure and thermochemical properties of the solvents are summarized in Table S1 of the Supplementary Material. Saline solutions were prepared by dissolving sodium chloride (ACS reagent grade NaCl, J.T. Baker, Phillipsburg, NJ) in deionized (DI) water from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA).

2.2. Equilibration of TSSE biphasic mixtures

Initial saline feed concentrations and temperatures were chosen to model the extraction and disengagement steps of TSSE. In the extraction step, the solvent preferentially draws water from the brine feed stream into the organic phase while rejecting most salts, and in the disengagement step, the organic extract phase demixes to yield the aqueous product water phase of low salinity. Extraction was experimentally simulated by equilibrating equal weights of 1.0 or 4.0 M NaCl brines, representative of hypersaline brine salinities, and DMCHA or DIPA in a glass media bottle at temperatures of 5–20 °C (at 5 °C intervals). The mixtures were continuously stirred in a cold temperature bath for a minimum of 10 min, followed at least 5 min of settling. Disengagement was experimentally simulated by equilibrating equal weights of 0.10 or 0.40 M NaCl aqueous solutions, representative of product water salinities that would be obtained from typical hypersaline desalination, and the solvents in glass media bottles at temperatures of 30–70 °C (at 10 °C intervals). These mixtures were equilibrated by vigorously hand-shaking and subsequent settling in a hot temperature bath for a minimum of 45 min.

2.3. Characterization of biphasic mixture composition

Water contents of the organic phase in the equilibrated TSSE biphasic mixtures were characterized using a Karl Fischer titrator (870 KF Titrino plus, Metrohm, Herisau, Switzerland) with the volumetric method [34]. Salt (NaCl) contents of the organic phases were analyzed by first evaporating a known weight of the organic phase in order to remove all the water and solvent. The residual salt was redissolved in an appropriate amount of DI water and quantified using a calibrated conductivity meter (Orion Star A121, ThermoFisher Scientific, Waltham, MA). In the simulated extraction experiments, Na^+ and Cl^- concentrations of the redissolved salt solutions were further quantified using ion chromatography (IC, Dionex, Sunnyvale, CA). Total organic carbon (TOC) contents of the aqueous phases were measured using a TOC analyzer (QbD1200, Hach, Loveland, CO) to determine the solvent concentrations.

3. Results and discussion

3.1. Productivity-selectivity tradeoff in solvent extraction desalination

Water and salt contents of the organic phases were evaluated for resultant biphasic mixtures from equal weights of solvent and aqueous saline solutions. Notations in subsequent discussions will use superscripts org or aq to denote the phase (i.e., organic or aqueous, respectively) and subscripts H_2O, amine, DMCHA, DIPA, NaCl, or ion to represent the component. Extraction was experimentally simulated by equilibrating equal weights of 1.0 or 4.0 M NaCl aqueous solutions and the solvents at temperatures of 5–20 °C (blue regions in Fig. 1), representative of feed brine salinities and temperatures typical to the extraction step in hypersaline TSSE desalination. In the simulated extraction experiments, water contents of the organic phases, $x_{H_2O}^{org}$, increase as temperature, T, decreases due to an increase in solvent polarity and concomitant ability to solvate H_2O (results for DMCHA are presented in Fig. 1A) [24,35]. At a given temperature, $x_{H_2O}^{org}$ decreases with increasing aqueous phase salt concentration. The increase from a 1.0 to 4.0 M NaCl brine feed lowers the chemical potential of water in the aqueous phase, reducing the driving force for water to partition into the solvent phase [16,24,36]. Salt contents of the organic phases, x_{NaCl}^{org}, increase as T decreases (Fig. 1B). Like $x_{H_2O}^{org}$, x_{NaCl}^{org} decreases at a given temperature as the aqueous brine concentration increases from 1.0 and 4.0 M NaCl. This relationship between x_{NaCl}^{org} and brine salinity is counterintuitive: the chemical potential of salt in the aqueous phase is higher with the 4.0 M NaCl solution and, hence, a greater portion of salt is expected to partition into the organic phase. However, x_{NaCl}^{org} is actually lower with the higher brine concentration. This behavior has been observed in phase diagrams of similar ternary systems [30,32,37]. However, the mechanism driving salt transport into the organic phase is still not well understood; the activity coefficient analysis in Section 3.5 will put forth an explanation to rationalize this trend.

Critically, x_{NaCl}^{org} is more thermoresponsive, i.e., sensitive to changes in temperature, than $x_{H_2O}^{org}$, as evident from the slopes of the trend lines. Fig. 1C shows water-salt selectivity, $n_{H_2O}^{org} : n_{NaCl}^{org}$, defined as the molar ratio of water to salt in the organic phase, as a function of $x_{H_2O}^{org}$, the mole fraction of water extracted into the organic phase (light blue triangle and dark blue circle symbols denote 1.0 and 4.0 M NaCl feeds, respectively). $x_{H_2O}^{org}$ is equivalently the amount of water extracted from the aqueous brine and is, hence, related to water productivity of TSSE desalination. The nonzero slopes indicate that salt and water do not partition into the organic phase at a constant ratio. The negative slopes of the trend lines signify a tradeoff between productivity and selectivity: as productivity increases, selectivity decreases. Additionally, the data points for 1.0 M NaCl are to the right of 4.0 M NaCl, indicating that the productivity-selectivity tradeoff is influenced by salinity of the aqueous brines, with a lower salinity yielding better productivity for similar selectivity. Permeability-selectivity tradeoffs are well-documented for membrane-based desalination [38,39]. The above results indicate that a similar productivity-selectivity tradeoff exists in solvent extraction desalination, which is expected to govern the desalination performance of TSSE.

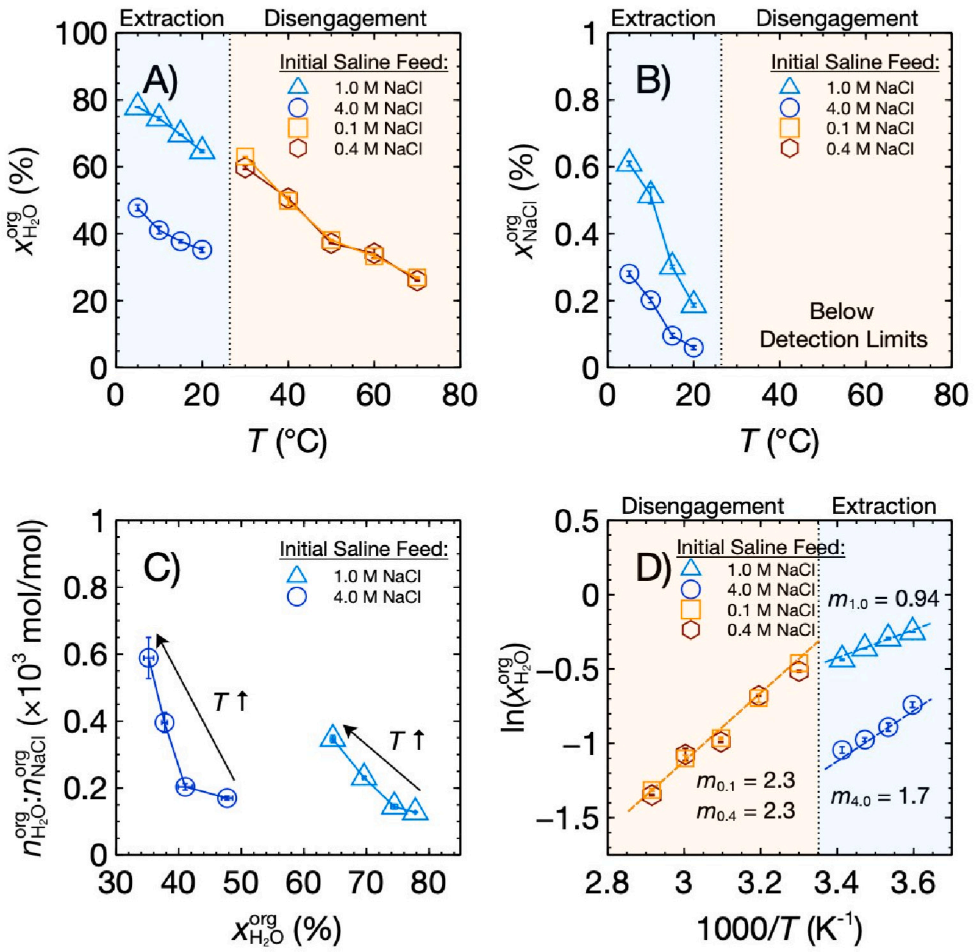

Fig. 1. Mole fractions of A) water and B) salt in the organic phase of biphasic mixtures, $x_{H_2O}^{org}$ and x_{NaCl}^{org}, respectively, as a function of temperature, T. Note that salt was not detectable in the organic phase of the mixtures in the simulated disengagement experiments. C) Molar ratio of water to salt in the organic phase, $n_{H_2O}^{org} : n_{NaCl}^{org}$, as a function of mole fraction of water in the organic phase. Straight lines connecting the data points are drawn in to serve as visual guides. D) Natural logarithms of $x_{H_2O}^{org}$ as a function of the inverse of absolute temperature, $1000/T$. Dashed lines are linear regressions, with labels m indicating slopes of the fitting lines and subscripts denoting the initial saline solution molarities. Typical extraction and disengagement temperatures (blue and orange regions, respectively) are demarcated by vertical dotted lines. Equal weights of DMCHA and saline solutions of 0.10, 0.40, 1.0, or 4.0 M NaCl (orange square, maroon hexagon, light blue triangle, and dark blue circle symbols, respectively) were equilibrated for all the biphasic mixtures. For all plots in this figure, data and error bars are means and standard errors, respectively, from duplicate experiments.

Disengagement was experimentally simulated by equilibrating equal weights of 0.10 or 0.40 M NaCl aqueous solutions and the solvents at temperatures of 30–70 °C (orange regions in Fig. 1), representative of product water salinities and temperatures typical to the disengagement step in hypersaline TSSE desalination. Extraction and disengagement are evaluated separately as temperature sensitivity of the system and order of magnitude differences in the initial aqueous solution salinities can potentially confound the analysis (blue and orange regions are included as visual guides and further details can be found in the Supplementary Material.) In simulated disengagement experiments, $x_{H_2O}^{org}$ also decreases with increasing T (Fig. 1A). The lower salinities favor partitioning of water into the solvent phase, with $x_{H_2O}^{org}$ for simulated disengagement experiments being, in some cases, comparable to or even higher than that of simulated extraction experiments (despite the greater preference of water to dissolve in the solvent phase at the lower extraction temperatures). Notably, $x_{H_2O}^{org}$-T trends are statistically indistinguishable between the 0.10 and 0.40 M NaCl aqueous solutions even though there is a ≈ 4× difference in the salt content. Crucially, salt was not detectable in the organic phases at any of the disengagement temperatures considered for both salinities (Fig. 1B). This further underscores the strong temperature sensitivity of x_{NaCl}^{org}, specifically, $x_{NaCl}^{org} \rightarrow 0$ at sufficiently high T. Therefore, in TSSE, practically no salt will remain in the solvent and be recirculated in the temperature swing cycles if adequately high disengagement temperatures are utilized. $x_{H_2O}^{org}$ trend lines for DIPA, however, do not fully overlap (results from experiments not shown) and, as will be discussed later, a detectable x_{NaCl}^{org} was observed at 30 °C.

Further quantitative analysis of these trends in thermoresponsiveness can offer additional insights into the interactions between the three primary components within hypersaline TSSE desalination. In this study, thermoresponsiveness of $x_{H_2O}^{org}$ is further assessed by plotting natural logarithm of the mole fraction of water in the organic phase as a function of the inverse of temperature (Fig. 1D, with $1/T$ scaled by 1000). Linear regressions exhibited excellent fits ($R^2 > 0.95$). Gradients of the regression slopes, labeled m, represent the sensitivities of the water content to changes in temperature. In both extraction and disengagement, the amount of salt in the system is observed to influence the partitioning behavior of water into the solvent. The thermoresponsiveness of $x_{H_2O}^{org}$ trends oppositely to the amount of salt in the organic phase. In extraction experiments, x_{NaCl}^{org}s in decreasing order are 0.19–0.61 % and 0.060–0.28 % for 1.0 and 4.0 M NaCl brine feeds, respectively (Fig. 1B), while the corresponding m are in increasing order of 0.94 ± 0.05 and 1.7 ± 0.2 (Fig. 1D). In disengagement experiments, x_{NaCl}^{org} and m are ≈0 % and 2.3, respectively, for both 0.10 and 0.40 M NaCl saline solutions. On the other hand, x_{NaCl}^{aq} did not appear to exhibit any observable trends on the thermoresponsiveness of $x_{H_2O}^{org}$. In particular, the DMCHA organic phases have no detectable levels of salt for the 0.10 and 0.40 M NaCl initial solutions and their $x_{H_2O}^{org}$ and slopes are statistically indistinguishable, despite the substantial difference in aqueous phase salt content. The DIPA organic phases, in contrast, have detectable x_{NaCl}^{org} and different $x_{H_2O}^{org}$ for the 0.10 and 0.40 M NaCl initial solutions. In other words, the amount of salt in the organic phase is a factor influencing water partitioning as the temperature is altered (note that x_{NaCl}^{org} also changes with T).

The presence of salt in the aqueous phases reducing water partitioning is well-known. These findings additionally suggest that the presence of salt in the organic phase also diminishes ability of the solvent to extract water at lowered temperatures. This relationship between x_{NaCl}^{org} and $x_{H_2O}^{org}$ can, in part, explain the plateauing of the productivity-selectivity tradeoffs at lowered temperatures. It is unlikely that the reduced water extraction is directly caused by local amine-salt interactions, as the number of salt molecules in the organic phase is ≈2–3 orders of magnitude lower than amine solvent molecules. Instead, we postulate that interactions between chloride ions and water disrupt the hydrogen bond network between solvent-water molecules in the organic phase (similar to Cl^- in pure water) [40], reducing the favorability of water partitioning into the organic phase [27,41]. The enthalpic and entropic contributions of x_{NaCl}^{org} to water partitioning are unable to be further deconvoluted and explicitly quantified (further discussions on the enthalpy and entropy of partitioning can be found in the Supplementary Material). However, DMCHA-H_2O systems exhibit a lower consolute temperature (LCST, also termed lower critical solution temperature), and the equilibrium partitioning behavior of water is, thereby, enthalpically-driven [42]. As such, the decrease in $x_{H_2O}^{org}$ with increasing x_{NaCl}^{org} is likely driven by a reduction in the enthalpic favorability of water partitioning into the organic phase.

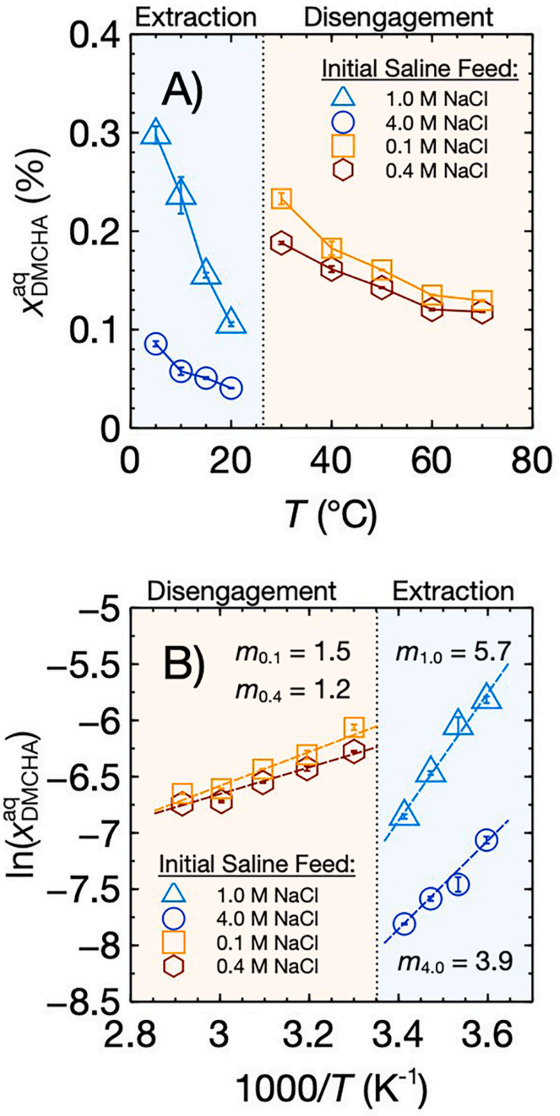

Fig. 2. A) Mole fractions of DMCHA in the aqueous phase of biphasic mixtures, x_{DMCHA}^{aq}, as a function of temperature, T. B) Natural logarithms of x_{DMCHA}^{aq} as a function of the inverse of absolute temperature, $1000/T$. Dashed lines are linear regressions, with labels m indicating slopes of the fitted lines and subscripts denoting the initial NaCl molarities of the aqueous saline solutions. Typical extraction and disengagement temperatures (blue and orange regions, respectively) are demarcated by vertical dotted lines. Equal weights of DMCHA and saline solutions of 0.10, 0.40, 1.0, and 4.0 M NaCl (orange square, maroon hexagon, light blue triangle, and dark blue circle symbols, respectively) were equilibrated for all the biphasic mixtures. Data and error bars are means and standard errors, respectively, from duplicate experiments.

3.2. Solvent losses become less thermoresponsive with increased salt concentrations

The partitioning of solvent into the aqueous phases in extraction and disengagement is representative of solvent loss through the dewatered brine raffinate and product water, respectively. Solvent partitioning was evaluated by characterizing the amine contents of the aqueous phases, $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ (results for DMCHA are presented in Fig. 2). As a weak base ($\mathrm{p}K_{\mathrm{a}} = 10.16$) [43], DMCHA is present almost entirely in unprotonated form (i.e., neutral molecule). As such, hydrogen bonding, as opposed to acid-base interactions, of DMCHA with H_2O molecules is the primary factor for partitioning of the organic solvent into the aqueous phase. The energy penalty incurred for DMCHA to form a cavity and partition into the aqueous phase is much larger than that incurred for H_2O to partition into the organic phase. Specifically, DMCHA must break apart relatively strong hydrogen bonds between several H_2O molecules in order to partition into the aqueous phase. On the other hand, interactions between DMCHA molecules are primarily weaker van der Waals forces as tertiary amines cannot form intermolecular hydrogen bonds [44]. H_2O, a comparatively smaller molecule, needs to break apart fewer van der Waals interactions between amine molecules in order to partition into the organic phase [18,45]. This difference in work of cavity formation contributes to $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ (Fig. 2A) being ≈2–3 orders of magnitude lower than $x_{\mathrm{H_2O}}^{\mathrm{org}}$ (Fig. 1A).

Across the same temperature ranges (i.e., separately considering extraction and disengagement), higher aqueous phase salt concentrations, $x_{\mathrm{NaCl}}^{\mathrm{aq}}$, result in lower $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ (Fig. 2A). That is, the greater presence of salt reduces the favorability of DMCHA to partition into the aqueous phase and lowers the miscibility (for the NaCl concentrations considered here). This salting-out phenomenon has been previously reported for other amine-water-salt systems as well [30,46]. However, there is no universally accepted explanation for the salting-out mechanism, and conjectures include, briefly: hydration (preferential hydration of electrolyte ions immobilizes H_2O molecules and diminish the ability of water to solvate nonelectrolytes), water dipole (electrolyte ion valence and structure result in unfavorable orientation of water molecules for interactions with nonelectrolyte molecules), and internal pressure (presence of electrolyte ions expands the aqueous solution and reduces space available for nonelectrolyte solvation, resulting in salting-out) [47–49].

Similar to two-component systems of amine and pure water, i.e., no salt, $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ decreases as temperature increases (negative slopes of Fig. 2A) [24]. The amount of salt in the system is also observed to influence the thermoresponsiveness of solvent partitioning into the aqueous phase. Quantitative analysis of thermoresponsiveness of $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ is performed similarly to that of $x_{\mathrm{H_2O}}^{\mathrm{org}}$ (Fig. 1D), by plotting the natural logarithm of $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ as a function of the inverse of temperature (Fig. 2B, with $1/T$ scaled by 1000). Linear regressions exhibited excellent fits ($R^2 > 0.95$). The thermoresponsiveness of $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ (represented by slopes of the linear fits) trends oppositely with $x_{\mathrm{NaCl}}^{\mathrm{aq}}$. Specifically, lower ms are observed when more salt is in the aqueous phase. In extraction experiments, $x_{\mathrm{NaCl}}^{\mathrm{aq}}$ ranges from 2.4 to 3.0 % and 8.0–8.5 % for 1.0 and 4.0 M NaCl brine feeds, respectively, while the corresponding m are 5.7 ± 0.3 and 3.9 ± 0.2. In disengagement experiments, $x_{\mathrm{NaCl}}^{\mathrm{aq}}$ increases from ≈0.2 % for 0.10 M to ≈0.8 % for 0.40 M NaCl saline solutions, with corresponding m decreasing from 1.5 ± 0.2 to 1.2 ± 0.1. As with the results presented in Fig. 1, extraction and disengagement (blue and orange regions, respectively) are evaluated separately as temperature sensitivity of the system and order of magnitude differences in the initial aqueous solution salinities can potentially confound the analysis (further details in the Supplementary Material.)

This inverse trend between thermoresponsiveness of $x_{\mathrm{DMCHA}}^{\mathrm{aq}}$ with $x_{\mathrm{NaCl}}^{\mathrm{aq}}$ further substantiates that DMCHA partitioning into the aqueous phase is energetically more unfavorable in the presence of greater salt content. Again, further deconvolution and more exact quantification of the relative contributions of $x_{\mathrm{NaCl}}^{\mathrm{aq}}$ to enthalpy and entropy are beyond the scope of the current analysis. However, the presence of an LCST in DMCHA-H_2O systems indicates that enthalpic hydrogen bonding of the amine molecules with water is a factor for equilibrium partitioning behavior of the solvent [42]. We postulate that, because Na^+ and Cl^- ions interact more strongly with polar water molecules than low-polarity DMCHA with H_2O, an increase in $x_{\mathrm{NaCl}}^{\mathrm{aq}}$ reduces the enthalpic favorability of amine-water hydrogen bonding in the aqueous phase. $x_{\mathrm{NaCl}}^{\mathrm{aq}}$ is, therefore, a key determinant in overall solvent loss in the TSSE process. While increasing extraction and disengagement temperatures in hypersaline TSSE desalination can aid in minimizing solvent loss, this strategy has diminishing returns as $x_{\mathrm{NaCl}}^{\mathrm{aq}}$ increases.

3.3. Productivity-selectivity tradeoff and solvent loss are influenced by amine properties

Equilibrium partitioning behaviors were also assessed for a second solvent of diisopropylamine (DIPA) with aqueous saline solutions of 4.0 and 0.40 M NaCl to simulate extraction and disengagement, respectively. In simulated extraction experiments, DIPA is able to extract more water than DMCHA at a given temperature, reflected by $x_{\mathrm{H_2O}}^{\mathrm{org}}$ (blue region of Fig. 3A). The thermoresponsiveness of $x_{\mathrm{H_2O}}^{\mathrm{org}}$ for both solvents, on the other hand, is similar, as suggested by the general slopes of the data points, and is confirmed by the statistically identical slope m of 1.6 ± 0.2 and 1.7 ± 0.2 for DIPA and DMCHA, respectively, in the $\ln x_{\mathrm{H_2O}}^{\mathrm{org}}$-$T^{-1}$ plots (Fig. S2A in the Supplementary Material). DIPA is more polar than DMCHA, with solvent polarity parameter $E_{\mathrm{T}}(30)$ of 33.7 and 32.7, respectively, and relative permittivity, ε_r, of 3.04 and 2.86 [50]. Additionally, DIPA is a secondary amine and able to both donate and accept hydrogen bonds, whereas DMCHA can only accept H-bonds as it is a tertiary amine. Thus, DIPA is able to extract more water from the aqueous saline solution (higher $x_{\mathrm{H_2O}}^{\mathrm{org}}$). However, the effectively same m indicates that the temperature sensitivities of water miscibility in the two solvents are similar.

$x_{\mathrm{NaCl}}^{\mathrm{org}}$s are also greater for DIPA than DMCHA but begin to converge at higher temperatures >≈15 °C (Fig. 3B). Like DMCHA, $x_{\mathrm{NaCl}}^{\mathrm{org}}$ is more thermoresponsive than $x_{\mathrm{H_2O}}^{\mathrm{org}}$ for DIPA, resulting in a productivity-selectivity tradeoff (filled blue symbols in Fig. 3C). Notably, the steeper slope signifies that $x_{\mathrm{NaCl}}^{\mathrm{org}}$ for DIPA is more sensitive to temperature change than for DMCHA ($\ln x_{\mathrm{NaCl}}^{\mathrm{org}}$-$T^{-1}$ plots are also presented in Fig. S2B). The combination of greater thermoresponsiveness of $x_{\mathrm{NaCl}}^{\mathrm{org}}$ with similar temperature-sensitivity of $x_{\mathrm{H_2O}}^{\mathrm{org}}$ results in superior TSSE extraction performance for DIPA in the temperature range considered: better productivities are achieved for similar selectivities (DIPA data points fall to the right of DMCHA at a given $n_{\mathrm{H_2O}}^{\mathrm{org}} : n_{\mathrm{NaCl}}^{\mathrm{org}}$ in Fig. 3C). Water and salt phase equilibrium data is often reported for several solvents at a single temperature [16,29] or for a single solvent across a range of temperatures [30–32]. For hypersaline desalination, the productivity-selectivity tradeoffs for different solvents across different temperatures enable performance comparisons spanning a range of operating parameters.

In simulated disengagement experiments, $x_{\mathrm{H_2O}}^{\mathrm{orgs}}$ are statistically indistinguishable for both organic solvents, suggesting that the polarities of DIPA and DMCHA are similar at sufficiently high temperatures despite the different molecular structures (orange region of Fig. 3A). We note that this behavior is only revealed through molar analyses, e.g., x, but is not readily evident from other metrics, such as mass fractions (Fig. S2C), which are often used for process operation considerations. For most disengagement temperatures examined, salt was not detectable in the organic phase for either solvent (orange region of Fig. 3B). This, again, demonstrates the strong temperature-dependence of salt partitioning behavior: increasing T rapidly drives practically all NaCl out of

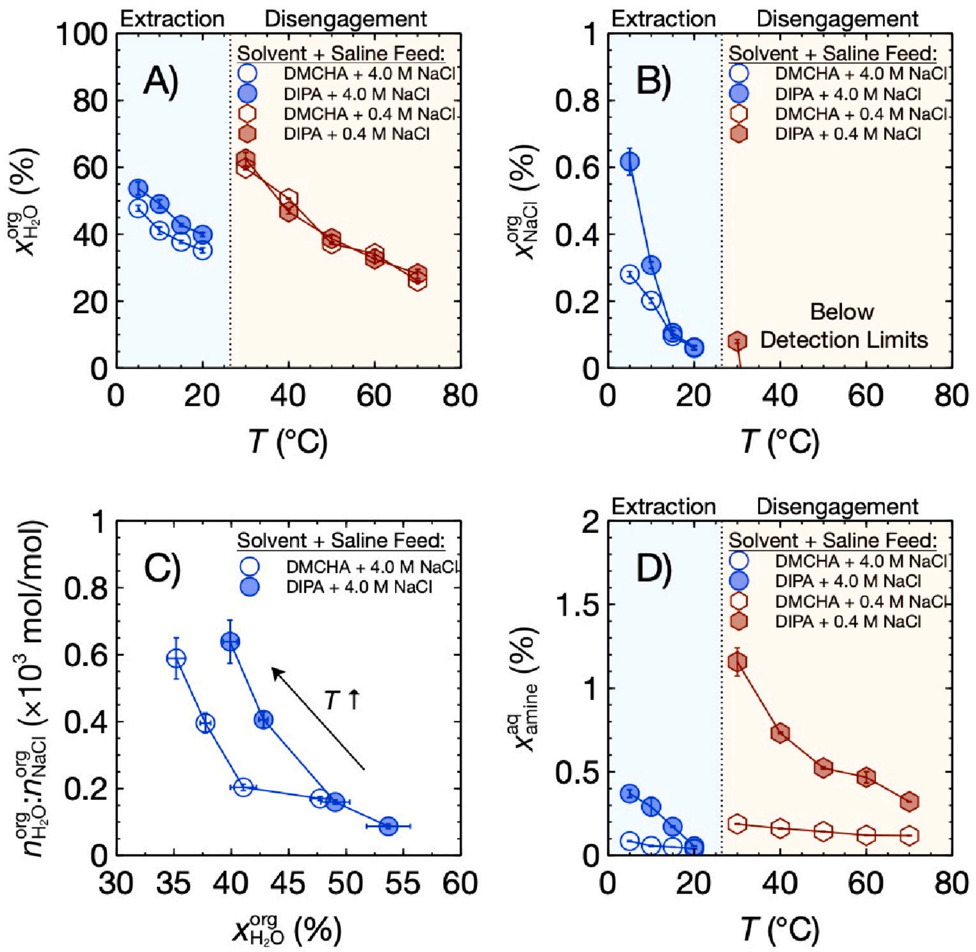

Fig. 3. Mole fractions of A) water and B) salt in the organic phase of biphasic mixtures, $x^{org}_{H_2O}$ and x^{org}_{NaCl}, respectively, as a function of temperature, T. Note that salt was only detectable in the organic phase of the mixtures in the simulated disengagement experiments with DIPA and an initial aqueous solution molarity of 0.40 M NaCl. C) Molar ratio of water to salt in the organic phase, $n^{org}_{H_2O} : n^{org}_{NaCl}$, as a function of mole fraction of water in the organic phase. D) Mole fractions of organic solvent x^{aq}_{amine}, as a function of temperature, T. Typical extraction and disengagement temperatures (blue and orange regions, respectively) are demarcated by vertical dotted lines. Equal weights of DMCHA or DIPA (open and filled symbols, respectively) and saline solutions of 0.40 and 4.0 M NaCl (open maroon hexagon and open dark blue circle symbols, respectively) were equilibrated for all the biphasic mixtures. For all plots in this figure, data and error bars are means and standard errors, respectively, from duplicate experiments.

the organic phase. The exception is DIPA at 30 °C, where a small but detectable x^{org}_{NaCl} was observed (no salt was detected at this temperature for DMCHA). Factors influencing the differences in x^{org}_{NaCl} for DIPA and DMCHA in extraction and disengagement will be further explored in Section 3.5.

In both simulated extraction and disengagement experiments, x^{aq}_{amine}s are ≈4× greater for DIPA than DMCHA (Fig. 3D). DIPA is a smaller molecule than DMCHA (molecular weights of 101.19 and 127.23, respectively, Table S1) and, therefore, the energy penalty incurred in forming a cavity for its dissolution in the aqueous phase is correspondingly lower [51–53]. As discussed earlier, DIPA is also more polar than DMCHA and can accept and donate H-bonds (whereas DMCHA can only accept). These effects contribute to the greater partitioning of DIPA into water. Thermoresponsiveness of x^{aq}_{amine} is also ≈3× larger for DIPA than DMCHA (from slopes m of the $\ln x^{aq}_{amine}$-T^{-1} plot, Fig. S2D). Again, this reflects the enthalpic favorability of DIPA to partition in the aqueous phase compared to DMCHA. In hypersaline TSSE desalination, the gain in water partitioning in the extraction step would need to be considered against the relative increase in solvent loss in both extraction and disengagement steps.

While thermoresponsiveness and corresponding water partitioning into the organic phase are similar for both solvents (Fig. 3A), solvent partitioning into the aqueous phase diverge significantly for DIPA and DMCHA (Fig. 3D). We postulate that this disparity in $x^{org}_{H_2O}$ and x^{aq}_{amine} partitioning behavior is due to differences in the work of cavity formation in the organic and aqueous phases, respectively. Water molecules are small and tend to be readily accommodated among the larger molecules of the organic solvent. Therefore, the difference between the work of cavity formation in DIPA and DMCHA organic phases is comparatively small. On the other hand, more work is required for the creation of a cavity among a highly structured network of hydrogen bonds between water molecules [18,45]. As such, the dissimilar thermochemical properties between DIPA and DMCHA, i.e., molecular size and hydrogen bonding ability, have a more pronounced effect on x^{aq}_{amine} and the thermoresponsiveness of x^{aq}_{amine}.

3.4. *Equimolar transport of sodium and chloride ions*

In the simulated extraction experiments, mole fractions of Na^+ and Cl^- ions in the organic phase, x^{org}_{ion}, were further analyzed and results for DMCHA and a 1.0 M brine feed as a function of temperature are presented in Fig. 4A. For these mixtures, the mole fractions of Na^+ and Cl^- are practically identical, signifying that the ions partition into the organic phase in equal molar concentrations (and, correspondingly, ions remaining in the aqueous phase are also at equal molar concentrations). This observation is consistent for both solvents and across all initial aqueous salt concentrations investigated: a unit change in $x^{org}_{Cl^-}$ ions is correlated with a 1.0 ± 0.0 change in $x^{org}_{Na^+}$ ($R^2 = 0.99$, Fig. 4B), with a fitted intercept of −0.015 ± 0.009, which is statistically indistinguishable from zero. These results provide compelling evidence that transport of Na^+ and Cl^- ions into the organic phase of biphasic mixtures is equimolar.

A 1966 study posited that water in the organic phase protonates amine molecules, which subsequently determines the transport of Na^+ and Cl^- ions to the organic phase [29]. In that study, the mole fraction of Cl^- in the organic phase, $x^{org}_{Cl^-}$, was found to be greater than $x^{org}_{Na^+}$ (mole

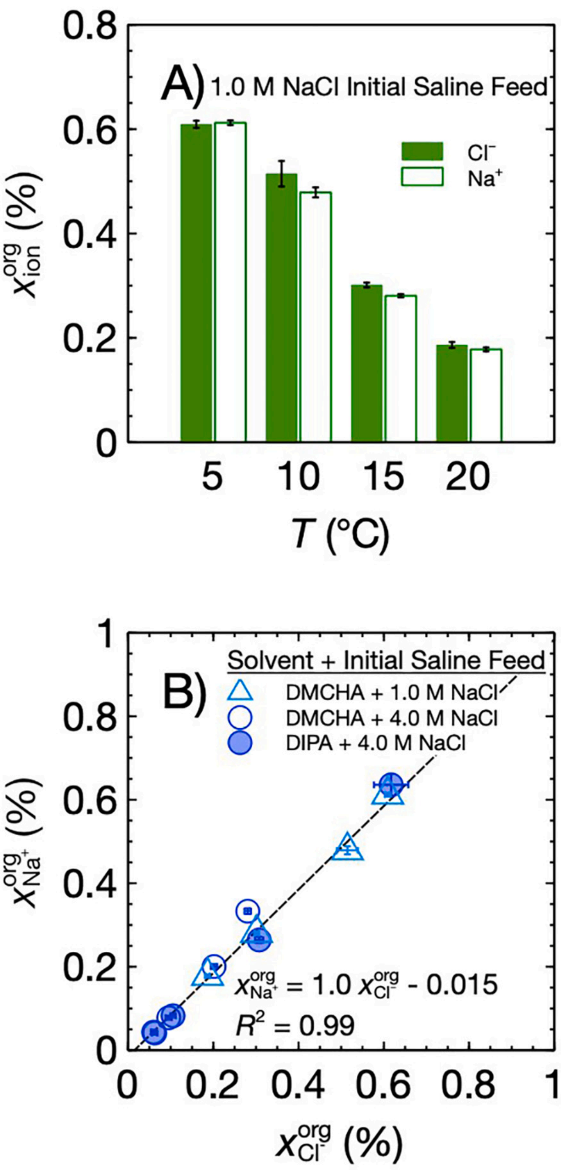

Fig. 4. A) Mole fractions of chloride and sodium ions (green and white columns, respectively) in the organic phase, $x_{\mathrm{ion}}^{\mathrm{org}}$, as a function of temperature, T. B) Mole fractions of sodium and chloride ions in the organic phase, $x_{\mathrm{Cl^-}}^{\mathrm{org}}$ and $x_{\mathrm{Na^+}}^{\mathrm{org}}$, respectively. Dashed line is a weighted least squares regression with slope of $m = 1.0 \pm 0.0$, intercept of -0.015 ± 0.009, and a coefficient of determination, R^2, of 0.99. DMCHA and DIPA are denoted by open and filled symbols, respectively, and aqueous brines of 1.0 and 4.0 M NaCl are indicated by light blue triangles and dark blue circle symbols, respectively. Equal weights of amine and aqueous saline solutions were equilibrated for all biphasic mixtures. For all plots in this figure, data and error bars are means and standard errors, respectively, from duplicate experiments.

fraction of Na^+ in the organic phase). The researchers attributed their finding to the higher solubility of protonated amines than Na^+ ions in the organic phase, leading to the selective partitioning of Cl^- ions. The study, however, relied on the experimental method of counting ^{22}Na and ^{36}Cl isotopic tracers from evaporated samples of the organic phase to quantify $x_{\mathrm{ion}}^{\mathrm{org}}$, a rudimentary technique by present standards. As $x_{\mathrm{NaCl}}^{\mathrm{org}}$ is often characterized by gravimetric measurements of the salt [30–33], concentrations of the individual cation and anion, $x_{\mathrm{Na^+}}^{\mathrm{org}}$ and $x_{\mathrm{Cl^-}}^{\mathrm{org}}$, are almost never assessed or reported for ternary amine-water-salt systems. The more advanced characterization method of ion chromatography (IC) utilized in this study enables more accurate quantification of ion concentrations. Fig. 4 shows that Cl^- was not selectively transported into the organic phase of biphasic mixtures, but rather partitions as a pair with Na^+. Additionally, protonated amine was not detected in the organic phase by IC, further substantiating that practically all solvent molecules remained as neutral amines and not ammonium salts. Therefore, for simulated extraction conditions representative of hypersaline desalination considered in this study, the subsequent redistribution of ions after amine protonation is not the primary mechanism for salt transport into the organic phase. Because of the high surface charge densities, Na^+ and Cl^- are not likely to exist as bare ions in the low-dielectric environments imposed by amine solvents [16,18–20]. Instead, we postulate that Na^+ and Cl^- ions partition into the organic phase with water molecules, i.e., the ions are "buffered" by water molecules in the low dielectric organic phase. This is supported by the negligible solubilities (below detection limits) of Na^+ and Cl^- ions in desiccated DIPA and DMCHA (results of experimental characterizations not shown), i.e., Na^+ and Cl^- ions are unable to exist in amines without water. The relationship between transport of water and salt into the organic phase will be further explored in the next subsection.

3.5. Activity coefficient of salt is correlated with organic phase water content

In the organic phase, the influence of salt on the thermoresponsiveness of water partitioning (Fig. 1D) suggests an underlying relationship between $x_{\mathrm{H_2O}}^{\mathrm{org}}$ and $x_{\mathrm{NaCl}}^{\mathrm{org}}$. However, as indicated by the nonzero slopes of the productivity-selectivity tradeoff trend lines (Figs. 1C and 3C), salt and water do not partition into the organic phase at a constant ratio, i.e., $x_{\mathrm{NaCl}}^{\mathrm{org}}$ is not a linear function of $x_{\mathrm{H_2O}}^{\mathrm{org}}$. Temperature and salinity of the aqueous solutions were observed to impact the distribution of both water and NaCl. To further elucidate the quantitative relationship connecting these two parameters, additional analysis was performed. Activity coefficients of salt in the organic phase, $\gamma_{\mathrm{NaCl}}^{\mathrm{org}}$, were determined and are presented in Fig. 5 (details on the calculation of $\gamma_{\mathrm{NaCl}}^{\mathrm{org}}$ are included in the Supplementary Material). Note that the experimental matrix was widened to include additional salt concentrations for the initial aqueous solutions, measured at 30 °C. NaCl concentrations of the organic phases were quantified using ion chromatography.

Na^+ and Cl^- ions, having high surface charge densities, generally do not exist as bare ions in low-dielectric environments [16,18–20]. As such, salts are effectively excluded from low-polarity amine solvents, which is the underlying principle for salt rejection in the extraction step

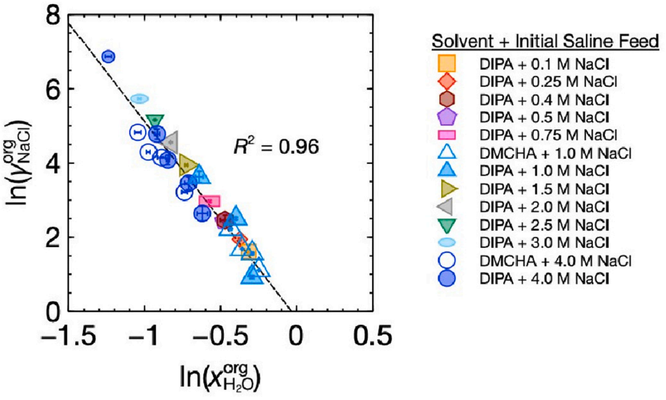

Fig. 5. Natural logarithms of activity coefficients of NaCl in the organic phase, $\gamma_{\mathrm{NaCl}}^{\mathrm{org}}$, as a function of mole fraction of water in the organic phase, $x_{\mathrm{H_2O}}^{\mathrm{org}}$. Dashed line denotes weighted least squares regression (R^2 of 0.96) with a slope of $m = -5.3 \pm 0.2$ and intercept of -0.2 ± 0.2. Equal weights of DMCHA or DIPA (open and filled symbols, respectively) and aqueous solutions over a range of NaCl concentrations were equilibrated for all biphasic mixtures. Data and error bars are means and standard errors, respectively, from duplicate experiments.

of TSSE [16]. However, as $x_{H_2O}^{org}$ increases, the relative permittivity of the organic phase (a measure of chemical polarity of the medium) increases. This, in turn, creates a more suitable environment, for salt ions [16,19,20]. Quantitative analysis of this relationship between increased solubility of Na^+ and Cl^- ions in the organic phase with the greater miscibility of water further reveals a linear correlation between the natural logarithms of $x_{H_2O}^{org}$ and γ_{NaCl}^{org}, as presented in Fig. 5 (natural logarithm scales are relevant to chemical potential, the Gibbs free energy of separation, and, thereby, desalination processes [9,54]; the same data is presented on a linear-linear scale in Fig. S3 of the Supplementary Material). As $ln\left(x_{H_2O}^{org}\right)$ increases to zero, $ln\left(\gamma_{NaCl}^{org}\right)$ diminishes linearly to -0.2 ± 0.2, a value statistically indistinguishable from 0. In other words, as $x_{H_2O}^{org}$ approaches unity, $\gamma_{NaCl}^{org} \rightarrow 1$, signifying NaCl in the organic phase is progressively behaving thermodynamically similar to the salt in an infinitely dilute aqueous solution (or, equivalently, ideal behavior), matching theoretical expectation. This relationship between $x_{H_2O}^{org}$ and γ_{NaCl}^{org} can explain the previously mentioned counterintuitive observation that, at a given extraction temperature, x_{NaCl}^{org} is lower with the higher brine concentration (Section 3.1). Increasing the feed salinity from 1.0 to 4.0 M NaCl lowers the chemical potential of water in the aqueous phase and reduces partitioning of water into the solvent phase. The lowered $x_{H_2O}^{org}$, in turn, creates a less suitable environment for salt in the organic phase. Crucially, the excellent fit of the weighted least squares linear regression ($R^2 = 0.96$) covers broad ranges of initial aqueous solution salt concentration (0.10 to 4.0 M), temperature (5 to 30 °C), and amine solvent (DIPA and DMCHA). The $ln\left(x_{H_2O}^{org}\right)$-$ln\left(\gamma_{NaCl}^{org}\right)$ relation holding across the divergent conditions (slope of regression line) and γ_{NaCl}^{org} approaching unity as $x_{H_2O}^{org} \rightarrow 1$ (vertical axis intercept) strongly suggest that salt partitioning is principally governed by water-ion interactions in the organic phase, with amine-ion interactions being relatively insignificant. We further posit that the slope of $ln\left(x_{H_2O}^{org}\right)$-$ln\left(\gamma_{NaCl}^{org}\right)$ (-5.3 ± 0.2 for NaCl in Fig. 5) is specific to the salt and is a quantitative measure of the water-ion interactions.

4. Implications for TSSE desalination

This study investigates the influence of temperature on equilibrium partitioning of amine, water, and salt in biphasic mixtures to provide insights into the underlying principles governing TSSE performance. The transport of water and salt is shown to be intrinsically related. Specifically, the relative permittivity of the organic phase increases with water content, thereby creating a more suitable environment for the partitioning of salt ions and consequently reducing salt rejection of TSSE desalination. In turn, salt in the organic phase reduces the ability of solvents to extract water at lowered temperatures, likely by disrupting the hydrogen bond network between solvent-water molecules in the organic phase and, thereby, reducing the enthalpic favorability of water partitioning. The inherently entwined relationship manifests in the productivity-selectivity tradeoffs that governs the overall performance of amine solvents in TSSE desalination.

The findings of this study suggest that, in the organic phase, ion-solvent interactions are relatively insignificant compared to water-ion interactions. Equimolar transport of Na^+ and Cl^- into the organic phase indicates that the salt ions are not interacting directly with protonated amines, as previously thought [36], but instead are more likely to be "buffered" by water molecules. In addition, the correlation between the natural logarithms of the water contents and the activity coefficients of salt in the organic phase, $ln\left(x_{H_2O}^{org}\right)$-$ln\left(\gamma_{NaCl}^{org}\right)$, was found to be applicable across different solvents. As such, amine properties indirectly affect salt partitioning behavior through their influence on water partitioning. These experimental results offer fundamental insight into the mechanism driving salt transport, filling in a crucial gap in understanding identified by molecular dynamic simulations [27,28]. Future analysis quantifying the effect of x_{NaCl}^{org} on the enthalpic favorability of water partitioning can offer additional insight into the nature of water-ion interactions in the organic phase. Water-ion interactions in the aqueous phase are influenced by ion properties, such as size, valence, and electronegativity [54–56]; water-ion interactions in the organic phase will likely be governed by similar ion characteristics. Analyzing the slopes of the $ln\left(x_{H_2O}^{org}\right)$-$ln\left(\gamma_{salt}^{org}\right)$ correlations for a broader range of ions with distinctly divergent properties can further shed light on the principal factors affecting water-ion interactions in the organic phase.

Notably, x_{NaCl}^{org}s are more sensitive to changes in temperature than $x_{H_2O}^{org}$. Rational selection of operating temperatures can take advantage of this difference in partitioning behavior to improve net TSSE desalination performance. Multi-stage processes with temperature steps, for example, can utilize the differences in temperature sensitives of water and salt to improve selectivity while maintaining high levels of overall productivity. Such an approach can expand the spectrum of viable solvents to include those that are seemingly unfeasible in single-stage operation (i.e., have high water productivity but inadequately low selectivity).

In TSSE systems with lower consolute temperatures, both water and solvent partitioning are driven by the same mechanism of enthalpic hydrogen bonding; therefore, solvent properties that contribute to higher water partitioning will likely also incur concomitant increases in solvent loss to the aqueous phase. Critically, the results of this study indicate that the relative gain in water partitioning will be much smaller than the proportional rise in solvent loss, plausibly because solvent properties affect the work of cavity formation more in the aqueous phase than in the organic phase. For example, DIPA, being a smaller and more polar molecule with greater hydrogen bonding capacity than DMCHA, can extract ≈10–20 % more water but experiences ≈4× greater solvent loss. Even though x_{amine}^{aq}s are ≈2 orders of magnitude smaller than $x_{H_2O}^{org}$s, amine loss will still impose nonnegligible additional costs and may require posttreatment of the raffinate and product streams to eliminate toxicity concerns. Strategic solvent design must therefore balance improving water extraction efficiency with elevated solvent loss. Increasing operating temperatures can help to suppress solvent loss but at the expense of decreased water partitioning during extraction and higher energy consumption for disengagement. In addition, this strategy has diminishing returns for high-salinity brine feeds: as the aqueous phase salt content increases, thermoresponsiveness of x_{amine}^{aq} decreases. Further analysis quantifying the effect of x_{NaCl}^{aq} on the enthalpic favorability of amine partitioning can offer additional insight into the nature of amine-water interactions in the aqueous phase.

A more complete understanding of the principal phenomena governing solvent extraction desalination can inform process design, selection of operating parameters, and identification of new solvents to maximize productivity and selectivity while minimizing solvent loss. Although the current study focuses on amines as the solvents and NaCl as the salt, the findings are generally applicable to different solvent classes, e.g., organic acids, ionic liquids and polyethers, as well as other electrolyte ions present in hypersaline feeds. The examination of additional solvent classes in future work can further deepen the understanding of the underlying mechanisms governing TSSE. Insight into the fundamental mechanisms of TSSE can inform advancement of the technology towards practical implementation for hypersaline desalination. More broadly, the findings of this study are applicable for liquid-liquid biphasic systems pertinent to other disciplines.

CRediT authorship contribution statement

Kinnari M. Shah: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing - Original Draft; Elizabeth Dach: Methodology, Formal analysis, Writing- Reviewing and Editing; Robert

Winton: Methodology, Investigation, Formal analysis; Hanqing Fan: Formal analysis, Writing- Reviewing and Editing; Ngai Yin Yip: Conceptualization, Supervision, Funding acquisition, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2022.116259.

References

[1] N. Ahmad, R.E. Baddour, A review of sources, effects, disposal methods, and regulations of brine into marine environments, Ocean Coast. Manag. 87 (2014) 1–7, https://doi.org/10.1016/j.ocecoaman.2013.10.020.

[2] J.M. Estrada, R. Bhamidimarri, A review of the issues and treatment options for wastewater from shale gas extraction by hydraulic fracturing, Fuel 182 (2016) 292–303, https://doi.org/10.1016/j.fuel.2016.05.051.

[3] M. Mickley, Membrane Concentrate Disposal: Practices and Regulation, Final Report, U.S. Department of the Interior, Bureau of Reclamation, Technical Service Center, Water Treatment Engineering and Research Group, 2001.

[4] B.K. Pramanik, L. Shu, V. Jegatheesan, A review of the management and treatment of brine solutions, Environ. Sci. Water Res. Technol. 3 (2017) 625–658, https://doi.org/10.1039/c6ew00339g.

[5] D.L. Shaffer, L.H. Arias Chavez, M. Ben-Sasson, S. Romero-Vargas Castrillón, N. Y. Yip, M. Elimelech, Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions, Environ. Sci. Technol. 47 (2013) 9569–9583, https://doi.org/10.1021/es401966e.

[6] A. Burbano, P. Brandhuber, The Water Research Foundation, Demonstration of membrane zero liquid discharge for drinking water system: a literature review. https://www.waterrf.org/resource/demonstration-membrane-zero-liquid-discharge-drinking-water-system-literature-review, 2012. (Accessed 11 February 2021).

[7] S.J. Khan, D. Murchland, M. Rhodes, T.D. Waite, Management of Concentrated Waste Streams from high-pressure membrane water treatment systems, Crit. Rev. Environ. Sci. Technol. 39 (2009) 367–415, https://doi.org/10.1080/10643380701635904.

[8] M. Mickley, WateReuse Foundation, Survey of High-recovery and Zero Liquid Discharge Technologies for Water Utilities, WateReuse Foundation, Alexandria, Va, 2008.

[9] K.M. Shah, I.H. Billinge, X. Chen, H. Fan, Y. Huang, R.K. Winton, N.Y. Yip, Drivers, challenges, and emerging technologies for desalination of high-salinity brines: a critical review, Desalination 538 (2022), 115827, https://doi.org/10.1016/j.desal.2022.115827.

[10] M. Mickley, Membrane Concentrate Disposal: Practices and Regulation, Final Report, U.S. Department of the Interior, Bureau of Reclamation, Technical Service Center, Water Treatment Engineering and Research Group, 2001.

[11] T. Tong, M. Elimelech, The global rise of zero liquid discharge for wastewater management: drivers, technologies, and future directions, Environ. Sci. Technol. 50 (2016) 6846–6855, https://doi.org/10.1021/acs.est.6b01000.

[12] A. Antony, J.H. Low, S. Gray, A.E. Childress, P. Le-Clech, G. Leslie, Scale formation and control in high pressure membrane water treatment systems: a review, J. Membr. Sci. 383 (2011) 1–16, https://doi.org/10.1016/j.memsci.2011.08.054.

[13] D. Brogioli, F. La Mantia, N.Y. Yip, Thermodynamic analysis and energy efficiency of thermal desalination processes, Desalination 428 (2018) 29–39, https://doi.org/10.1016/j.desal.2017.11.010.

[14] D.W. Hood, R.R. Davison, The place of solvent extraction in saline water conversion, in: SALINE WATER Convers, American Chemical Society, 1960, pp. 40–49, https://doi.org/10.1021/ba-1960-0027.ch006.

[15] A. Bajpayee, T. Luo, A. Muto, G. Chen, Very low temperature membrane-free desalination by directional solvent extraction, Energy Environ. Sci. 4 (2011) 1672, https://doi.org/10.1039/c1ee01027a.

[16] C. Boo, R.K. Winton, K.M. Conway, N.Y. Yip, Membrane-less and non-evaporative desalination of hypersaline brines by temperature swing solvent extraction, Environ. Sci. Technol. Lett. 6 (2019) 359–364, https://doi.org/10.1021/acs.estlett.9b00182.

[17] C. Boo, I.H. Billinge, X. Chen, K.M. Shah, N.Y. Yip, Zero liquid discharge of ultrahigh-salinity brines with temperature swing solvent extraction, Environ. Sci. Technol. (2020), https://doi.org/10.1021/acs.est.0c02555.

[18] Y. Marcus, The Properties of Solvents, John Wiley & Sons, 1999.

[19] V.S. Kislik, Solvent Extraction: Classical and Novel Approaches, Elsevier, 2011.

[20] T.R. Griffiths, D.C. Pugh, Correlations among solvent polarity scales, dielectric constant and dipole moment, and a means to reliable predictions of polarity scale values from current data, Coord. Chem. Rev. 29 (1979) 129–211, https://doi.org/10.1016/S0010-8545(00)82109-8.

[21] Z.H. Foo, C. Stetson, E. Dach, A. Deshmukh, H. Lee, A.K. Menon, R. Prasher, N. Y. Yip, J.H. Lienhard, A.D. Wilson, Solvent-driven aqueous separations for hypersaline brine concentration and resource recovery, Trends Chem. (2022), https://doi.org/10.1016/j.trechm.2022.09.004.

[22] J.C.N. Kimberlin, R.W. Richardson, Desalination by Solvent Extraction, US3177139A, 1965.

[23] R.R. Davison, W.B. Harris, W.H. Smith, A solvent extraction desalination pilot plant, Desalination 3 (1967) 17–26, https://doi.org/10.1016/S0011-9164(00)84020-5.

[24] R.R. Davidson, W.H. Smith, D.W. Hood, Structure and amine-water solubility in desalination by solvent extraction, J. Chem. Eng. Data 5 (1960) 420–423, https://doi.org/10.1021/je60008a005.

[25] J. Guo, Z.D. Tucker, Y. Wang, B.L. Ashfeld, T. Luo, Task-Specific Ionic Liquid Enables Highly Efficient Low Temperature Desalination by Directional Solvent Extraction, 2020, https://doi.org/10.26434/chemrxiv.11840025.v1.

[26] A. Bajpayee, S.J.P. Kress, K. Kleinguetl, G. Chen, M. Fowler, Water Extraction Using a Directional Solvent, US9428404B2, 2016.

[27] O. Choi, M. Kim, A.E. Cho, Y.C. Choi, G.D. Kim, D. Kim, J.W. Lee, Fates of water and salts in non-aqueous solvents for directional solvent extraction desalination: effects of chemical structures of the solvents, Membr. Water Treat. 10 (2019) 207–212, https://doi.org/10.12989/mwt.2019.10.3.207.

[28] G.D. Barbosa, X. Liu, J.E. Bara, S.T. Weinman, C.H. Turner, High-salinity brine desalination with amine-based temperature swing solvent extraction: a molecular dynamics study, J. Mol. Liq. 341 (2021), 117359, https://doi.org/10.1016/j.molliq.2021.117359.

[29] R.R. Davison, W.H. Smith, D.W. Hood, Phase equilibria of desalination solvents: water-NaCl-amines, J. Chem. Eng. Data 11 (1966) 304–309, https://doi.org/10.1021/je60030a005.

[30] R. De Santis, Phase equilibriums of the water-sodium chloride-triethylamine system, J. Chem. Eng. Data 21 (1976) 328–330, https://doi.org/10.1021/je60070a009.

[31] D. Cherkasov, V. Danilina, K. Ilin, Phase equilibria, critical phenomena, and extractive crystallization of the salt in the sodium Chloride–Water–Diisopropylamine ternary system, Russ. J. Inorg. Chem. 66 (2021) 883–890, https://doi.org/10.1134/S0036023621060073.

[32] A.M. Ting, S. Lynn, J.M. Prausnitz, Liquid-liquid equilibria for aqueous systems containing N, N-diethylmethylamine and sodium chloride or sodium sulfate, J. Chem. Eng. Data 37 (1992) 252–259, https://doi.org/10.1021/je00006a032.

[33] A. Cartón, S. Bolado, M. Marcos, Liquid−Liquid equilibria for aqueous solutions of lithium sulfate or lithium formate and triethylamine or diisopropylamine, J. Chem. Eng. Data 45 (2000) 260–264, https://doi.org/10.1021/je990235u.

[34] Standard Test Method for Water Using Volumetric Karl Fischer Titration, ASTM International, West Conshohocken, PA, 2017.

[35] R.T. Berry, E. Dach, J.A. Melhorn, N.Y. Yip, L. Soh, Assessing the temperature-dependent tunable polarity of N, N-dimethylcyclohexylamine (DMCHA) and water mixtures, ACS Sustain. Chem. Eng. 10 (2022) 3726–3734, https://doi.org/10.1021/acssuschemeng.2c00293.

[36] R.R. Davison, D.W. Hood, Thermodynamic cycles for recovery of water by solvent extraction, Ind. Eng. Chem. Process. Des. Dev. 3 (1964) 399–404, https://doi.org/10.1021/i260012a023.

[37] T. Takamuku, A. Yamaguchi, D. Matsuo, M. Tabata, M. Kumamoto, J. Nishimoto, K. Yoshida, T. Yamaguchi, M. Nagao, T. Otomo, T. Adachi, Large-angle X-ray scattering and small-angle neutron scattering study on phase separation of Acetonitrile−Water mixtures by addition of NaCl, J. Phys. Chem. B 105 (2001) 6236–6245, https://doi.org/10.1021/jp003011n.

[38] G.M. Geise, H.B. Park, A.C. Sagle, B.D. Freeman, J.E. McGrath, Water permeability and water/salt selectivity tradeoff in polymers for desalination, J. Membr. Sci. 369 (2011) 130–138, https://doi.org/10.1016/j.memsci.2010.11.054.

[39] H.B. Park, J. Kamcev, L.M. Robeson, M. Elimelech, B.D. Freeman, Maximizing the right stuff: the trade-off between membrane permeability and selectivity, Science 356 (2017), eaab0530, https://doi.org/10.1126/science.aab0530.

[40] Y. Marcus, Effect of ions on the structure of water: structure making and breaking, Chem. Rev. 109 (2009) 1346–1370, https://doi.org/10.1021/cr8003828.

[41] J.M. Sangster, Octanol-Water Partition Coefficients: Fundamentals and Physical Chemistry, John Wiley & Sons, 1997.

[42] J. Bianga, K.U. Künnemann, T. Gaide, A.J. Vorholt, T. Seidensticker, J. M. Dreimann, D. Vogt, Thermomorphic multiphase systems: switchable solvent

mixtures for the recovery of homogeneous catalysts in batch and flow processes, Chem. Eur. J. 25 (2019) 11586–11608, https://doi.org/10.1002/chem.201902154.

[43] W.M. Haynes, CRC Handbook of Chemistry and Physics, 97th ed., 2016.

[44] R.J. Ouellette, J.D. Rawn, Principles of Organic Chemistry, Academic Press, 2015.

[45] Y. Marcus, Solvent Mixtures: Properties and Selective Solvation, CRC Press, 2002.

[46] R. Sargent, W. Rieman, Salting-out chromatography: amines, Anal. Chim. Acta 17 (1957) 408–414, https://doi.org/10.1016/S0003-2670(00)87057-9.

[47] P.K. Grover, R.L. Ryall, Critical appraisal of salting-out and its implications for chemical and biological sciences, Chem. Rev. 105 (2005) 1–10, https://doi.org/10.1021/cr030454p.

[48] A.M. Hyde, S.L. Zultanski, J.H. Waldman, Y.-L. Zhong, M. Shevlin, F. Peng, General principles and strategies for salting-out informed by the hofmeister series, Org. Process. Res. Dev. 21 (2017) 1355–1370, https://doi.org/10.1021/acs.oprd.7b00197.

[49] F.A. Long, W.F. McDevit, Activity coefficients of nonelectrolyte solutes in aqueous salt solutions, Chem. Rev. 51 (1952) 119–169, https://doi.org/10.1021/cr60158a004.

[50] J.P. Cerón-Carrasco, D. Jacquemin, C. Laurence, A. Planchat, C. Reichardt, K. Sraïdi, Solvent polarity scales: determination of new ET(30) values for 84 organic solvents, J. Phys. Org. Chem. 27 (2014) 512–518, https://doi.org/10.1002/poc.3293.

[51] J. Konicek, I. Wadsö, Thermochemical properties of some carboxylic acids, amines, and N-substituted amides in aqueous solution, Acta Chem. Scand. 25 (1971) 1541–1551.

[52] T. Magsumov, I. Sedov, Thermodynamics of cavity formation in different solvents: enthalpy, entropy, and the solvophobic effects, J. Mol. Liq. 331 (2021), 115738, https://doi.org/10.1016/j.molliq.2021.115738.

[53] D. Chandler, Interfaces and the driving force of hydrophobic assembly, Nature 437 (2005) 640–647, https://doi.org/10.1038/nature04162.

[54] K.S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations, J. Phys. Chem. 77 (1973) 268–277.

[55] J. Li, H.M. Polka, J. Gmehling, A gE model for single and mixed solvent electrolyte systems: 1. Model and results for strong electrolytes, Fluid Phase Equilib. 94 (1994) 89–114, https://doi.org/10.1016/0378-3812(94)87052-7.

[56] P. Debye, E. Hückel, Theory of electrolytes 1. Freezing point lowering and related phenomena, Physik. 24 (1923) 185–206.