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Changing the World's Energy Future

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Trends in Chemistry

Feature Review

Solvent-driven aqueous separations for hypersaline brine concentration and resource recovery

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Solvent-driven separation processes can extract water and high-value minerals from high salinity or contaminated brines, simultaneously reducing the environmental impact of brine disposal and enabling resource recovery. The efficient dewatering of hypersaline brines is essential for the sustainable minimal and zero liquid discharge processing of industrial wastewaters. Fractional crystallization can selectively extract ions from contaminated waste streams, allowing critical materials to be recycled, including transition and lanthanide metals required for renewable energy generation and storage. Mass transfer in solvent-driven water extraction occurs across a liquid–liquid interface, eliminating the scaling and fouling of membrane and heat exchanger surfaces and limiting the need for extensive pretreatment. Solvent-driven fractional crystallization can leverage sequential treatment and control of process conditions to rapidly recover salts without requiring evaporation of water. Despite promising applications, the principles and potential of solvent-driven aqueous separations remain poorly understood. This critical review explores the opportunities presented by solvent-based aqueous separations from the molecular to process scale, evaluating the chemistry of solvation and system design in the broader context of desalination, resource recovery, water softening, and mineral production.

Highlights

Solvent-driven aqueous separations enable resource recovery and zero liquid discharge desalination from hypersaline or contaminated aqueous brine, mitigating environmental impacts of brine disposal.

Promising solvents include thermoresponsive and volatile organic solvents, which selectively solvate water while dissolving minimally into the aqueous retentate; critical materials, including transition and lanthanide metals, may be recovered simultaneously through fractional crystallization.

Effects of intermolecular interactions and phase kinetics that control macroscopic separation efficacy are identified to elucidate key process-level design considerations for energy-efficient solvent-driven aqueous separations.

Solvent regeneration processes bypass traditional limitations associated with direct water vaporization and membrane separation. Process optimization is evaluated in terms of recycled sensible heats, reducing net energy consumption while mitigating solvent depletion.

Motivations for solvent-driven separations

Population growth, climate change, and rising economic standards are rapidly exacerbating resource scarcity [1]. Globally, water stress has a cascading impact on several critical resources, including the irrigation of farmland for food production, the manufacturing of photovoltaics for clean energy generation, and the extraction of metals for batteries and magnets. Aqueous water–salt and ion–ion separations play a central role in alleviating water scarcity, by augmenting and protecting freshwater supplies and by maximizing resource recycling from industrial waste streams. Sustainable water management and resource recovery systems must be energy, atom, and carbon efficient, to minimize environmental impact [2].

Freshwater supplies can be augmented using nontraditional sources, including saline aquifers, high **total dissolved solids (TDS)** (see Glossary) surface waters, municipal wastewaters, and aqueous industrial wastes. Fresh water can be produced from these sources with membrane systems such as **reverse osmosis (RO)**, the most widely used and generally the most energy efficient **desalination** technology [3]. Currently, RO is extensively employed in brackish and seawater desalination. However, the hydraulic pressure limitations of conventional RO restrict the feed TDS levels to be under ~70 000 ppm, although emerging variants of RO may accept

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somewhat more saline feed streams (up to 150 000 ppm TDS) [4,5] with proper softening. Another bottleneck for RO is brine disposal, especially from inland desalination plants, which requires environmentally responsible discharge to unlock these nontraditional sources [6,7]. Industrial activity also creates a wide spectrum of solute-containing chemical wastes. Often, these waste streams can contain valuable minerals and organic compounds, but are near saturation, prone to scaling, and otherwise incompatible with conventional membrane processes [8,9]. Accessing critical materials dissolved in these saline streams is a key step towards realizing a circular economy of water and minerals, while alleviating existing resource stress.

Thermal distillation is the predominant approach to desalinate **hypersaline brines**, including complete dewatering for **zero liquid discharge (ZLD)** [10–13]. However, evaporative technologies have low thermodynamic efficiency as a result of unavoidable entropy production in economically sized heat exchangers [14]; additionally, most evaporative technologies are challenged by scaling and corrosion on the surfaces of heat exchangers [15]. Alternative proposed technologies for treating hypersaline streams include forward osmosis (FO), membrane distillation (MD) [16], electrodialysis [17], high-pressure RO [18], cascading osmotically mediated RO, and counterflow RO [19]. Unfortunately, these technologies are all based on membrane separations. Hence, they are likely to be afflicted by the aforementioned practical problems, particularly degraded performance as contaminants accumulate on the membrane surface.

In the implementation of hypersaline brine desalination, solvent-based technologies are an emerging class of aqueous separations with two notable advantages over traditional approaches: (i) they are not constrained by the practical limitations of membrane systems, and (ii) they avoid the high latent heat of vaporization of water during extraction and regeneration. Conceptually, solvents can be used in two distinct processes: either in: (i) **solvent-driven water extraction (SDWE) (**Figure 1A); or in (ii) **solvent-driven fractional crystallization (SDFC)** (Figure 1B).

In SDWE desalination (Figure 1A), the solvent selectively solvates water over salt through directional solubility, thereby extracting water into the organic-rich phase (dark blue phase) while retaining the inorganic salts in the aqueous-rich phase (green phase). Subsequently, to recover the extracted water, less energy-intensive phase transitions based on solvent–water liquid–liquid equilibrium (LLE) or vapor–liquid equilibrium (VLE) can be leveraged in place of conventional evaporative technologies [20–22]. The selective extraction of water into the organic phase drives the aqueous phase toward saturation, inducing precipitation of inorganic minerals from the brine at solid–liquid equilibrium (SLE). Recent studies demonstrate that solvent extraction can recover water from hypersaline brines (~200 000 ppm TDS) and can be designed to achieve ZLD and simultaneously recover valuable minerals [21,23,24].

In SDFC, as illustrated in Figure 1B, a water-miscible solvent (dark blue phase) is used to induce solute saturation (SLE) in an aqueous solution (green phase). Unlike SDWE, the liquid portion of the mixture remains a single phase from which precipitated solids are isolated. Empirical studies suggest that target solutes can be precipitated by the organic solvent on a near one-to-one molar basis, allowing for efficient solute recovery with minimal solvent addition [23]. In practice, SDFC can be used to efficiently recover critical materials from industrial wastewater streams, recycle materials like nickel and cobalt, or produce lithium and other inorganic ions from hypersaline brine. As compared with conventional solvent extraction and ion exchange treatments, the adverse environmental impact from these raw material extractions [25] can be minimized due to reduced volumes of liquid waste residuals [26] and the reduced usage of consumable reagents [27].

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In this review, we explore the chemistry of solvent-driven aqueous separations and analyze the material classes and **solvent regeneration** mechanisms that have been studied to date. Using a molecular- to system-scale approach based on state-of-the-art chemical theories, we discuss the effects of intermolecular interactions, solution thermodynamics, and kinetics that control macroscopic separation efficacy. Molecular-level understanding is then used to elucidate key process-level design considerations necessary for energy-efficient extraction and solvent regeneration. Finally, we highlight important areas of future research that may accelerate the development and adoption of effective solvent-driven aqueous separations for water extraction and resource recovery from brines.

Water extraction for desalination and brine concentration

A historical overview of SDWE

SDWE (Figure 1A) was reported in the literature as early as 1953 by Davison and Hood [28,29], underwritten by the United States Government's Office of Saline Water. While initial developments of solvent-driven desalination were demonstrated at the pilot scale in 1964 [29], the technology was never fully commercialized. The development of the Puraq process in the 1980s revived interest in the field [30]; this was followed by advancements in directional solvent extraction (DSE) by Chen [31], application of **ionic liquids** for DSE desalination [22,32–34], and water softening and desalination with **thermally responsive solvents** by Yip [21,35] and others [36–44]. Water extraction processes using multiple and/or mixed solvents have also garnered recent industrial interest [45,46]. The spectrum of solvent functional groups explored for SDWE and SDFC is summarized in Figure 2.

Thermally responsive solvents for water extraction

In desalination, solvents used for directional or temperature-swing extraction exhibit a strong temperature-dependent solubility of water (i.e., they display thermo-responsive or thermomorphic solubility of water, while having a limited solubility in water). Detailed working principles of this liquid–liquid extraction process can be found in the literature [21,30,31,47–51] and are summarized here.

In the extraction step, the thermo-responsive solvent contacts a brine at a favorable temperature for water extraction, functioning as a liquid desiccant. At thermodynamic equilibrium, the two liquids (i.e., aqueous brine and organic solvent) are not fully miscible and form bilayered liquid phases [21,35,52]. After the water-laden organic solvent is physically separated from the **raffinate** (in this case, a concentrated brine), an induced temperature change decreases the solubility of water in the organic solvent phase. The extracted water thereby demixes and stabilizes to form an immiscible layer of desalinated product water. Depending on the organic solvent's properties, the solubility of water in the organic solvent can increase or decrease monotonically with temperature or display an asymptotic behavior beyond a critical temperature.

An ideal directional solvent should have a high water solubility that is acutely sensitive to temperature changes, such that a moderate temperature swing would produce a large yield of desalinated water. To achieve desalination, these solvents require high solvation selectivity for water over dissolved ions in the brine (i.e., a low salt solubility in the organic solvent). To suppress the undesirable solvent loss to the aqueous raffinate and product water streams, low solubility of the organic solvent in water is imperative (Figure 3A); this stark difference in mutual solubility between the organic solvent and water is the basis of directional solubility. Operationally, the solvent should be thermally stable to allow for solvent recycling between extraction and demixing temperatures.

Glossary

Anti-solvent crystallization: a process by which a solvent, commonly a molecular liquid, is used to precipitate a solute from a solution. The anti-solvent promotes solute crystallization due to the poor solubility of precipitated solute. Recent analyses suggest, however, that this solvation mechanism is incomplete and is unable to account for the solute's behavior at low concentrations.
Desalination: a process by which purified water is separated from an aqueous salt solution. Commercial technology is dominated by reverse osmosis for feed solutions with salt concentration up to up to 4 wt%.
Hypersaline brine: an aqueous solution with concentrations (total dissolved solids) greater than the ocean, generally ranging from 3.5 to 30.0 wt% (35 000–300 000 ppm). In the context of water treatment, hypersaline solutions typically have concentrations greater than ~7.0 wt% and require treatment technologies beyond those typically used for sea water desalination.
Ionic liquid: a solvent comprising salt in the liquid state. By selecting the appropriate molecular ions, ionic liquids can be hydrophilic or hydrophobic and feature water solubilities that are thermal responsive.
Raffinate: a liquid residual or by-product from impurity removal by solvent extraction.
Reverse osmosis (RO): a pressure-driven process in which a semi-permeable membrane is used to separate water from an aqueous solution. The membrane is usually made of a thin layer of aromatic polyamide that is hydrophilic.
Solvent depletion: any pathway by which useful solvent is lost, including entrainment in products (water, solutions, and solids), volatile losses to the atmosphere, and chemical contamination/degradation caused by the operating environment or conditions that renders the degraded solvent unusable.
Solvent-driven fractional crystallization (SDFC): a process by which a solvent dissolves into a concentrated aqueous solution, inducing the crystallization of salt fractions contained therein.
Solvent-driven water extraction (SDWE): a process by which a solvent selectively removes water from an aqueous brine, simultaneously

To date, a wide range of solvents demonstrating temperature-dependent solubility of water have been investigated for solvent-driven desalination, including alcohols [47,48], aliphatic acids [31,50], amines [35,51], epoxide-based polymers [30], ethers [23,52], and ionic liquids [22,33,34]. These organic solvents possess hydrophilic moieties that form hydrogen bonds and other polar interactions between the extracting solvent and water molecules, allowing for selective solvation of water from the brine. To enable the formation of biphasic mixtures at equilibrium, the solvent and brine must not be highly miscible. The desired phase separation is usually accomplished by selecting solvents with hydrophobic hydrocarbon substituent groups, which can sterically hinder the intermolecular interactions with water molecules. Further, in systems where directional bonding facilitates solubility of water, the intermolecular directional bonds can be entropically disrupted at higher temperatures [53–55]. For example, the hydrogen bond between water and an organic amine facilitates solubilization of water at low temperature; as temperatures increase, these bonds are broken, leading to reduced solubility and even lower-critical solution temperature behavior in some systems [56,57]. The relevant bonds can also be modified via inductive or conjugated electron donation to the bonding lone pair. For example, replacing a proton on an amine with an electron-donating unconjugated aliphatic group yields stronger hydrogen bonds with water.

To derive fundamental thermodynamic insights for water-organic liquid–liquid phase equilibria, molecular modeling with molecular dynamics simulation [22,58–60] and grand canonical Monte Carlo simulations have been extensively explored [61–64]. The intermolecular and interionic attractions can be parameterized based on free-energy formulations derived from density functional theory, or mathematically described using molecular force fields [62,65].

While existing empirical potentials cannot fully represent the spectrum of organic solvents explored in SDWE, they elucidate structure–function relationships between the equilibrium phase properties of solvent–water mixtures and the molecular structure and composition of the solution. In particular, steric hindrance effects are shown to be temperature-dependent (e.g., the free rotation of alkyl groups increases at higher temperatures), which can desirably heighten the sensitivity of the water dissolution in response to heat [35,54,56,66,67]. In such systems thermally driven molecular motion interrupts the hetero-interactions between water and solvent, reducing water dissolution in the solvent with

concentrating the brine and inducing the precipitation of dissolved solids.
Solvent regeneration: a process by which the product water (or solution) is removed and the solvent (or a solvent-rich composition) is recovered for reuse.
Thermal distillation: a process by which water is vaporized and separated from an aqueous solution using thermal energy from a heat source, driven by the volatility difference between the solvent and the solutes.
Thermally responsive solvent: a solvent whose physical and chemical properties alter significantly with temperature; the present work focuses on temperature-dependent changes in a solvent's ability to dissolve water.
Total dissolved solids (TDS): a measure of the content of dissolved solutes in a liquid. Solutes can include common salts and minerals such as sodium chloride and dissolved silica and critical minerals such as cobalt sulfate.
Volatile organic solvent (VOS): a carbon-based molecular solvent with a high vapor pressure, indicative of a low boiling point.
Zero liquid discharge (ZLD): a process that converts an aqueous waste solution into purified water and a solid product or solid waste.

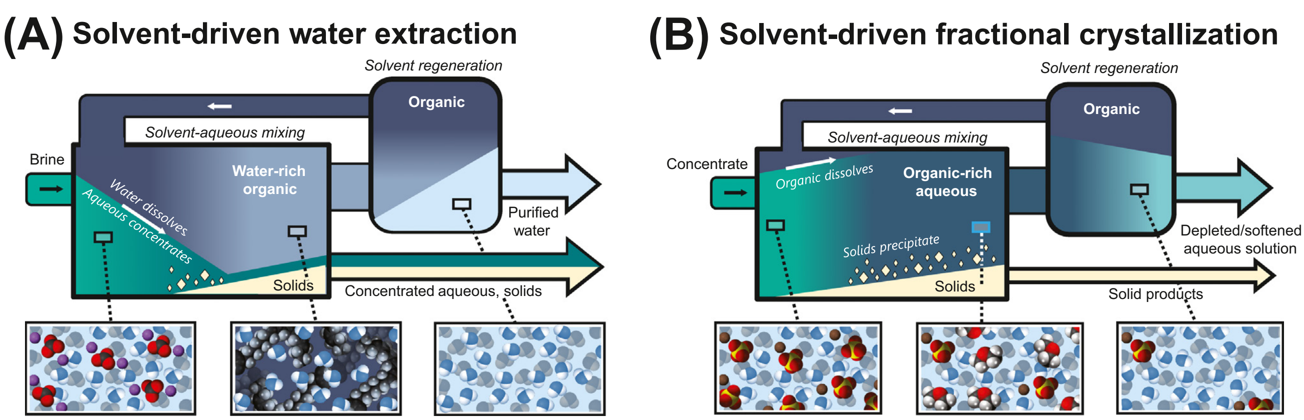


Figure 1. Schematic process diagrams for practical implementation of solvent-driven separation processes. Simplified schematic process diagrams of (A) solvent-driven water extraction (SDWE) and (B) solvent-driven fractional crystallization (SDFC). The incoming hypersaline brine (green solution) contacts the recycled organic solvent (dark blue) and attains liquid–liquid and solid–liquid phase equilibria for SDWE and SDFC, respectively. In SDWE, the water-rich organic phase is siphoned out and regenerated through a temperature or pressure swing and the product desalinated water (light blue) is collected. In SDFC, the settled solid slurry (light yellow) is collected and passed for post-treatment.

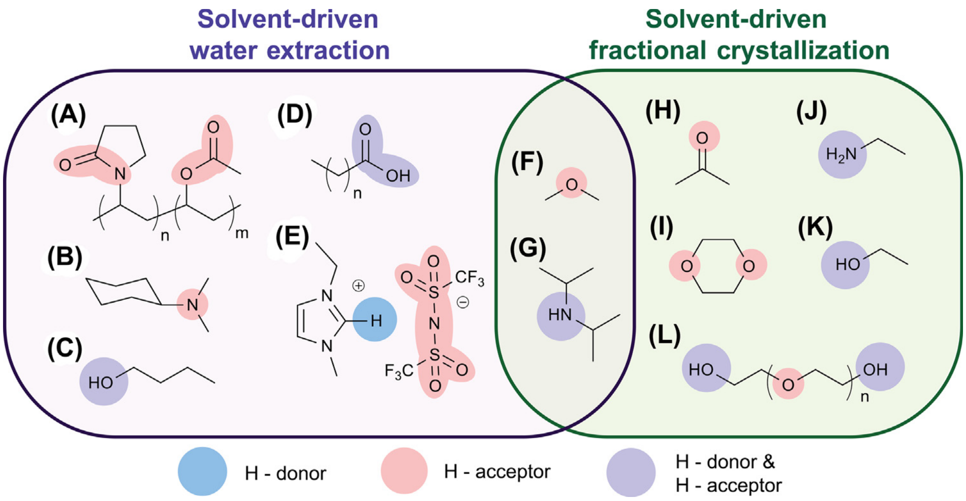


Figure 2. Solvent chemistry and functional groups relevant for solvent-driven water extraction and fractional crystallization. Solvent molecules investigated for solvent-driven separation processes in the literature, including: (A) polyvinylpyrrolidone-vinyl acetate (PVP/VA), (B) *N,N*-dimethylcyclohexylamine, (C) 1-butanol, (D) aliphatic carboxylic acid, (E) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (F) dimethyl ether, (G) diisopropylamine, (H) acetone, (I) 1,4-dioxane, (J) ethylamine, (K) ethanol, (L) polyethylene glycol. Solvents with polar functional groups capable of hydrogen bonding are selected to enhance water–solvent interactions. This is balanced against the nonpolar functionality of the hydrocarbon substituents to ensure the formation of a biphasic mixture and facilitate solvent recovery from water at equilibrium.

increased temperature. Directional homo-interactions between solvent molecules can be disrupted by increased temperature, enhancing water dissolution in the solvent. For instance, with carboxylic acids, increasing temperatures can disrupt the stable dimers between organic carboxylic acid [68] molecules, allowing for more interaction with water. Thus, the solubility of water in a variety of aliphatic carboxylic acids increases with temperature. Simultaneously, the homo-bonding between water molecules weakens at higher temperatures, making it more conducive to solubilization with an organic system [69]. Ionic liquids, on the other hand, can exhibit temperature-driven phase changes across a lower or upper critical solution temperature [22,70,71]. Consequently, they can display enhanced water miscibility with temperature increase or decrease.

The mechanism of salt selectivity of the organic solvent is more nuanced. Thermodynamic mechanisms have been proposed to explain the observed differences in salt solubilities, including the affinity of ions for the higher dielectric constant of the water as compared with the extracting solvent [31]. A detailed mechanistic understanding of salt rejection and water selection, via roles played by solvent structure and ion properties, would benefit the design and selection of solvents for water extraction [49].

Volatile organic solvents for water extraction

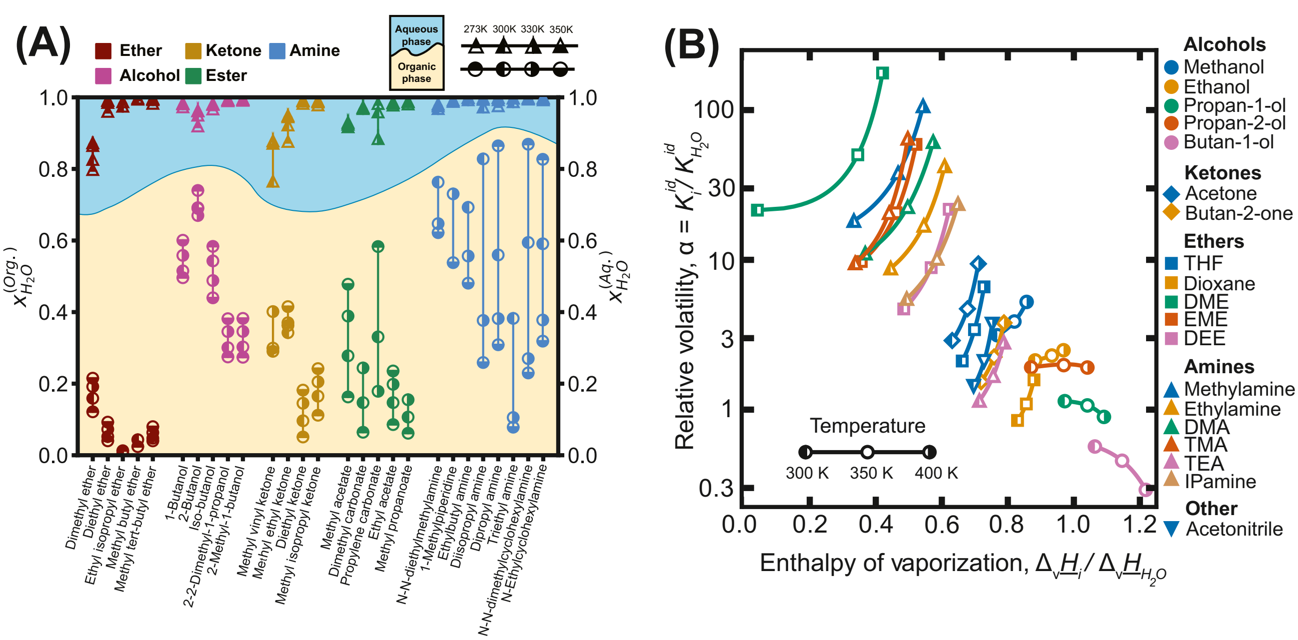
As an alternative to exploiting the temperature sensitivity of water solubility in solvents, the large volatility differences between water and aprotic organic solvents can be leveraged to allow for rapid and efficient separation of the water–solvent mixtures; in other words, exploiting the VLE behavior in place of temperature-dependent LLE. In these systems, the **volatile organic solvent (VOS)**, which can be largely vapor at standard temperature and pressure, are first pressurized and liquefied before contacting the incoming saline feed in a liquid–liquid extraction system. The chemistry of selective solvation for VOS systems is like that of the thermo-responsive solvents: a portion of the water from the saline feed is selectively solvated into the organic phase, while NaCl and other dissolved ions are retained in the aqueous phase due to the low polarity of the organic solvent. The water-laden organic phase is siphoned off and passed into a solvent regeneration system, where the organic solvent is stripped and recycled, yielding a purified water stream. The high vapor pressure of VOS enables the use of ultra-low-grade or 'waste' heat sources (<50°C) during solvent regeneration; the low VOS boiling points can be leveraged to minimize fugitive solvent losses in the concentrated aqueous brine by a pressure swing beneath the solvent's saturation pressure.

To facilitate water–VOS separation from the organic and aqueous phases, the relative volatility ratio between the VOS and water should be large (ideally >10); organic molecules with low molecular polarity and weight are ideal due to their large vapor pressure differences with water (Figure 3B). Simultaneously, to allow for water uptake, these organic molecules should possess hydrophilic moieties to interact with water and achieve high water recoveries. For instance, a sterically unhindered lone pair on a highly electronegative atom (N or O) can hydrogen bond with water to improve solvation. Solvents having a limited water miscibility generally form asymmetric hydrogen bonds with water. For example, aprotic solvents lack hydrogen atoms that can hydrogen bond with the oxygen in water. The combination of these factors inherently favors short-chain amine, ether, and ketone molecules (Figure 3A,B).

Fractional crystallization for ZLD and critical material recovery

A historical overview of SDFC

SDFC (Figure 1B), also termed solvent-driven fractional precipitation, 'solventing-out' of electrolytes, 'drowning-out' crystallization, or **anti-solvent crystallization** [72,73], is the process in which



Trends in Chemistry

Figure 3. Key chemical properties of solvents relevant to solvent-driven separations. (A) Composition of the aqueous- and organic-rich phases of liquid–liquid equilibria (LLE) of binary aqueous-organic solvent mixtures, for temperatures ranging between 273 and 350 K. These organic solvents, including short-chain ethers, alcohols, ketones, esters, and amines, are chosen due to their directional solubility characteristics [138–142]. (B) Relative volatility as a function of normalized enthalpy of vaporization for fully or partially water-miscible organic solvents, including alcohols (circles), ketones (diamonds), ethers (squares), amines (up triangles), and acetonitrile (down triangles). Temperature increases from 300 to 400 K. Relative volatility values are determined using saturation pressures calculated as a function of temperature using the Riedel equation.

targeted solutes are selectively precipitated from multicomponent solutions upon the addition of an external organic solvent. For instance, selective precipitation of potassium chloride from mixed salt solutions upon alcohol [74] and ammonia [75] addition have been previously reported. SDFC was dominant in the early development of the potassium fertilizer industry [76], where organoamines were deliberately added to hypersaline brines to selectively precipitate potassium chloride from a sodium chloride-rich solution [77].

In fractional crystallization, organic solvents have been widely explored to saturate aqueous solutions and influence the solubility limits of dissolved solutes. Beginning in the 1990s, Ng [73,78,79] and Cisternas [80–82] advanced generalized processes for fractional crystallization that included organic solvents and other inorganic reagents. Alfassi's work with SDFC for the separation of specific salts systematically explored water-miscible organic solvents such as propylamine and isopropylamine [72,83–85], leading to the development of a solubility model for fractional crystallization processes [86].

Since then, several water-miscible solvents have been studied, including ethanol [74], dioxane [87,88], organoamines [21,35,72,77,83–85,88], acetone [89], and polyethylene glycol [90]. Ireland and colleagues used ethylamine to induce precipitation of sodium chloride from hypersaline brine, reporting greater NaCl precipitation per unit mass of solvent addition than acetone and acetonitrile [91]. SDFC has been deployed in the treatment of liquid waste streams and water softening in both academic [92–94] and industrial [95,96] research. Others have applied fractional crystallization through hybridization with membranes for pharmaceutical [97], ammonization [98], and crystallization applications [99]. Condensable gases, namely short-chain ethers and amines, have recently been demonstrated as organic solvents for fractional crystallization and are being explored for a variety of applications [23,24].

Governing mechanisms for SDFC

Prior work in SDFC has identified the importance of solvent selection [88,90,95]. An ideal solvent for fractional crystallization induces an SLE boundary with minimal solvent addition and is subsequently removed rapidly from the aqueous solution with a high solvent recovery ratio [23]. However, the optimal solvent for a given process depends on the interaction between the solvent, aqueous system, and ions contained therein [88,90,95]. The complexity of solvent–solute interactions is demonstrated in the work by Goodenough and Harry, on the precipitation of KCl from a NaCl-rich solution via ammonia addition [75]. In the aqueous solution containing ammonia, molecular ammonia-solute interactions were found to increase the solubility of NaCl, while simultaneously decreasing the solubility of KCl, thereby initiating selective precipitation of KCl [100]. Notwithstanding the complexity of these systems, theoretical frameworks have been developed to interpret and predict fractional crystallization processes.

A prominent theory to interpret fractional crystallization regards the organic solvent as an anti-solvent [88,90,95], whose role parallels that of the anti-solvent used in phase inversion of a polymer [101]. This theory argues that the mixed solvent solution cannot maintain ionic solutes in a solvated state due to the altered dielectric properties of the system. As an example, under this type of theory, adding ethanol to an aqueous nucleic acid solution lowers the solution dielectric constant, as ethanol has a lower dielectric constant than pure water (24 for ethanol and 80 for water) [102]. This argument contends that the force of attraction between sodium ions and phosphate groups in the nucleic acids is magnified, permitting sodium ions to penetrate water solvation shells; as a result, the charges of the phosphate groups are neutralized by the mobile sodium ions, inducing the aggregation and precipitation of ion-paired nucleic acid salts from the solution [103,104]. However, recent studies indicate that the SLE boundary defined by solvent-induced fractional crystallization occurs on a molar basis, independent of the solvent's identity, thus contesting the proposed dielectric-based theories [23].

Empirical models developed by Alfassi and Ata showed that the mass ratio of a water-miscible organic solvent in a solvent–water mixture can be correlated with the fraction of salt precipitated from a saturated brine (SI.2 in the supplemental information online), to determine the fractional crystallization behavior of a particular solvent in interaction with various electrolytes [105]. The fraction of solute precipitated was shown to have a natural logarithmic dependence on the amount of solvent added. Alfassi and Ata described this process as 'solventing out' [105], an inversion of the 'salting out' process, whereby addition of electrolytes induces the precipitation of other solutes, frequently large biomolecules [106,107]. Subsequent experimental study and empirical modeling by Bader and colleagues explored solution thermodynamics to understand fractional crystallization in mixed-solvent systems [93]. However, these results suggest that the fraction of precipitated salt remains unchanged, despite varying initial salt concentrations, and that these fractions are independent of the individual salt in solution [93,108]. These findings are inconsistent with studies performed by Alfassi and Ata [105], which utilized the same miscible organic solvent (isopropyl amine), and are also inconsistent with the expected predictions for a process defined by a thermodynamic SLE endpoint.

Solvent recovery and regeneration

Thermally driven liquid phase regeneration

A thermo-responsive solvent used in water extraction from brines must be restored to its original composition before reuse in subsequent dewatering cycles. The water released from this regeneration step is the desalinated product water. Regeneration of thermally responsive solvents depends on the inherent temperature sensitivity of the organic solvents (i.e., temperature-driven equilibrium partitioning behavior) and the rate of demixing (i.e., the kinetics of phase separation). From an operational standpoint, the quicker the organic solvent–water mixture separates into product water and regenerated organic solvent, the higher the throughput of the process and, correspondingly, the smaller the reactor size requirement. Using low viscosity solvents has the additional benefit of reducing pumping energy and associated costs. In laboratory-scale experiments, phase disengagement times ranging from 10 min to 72 h have been reported [21,22,31,34,35]. The optimization of demixing time is an important design consideration for practical implementation.

The temperature sensitivity of a solvent varies by solvent class. For alcohols, aliphatic acids, and imidazolium-based ionic liquids, the solvent contacts the brine at an elevated temperature. Decreasing the solution temperature decreases the solubility of water in the solvent, releasing desalinated product water [49]. Amine and ether-based polymers display the opposite behavior, solubilizing water at lower temperatures and releasing water at elevated temperatures.

Recovery of the thermally responsive solvents can be achieved by temperature swinging. As illustrated in Figure 4A, the organic phase from the liquid–liquid separator (LLS) is siphoned out and its temperature raised through a series of heating and thermal energy recovery stages. At its elevated temperature, the mixture spontaneously separates into two phases in the decanter: a high purity organic-rich phase and a residual aqueous-rich phase. The regenerated organic phase is subsequently cooled before injection into the liquid–liquid extractor, while the aqueous phase is passed into post-treatment processes to derive pure water [21,22,109].

Volatility-based vapor–liquid separation

Volatile solvents used in extraction or fractional crystallization can be regenerated using vapor–liquid separation processes, ranging from evaporator-condenser systems to organic mechanical

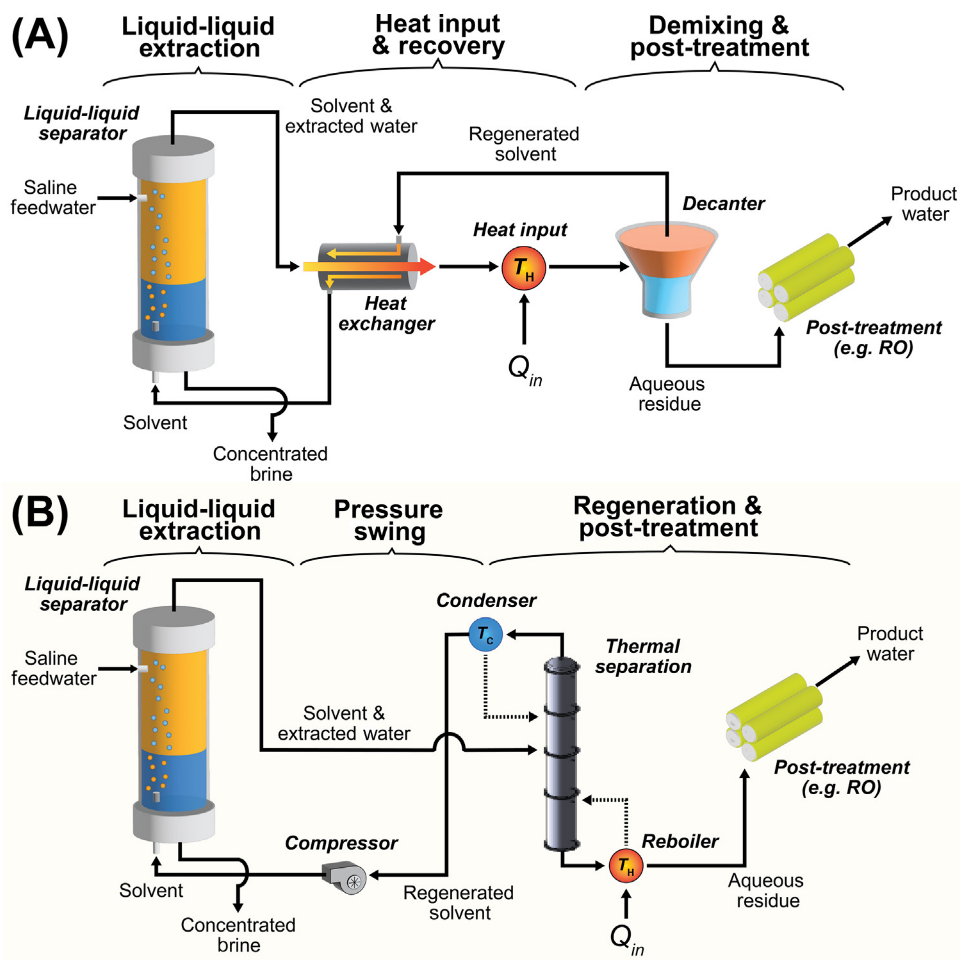


Figure 4. Process schematic diagrams for solvent regeneration. (A) High salinity water extraction using thermally responsive solvents. Solvent regeneration is accomplished by leveraging the difference in solubility of water during temperature swing. Thermal energy input is provided as an external heat source (T_H). (B) High salinity water extraction using volatile organic solvents. Solvent regeneration is accomplished by leveraging differences in organic phase volatility using pressure swing. Thermal energy input is provided in the reboiler (T_H), while the condenser is used for reflux and liquefaction. For both systems, if required, the aqueous residue can be post-treated with conventional membrane processes to obtain solvent-free product water. Abbreviation: RO, reverse osmosis.

vapor compression (OMVC), as illustrated in Figure 4B. Volatility-based separations typically comprise two steps. First, heat is used to partially vaporize the water-laden organic stream from the LLS in a boiler or evaporator, yielding a water-rich liquid phase and an organic-rich vapor phase. The liquid phase exiting the boiler forms the desalinated product water. The boiler temperature and pressure are selected to ensure that a water-rich, rather than an organic-rich, liquid phase is formed at the VLE. In the second step, the vapor phase containing the VOS is liquified in a condenser and recycled into the LLS. Additional processing may be required to remove residual solvent (see the ‘Membrane-based water-solvent separation’ section). Strategic VOS selection can minimize the energy required for solvent regeneration, while also tailoring the operation temperature.

Low molecular weight ethers and amines are particularly well-suited to volatility-based solvent regeneration, combining a high relative volatility with a lower enthalpy of vaporization than water. Higher relative volatility allows for fewer separation stages and lower residual solvent loss in the solvent regeneration system. Furthermore, choosing a VOS with a lower enthalpy of vaporization may reduce the energy consumption that results from imperfect heat recovery between the evaporation and condensation steps of a solvent regeneration process. Relative volatility values can be determined using saturation pressures calculated as a function of temperature using the Riedel equation with parameters from the literature (Figure 3B, see SI.1 in the supplemental information online). The most promising VOS candidates are organic compounds that form asymmetric hydrogen bonds with water, including dimethyl ether (DME) and trimethyl amine (TMA), which are an order of magnitude more volatile than water at 300 K.

Membrane-based water–solvent separation

Although thermally driven solvent regeneration systems (Figure 4A,B) can reduce the organic content in the water substantially, full removal (to ppm concentrations or lower) will likely require further post-treatments. Membrane processes generally achieve lower rejection of neutral solutes when compared with equivalent molecular mass electrolytes. Through multi-staging, membrane processes can potentially be employed as a final treatment process, to recover and recycle ~99% of the dissolved organic solvent in the product water. This method produces high-purity water while regenerating nearly all the organic solvent for further use. Selective membranes separations, both pressure- and temperature-driven, have been successfully deployed in the removal of dissolved high-molecular weight organics from aqueous streams. By tuning the membrane pore size distribution and porosities, FO, nanofiltration and ultrafiltration have been used to remove trace amounts of dissolved organic solvents, using a variety of counter-solvents as draw and osmotic agents [22,33]. Variants of conventional MD have recently been investigated for the recovery of low molecular weight organics, such as ammonia [110–112]. Pervaporation is also an effective means to remove trace organics from an aqueous solution [113–115]. Solvent-driven crystallizers that incorporate membrane-based filtration for high-efficacy solvent regeneration are under development for applications in water adsorption and recovery.

Process design considerations

Energy requirements

Solvent regeneration accounts for the bulk of energy consumption in SDWE and SDFC systems. Despite its thermal energy dependence, regeneration of thermo-responsive solvents can require less energy than evaporative thermal distillation [35,116]. Temperature-swing solvent regeneration avoids direct water vaporization, bypassing the large latent heat of vaporization needed for conventional water–salt separation [116]. Instead, thermal energy is expended to induce liquid phase temperature changes of the organic-rich phase (requiring only sensible heat and a small latent heat), yielding product water at a new LLE point. For instance, the Puraq process consumes up to 97.4 kWh_t/m^3 for a water recovery of 50%, using heat sources at 51°C [30]. Further, the direction of the temperature swing impacts energy and regeneration efficiencies; thermo-responsive solvents require less heat when operated at lower temperatures (close to ambient), as the saline feed and organic-rich phase need not be preheated. Assuming a 90% heat recovery, the specific thermal energy consumption (SEC) required to achieve 50% water recovery from a 1.5 M NaCl solution with DIPA is estimated to be between 39 and 77 kWh_t/m^3, using a heat source at 68°C [35]. The SEC for decanoic and octanoic acid systems is reported to be similar, at 170 and 80 kWh_t/m^3 when using a heat source at 80°C [38]. With imidazolium-based ionic liquids like [1-ethyl-3-methylimidazolium] [bis(trifluoromethylsulfonyl) imide], the exergetic demand of water extraction is estimated to be 2.4 kWh_t/m^3 at 45°C and 5.9 kWh_t/m^3 at 75°C, when calculated using ideal Carnot efficiencies [34].

Correspondingly, VOS extraction systems leverage vapor–liquid phase transition to recover pure VOS vapor from a water-rich mixture. The energy expended for VOS regeneration is minimized by selecting solvents with high relative volatilities (Figure 3B). To optimize thermal efficiency, integrated heat recovery systems, such as OMVC cycles, can be leveraged to transfer heat directly from condensing VOS vapors to the evaporating water–VOS liquid mixtures [52]. Also, heat pumps are used to transfer heat from VOS condensers to boilers. As a result, high purity water (>99% by moles) can be extracted from hypersaline NaCl solutions; an integrated DME-based OMVC cycle demonstrated 50% net water recovery from a 2.5 M NaCl feed solution, with a corresponding electricity consumption ranging from 30 to 65 kWh_e/m^3 [116].

For an incoming brine feed, the exact extraction and solvent regeneration temperatures are critical in determining both desalination performance and energy requirements. Solvent-driven processes utilize thermal energy at moderate temperatures between 25^{oC} and 80^{o}C. Thus, sustainable heat sources, including low-grade industrial heat, shallow-well or low-grade geothermal heat, and solar energy (e.g., non-tracking collectors [143] and photo-thermal converters [22]), are favorable for deployment [35]. The associated heating and insulation costs are also reduced when operating temperatures are near ambient conditions. Ultimately, fine-tuning of these operating conditions may optimize the balance between water selectivity and energy costs.

Solvent depletion

Solvent loss through entrainment into the aqueous-rich brine discharge [117] and crystallized solids [118], for SDWE and SDFC, may incur significant material and economic losses. To enable continuous operation, solvent replenishment following loss and/or degradation is unavoidable. Considering a hypothetical solvent in an SDWE system with a 10 wt% water carrying capacity, and material cost of US\$1 per kg, the estimated cost of solvent loss would be \$1/m^3 of purified water, with an idealized recovery ratio of 99.99%. The cost rises quickly to \$100/m^3 of purified water when recovery ratio falls to 99.00%, underscoring the importance of solvent recovery in ensuring economic viability.

When exposed to prolonged elevated temperatures, **solvent depletion** through chemical degeneration represents another major source of solvent loss [119]; amines oxidize through dealkylation, demethylation, and carboxylic acid formation, producing volatile compounds such as ammonia and short-chain amines. Glycols oxidize into carboxylic acids [120], while ethers decompose into alkanes, hydrogen, and carbon monoxide [119]. Ketones undergo decomposition to form ketenes, which subsequently form methane, ethylene, and carbon dioxide [121].

Adverse catalytic degradations have been reported at unfavorable solution pH. For instance, ketones undergo acid- and base-catalyzed degradation to form enols and enolates [122] [123] and ethers hydrolyze in acid to form alcohols and alkyl halides. Amines are oxidized by dissolved oxygen [124], as are ethers, forming peroxides through a slow oxidation process [125]. Catalytic surfaces and metal ion centers also contribute to solvent degeneration [126]. These may originate from corrosion within the system and surfaces in contact with the solvent, contaminants, or combinations thereof. For many feed waters, these materials will not be an issue; however, for some industrial wastewater treatments, mineral isolation processes, and material production pathways, the presence of deleterious catalytic materials will be an important concern.

Kinetic considerations

The mixing of two immiscible liquids in SDWE results in liquid phase emulsification, dispersing water droplets (dispersed phase) in the organic solvent (continuous phase) [127–129]. In the chemical separation industry, emulsion formation is ubiquitous and is carefully managed to avoid operational challenges arising from unexpected rheological behavior and slow transport kinetics. The thermodynamic stability of emulsions is characterized by droplet size distribution;

mixtures with high interfacial energies form unstable emulsions, with average droplet sizes greater than 0.1 μm [130]. In unstable emulsions, the interfacial area is reduced and the two liquids coalesce and separate into distinct phases over time. Here, we underscore the importance of controlling emulsification in optimizing SDWE by considering: (i) the kinetics of water uptake by the organic solvent during extraction, and (ii) the rate of phase stabilization during solvent recovery.

During the extraction phase in SDWE, the organic solvent contacts an incoming aqueous brine at a favorable temperature, forming water-in-organic emulsions (Figure 5). Water transport occurs between the two phases driven by the gradient of its free energy [131]. Smaller droplets accelerate water uptake by improving the interfacial-area-to-volume ratio [132]. In SDWE, opportunely, the inorganic salts stabilize the aqueous phase and ameliorate the interfacial tension, leading to reduced emulsion droplet sizes. At higher salinities, however, droplet elasticity and deformation results from the weakened interfacial tension, attenuating water transport kinetics due to fluid instability and coalescence [133,134].

Liquid phase stabilization/separation following water extraction is needed to regenerate the organic solvent for recycling. The mixture's sedimentation velocity quantifies the kinetics of phase stabilization and is dependent on buoyancy and frictional effects, as described analytically by Stokes's law (see SI.3 in the supplemental information online) [135]. To accelerate solvent regeneration, low viscosity organic solvents are used preferentially at higher temperatures to enhance droplet collision frequencies. Alternatively, effective demulsification through mechanical, electrical, thermal, and chemical agitation is also widely employed in the chemical separation industry [127].

Economics and safety

Practical factors influencing solvent selection are delineated in Table SI.1 (see the supplemental information online, also SI.4). To enable safe and cost-effective dewatering of hypersaline brine, the ideal solvent must be biologically and ecologically inert, while minimizing material and equipment costs [136]. Further, the carbon footprint from solvent manufacturing should not offset potential carbon savings from SDWE and SDFC. Organic solvents that are by-products from existing chemical manufacturing are ideal for valorization, reducing net chemical wastage and cost of solvent consumption. While VOS (e.g., ethers and alcohols) are widely produced at low carbon and production costs, they require additional safety measures in practice due to their

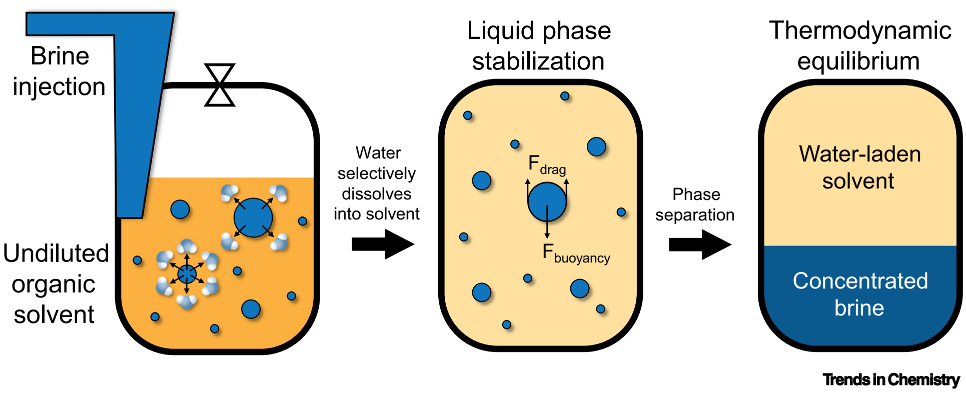


Figure 5. Kinetic limitations on water uptake due to interfacial transport dynamics. Schematic diagram illustrating the emulsification in water recovery and solvent regeneration for solvent-driven water extraction. Smaller emulsion droplet sizes lead to faster water uptake, but results in slower settling speed during solvent regeneration. The ideal organic solvent should form low interfacial tension with water and have low dynamic viscosity and large density differences with water [134].

relative high flammability. Correspondingly, while thermo-responsive solvents (e.g., amines and carboxylic acids) are biologically and physically stable in operation, they suffer from higher production costs and environmental carbon footprint. Detailed analysis of the competing requirements based on the specific application is vital to minimize net process costs of SDWE and SDFC.

Further, we stress that the regulatory frameworks for solvent usage and discharge remain underdeveloped in many applications. The toxicity standards developed for the same solvents in the chemical industry, for instance, may be inadequate to guide the production of potable water and inform disposal limitations. The chemical reaction pathways should be elucidated on potential solvent classes under the harsh conditions encountered in practical usage to rule out formation of harmful or carcinogenic by-products. The long-term environmental effects should be ascertained from life cycle analysis, to identify next-generation solvent candidates that are safer and more environmentally benign.

Concluding remarks

SDWE and fractional crystallization (SDWE and SDFC) represent a promising class of separation processes to recover critical minerals and achieve ZLD desalination from hypersaline brine. Here, we identify three open areas of research critical in enabling commercial realization of SDWE and SDFC (see Outstanding questions).

First, the thermodynamics of directional solubility and the fundamental phenomena governing the process require further investigation; in particular, potential adverse effects, arising from transport coupling in multicomponent brines [137] (including organic molecules and inorganic ions other than Na^+ and Cl^-), on water selectivity remain unquantified. Data on the effect of temperature on the multinary phase equilibria is limited, and mechanistic understanding of the molecular interactions in water–solvent–salt systems is incomplete. Advancing the science and engineering of these areas will enable the informed identification of novel solvent candidates for the selective recovery of water from multicomponent brine systems.

Second, thermodynamic and first principles-based research are also required to establish the mechanism of fractional crystallization (as described in the 'Fractional crystallization for ZLD and critical material recovery' section) between a single salt and solvent, as well as for complex systems with multiple salts. When an organic solvent and aqueous brine are combined, two separations are possible: the solvents can induce fractional crystallization of salts (SLE), or the salts can also induce solvent phase separation (LLE) [24]. For example, a solvent may precipitate a large fraction of a sparingly salt like $CaSO_4$ from a solution consisting of only water and $CaSO_4$; however, in the presence of a high solubility salt like NaCl, the solvent may phase separate with limited precipitation of gypsum. Knowledge of these variations, and the limitations they impose, is essential for many separation processes.

Finally, process design and corresponding energy consumption calculations for SDWE and SDFC processes are necessary. These process assessments need to account for heat recovery (or the lack thereof) and necessary post-processing steps for residual solvent removal and recovery. Solvent recycling is especially important, given solvent waste has historically been a shortcoming of solvent-driven aqueous treatments.

Outstanding questions

Solvent-driven aqueous separation processes enable bulk recovery of critical metals and minerals, and can achieve zero liquid discharge desalination, from hypersaline brine. How can we leverage our prior understanding of the water–solvent–salt systems to select novel solvent candidates for the targeted separation of specific ions?

Intermolecular interactions between the inorganic ions, organic solvent, and water, dictate the selectivity and water recovery potentials of liquid phase solvent-driven processes. A comprehensive data set of the multinary phase equilibria of such systems is lacking. What other solvent and salt systems should be investigated to reduce existing knowledge gaps?

What is the fundamental mechanism of fractional crystallization between the organic solvent and a mixture of inorganic ions? How do inorganic ions promote solvent phase separation (liquid–liquid equilibria) between two miscible organic solvents and water?

Efficient solvent recovery systems reduce treatment costs and enable continuous closed-loop operations. How does the choice of solvent affect the quality and quantity of energy consumed for recovery? How can such systems be designed and scaled to ensure economic and operational viability of solvent-driven aqueous separation?

A solvent must be biologically and environmentally inert to enable its safe discharge. What toxicity metrics should be developed to guide the selection of next-generation solvent candidates that are safer and more environmentally benign? What are the possible changes in a solvent's degradation pathway under the conditions typical of practical implementations?

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Declaration of interests

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.

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