

Liquid-Liquid Extraction Method for Low-cost, Low-energy Desalination of Seawater and Brackish Water

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Abstract

More than a third of the world's population lives in countries that use more than 40% of their available supply of freshwater each year, an unsustainable level of demand. Most such countries have access to a sustainable water resource: seawater. However, desalination is currently too expensive for many of the communities that need it most. This paper presents a new desalination method: solvent-based liquid-liquid extraction that exploits the selective solubility of freshwater over saltwater in a particular class of polar organic solvents at certain temperatures below 100°C. For once such solvent, *N*-cyclohexyl pyrrolidone, the calculated desalination efficiency at 3 hours was 99.6%. Optional purification with a standard material yielded acceptably pure water. The method holds promise for development as a simple, low-energy, low-cost, low-waste process that can make desalination feasible in a broader range of coastal and marine applications.

Keywords: Desalination, Liquid-liquid extraction, Seawater, Brackish water, Polar organic solvent, Sustainable water supply

1. Introduction

Of the vast amount of water on Earth, only a tiny fraction—about 1.1%—is found in surface sources and aquifers, according to observations made in 2002–2008 (Trenberth, et al., 2011). Those sources are inequitably distributed, and many regions of the world struggle with inadequate supplies of freshwater for household, agricultural, and industrial use. According to the World Research Institute, 17 countries experience “extremely high” water stress. That is, they typically withdraw more than 80% of the available supply annually (Hofste, et al., 2019), leaving little margin for extreme events. These countries represent one-quarter of the world's population. When the criterion is merely “high” stress—that is, 40% or more of available supply is

withdrawn annually—the number of at-risk countries jumps to 44, home to one-third of the global population (Hofste, et al., 2019). The issue is not just drinking water: according to the United Nations, 69% of global water withdrawal is used for agriculture; regionally that rate can be far higher, e.g., in Africa and Asia (Food and Agricultural Organization, 2020; Gleick and Cooley, 2021). Much of this water is being drawn from nonrenewable groundwater reserves at an unsustainable rate (Bierkens and Wada, 2019).

Most at-risk countries have easy geographical access to a potential solution: desalination of saltwater. Industrial-scale desalination was essentially nonexistent before the mid-1970s but expanded rapidly after 2000 (Gleick and Cooley, 2021, Fig. 10), as technologies improved and costs declined. The

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decline in cost has been just enough for affluent nations to access desalination. Today there are approximately 15,900 desalination facilities in operation, producing about 95 million cubic meters of usable water per day; about 48% of that output is produced in North Africa and the Middle East (Jones, et al., 2019). However, with current technology, desalination plants are both expensive to build and expensive to operate. As a result, this plentiful resource is out of reach for many of the people who need it.

The search for alternatives includes extraction approaches. One emerging method is based on nonionic surfactant extraction (Chakrabarti, 1997). This method shows good desalination efficiency but has limitations in the context of producing drinking water at scale: the water yield is low given the amount of nonionic surfactant used, the kinetics of separating the freshwater are too slow, and removing trace surfactant from the freshwater is difficult. The objective of this work was to overcome these limitations by using a solvent extraction method based on a principled choice of solvent (section 1.2).

1.1 Desalination Methods

Desalination refers to removal of salt from seawater or brackish water, rendering it usable for human activities. Typical seawater has a salinity of about 3%–3.5% salt (30–35 g/kg or parts per thousand [ppt]). The salinity of brackish water (typically found where freshwater meets seawater and in some groundwater reserves) is about 0.05%–2.9% (0.5–29 ppt).

The two most common technologies used for industrial desalination are reverse osmosis and distillation, at 69% and 25% of global capacity, respectively (Jones, et al., 2019, Fig. 5). In the reverse osmosis method, water is pumped through a semipermeable membrane that blocks dissolved salts but allows water to pass through. Distillation involves bringing seawater to its boiling point, heating further to convert water into vapor, then condensing the vapor back into water.

Both processes are costly. In reverse osmosis, the water is pumped through the membrane at high pressure, typically 800–1000 pounds per square inch,

which requires significant energy; operating the high-pressure pumps accounts for about 25% - 40% of the cost of water produced by reverse osmosis (LiVecchi, et al., 2019). Because of high pressures and sophisticated membrane technologies, reverse osmosis plants are also expensive to build. The ballpark figure has historically been \$1,100 per $1\text{ m}^3/\text{d}$ capacity, though that is dropping as technology improves (Gasson, 2020). Thus, construction costs for a plant producing $600,000\text{ m}^3/\text{d}$ might be close to \$700 million dollars. For perspective, in Libya, a coastal country under “extremely high” water stress, such a plant could replace about 10% of the 6.5 million cubic meters drawn daily from desert aquifers by the Great Man-Made River Project (Chibani, 2022). But construction would cost roughly 1% of the country’s gross domestic product, which is about \$48.7 million (PopulationU, n.d.).

In thermal distillation, significant energy is required first to heat the water to boiling and then to drive the phase change from liquid to vapor. As result, a thermal distillation plant uses on the order of 10 times more energy than a typical seawater reverse osmosis plant (Service, 2006). For this reason, most newer plants, especially outside the Middle East, use reverse osmosis (Jones, 2019).

1.2 Extractive Desalination

The present desalination technique (Chakrabarti, 2022) centers on a solvent-based liquid-liquid extraction method that exploits the solubility characteristics of a particular class of polar organic solvents. In particular, this method exploits the solubility of water, with an inverse temperature–solubility relation, in these solvents. In addition, like all organic solvents, this particular class of organic solvents does not dissolve salt (NaCl). The appropriate solvent is characterized by the following properties:

- dissolves water at or above 10% w/w at room temperature,
- has a boiling point above that of water, preferably above 150 °C under atmospheric pressure,
- has decreasing water solubility with increasing temperature (counter to typical solubility

behavior),

- is a liquid at room temperature,
- has differential solubility characteristics in saltwater and freshwater, such that the cloud point (the temperature at which two phases separate) is lower in saltwater than in freshwater, with the two cloud points being within about 20–100°C.

The last property is the key to the extraction methodology. At low temperature (i.e., ambient temperature) solubility of water in the solvent is high. The temperature is raised to the first cloud point and then to the second cloud point of the solvent. The different solubility of water in the solvent at the two cloud points permits separation of water from salts, as described next. The modest temperature range between the first cloud point and the second cloud point is important for cost-effectiveness.

The process is as follows. Starting with a solvent–saltwater mixture (Figure 1, A), desalination is carried out by phase separation in two steps, followed by an optional purification step.

1. The temperature of the solvent–saltwater mixture is raised to just above the solvent’s cloud point in saltwater. Just beyond the cloud point, the mixture separates into two clear phases: a freshwater-rich solvent phase (B) and a denser saltwater (brine) phase (C). During this phase separation, freshwater is extracted by the solvent and the water phase becomes salt-rich. The upper phase is processed in Step 2, and the lower phase is removed and discarded. Prior to being discarded, the brine phase can be passed through a biological treatment pond to biodegrade any trace residual solvent.
2. The freshwater-rich solvent phase (B) is heated to the solvent’s second cloud point, for freshwater, causing it to separate into two new phases: a solvent phase and a denser freshwater phase. After separation is complete, the new upper phase (D), now containing practically all the solvent, is recovered for reuse in Step 1. The freshwater lower phase (E) can be used directly (e.g., for agriculture or industry) or purified to potable levels in Step 3. Note that because solvent loss is extremely low, the bulk of the solvent can be reused repeatedly.

3. The freshwater phase (E) may be purified using conventional adsorption methods for removing polar organic solvents (e.g., activated carbon or bentonite clay), yielding water meeting drinking water standards. The adsorption media (activated carbon, clay, etc.) can be reused repeatedly, as in standard industrial purification. The trace amounts of solvent that are adsorbed would be disposed of in a customary industrial manner after the adsorption media loses its efficiency.

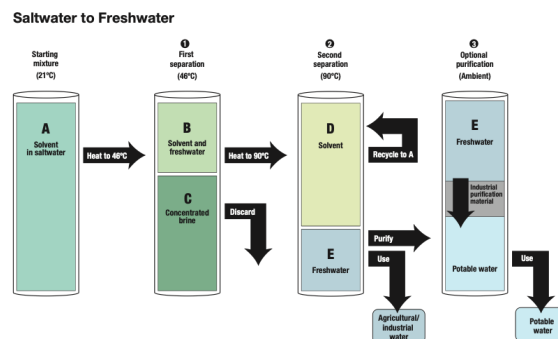


Figure 1. Schematic of novel extraction-based desalination with a dual-solubility polar organic solvent as reported here. (Proportions not to scale.)

2. Methods

2.1 Solvent Selection and Experimental Design

Candidate solvents were identified by searching the literature for compounds with appropriate characteristics. Screening focused first on polar solvents with low cloud points. Results of initial testing narrowed the focus to polar aliphatic compounds (either cyclic or acyclic). Because solubility data for some candidate compounds were unavailable or outdated, solubility curves were reconstructed or confirmed.

Promising candidates were tested to confirm the needed solubility characteristics. Initial tests broadly explored the efficiency of salt extraction (Step 1) and the extraction kinetics. In this initial screening, three candidates were tested: NP-9 (Dow Chemical), 2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol (Triton X-100, Dow Chemical), and *N*-cyclohexyl pyrrolidone (CHP, Dow Chemical). CHP had the best efficiency, and all remaining tests focused on this solvent. Next, small-volume tests with CHP were

done for several separation times to further test kinetics. Finally, both extraction steps were performed with CHP to obtain the final purity.

2.2 Measurement Methods

For all tests reported here, the solvent was mixed with a salt solution of approximately 3.5% salinity. In all cases, the solvent–brine mixture was initially held at 21°C in a constant-temperature water bath (1-chamber, 3-liter Digital Thermostatic Water Bath, Joan Lab Equipment Co., Ltd, Huzhou City, People’s Republic of China).

Separation of water from brine (Step 1) was achieved by heating the solvent–brine mixture to an appropriate temperature in the water bath (46°C for CHP) and holding at that temperature for the duration of the separation. After the separation period, the aqueous (lower, brine) phase was removed and measured for salinity using a water quality meter (3-in-1 digital pH meter with pH/total dissolved solids/temperature, unbranded). A calibration curve was generated (Figure 2) and used to determine salinity values.

Separation of freshwater from solvent (Step 2) was achieved by heating the first solvent (upper) phase from Step 1 to 90°C. The resulting second aqueous (lower, freshwater) phase was removed, and the volume was recorded to 2 significant figures. The salinity of the second aqueous phase was calculated by mass balance using the amount of NaCl present in the brine phase (to 3–4 significant figures; GEMINI-20 Portable Precision Digital Milligram Scale), and its solvent concentration was calculated using the solvent solubility curve.

Desalination efficiency was calculated by first drying the aqueous (brine) phase from the first separation step and weighing the amount of dry NaCl present. Then the percent desalination was calculated as weight of NaCl in aqueous phase divided by the calculated weight of starting NaCl (NaCl wt% x volume).

Purification of the freshwater (optional Step 3) was demonstrated with activated charcoal and bentonite clay. A solution was created that mimicked the <0.1% final CHP concentration in several of the extraction tests. The solution was agitated for 2

minutes with the charcoal or clay and then vacuumed twice through a Büchner funnel/filter setup. The amount of solvent was measured by boiling off the remaining water and weighing the excess material to 2 significant figures.

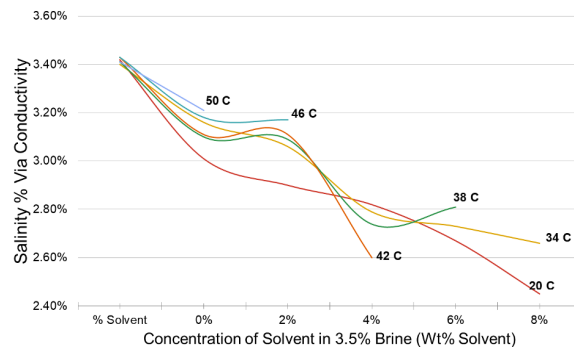


Figure 2. Salinity meter calibration curve, giving salinity vs. temperature and solvent concentration for *N*-cyclohexyl pyrrolidone (CHP, Dow Chemical).

3. Results

Solubility curves were recreated or confirmed for the candidate solvents. The curve for CHP is given in Figure 3.

In a screening test of desalination efficiency and kinetics, CHP far outperformed two other common nonionic surfactants, NP-9 and Triton X-100. Over a separation time of 3 hours, CHP reached 100% extraction (20% solvent; 46°C). In contrast, NP-9 had reached only about 60% extraction at 3 hours (5%, 60°C), and Triton X-100 showed no extraction at all (5%, 68°C). The test with Triton X-100 was allowed to run to completion: it took about 24 hours to reach 100% extraction. (Concentrations and temperatures for these tests were selected on the basis of solvent properties.)

Initial small-volume testing of the first extraction step showed that CHP had a calculated desalination efficiency of near 100% for all separation times tested (Table 1). Testing of the full process with a larger volume yielded a calculated desalination efficiency over 99% for a separation time of 3 hours (Table 2).

Purification tests with activated charcoal and bentonite clay confirmed that conventional purification methods yielded highly pure freshwater.

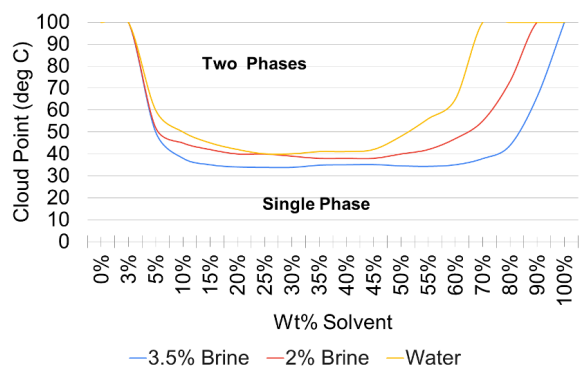


Figure 3. Solubility curve of *N*-cyclohexyl pyrrolidone (CHP, Dow Chemical) in 3.5% brine, 2% brine, and water. Solubility of the solvent is indicated by its cloud point: the temperature at which a solution (single phase) separates into water and solvent (two phases). The cloud point varies with the amount of solvent in the solution; this variation is shown in the shape of the solubility curve. The cloud point is also affected by the salt concentration of the solution, as shown by the different curves for 3.5% brine, 2% brine, and water (0% brine).

Table 1. Effect of first extraction duration on desalination efficiency with CHP.^a

Solvent Volume (mL)	Brine Volume (mL)	Solvent Load (%)	Salinity, Initial Brine (%)	Separation Time, Step 1, 46°C, (hours)	Salinity, Extracted Brine (%)	Calculated Desalination Efficiency (%)
2.8	11.2	20	3.51%	1	3.96	98.9
2.8	11.2	20	3.51%	2	4.18	100
2.8	11.2	20	3.51%	3	4.17	100

^aSolution held at 21°C in constant-temperature water bath until extraction protocol launched.

Table 2. Freshwater extraction from brine with CHP.^a

Solvent Vol. (mL)	Brine Vol. (mL)	Initial Brine Conc. (%)	Total NaCl (g)	Separation		Separation			Desalination Efficiency (%)	
				Time, Step 1, 46°C (h)	Adjusted Salinity, Extracted Brine (%)	Time, Step 2, 90°C (h)	Total NaCl in Brine Phase (g)	Total NaCl in Freshwater (mg)		Volume Efficiency (%) ^b
10	40	3.51	1.40	1	4.08	1.40	2	1.87	11	99.0
20	80	3.51	2.81	1	3.97	2.78	2	29.18	10	91.7
20	80	3.51	2.81	2	4.04	2.79	2	15.00	11	96.0
20	80	3.51	2.81	3	4.07	2.81	2	1.49	11	99.6

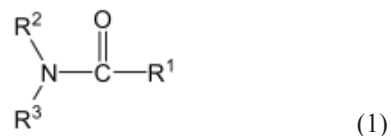
^a Solution held at 21°C in constant-temperature water bath until extraction protocol launched.

^b Volume efficiency calculated as volume of freshwater recovered per unit of input brine (i.e., units of freshwater per unit of saltwater).

4. Discussion

4.1 Surfactant Chemistry

Both aromatic or aliphatic solvents can be suitable, but aliphatic structures (either cyclic or acyclic) are preferred for biodegradability considerations. Structures include amides (Eq. 1), sulfones and sulfoxides (Eq. 2), and alcohols (Eq. 3):



where suitable structures of the R groups are defined in Chakrabarti (2022). These R groups are used to balance the overall polarity of the molecule and thereby determine the total solubility of the molecule in water.

To be usable for desalination using this method, the solvent must, in addition to the physical properties noted in section 1, derive its polarity from one or more groups selected from amide, substituted amide, sulfoxide, sulfone, hydroxyl, and ether groups.

Optimal candidates determined to date are shown in Table 3. Note that although the structure options specified in Chakrabarti (2022) serve to define an envelope of suitable structures, actual solubility properties and extraction efficiency must be verified by testing.

Table 3. Candidate polar organic solvents for low-temperature solvent-extraction desalination.

Compound
cyclohexyl pyrrolidone <i>also known as</i> <i>N</i> -cyclohexyl-2-pyrrolidinone <i>N</i> -cyclohexyl pyrrolidone
<i>N</i> -dodecyl pyrrolidone ethylene glycol monobenzyl ether 2-ethyl-butyl glycol <i>N</i> -hexyl glycol 4-methoxy-4-methyl-penta <i>N</i> -2-ol <i>also known as</i> 4-methoxy-4-methyl-pentanol-2

4.2 Benefits of This Extractive Approach

The properties of the solvents were chosen with a view to making the process practical for the widest possible range of applications and communities. The following were among the considerations.

The high extraction efficiency demonstrated for this class of solvent is important for three reasons. First, the process directly and relatively rapidly produces agriculturally usable water, without further treatment. Second, the very low concentration of solvent left in the freshwater fraction means that well-established industrial purification methods can be used to reach the purity required by regulatory bodies for drinking water (e.g., in the United States, the limit for foaming agents, i.e., surfactants, is 0.5 mg/L (U.S. Environmental Protection Agency, 2022). Purification tests confirmed complete or near-complete removal of the solvent, indicating that solvent concentration in treated water would be far

below the regulatory limit. Third, the completeness of the solvent–freshwater separation means the solvent can be reused many times before needing to be replaced, for lower operating costs.

In general, the process makes desalination accessible to communities across a broader range of geographic and economic conditions. Overall capital costs will be low because the process will use standard industrial extraction equipment. The relatively low solubility temperature limits the energy requirements for the process compared to distillation. The energy requirements are also low compared to reverse osmosis because no pressurization is required. As a result, this method would be feasible for communities whose access to fuel is limited by economics or geography (e.g., islands or remote coastal areas). Together, low-energy operation and closed-loop solvent design mean that a desalination option is now available for ecologically sensitive regions. Finally, the process will work for water with low initial salinity (brackish water); this characteristic, along with the low ecological impact, means that desalination becomes an option in relatively sensitive tidal river ecosystems.

Separate from municipal water supply and agricultural needs, a simple extraction method would also have advantages for marine applications where weight and energy consumption preclude use of existing technology.

5. Conclusion

The present work points the way to low-cost, energy-efficient desalination at industrial scale. Because extraction processes are ubiquitous, equipment design should not be a significant barrier to scale-up. However, because the process depends on solubility behavior with temperature, it will be important to explore the sensitivity of the extraction to temperature control. For designing for high throughput, the fast kinetics of CHP are promising: because extraction reaches 100% in 3 hours, there is room for optimizing dwell time vs. yield. For industrial scale-up, development will be required to optimize solvent recycling for long-term use. For example, potential regeneration cycles and replacement intervals will need to be investigated.

Predicting future water supply and demand on a global level is difficult because of the complex interactions among population growth, trade, industrialization, politics, climate change-related disruptions in precipitation, and improvements in conservation and efficiency (Oki and Kanae, 2006). Nevertheless, at the community and regional level, expanding the availability of usable water will open opportunities for economic development, improved quality of life, and greater resilience in areas that currently operate within a narrow and vulnerable window of viability.

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