

# Analysis of saline water desalination by directed solvent extraction using octanoic acid



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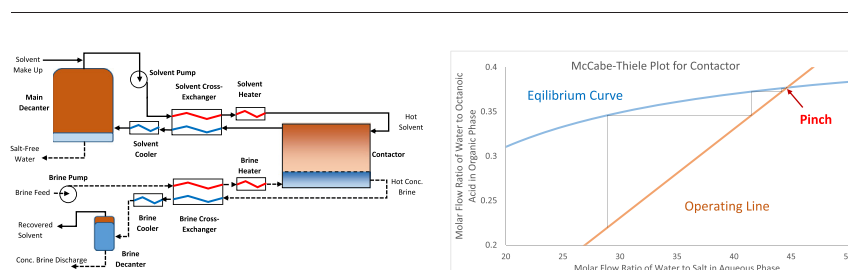
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## HIGHLIGHTS

- Feasibility study of extractive desalination using octanoic acid directional solvent
- Experimental water partitioning data fitted to extended UNIQUAC model
- Process severely pinched; contactor offers a maximum of only 3 theoretical stages.
- Extractive desalination over 25-fold more capital intensive than reverse osmosis
- Extractive desalination over 10-fold more energy intensive than reverse osmosis

## GRAPHICAL ABSTRACT



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## ABSTRACT

The thermodynamics of partitioning of water between saline aqueous phase and organic phase was studied to determine the feasibility of desalination by directed solvent extraction using octanoic acid as the solvent. The experimental results were fitted to an extended UNIQUAC model and used in process calculations. Extractive desalination was found to have an order of magnitude higher consumption compared to the state-of-the-art in desalination using reverse osmosis. The equivalent electricity consumption in extractive desalination is estimated to be approximately 30 kWh/m<sup>3</sup> of salt-free water as opposed to 3–5 kWh/m<sup>3</sup> for a reverse osmosis process. Capital costs for the heat exchangers alone are 25-fold higher than the total capital expenditure for an equivalent reverse osmosis process. A fundamental thermodynamic obstacle to the performance of extractive desalination was discovered; the contactor, the device used to countercurrently contact the organic phase with the saline aqueous phase in order to extract water into the former, is severely pinched and can yield only three effective theoretical contact stages. This leads to excessively large circulation of solvent and the concomitant losses in pumping and temperature swing.

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## 1. Introduction

The United Nations General Assembly declared access to water and sanitation as a fundamental human right in 2010, effectively giving each person a right to 50–100 l of potable water per day at costs not exceeding 3% of the household income [1]. Current supplies of fresh-water in the form of rain, surface-waters and ground-water reserves are

already under severe pressure in many parts of the world; and at least one study claims credibly that the evapo-transpiration mechanism, that supplies most of the world's fresh-water through precipitation, will not be able to keep up with freshwater demands of the rising population [2]. In this context, winning freshwater from the unpotable sea-water (30–40 g of salt per liter of water) seems to be a conceptually attractive proposition; and even now, large fractions of the populations of the countries of the Persian Gulf rely on desalination of sea-water for their freshwater.

Around 2012, global desalination capacity was 66.4 Mm<sup>3</sup>/day and by 2015 is expected to increase around 100 Mm<sup>3</sup>/day. About 64% of this global production is based on membrane processes while the rest is based on thermal methods [3]. A major concern with both approaches is capital and operating costs: the cost of a thermal/membrane based desalination plant would be US\$ 1000 for every m<sup>3</sup>/day capacity and the production cost would be US\$ 0.7/m<sup>3</sup> of fresh water [4]. These numbers are large enough for several researchers to be skeptical of the use of desalination to meet the world's freshwater needs [2,5]. Although the current state-of-the-art is more than adequate to address the mandate of the UN General Assembly for freshwater for personal consumption,<sup>2</sup> it cannot meet the requirement of irrigation which is an order of magnitude higher [6].

Both the thermal and membrane-based techniques have been adequately reviewed elsewhere [4,7–9]. Very briefly, the thermal methods remove salt-free water from saline water by vaporization followed by condensation while the membrane methods force water through a membrane that is impermeable to ions. A major challenge faced by thermal methods is the requirement of provision of extended metallic surfaces for heat transfer which must also be resistant to salt-water corrosion. Membrane methods must also provide extended semi-permeable surfaces that must stand up to high pressure differential (as much as 50–100 bar) and must be fed a thoroughly pretreated brine to prevent fouling and/or membrane matrix degradation. Hence, the current state-of-the-art in desalination faces essentially a problem of materials. Further, plants operating both types of technologies, but especially the membrane-based technologies, require highly trained staff; which make it difficult to implement these solutions in locations deemed undesirable e.g. remote villages.

There are several alternatives to the above two strategies, notably freezing, electro-dialysis, solar-stills which have found niche applications. However, these and the two main desalination strategies have been around for several decades and can be considered mature i.e. only incremental improvement may be expected of them.

Recently however, directed-solvent desalination has been revived as a technology [10–12]; where water is extracted into an immiscible solvent at high temperature and removed from it by phase decantation at a lower temperature. Desirable characteristics of such a directional solvent are high capacity for water, high temperature variation of capacity for water, negligible solubility of solvent in water and insolubility of salt in solvent. The idea of directed solvent desalination received much interest in the 1960's when tertiary and branched secondary amines (5 to 6 carbon atoms long) were considered most promising [13,14] but fell out of favor due to the expense as well as the relatively high water-solubility of these amines. Later, extraction into a hydrophilic-hydrophobic co-polymer gel was attempted [15] but was rejected for co-dissolution of an unacceptably high amount of salt. The important breakthrough for this technology was the discovery in 2010 that the lower fatty acids are excellent directional solvents for desalination, having a reasonable capacity for water, inability to dissolve salts and having a low solubility in water and further being benign to human health at several times these concentrations (for example, octanoic

acid is found to the extent of 7% in coconut oil [16] and at the level of ~1000 ppm in milk [17]).

To obtain a quantitative estimate of the feasibility of this technology, we considered it an interesting problem to try to quantify the liquid-liquid equilibria of octanoic (caprylic) acid, which was identified as promising for further development [11]. We have performed simple process calculations to evaluate the feasibility of extractive desalination using this solvent and have discovered that, per cubic meter of salt-free water generated, the process consumes work equivalent to ~30 kWh and loses ~3 kg of octanoic acid via dissolution in the aqueous phase. Further, the cost of the heat-exchangers alone amounts to ~US\$ 25,000 per cubic-meter-per-day capacity. Both the consumptions and the capital expenditure are an order of magnitude higher than the current state-of-the-art; which rules out widespread use of this technology in its present state. We have further shown that even under the most ideal conditions, extractive desalination with octanoic acid as a solvent is only as efficient as commercialized reverse osmosis processes owing to a fundamental thermodynamic obstacle to the performance of directed solvent desalination with octanoic acid: the solvent-water contactor is severely pinched and can yield only three effective contacting stages.

## 2. Experimental

The experimental protocols for generating liquid-liquid equilibrium data for octanoic acid with aqueous solutions of sodium chloride is described below.

### 2.1. Materials

Octanoic acid (99%) was purchased from VVF Ltd. Sodium chloride (Extra pure AR grade) was purchased from SD Fine-Chem Ltd. Deionized water was obtained from a DI water plant (Sartorius Stedim Biotech, Arium 611VF).

### 2.2. Contacting and equilibration protocol

Aqueous solutions of sodium chloride of concentrations 3, 5, 7 and 10 (%w/w-water) were prepared. Octanoic acid, the directional solvent, composed the bulk of the organic phase. For each experimental run, 5 ml of one of the aqueous sodium chloride solutions along with 5 ml of octanoic acid was added in a 15 ml glass sample bottle with screw cap. Sample bottles were agitated in a temperature controlled orbital shaker (Orbitek, Scigenics Biotech) at 380–400 rpm for 1 h to equilibrate the samples. Four different temperatures were investigated: 26, 40, 50 and 60 °C. After equilibration, the samples were kept still for phase separation while maintaining their respective temperatures. Two distinct phases formed after approximately another hour. A sample from each phase was taken out for analysis using a plastic syringe.

### 2.3. Analytical methods

#### 2.3.1. Organic phase

The organic phase was octanoic acid saturated with water. The water content of this phase was analyzed using Karl-Fischer titrations. The sample was heated back to the equilibration temperature to ensure homogeneity before being injected into the Karl-Fischer apparatus (795 KFT Titritino, Metrohm).

#### 2.3.2. Aqueous phase

Only trace amounts of octanoic acid partitioned into the aqueous sodium chloride phase. Since octanoic acid was the only organic material in the system, total organic carbon (TOC) concentration, obtained from a TOC analyzer (SGC ANATOC Series II), was used for quantifying its aqueous phase concentration. The samples were heated to their equilibration temperatures to ensure homogeneity prior to analysis. The

<sup>2</sup> A simple back-of-the-envelope calculation shows that meeting the UN-General Assembly's mandate would require a per-capita investment of US\$ 50.00 and per-capita yearly expenditure of US\$ 13.00 i.e. less than 3% of US\$ 600 which is the per capita GDP of even a low income country like Somalia.

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