SUPPLEMENTARY INFORMATION

Very Low Temperature Membrane Free Desalination by Directional Solvent Extraction

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Supplementary Text

Materials and Methods

A 3.5% w/w solution of sodium chloride in distilled water was made to simulate sea water. The materials were heated and stirred on a digital hot plate (HS 40, Torrey Pines ® Scientific, Carlsbad, CA). 200 ml of decanoic acid was heated in a beaker to different temperatures between 40 and 80 °C (Fig.1A). 10 g of salt solution was mixed with the solvent while stirring and as an emulsion formed the clear beaker contents turned cloudy (Fig.1B). Stirring was continued at elevated temperature for 60 minutes. During this time some water dissolved into the solvent, leaving behind water droplets highly concentrated with salt, as the emulsion becomes clearer due to shrinking of saline water droplets (Fig. 1C). The un-dissolved water droplets, being denser than decanoic acid, gravitationally separated to form a layer of brine at the bottom of the beaker, leaving a clear layer of decanoic acid containing dissolved water above (Fig.1D). This clear upper layer was then decanted by carefully pouring off into conical tubes maintained at 34 °C in a water bath (Fig.1E). The cooling of decanoic acid reduced the solubility of water in it facilitating precipitation of pure water droplets. The contents of the conical tubes appeared to turn cloudy again providing visual evidence of this precipitation (Fig.1F). These tubes were allowed to stand at 34 °C for 72 hours to permit for complete precipitation of water and its gravitational separation from the acid. When most of the precipitated water had separated, two clear layers made of water (bottom) and decanoic acid (top) were observed (Fig. 1G) This water was recovered by piercing a hole in the bottom of the conical tubes and carefully collecting in another tube (Fig. 1H). Care was taken to ensure that no solvent was collected along with the precipitated water. The salinity of the recovered water was measured using an ATAGO® salt meter (Atago USA Inc., Bellevue, WA). The weights of recovered water and of decanoic acid in the conical tubes were also recorded to calculate yield of pure water per unit volume of decanoic acid.

To determine the effect of salt presence on water yield, the saline solution was replaced with distilled water and the above steps, except salinity measurement were repeated. Furthermore to obtain a baseline estimate of solubility of water in decanoic acid at the lower process temperature (34 °C), 10 g of decanoic acid was maintained at 34 °C and while stirring distilled water was added to it in increments of 0.2 g, 0.1, and several increments of 0.01 g until no more water dissolved after stirring for 180 minutes.

Samples of recovered water were collected and allowed to stand for 72 hours. In order to check whether any decanoic acid was left in the recovered water, a small sample (137.595 mg) was measured on a UMT 2 scale (Mettler Toledo, Columbus, OH) and heated on a VWR 575 Hot Plate (VWR Scientific, Westchester, PA) to 120 °C. This was done to boil off the water until a brownish white residue was left behind. The sample was weighed again to obtain the weight of the remaining salt and decanoic acid. This was found to be 0.087 g. Since the salt concentration of the original sample was known (0.06% = 0.082g) the difference was subtracted to calculate the weight of the residual decanoic acid. This was calculated to be 0.005 mg which is equivalent to a concentration of 36 ppm.

Illustration of Hydrogen Bond Formation between Water and Decanoic Acid

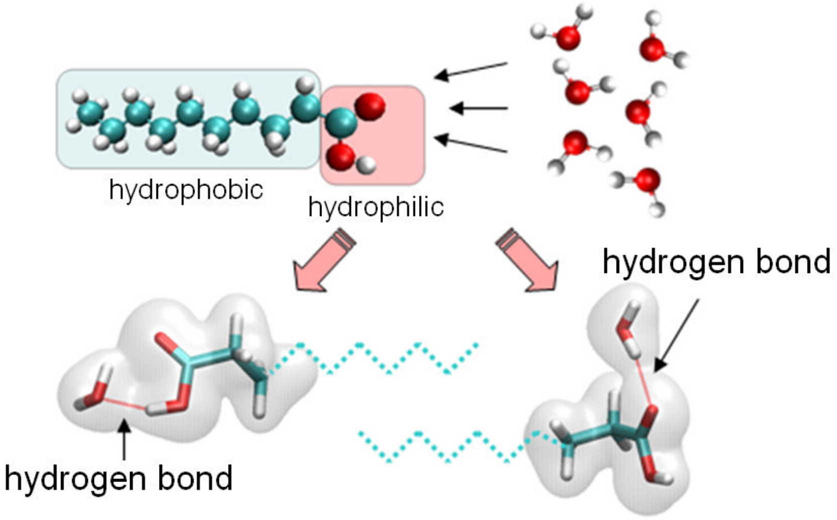

Figure S1. Illustration of hydrogen bond formation between water and decanoic acid. Blue = Carbon; Red = Oxygen; White = Hydrogen.

Molecular Dynamics Simulation and Solvation Free Energy Calculation

Molecular dynamics simulations are performed using Gromacs[S1] on Ranger cluster of Texas Advanced Computing Center. The optimized potential for liquid simulation (OPLS)[S2] together with the TIP5P[S3] water potential model is used to simulate the decanoic acid and water, respectively. The bonds are constrained by the Parallel Linear Constraint Solver (P-LINCS)[S4] so as to make the time step 2 fs. Amorphous decanoic acid is generated using the modified Markov process[S5].

To describe a solution from the thermodynamics point of view, we calculate the free energy of salvation using the thermodynamics integration (TI) with the coupling parameter method. The details of this method can be found in different sources such as[S6]. Here, a brief description of the TI method is presented.

The Hamiltonian of the system, H, is artificially changed through a coupling factor λ using the soft-core method[S7]. The free energy difference in any two states, ΔG_{1-2}, can be calculated using the coupling factor method:

$$\Delta G_{1-2} = \int_{\lambda_1}^{\lambda_2} \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle d\lambda \tag{S1}$$

Since free energy is a state parameter which does not depend on the path of state change, we can take any route to perform the integration.

The salvation free energy is the work required to transfer a molecule from the bulk phase into solution and can be calculated using a certain thermodynamic cycle. Figure S2 shows an example of such thermodynamic cycle which describes a decanoic acid molecule dissolves in water. As depicted in Fig. S2, the dissolution of a decanoic acid molecule in water is equivalent to the following three steps: (1) The decanoic acid molecule is changed from the real entity to its dummy in vacuo (ΔG_1); (A "dummy" molecule is a fictitious molecule without non-bond interactions with itself and its environment.) (2) The dummy decanoic acid is inserted into the water solution (ΔG_2); (3) The dummy decanoic acid recovers the non-bond interaction with itself and the surrounding water molecules in the solution ($-\Delta G_3$), changing into its real state. Since the dummy decanoic acid does not interact with the environment, the work required to put a dummy molecule to the solution does not require any work, meaning $\Delta G_2 = 0$. As a result, the solvation free energy is expressed as:

$$\Delta G_{solv} = \Delta G_1 - \Delta G_3 \tag{S2}$$

By calculating ΔG_1 and $-\Delta G_3$ separately using eq. (S1) through molecular dynamics simulation, the free energy of salvation can be calculated.

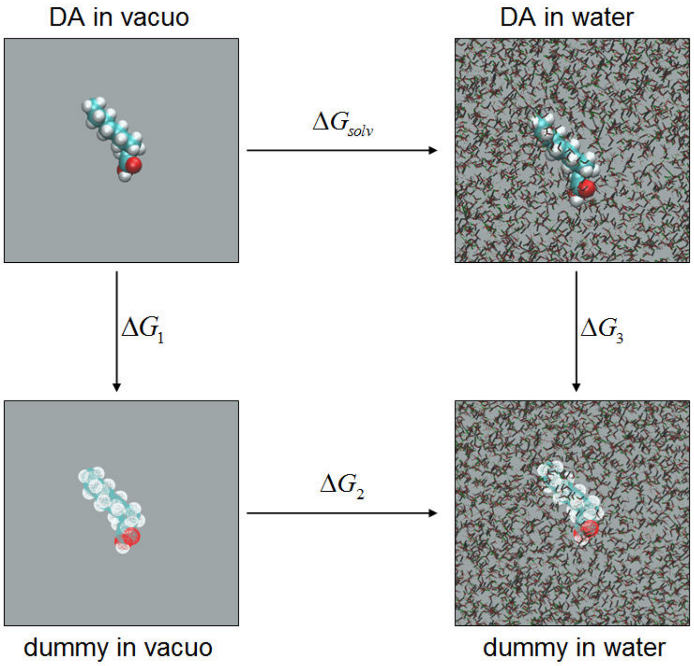

Figure S2. Thermodynamic cycle describing decanoic acid solve in water.

In a Gromacs free energy calculation, changing a molecule from its real entity to dummy is achieved by gradually switching off its non-bond interactions with the environment and itself, including van der Waals (vdW) and electrostatic interactions. This is done through appropriate formulation of the λ dependent non-bond interactions (see Gromacs manual[S7] for details of the λ dependent Hamiltonian) with $\lambda = 0,1$ corresponding to the real state and the dummy state, respectively. A number of discrete λ points are chosen between 0 and 1, and $\left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle$ is evaluated analytically in each molecular dynamics simulation with different λ values. Numerical integrations are then performed to get the free energy difference according to eq. (S1). Due to the hydrogen bond between the solvent and solute, a very dense λ point grid is needed near $\lambda = 0$. In our calculations, 60-80 λ points are used for each free energy calculation. Errors are analyzed using block averaging.

Amount of Decanoic Acid Dissolved in Water

Molarity of decanoic acid in water solution S is calculated as

$$S = \exp\left(-\Delta G/RT\right)/V_m \tag{S3}$$

where ΔG is the free energy difference, R ideal gas constant, T temperature and V_m molar volume of bulk amorphous decanoic acid. By taking $\Delta G = 16.04 - 9.82 = 6.22 Kcal/mol$, $V_m = 191.96 cc/mol$, and $T = 300K$, we found $S = 1.6391\times10^{-7} mol/cc = 2.8192\times10^{-5} g/cc\_water = 28.192 ppm$.

Exergy Analysis

The energy consumption of the laboratory batch process described herein was calculated and then extrapolated to estimate the energy requirement of a continuous industrial process at a directional solvent desalination plant.

The experiments were cycled between a lower temperature of 34 °C (T_o) and a varying top brine temperature (T_{TBT}). Thus, the energy consumption of the process for heating up the decanoic-saline solution mixture per unit mass of recovered fresh water is simply given by:

$$Q_{lab} = (\frac{C_{DA}}{Y_w} + C_w)\left(T_{TBT} - T_o\right) \tag{S4}$$

where Y_w represents fresh water yield and C_{DA} and C_w represent the specific heats of decanoic acid and water respectively.

In a continuous industrial process heat is exchanged between streams of decanoic acid, one of which is cooling down and the other is heating up. The amount of energy lost in this heat transfer will be determined by the effectiveness (η_{HE}) of the heat exchanger, and the energy requirement will then be given by:

$$Q_{ind} = Q_{lab}(1-\eta_{HE}) \qquad \text{(S5)}$$

In this case a practical heat exchanger effectiveness of 0.8 is assumed[S8].

To appreciate the benefit of using low temperature sources it is imperative is calculate the exergy consumption, i.e. the maximum work that can be derived from the energy consumed. This depends on the TBT of the process is given by:

$$E = Q_{ind}(1-\frac{T_O}{T_{TBT}}) \qquad \text{(S5a)}$$

Equation (S5a) may be re-written as

$$E = (\frac{C_{DA}}{Y_w} + C_w)(1-\eta_{HE})(T_{TBT} - T_o)(1-\frac{T_O}{T_{TBT}}) \qquad \text{(S5b)}$$

This gives the maximum amount of work that may be extracted from the heat used to fuel the process and provides for fair comparison with the power requirements of RO and MSF processes.

Supplementary References

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