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Directional solvent for membrane-free water desalination—A molecular level study

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Directional solvent for membrane-free water desalination—A molecular level study

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Development of desalination technologies has been identified as vital to fulfilling future water demand. In this paper, we use molecular simulation to demonstrate that decanoic acid can dissolve water but reject salt, and itself is insoluble in water. We have recently demonstrated that the directional properties of decanoic acid together with the temperature dependence of water solubility in decanoic acid can be utilized to design a desalination process which extracts water molecules, using the decanoic acid as a directional solvent, from saline source at a higher-than-ambient temperature, and precipitate out the water from the solvent at a lower temperature to recover pure water. Such a desalination process is membrane-free and can make use of low temperature heat sources. Solubility properties between water and decanoic acid are characterized through free energy calculations, and water-decanoic acid interdiffusion processes are studied by molecular dynamics simulations. This work also exemplifies an approach to characterize other possible directional solvents. © 2011 American Institute of Physics. [doi:10.1063/1.3627239]

I. INTRODUCTION

By the year of 2025, two thirds of the world population will be living in water stressed conditions, if the present global consumption patterns continue.¹ Ocean contains 97.5% of the global water, thus making desalination of the seawater a promising route to meet the future demand in water supply. However, <1% of the total world water consumption is produced by desalination plants as reported in 2002.² The main reason is that desalinations of all types are capital-³ and energy-intensive,⁴ making their products about 3.5 times more expensive than water from existing sources.⁵ The National Research Council roadmap for water desalination sets a target of 50–80% reduction in desalination costs by 2020, which may not be achieved by incremental improvements of current technologies.⁴ Development of novel and inexpensive desalination processes is thus imperative.

Currently, the most widely used desalination technologies are reverse osmosis (RO) and multistage flash (MSF).^{6,7} However, membrane-based RO uses high grade electrical energy,⁵ and the membranes are prone to fouling and need frequent replacement.⁶ Research on high-flux membranes based on carbon nanotubes⁸ can potentially reduce the energy consumption, and a recent microdevice using ion concentration polarization⁹ could potentially avoid the fouling. Thermal energy based MSF needs high temperature thermal source (~90 °C) to evaporate water, which make desalinated water expensive.⁵ As an alternative to MSF, multiple effect distillation is gaining popularity because it has higher efficiency and lower top brine temperatures (~70 °C).¹⁰ Forward osmosis is a promising process that utilizes low temperature (~60 °C) heat sources but still need to use membranes.^{11,12} Other technologies, like solar thermal distillation desalina-

tion¹³ and humid air desalination¹⁴ are also promising technologies especially for inland places.

Ideas of solvent extraction for desalination were explored by Hood and Davison in the 1960s^{15,16} who used amines as solvents and by Johnson in the 1970s¹⁷ who proposed mixtures of alcohols and nitriles as primary solvents and mixtures of alkyl benzenes and paraffinic compounds as secondary solvents. These were discounted as effective techniques due to the significant residual presence of solvents in the recovered water.¹⁸ Lazare established a pilot plan using a technology combining liquid–liquid extraction and membranes,^{19,20} and estimated a cost of 1 dollar per 1000 gallons of fresh production.²¹ This process, however, still rely on the use of membranes.

Recently, we have demonstrated a membrane-free, low temperature directional solvent extraction (DSE) desalination technology²² which has the potential to impact the desalination industry by eliminating membranes and utilizing low temperature sources that are readily available from solar or waste heat. When operated at lower temperature, this desalination process is estimated to consume less exergy (the maximum theoretical work that can be extracted, at Carnot efficiency, from the heat used to fuel the process) compared to both RO and MSF.

The DSE technology uses directional solvents going through a cyclic process that consists of first forming a saline water-in-solvent emulsion, heating the emulsion so that pure water is dissolved into the solvent, removing the brine-phase, and cooling the solvent to precipitate out pure water. The key to this process is the directionality of the solvent, meaning it should have the ability of dissolving water while rejecting salt and itself being insoluble in water.

In general, fatty acids dissolve water due to the presence of carboxylic acid group (COOH). The highly polar C=O and O-H groups facilitate the formation of hydrogen bonds between the COOH ends and water molecules (see Fig. 1). While this chain end is hydrophilic, the rest of the fatty acid

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molecule consisting of CH₂ and CH₃ segments is hydrophobic. Fatty acids with very small chain lengths are miscible with water because the hydrophilic COOH group outplays the hydrophobic feature of the carbon backbone. However, as the chain length increases, the solubility of both substances in each other decreases significantly due to the more pronounced effect of the hydrophobic carbon backbone. In order to use a solvent for directional solvent extraction purpose, a balance among the solubility of solvent in water, the solubility of water in solvent and the solubility of salt in solvent must be met so that the solvent can effectively extract water while leave as little as possible residue in the recovered fresh water.

In this work, we carry out free energy calculations and molecular dynamics simulations to demonstrate that decanoic acid [CH₃(CH₂)₈COOH] has these directional features. This atomistic modeling provides guidance of searching for other directional solvents that could be used for DSE desalination technology.

II. COMPUTATIONAL MODEL

In the present work, molecular dynamics simulations are performed using GROMACS (Groningen machine for chemical simulations).²³ The optimized potential for liquid simulation (OPLS)²⁴ together with the TIP5P²⁵ water potential model is used to simulate the decanoic acid and water, respectively. A cutoff of 0.9 nm for the van der Waals (vdW) and short-range electrostatic interaction is used. For the long-range electrostatic interactions, we used the fast particle-mesh Ewald (PME)²⁶ method with a 0.12 nm spacing for the fast-Fourier transformation (FFT) grid and a 6th-order interpolation scheme. The bonds are constrained by the parallel linear constraint solver (P-LINCS).²⁷ A time step of 2 fs is used. More detailed descriptions of the simulation setup and procedures for different cases are described in the following sections.

III. FREE ENERGY CALCULATION

To characterize the solubility of materials in different solvents, we calculate the free energy of salvation using the thermodynamics integration (TI) with the coupling parameter method. Details of this method can be found in different

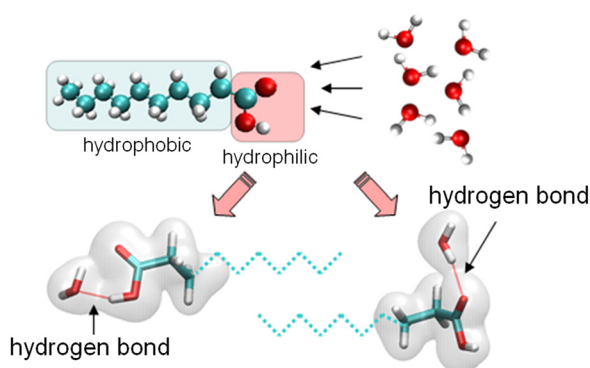


FIG. 1. (Color online) Illustration of hydrogen bonds between water and decanoic acid.

sources such as Ref. 28. Here, a brief description of the TI method is presented.

In the TI method, to calculate the free energy difference between two states, the Hamiltonian of a system, H , is artificially changed through a coupling factor λ using the soft-core method.²⁹ The free energy difference, ΔG_{1-2} , can be calculated using the coupling factor method:

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

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

The solvation free energy can be regarded as the work required to extract a solute molecule from its bulk phase and insert it into a solution. It can also be regarded as an energy difference which indicates the relative stability between states. The free energy can be calculated using a certain thermodynamic cycle. Figure 2 shows an example of such thermodynamic cycle which describes a decanoic acid molecule dissolving in water. As depicted in Fig. 2, 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 which has no nonbonded interactions within itself and with its environment.) (2) The dummy decanoic acid is inserted into the water solution (ΔG_2); (3) The dummy decanoic acid recovers the non-bonded interactions within itself and with 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, putting 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:

$$\Delta G_{\text{solv}} = \Delta G_1 - \Delta G_3. \quad (2)$$

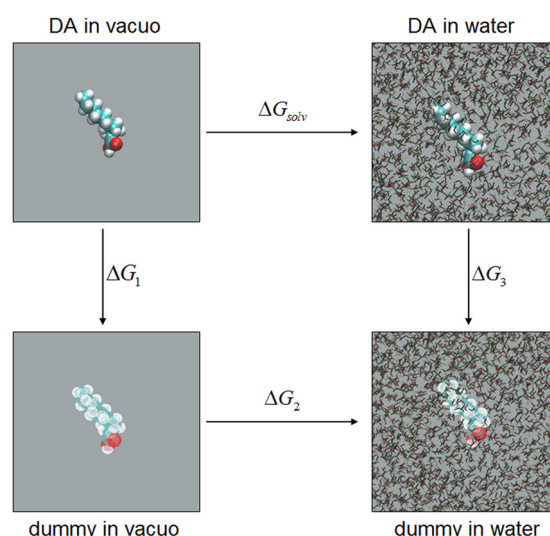


FIG. 2. (Color online) Thermodynamic cycle describing a decanoic acid molecule dissolving in water. (DA=decanoic acid)

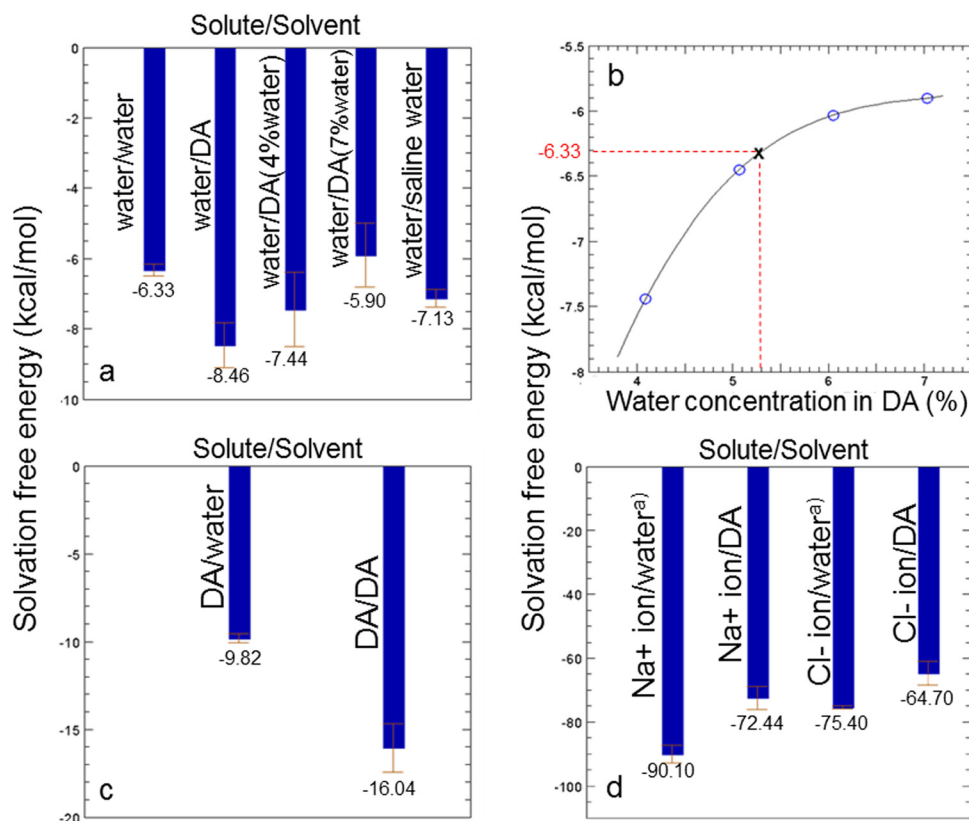


FIG. 3. (Color online) Solvation free energy of (a) water in different solvents; (b) water in decanoic acid solvent with different water concentrations (circles—calculated values; solid line - polynomial fit; cross—interpolated water solubility limit in DA); (c) decanoic acid in water and decanoic acid; and (d) ions in water and decanoic acid. [DA=decanoic acid. (a)—Ref. 36].

By calculating ΔG_1 and $-\Delta G_3$ separately using Eq. (1) through molecular dynamics simulations, the free energy of solvation can be calculated.

In a GROMACS free energy calculation, changing a molecule from its real entity to dummy is achieved by gradually switching off its nonbond interactions, including van der Waals (vdW) and electrostatic interactions. This is done through appropriate formulation of the λ dependent nonbonded interactions with $\lambda = 0, 1$ corresponding to the real state and the dummy state, respectively (see Ref. 29 for details of the λ dependent Hamiltonian).

A number of discrete λ points are chosen between 0 and 1, and $\langle \partial H(\lambda) / \partial \lambda \rangle$ is evaluated analytically in each molecular dynamics simulation with different λ values. In each simulation, the simulation system is firstly equilibrated for 100 ps followed by a 25 ns production run where the derivative $\langle \partial H(\lambda) / \partial \lambda \rangle$ is evaluated and time averaged. After collecting all the derivatives at each λ point, trapezoidal numerical integrations are then performed to obtain the free energy difference according to Eq. (1). Due to the hydrogen bonds 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. According to tests, even denser λ grid have no improvement on the calculated free energy. Errors are analyzed using block averaging. All simulations are performed at 300 K.

The calculated values of solvation free energy depicted in Fig. 3(a) show that a water molecule is more stable in a decanoic acid solution (-8.46 Kcal/mol) than in its bulk phase (-6.33 Kcal/mol), suggesting that water is likely to dissolve into decanoic acid. However, as the concentration

of water in the acid increases, it becomes difficult for successive water molecules to dissolve as seen from the increasing free energy values (4% water in acid: -7.44 Kcal/mol and 7% water in acid: -5.90 Kcal/mol). Such a trend will lead to an equilibrium state in which a water molecule has the same solvation free energy in bulk water as that in decanoic acid. This equilibrium corresponds to the water solubility limit in decanoic acid. We calculated solvation free energy of a water molecule in decanoic acid with a series of water concentrations [see Fig. 3(b)], and we predicted the water solubility limit in decanoic acid at 300 K to be 5.3% [black cross in Fig. 3(b)] through polynomial interpolation.

A water molecule in a saline solution (3.5% NaCl w/w) has lower solvation free energy (-7.13 Kcal/mol) than in pure water (-6.33 Kcal/mol) [see Fig. 3(a)] because of the extra Coulombic interactions among water molecules and salt ions. As water diffuse into decanoic acid from the saline solution, the salinity of the saline phase will increase, and a water molecule will be more stable in the saline phase. Due to the change of the relative stability of water in saline water and in decanoic acid, water molecules from the saline phase are expected to dissolve into decanoic acid until equilibrium is attained when the free energy of water in saline solution becomes equal to that of water in decanoic acid. To have more water molecules dissolve into decanoic acid from the saline water, additional energy is required. An increase in temperature can supply this energy and allow further dissolution of water, and thus increase the solubility.

Another important feature of the directional solvent is that there should be negligible residue in the recovered fresh water. This feature requires the solvent not being able to

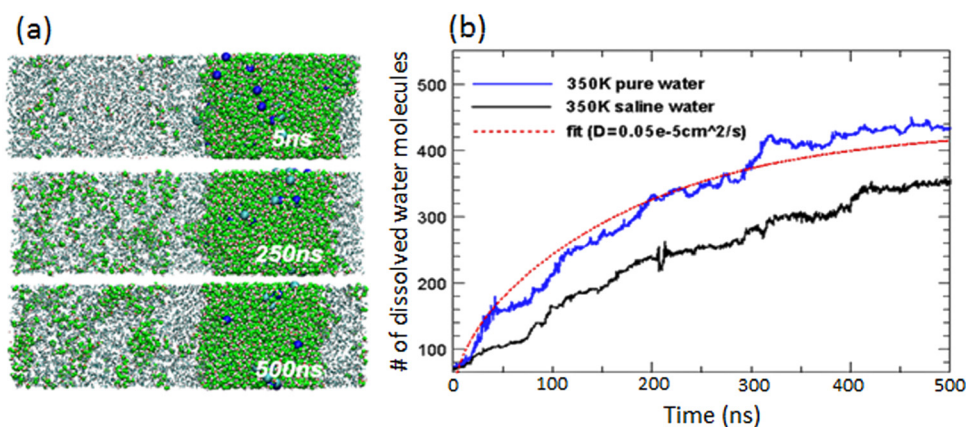


FIG. 4. (Color online) (a) Molecular dynamics simulation of dissolution of water (right block) into decanoic acid (left block) from a saline water-decanoic acid interface; salt ions (large balls in water block) remain in solution and no decanoic acid dissolves into water; (b) number of dissolved water molecules in decanoic acid as a function of time for pure water-decanoic acid and saline water-decanoic acid systems at 350 K.

dissolve in water. Based on the free energy calculation of a decanoic acid molecule in its bulk phase and in water [Fig. 3(c)], a decanoic acid molecule in its amorphous bulk phase (-16.04 Kcal/mol) is much more stable than when it is dissolved in a water solution (-9.82 Kcal/mol), suggesting that decanoic acid is unlikely to dissolve in water. Furthermore, the directional solvent should also have the ability to reject salt ions. As we can see from Fig. 3(c), there are large energy barriers preventing salt ions from diffusing into decanoic acid from the saline solution (-90.1 Kcal/mol for a sodium ion in water compared to -72.44 Kcal/mol in decanoic acid, and -75.4 Kcal/mol for a chloride ion in water compared to -64.7 Kcal/mol in decanoic acid^{30,31}).

Since decanoic acid is unlikely to dissolve into water from its bulk phase as suggested by the above calculated free energies, we can use the following formula to calculate its solubility limit in water assuming dilute limit:³²

$$S = \exp(-\Delta G/RT)/V_m, \quad (3)$$

where ΔG is free energy difference, R is the ideal gas constant, T is temperature, and V_m is molar volume of bulk amorphous decanoic acid. By taking $\Delta G = -9.82 - (-16.04) = 6.22$ Kcal/mol, $V_m = 191.96$ cc/mol, and $T = 300$ K, we found $S = 1.6391 \times 10^{-7}$ mol/cc = 2.8192×10^{-5} g/cc = 28.192 ppm, which is a negligible concentration. This value agrees well with our measurement²² which yield a value of 36 ppm and available reference values ranges from 30–150 ppm.^{33,34} To put this in perspective, whole milk contains about 1300 ppm of decanoic acid.³⁵

IV. DIFFUSION SIMULATION

A. Diffusion at a water-decanoic acid interface

Dissolution is essentially a solute-solvent interdiffusion process. To better understand this process, we used molecular dynamics simulations to model the transient interdiffusion between water and decanoic acid across a water-decanoic acid interface. We prepared a system consists of one layer of water and one layer of decanoic acid (see Fig. 4). The simulation procedure is as follow: (1) An 8.5 nm-thick amorphous decanoic acid layer consisting of 480 decanoic acid molecules is constructed using the modified Markov process³⁶ in a supercell with dimensions of

$4.25 \times 4.25 \times 14.00$ nm³. Periodic boundary conditions (PBC) are used in all spatial directions with a vacuum gap of 5.5 nm thick between the decanoic acid layer and its image in the z -direction. (2) The vacuum gap is then filled with water molecules. (3) The interface is optimized by relaxing the decanoic acid layer in NVT ensemble with the water molecules fixed, and then relaxing water layer with decanoic acid layer fixed. (4) For saline water simulation, 3.5% w/w of sodium and chloride ions are dispersed in the water layer. (5) An equilibrium run is performed in NPT ensemble for 5 ns. (6) A production run is then performed at 350 K in NPT ensembles for at 500 ns.

Figure 4(a) shows three snapshots of the MD simulation of a saline water-decanoic acid system. Throughout the simulation, there are no decanoic acid molecules diffusing into water, but water molecules diffuse into decanoic acid as seen in the snapshots. The same observations are found in simulations of pure water-decanoic acid systems at different temperatures. We also find that there are no salt ions diffusing into decanoic acid from the saline water layer. All these observations agree with those suggested by the free energy calculations in Sec. III.

To estimate the water solubility in different cases, we monitored the number of water molecules diffused into decanoic acid during the simulations. As we can see from Fig. 4(b), the diffusion of water into decanoic acid has reached a steady state suggested by the plateau starting from around 450 ns. We estimated the solubility of water in decanoic acid based on the number of dissolved water, and found the solubility limits at 350 K to be 8.8% and 7.1% for the case of pure water and saline water, respectively. As expected in the free energy calculation, the saline water has less water dissolved into decanoic acid due to the extra Columbic interactions among water molecules and ions. Taking the predicted water solubility in decanoic acid at 300 K from the free energy calculations (5.3%) and assume a linear relation between the solubility and temperature, we roughly estimation the solubility at 307 K (34 °C) to be 5.8%. The yield at 350 K with respect to 307 K is then 3.0%. This value is comparable to the experimental value of 2%,²² and the estimation of 2.4% based on Hoerr's data.³⁷

As an order of magnitude estimation of the water diffusion constant (D) in decanoic acid, we fit the curve in Fig. 4(b) to one-dimensional Fick's law and found

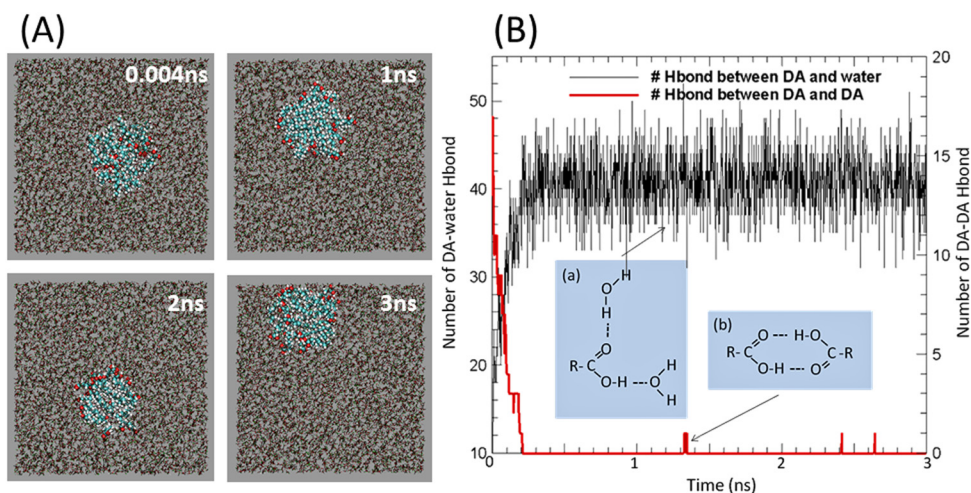


FIG. 5. (Color online) Decanoic acid droplet in water: (A): snapshot of decanoic acid droplet in water at 350 K (dark dots on the background are water molecules. The blue and red spheres consist the decanoic acid molecules, with red spheres being the O atoms in the COOH end groups and blue spheres being the C chain tails); (B): number of hydrogen bonds among decanoic acids and between decanoic acid and water. Inset (a) a sketch of COOH-water hydrogen bonds; (b) a sketch of COOH-COOH hydrogen bonds (dashed line—hydrogen bonds).

$D \sim 0.05 \times 10^{-5} \text{ cm}^2/\text{s}$. We also calculate this diffusion constant using Einstein's relation through MD simulation and found $D \sim 0.02 \times 10^{-5} \text{ cm}^2/\text{s}$. Considering the uncertainty in fitting and simulations, these two values agree reasonably to each other.

B. Decanoic acid droplet in water

To study the mechanism of decanoic acid being insoluble in water, we simulate the time evolution of a decanoic acid droplet in water. The simulation procedure is similar to that of the interface simulation in Sec. IV A. In the simulation, a droplet of the size $2.5 \times 2.5 \times 2.5 \text{ nm}^3$, consisting 20 decanoic acid molecules, is placed in the center of a cubic cell of water with a size of $6 \times 6 \times 6 \text{ nm}^3$ (~ 7158 water molecules). Throughout the 40 ns simulations, there is no decanoic acid molecule diffuse into the water, and they stay as a droplet [see snapshots at Fig. 5(A)]. We also found that such insolubility of decanoic acid is independent of temperature as observed in simulations at 300, 330, and 350 K. These findings are consistent with our free energy calculations and interface simulations.

In nonpolar solutions, decanoic acid will dimerize,³⁸ forming COOH-COOH hydrogen bonds [see Fig. 5(B) inset (b)]. In water, which is a polar solution, the dimerization does not happen as is proven by the number of hydrogen bonds among decanoic acids, which rapidly decays to 0 as the simulation starts [see red line in Fig. 5(B)]. Instead, all the COOH ends are found to be on the droplet surface like a surfactant, forming hydrogen bonds with water molecules, which stabilize the droplet. This observation is quantified by the number of hydrogen bonds between decanoic and water [see Fig. 5(B)]. The 20 decanoic acid molecules form almost exactly 40 hydrogen bonds with water molecules, given each COOH end group can form two hydrogen bonds with two water molecules, as sketched in inset (a) of Fig. 5(B).

V. CONCLUSION

In this paper, we have shown, using free energy calculations and molecular dynamics simulations, that decanoic acid is a directional solvent, which has the ability of dissolving water molecules, rejecting salt ions, while being insoluble

in water. Because the water solubility in directional solvent increases with temperature, the difference in the amount of dissolved water at different temperatures (i.e., yield) allows us to design a directional solvent extraction (DSE) process, in which we extract water from saline source at high temperature and precipitate out the dissolved fresh water at a lower temperature.²² This desalination technology is membrane-free and can utilize low temperature heat sources which can be readily obtained from solar energy or waste heat. It has been proven that the DSE technology, with the current yield, is more exergy efficient than the current desalination technologies such as RO and MSF.²² With solvents which has higher yield, the process will be even more energy efficient, and this work presents a route to characterize such directional solvents.

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