

## **Interactions of water and salt with non-aqueous solvent in directional solvent desalination**

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### **ABSTRACT**

Non-aqueous solvents (NAS) is generally known to be barely miscible and reactive with a polar compound, e.g. water. However, water can interact with some NAS, which can be used as new means for water recovery from saline water. This study explores the fate of water and salt in NAS when the saline water is mixed with NAS. Three amine solvents with same molecular formula were selected as NAS and they were differentiated by their molecular structures as follows: 1) solvent 'A' having the hydrophilic group (NH<sub>2</sub>) at the end of the straight carbon chain, 2) solvent 'B' with symmetrical structure and having the hydrophilic group (NH) at the middle of the straight carbon chain, 3) solvent 'C' having the hydrophilic group (NH<sub>2</sub>) at the end of the straight carbon chain but possessing a hydrophobic ethyl branch in the middle of the structure. In batch experiments, 0.5 M NaCl water was blended with NAS, and then the contents of water and salt in the NAS were measured. Water absorption efficiency by solvent 'B' and 'C' was 3.8 and 10.7%, respectively, however salt rejection efficiency was 98.9% and 58.2%, respectively. While, solvent 'A' exhibited a higher water absorption efficiency of 35.6% despite a worse salt rejection efficiency of 24.7%. Molecular dynamic (MD) simulation showed different interaction of water and salts with each NAS. The solvent 'A' forms a lattice structured clusters with the hydrophilic group located outside and captures a large numbers of water molecules together with salt ions inside the cluster pockets. The solvent 'B' forms a planar-shape cluster where only some water molecules but none of salt ions migrated to the solvent cluster. The solvent 'C' with an ethyl group branch forms a similar shape of cluster with solvent 'B', however, the boundary surface of the cluster looks higher than that of 'C' due to the branch structure in solvent. The MD simulation was helpful for understanding the experimental

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results for water absorption and salt rejection by demonstrating changes in interactions of water molecules and salts with NAS types.

## **1. INTRODUCTION**

Climate change causes depletion of available freshwater resources and water scarcity in many regions. It was reported that about 40% of the global population lives in water stressed areas (Marchal et al., 2011). Without securing alternative water resources, it is anticipated that 90% of the total available freshwater in the world will be used up by 2025 (Hoffmann, 2009; Harrison, 1997). Thus, global interests in securing water resources tends to increase year by year. To respond the water security, desalination technology has been developed for centuries, and has been further advanced over the last decades. Cost for seawater desalination has decreased by approximately nine times since the 1950s and the total capacity of seawater desalination plants is expected to increase over 28 million m<sup>3</sup>/day by 2025 (Zhou and Tol, 2005).

Desalination technologies developed to date include evaporative process, membrane process, electrodialysis (ED), and capacitive deionization (CDI) etc. Of these, multi-stage flash distillation (MSF) and reverse osmosis (RO) have been widely applied and practiced in the world (Shannon et al., 2008; Service, 2006). MSF is a thermal desalination process and has been long applied in the full-scale process due to its capacity for large production. Nevertheless, evaporation requires abundant energy to overcome the latent heat (539 kcal/kg) of water (Elcock, 2010). Energy consumption for vaporizing water accounts for 40~50% of the total operational cost in MSF (Miller, 2003; Rajvanshi, 1981; Thomas, 1997). In addition, crystallization of calcium in the MSF system often causes a scaling problem, which reduces the facility lifetime. On the other hand, RO is a fastest-growing technology in desalination due to its high performance, convenience of operation with a less energy consumption than MSF, and flexibility in applicable scale from small- to large-size plants. In spite of many benefits in the RO process, it needs high pressure to induce osmotic pressure. Electrical energy for this accounts for 44% of the total costs for seawater RO (SWRO) process (Banat and Jwaied, 2008). In addition to energy consumption, RO membranes are susceptible to fouling problem which results in frequent cleaning or replacement of membrane (Shannon et al., 2008). ED is a membrane-based technology in which charged cations and anions can separately migrate across the ion-exchange membranes by electrical potential differences (Miller, 2003). However, application of ED in the desalination process is limited to only low TDS water (i.e. brackish water) treatment due to high energy consumption (Speigler and Sayed, 1994). Recently, forward osmosis (FO) has gained an increasing attention due to its potentially low energy consumption compared to SWRO (Mazlan et al., 2016). FO uses the osmotic pressure difference between the feed solution and draw solution as a driving force to induce water transport across a semi-permeable membrane (Sun et al., 2017). In addition to a lower energy consumption, FO technology has other benefits such as low fouling propensity and ease of cleaning. Nonetheless, mechanisms of FO have not been clearly understood yet and it still needs understanding molecular-level behaviors of water and ions

between membranes (Yip et al., 2010; Tiraferri et al., 2011; Qiu et al., 2012). Also, effective recovery of the draw solution in FO process should be solved in order to expand its application to full-scale plants.

A desalination method by using solvent extraction is very recently attempted and sometimes called as a directional solvent extraction process (Kleinguetl, 2011; Alotaibi et al., 2017). This method separate the water from a saline water by using the difference in the solubility between water and solvent according to the temperature change. The idea of this directional solvent extraction for desalination was firstly proposed in the 1960s (Davidson et al., 1960). However, since it was firstly proposed, the relevant technologies have been rarely developed to date. This method may have several benefits such as flexibility of its process scale, simplicity in process configuration, and less energy consumption compared to the other desalination processes. However, its technological state is still immature and not robust, and its application was limited to some specific water recovery from a low salinity water of 5,000 ppm or much less than that of seawater (Davidson and Hood, 1964). A limited number of study has been done for this so far due to lack of understanding in molecular interactions among water, salt ions and solvent. Recently, Bajpayee (2011) found that some edible oils and long chained carboxylic acid could absorb water while rejecting the other soluble substances including NaCl. They described such phenomena at thermodynamic aspect by using free energy for the interaction of water-solvent-ions.

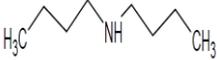
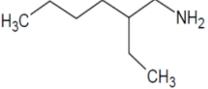
The goal of this study was to investigate the potential of desalination by solvent extraction using three NAS with different molecular structures. Desalination performance of these three NAS was experimentally assessed in terms of water absorption and salt rejection. Also, the fates of water and salt in three NAS were analyzed by using molecular dynamic (MD) simulation method which illustrates interaction of water and salt ions with NAS.

## **2. MATERIALS AND METHODS**

### *2.1. Selection of NAS*

Three amine compounds were selected as the candidate NAS for direction solvent desalination. These three NAS have the same molecular formula with C8 organic carbon links where one amine group (N-H) bonded at different position. This amine group (N-H) possesses a strong hydrogen bonding which may allow the interactions with water or ions. The selected NAS are differentiated by chemical structures. The N-H group in the solvent 'A' is located at the end of the organic chain, whereas that of the solvent 'B' is located at the center of the organic chain. The solvent 'C' of which the N-H group was located at the end of the chain like the solvent 'A', has an ethyl group (CH<sub>3</sub>CH<sub>2</sub>) as a branch in the middle of the organic chain. Table 1 shows the major properties of three selected NAS. Three amine compounds have the same molecular formula but different properties (i.e. boiling point, solubility) due to their structural difference. In particular, solvent 'A' and 'C' are very low insoluble in water, however, solvent 'B' has a slightly higher solubility values than the other two solvents even though it is immiscible with water.

Table 1 Chemical properties of three selected solvents used for desalination experiment

	Solvent 'A'	Solvent 'B'	Solvent 'C'
Chemical formula	 <chem>CCCCCCCCN</chem>	 <chem>CCCCNCCCC</chem>	 <chem>CCCCNCC</chem>
	<chem>C8H19N</chem>	<chem>C8H19N</chem>	<chem>C8H19N</chem>
Molecular weight (g/mol)	129.25	129.25	129.25
Density (g/mL)	0.78	0.77	0.79
Boiling point (°C)	180	160	169
Solubility (g/L)	0.2	3.5	< 1

## 2.2. Experiments for desalination using the selected NAS

Synthetic saline water was prepared by dissolving sodium chloride in the distilled water at 0.5 M which is close to the concentration of seawater. 100 mL of each solvent (NAS) and synthetic saline water were separately added into a 500 mL beaker and mixed at 300 rpm using magnetic stirrer for 10 min. After mixing finished, the mixture were quickly separated into two phases (solvent and brine phase) due to differences in the density and polarity between the solvent and water. Separation was continued under quiescent condition for 5 min, thereby the solvent (upper phase) was carefully taken. Desalination performance was estimated in terms of water absorption efficiency and salt rejection efficiency. The water content in the solvent was measured by using Karl-Fischer analysis (KF-890, Metrohm, Switzerland).

The water absorption efficiency of the solvent means the content of water increase in the solvent and the salt rejection efficiency means the change of the concentration of the  $\text{Cl}^-$  ion in the synthetic saline water before and after desalination experiment and can be defined as follows:

$$\text{Salt rejection efficiency(\%)} = \frac{\text{Residual mass of } \text{Cl}^- \text{ in the brine phase}}{\text{Initial mass of } \text{Cl}^- \text{ in saline water}} \times 100$$

$\text{Cl}^-$  concentrations in the solvents and residual water (brine) were measured by using Ion chromatograph (ICS-900, Dionex, USA).

## 2.3. MD simulation for desalination with solvent extraction

Molecular dynamic (MD) simulations were conducted using Desmond molecular dynamics package (Schrödinger Release, 2018-2). Three-dimensional structure of each NAS was prepared using 2D-Sketcher in Schrödinger suites and were optimized using quantum mechanics (QM) application called as Jaguar in Schrödinger suites. In the QM calculation, density functional theory (DFT) was used with B3LYP hybrid functional and 6-31G\*\* basis set. Atomic partial charges of the NAS were also calculated using electrostatic potential (ESP) fitting method. Desmond system builder was performed to build the initial system for MD simulation. First, 1,000 NAS molecules were randomly arranged in a three-dimensional space. Then, water molecules were

also randomly arranged in a 1:1 ratio (v:v) of water and NAS by using TIP3P water model. Concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  ions were set to be 0.5 M, respectively. OPLS3 force field was employed to describe all the molecules and calculate explicit interactions among atoms. The NPT ensemble was employed in MD simulations. To maintain a constant temperature and pressure during MD simulations, the Nose-Hoover thermostat method was set at the reference temperature of 300 K and the Martyna-Tobias-Klein barostat was set at the reference pressure of 1 bar. After performing a series of minimizations to relax the MD system, MD simulations were run for 100 ns.

### 3. RESULTS AND DISCUSSION

#### 3.1. Experimental results of directional solvent extraction

In order to investigate the desalination capability of NAS, we examined the transfer of water from 0.5 M synthetic saline water into each NAS selected. After mixing, NAS and saline water mixture were rapidly separated into two phases of solvent and brine. The volume of solvent phase in the upper layer slightly increased indicating that water molecules migrate to the solvent phase. After carefully recovering the upper solvent phase, the volume of solvent 'B' and 'C' increased by approximately 5% and 10% of its initial volume, whereas that of the solvent 'A' increased by 50% (see in Fig. 1). Water content in the solvent was more precisely measured by Karl-Fisher analysis. Water absorption efficiency in the solvent 'A', 'B' and 'C' resulted in 35.6%, 3.8% and 10.7%, respectively. The increment of water content in every solvent was not exactly same to that of the observed volume. This is presumably because a little amount of solvent transferred to the brine phase while the water molecules transferring to the solvent phase.

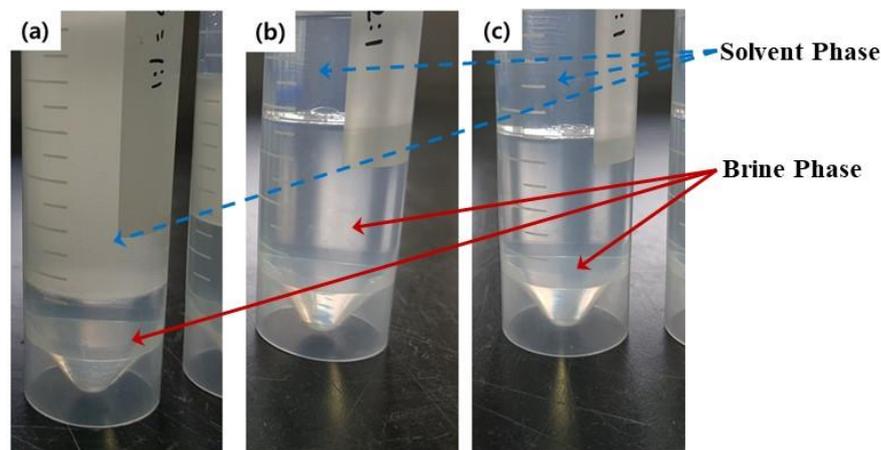


Fig. 1 Phase separation after mixing into solvent and brine in use of (a) solvent 'A', (b) solvent 'B', (c) solvent 'C'

Similar to water content,  $\text{Cl}^-$  ion concentration in each brine phase was analyzed. Concentration of  $\text{Cl}^-$  in the brine phase can be an index for interaction of salt ions with solvent and decrease in  $\text{Cl}^-$  concentration in the brine phase indicates migration of salt into the solvent phase. Salt rejection efficiency for each solvent is shown in Fig. 2. Low

Cl<sup>-</sup> concentration relative to water content in the solvent means that the solvent is capable of selectively absorbing water and rejecting salt ion during the desalination process. In spite of the highest water absorption efficiency, solvent 'A' exhibited the lowest salt rejection efficiency at 24.7% implying that it is not suitable for desalination. On the contrary, solvent 'B' with the lowest water absorption efficiency showed the excellent salt rejection capability with 98.9% efficiency. Solvent 'C' exhibited a moderate desalination capability in terms of water absorption and salt rejection efficiencies in between solvent 'A' and 'B'. Considering both sides of desalination capabilities, solvent 'B' can be the best suitable solvent among the selected NAS candidates for directional solvent desalination.

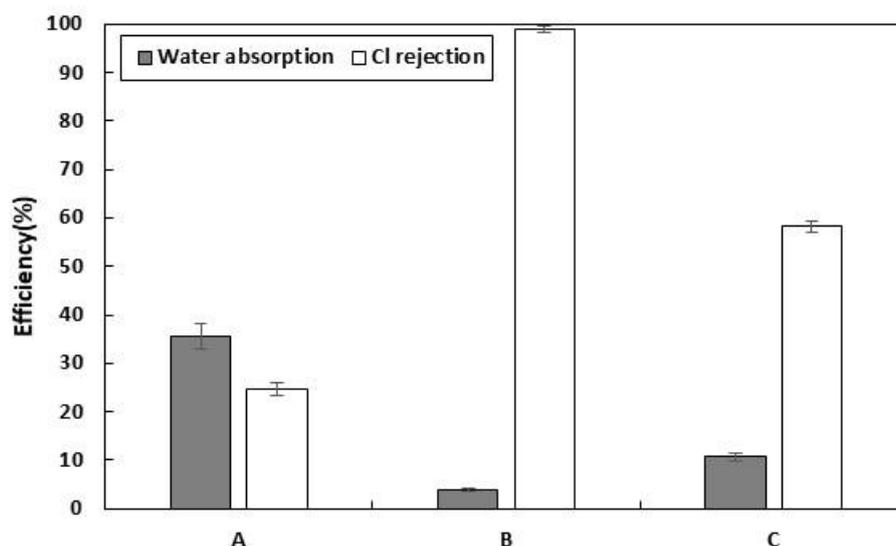


Fig. 2 Comparison of water recovery and salt rejection efficiency of selected solvent

Unexpectedly, as shown in Fig. 1(a), when solvent 'A' was mixed with saline water, the viscosity of the mixture increased and then the mixture turned into a gel. The principle of gelation of solvent 'A' with saline water could not be clearly explained in this study, however, there were many previous studies reporting the formation of gelatin in a mixture of organic solvent and water (Dastidar et al., 2004; Mahapatra and Dey, 2016). It can be hypothesized that the solvent 'A', having the hydrophilic group at the end of the carbon chain, enables to form a semi-solid structure such as a cell membrane bilayer, which in turn forms a pocket (a kind of vesicle) where a large numbers of water molecules and ions can be captured (see in Fig. 3).

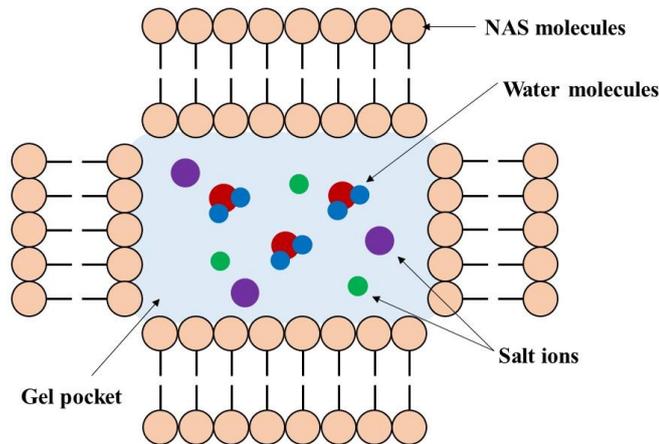


Fig. 3 Predictions for water molecules and salt ions captured inside a bilayer of solvent 'A'

### 3.2. MD simulation for interaction of water and salts with NAS

In order to demonstrate the interaction of water and salts with NAS in directional solvent desalination at atomic scale, the molecular dynamics (MD) simulation was carried out. MD simulation is a computer simulation method for representing the physical movements of molecules with time. MD simulations were performed at the initial states where the NAS, water molecules and salt ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) were uniformly distributed. To check the phase changes of the mixture during MD simulations, we measured the positional changes of the NAS by the root-mean-square deviation (RMSD) of atomic positions. Based on the RMSD data, all the NAS reached an equilibrium state after 5 ns and the RMSD values were stabilized (Fig. 4). Stabilization of RMSD means that NAS probably reached a steady state condition for interaction with water and salt ions.

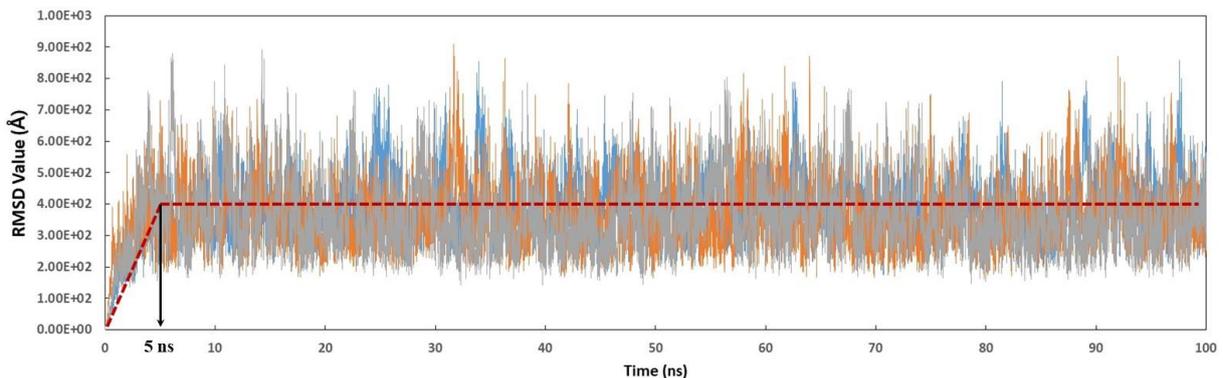


Fig. 4 RMSD results of MD simulations

100 ns snapshots of MD simulations are shown in Fig. 5. Solvent 'A' formed a cross-shaped cluster surrounded by water molecule clusters. As hypothesized from the experimental results, the hydrophilic amine group (N-H) contacts with the water molecules and the hydrophobic carbon chains are aggregated together forming the

clusters. The NAS cluster contains many water molecules inside and the water molecules might bond each other by their hydrogen bonding network. Based on the experimental results, solvent 'A' exhibited the highest water absorption capacity and lowest salt rejection efficiency, which means no selective absorption of water from saline water. However, in MD simulation, no NaCl ion was found inside the solvent cluster. In order to see the clusters at a macro-scale view, we extended the boundary of the system scale of MD to 3 x 3 system by making replicas of the cluster spaces. In the extended system, the solvent clusters formed a lattice structure which surrounded many pockets (vesicles) that can contain water molecules and NaCl ions together (Fig. 6(a)). Interestingly, the lattice structure of the solvent cluster looks very similar to the general gel structure (Fig. 6(b)), which supports the observation of gelatin formation during the experiment.

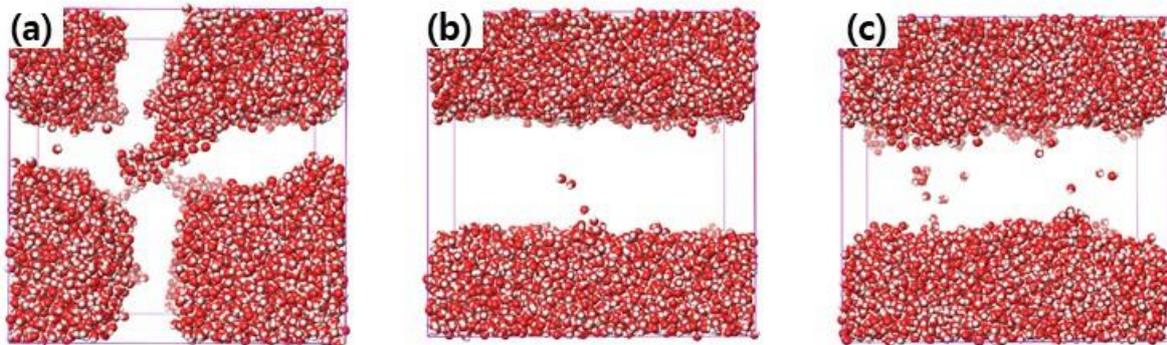


Fig. 5 MD simulation results for directional solvent desalination using (a) solvent 'A', (b) solvent 'B', (c) solvent 'C'. The red and white symbol represent the water molecules and the vacant space is the solvent layer

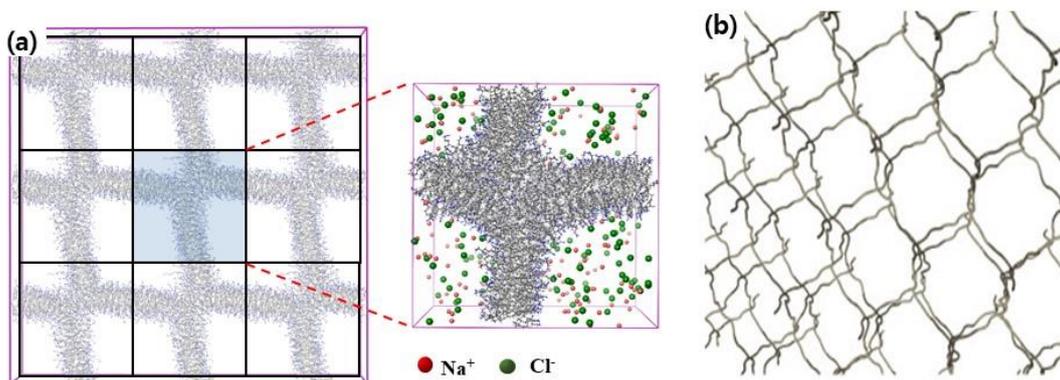


Fig. 6 Comparison of the lattice-structure of solvent 'A' (a) and general structure of gelatin (b) (reproduced from Sakai T., 2013). The red and green symbol represent the salt ions and the gray layer is the solvent.

Different from solvent 'A', solvent 'B' and 'C' formed a planar-shape cluster structures (Fig. 5(b), (c)). Although both solvents did not form any vesicle within the solvent clusters, small numbers of water molecules were found to migrate inside the solvent clusters. The water absorption efficiency could be analyzed by counting the number of water to migrate to the solvent clusters, and it resulted in 1.29 and 2.13% for solvent 'B' and 'C', respectively. There were a significant difference in water absorption efficiency between the experimental results and MD simulation probably due to limit of scale in MD simulation. Also, in spite of a similar shaped cluster, solvent 'C' shows a greater water absorption capacity due to presence of ethyl branch. The branch-type structured solvent 'C' looks like forming a rougher surface of clusters than a straight chain structure of solvent 'B'. Increase in the interfacial surface area between water and solvent 'C' clusters may lead to enlarging the transferring opportunity of water and salt ions into solvents.

Different from the experimental results, it has not been clearly demonstrated for movement of  $\text{Na}^+$  and  $\text{Cl}^-$  ions into solvent clusters through MD simulation. In order to clarify the fate of salt ions together with water molecules through MD simulation, it is necessary to expand the scale of system and to simulate it under more diverse conditions associated with directional NAS desalination.

#### **4. CONCLUSIONS**

Directional solvent desalination can be a cost-effective and flexible technology completely different concept from the current technical approaches for desalination even though its technical state is not still robust. Three non-aqueous solvents (NAS) are amine group organic solvents with the same molecular formula but different structural formula each other. Different structures of NAS lead to different desalination performances. Solvent 'B' with amine group in the center of the straight C8 chain showed the best desalination performance considering both water absorption and salt rejection efficiency. Solvent 'A' exhibited the substantially higher water absorption efficiency but the lowest salt rejection efficiency due to formation of water pockets (vesicles) inside the solvent clusters which was well demonstrated by molecular dynamics (MD) simulation. The MD simulation results relatively well matched with the experimental results even though it needs still to modify by expanding the scale and diversifying condition for simulation. Mechanisms for interaction of water and salt ions with NAS in directional solvent desalination have been rarely understood yet. Experiment supported by MD simulation will be helpful for clearly understanding the mechanisms of directional solvent desalination and enhancing its performance in the future.

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