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液液界面のイオン輸送における微量水の触媒効果

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Catalytic Effect of Trace Water on Ion Transport through Liquid-Liquid Interface --- Water Finger Formation and Hydration.

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Introduction

Transport of ions through liquid-liquid interfaces, often called the interface between two immiscible electrolyte solutions (ITIES), plays versatile roles in a number of phenomena, but the elementary kinetics and mechanism of the ion transport at ITIES remain largely unknown. Appearance of micropipette apparatus enabled the kinetic study of ion transfer experimentally by allowing us to control the amount of water dissolved in the oil phase up to its saturation limit[1] and thereby revealing that even a trace amount of water dissolved in the hydrophobic phase brings about remarkable facilitation for the ion transfer from the water phase to the hydrophobic one.[2]

We have elucidated the microscopic mechanism for phase transfer catalyst to facilitate the ion transfer process using molecular dynamics (MD) simulation before. [3] This time, the purpose of our research is to elucidate the catalytic mechanism of the trace water.

Method

It is conceivable that the concentration of the trace water will affect the number of hydrated water surrounding an ion in the equilibrium oil phase. This is experimentally supported that the measured conductance of the ions in the oil phase decreases with concentration of trace water.[2] This is considered to be a result of the formation of larger ion cluster which decreases the conductance in the bulk phase. However, the lower conductance in the oil phase is at odds with the facilitated ion transfer by the trace water. Therefore, the catalytic effect of the trace water should attribute to the interfacial effect rather than in the oil bulk. Straightforward MD is not useful in this situation due to its temporal and spatial limitation. It is obvious that in order to model the trace amount of water (100μM) dissolved in the oil phase, one will need a cubic box with a side length of at least 26nm ($100 \times 10^{-6}M \times 6.022 \times 10^{23}mol^{-1} \times 10^3 L \cdot m^{-3} =$

$26 nm$) , which is prohibitively large for conventional MD. This means we need an alternative method to study the role of trace amount of water.

In order to understand the catalytic effect by encompassing the microscopic ion transfer dynamics at the interface, we need both the information about the distribution of hydrated ion clusters in the bulk oil phase and the molecular details near the interface.

The hydrated ion clusters should follow the grand canonical distribution:

$$P_s(N) \propto e^{-\beta(\Delta E_s(N) - \mu N)} \tag{1}$$

Here, μ is the chemical potential of water in the bulk oil that can be calculated from the number density of water in the bulk oil (ρ):

$$\mu = G^*(W) + kT ln(\rho \Lambda_w^3) \tag{2}$$

$\Delta E_s(N)$ is the free energy for taking one water from the cluster :

$$\Delta E_s(N) = E_s(N) - [E_s(N - 1) + G^*(W)] \tag{3}$$

This free energy is estimated using the free energy perturbation method on hydrated ion clusters with number of water molecules ranging from 0 to 20. With the information of ρ and $\Delta E_s(N)$, the distribution of hydrated ion cluster in the bulk oil phase is retrieved.

The molecular details near the ITIES is sampled using replica-exchange molecular dynamics (REMD). Different replica corresponds to different water finger status (the breaking position and the number of water molecules in the breaking away hydrated ion cluster). With the efficient sampling using REMD, we obtain the 2-D energy surface of the ITIES.

Result

We adopted the picture of free energy surface in relation to the hydration number of the ion. When the ion moves into the oil phase, the water finger is formed and broken to leave some hydrated water molecules around the ion in the oil phase. It is shown in the research that coupling of water finger formation/destruction and the hydration number of ions plays a key role to bring about the catalytic effect of the trace water. The detailed result will be presented on the day of presentation.

References

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