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液液界面付近の水和イオンクラスター分布

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Distribution of hydrated ion clusters near the liquid-liquid interface

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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 due to scarcity of experimental techniques that are able to selectively probe microscopic dynamics at ITIES. For example, the 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] but the mechanism of this phenomenon is still unsolved.

Method

In order to understand the mechanism of facilitation of ion transfer process by increased water concentration inside the bulk oil, the distribution of hydrated ion clusters in bulk oil with different water concentration is calculated using molecular dynamics (MD) simulation. Straightforward MD is not useful to reproduce the equilibrated hydrated cluster distribution due to the prohibitively large temporal and spatial requirement of this problem. This means we need an alternative method to study the distribution of hydrated ion clusters. In this case, if we treat the clusters dispersed in bulk oil as individual μVT ensembles, the distribution of cluster with hydration number N can be calculated from grand canonical distribution as

$$P(N) \propto \frac{e^{-\beta(G^*(N)-N\mu_w)}}{N!\Lambda_N^3}. \quad (1)$$

Here, Λ_N is the thermal de Broglie wavelength of the cluster, μ_w is the chemical potential of water in the bulk oil that can be calculated from the concentration of water ρ_w as

$$\mu_w = \mu_w^* + k_B T \ln \rho_w \Lambda_w^3 \quad (2)$$

and $G^*(N)$ is the free energy of the cluster that can be calculated using MD simulation. The free energy change $\Delta G^*(N)$ of the following process,

$$AW_{n-1} + W(vacuum) \xrightarrow{\Delta G^*(n)} AW_n, \quad (3)$$

can be calculated using free energy perturbation (FEP). Then $G^*(N)$ can be calculated as

$$G^*(n) = \sum_{m=1}^{n} \Delta G^*(m) + G^*(0) \quad (4)$$

by considering a series of processes of water molecule adding to the cluster,

$$[G^*(0) \xrightarrow{\Delta G^*(1)} G^*(1) \xrightarrow{\Delta G^*(2)} G^*(2) \xrightarrow{\Delta G^*(3)} \dots \xrightarrow{\Delta G^*(n-1)} G^*(n-1) \xrightarrow{\Delta G^*(n)} G^*(n)]. \quad (5)$$

Result & Discussion

The $\Delta G^*(N)$ and $G^*(N)$ for $N = 1{\sim}10$ are calculated (Fig.1). Based on the calculated free energy, the cluster distribution in water-saturated dichloromethane (DCM) is retrieved (Fig.2). The result shows that the average hydration number of ion clusters deceases as the water concentration decreases. In our previous research, the distribution of hydrated ion clusters near the interface right after the break of water finger was retrieved using replica-exchange MD.[3] It is shown that the corresponding water concentration to this near interface environment is 4.5M (Fig.3), which is in between the water-saturated DCM concentration (130mM) and the pure water concentration (55M).

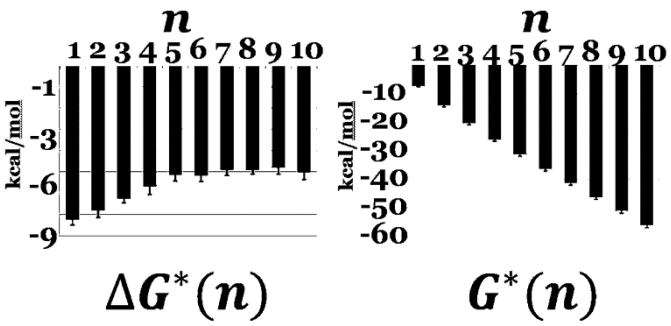
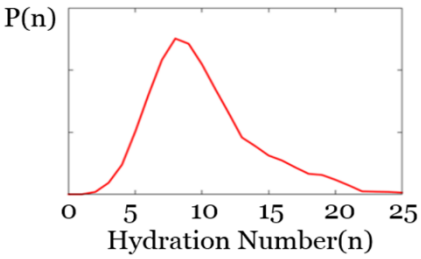


Fig. 1. Calculated $\Delta G^*(N)$ and $G^*(N)$ for $N = 1{\sim}10$.



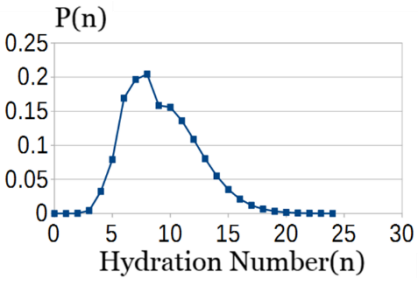


Fig. 2. Distribution calculated as $\rho_w = 130mM$.

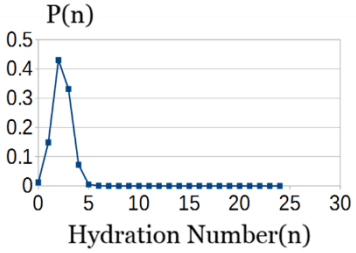


Fig. 3. Up: near interface distribution calculated using REMD (Ref.3) Down: distribution calculated as $\rho_w = 4.5M$.

References

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