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自由エネルギー計算による親水性イオンの界面間輸送プロセスにおける水和効果の究明

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Unveiling the role of hydration during the interfacial transport process of hydrophilic ion using free energy calculation

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【Abstract】 In this study, we calculated the multidimensional free energy surfaces of ion transport through liquid-liquid interfaces. The calculation revealed the hydration status of the interfacial ions and evaporation kinetics of hydration along the diffusion in the oil phase. The role of evaporation kinetics in relation to the efficiency of the interfacial transport is discussed in details, and thus the catalytic effect of water during the interfacial transport process of hydrophilic ions is elucidated.

【Introduction】 Recent experimental measurement of interfacial kinetics using micropipette apparatus revealed 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,1 but the mechanism of this phenomenon is still unsolved. In order to understand the mechanism of facilitation of ion transfer process, we use molecular dynamics (MD) to look into microscopic details of the ion transport process near the interface.

【Method】 The transport process of hydrophilic ions through water-oil interface is accompanied with characteristic transient structural fluctuation of water molecules near the interface, called “water finger”. The interfacial transport is properly described with two coordinates: the distance between ion and the interface z, and the water finger coordinate w to account for the status of “water finger”.[2] We calculated the 2D free energy surface along z and w using the Hamiltonian replica exchange molecular dynamics (HREMD).

The MD simulation was carried out with Cl^- ions through the interface between water and 1,2-dichloromethane. The distribution of hydrated ion clusters with different hydration number immediately after the break of “water finger” is retrieved by analyzing the trajectory of HREMD simulations. The free energy profiles with restricting the hydration number to a specific value in the exit channel are also calculated.

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【Result & Discussion】 The calculated 1D free energy curves along *z* under different conditions are shown in Fig 1. Each curve in the figure has a break point in the oil region (*z*=10~30 Å) where the water finger is broken. The *n*=0 and *n*=1 curves in Fig. 1 show the free energy curves with restricting the exit channel to a specific number of hydration *n*, indicating that the water finger tends to last longer when the break generates a naked ion (*n*=0) or a small cluster (*n*=1). Figure 2 shows the distribution of clusters with different hydration number immediately after the break of "water finger". The nascent clusters tend to have more hydrated water than that in the equilibrated bulk oil.[3] The subsequent kinetics of water evaporation/adsorption should take place after the break of water finger, and the kinetics competes with the diffusion and the recapture by the water finger. The comprehensive picture of the kinetics of hydrated ion clusters is proposed in the presentation.

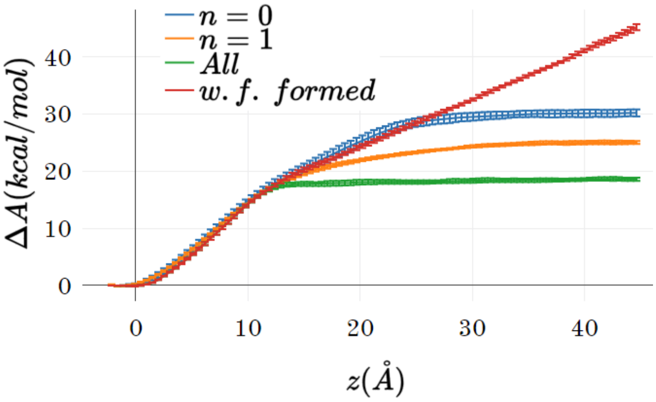

Fig 1. 1D free energy curves under different conditions. The green line is the ordinary curve. The red line represents the situation when "water finger" keeps being formed.

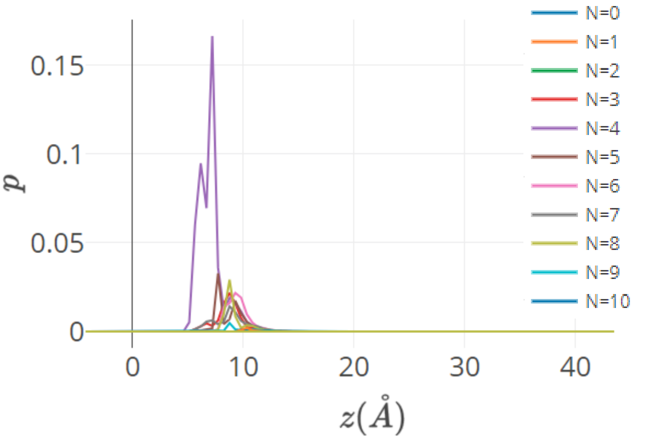

Fig 2. The distribution of clusters with different hydration number immediately after the break of "water finger".

【Acknowledgment】

This work was supported by the Grants-in-Aids (JP26288003, 25104003). The computation was carried out using the Research Center for Computational Science, Okazaki.

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