1E10

液液界面で起こるイオン輸送過程の水和状態に関する研究

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Study of ion hydration status during the transport through liquid-liquid interface

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【Abstract】 In order to understand the effect of hydration on the ion transport process, we first calculated the distribution of hydrated ion clusters in the bulk oil corresponding to different water concentration states. We then calculated the free energy surface in relation to hydration number of the ion and the distance between transported ion and the interface to gain further knowledge on the hydrated ion cluster stability under different situations. Combining the results from these two researches, we managed to explain the mechanism of the catalytic effect of trace water on ion transport process.

【Introduction】 Ion transport process through liquid-liquid interfaces plays versatile roles in a number of physical chemical phenomena, but the elementary kinetics and mechanism of it remain largely unknown due to insufficient spatial and temporal resolution from experimental approaches. Molecular dynamics simulation is adopted in this research to unravel the microscopic details of ion transport process. The widely accepted ion transport mechanism includes the formation and break of the water finger, a finger like structure formed by water molecules surrounding transported ion. The hydration number of ion clusters throughout the ion transport process is of particular importance to its free energy nature.

【Method】 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. The free energy surface in relation to hydration number of the ion and the distance between transported ion and the interface is calculated using Hamiltonian replica exchange method for cluster hydration number (N_w) of 0 and 1.

【Result & Discussion】 The calculated distribution of hydrated ion clusters under different water concentration value is shown in Figure 1. Previous study shows that the average hydration number of the clusters near the interface is much higher[1] than the equilibrated distribution in the bulk oil. Figure 2 shows the 1D free energy curve of the system with clusters' hydration number N_w is restricted to 0 (red) / 1 (pink), or with intact water finger structure (brown). The line representing the intact water finger structure keeps rising due to the increase of surface tension introduced by prolonged finger structure, while the lines representing clusters with restricted hydration number flattens out from a certain z position. This offers some explanation for previous experimental observation of facilitated ion transfer process by staining oil with water[2].

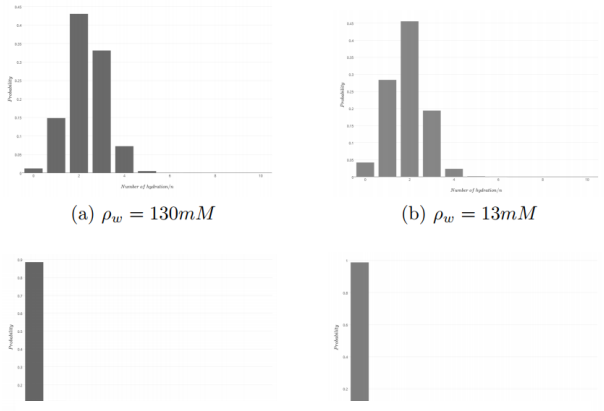

Figure 1. *Distribution of hydrated ion clusters for different ρ_w in the bulk organic phase*

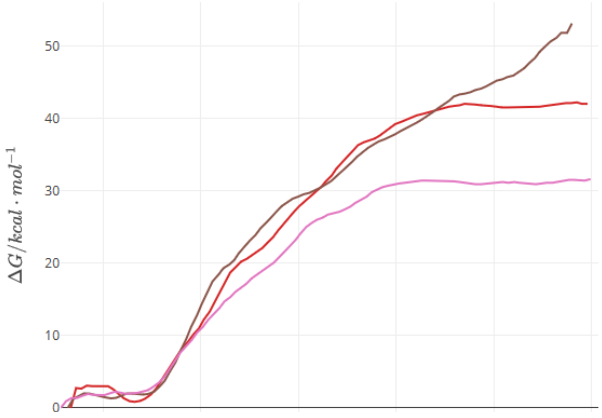

Figure 2. *Free energy curve for N_w=0(red) and 1(pink) and connected water finger (brown)*

【References】

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2. Sun, P., Laforge, F. O. & Mirkin, M. V. Role of Trace Amounts of Water in Transfers of Hydrophilic and Hydrophobic Ions to Low-Polarity Organic Solvents. *J. Am. Chem. Soc.* **129**, 12410–12411 (2007).