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液液界面のイオン輸送における水和と蒸発の効果

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The role of hydration and evaporation in the ion transfer process through water/oil interface

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Ion transfer process through liquid-liquid interface is of great importance for many electroanalytical applications such as sensors, batteries and filtrations. Molecular dynamics (MD) simulation is quite powerful to investigate the microscopic transfer mechanism. It revealed a transient interfacial structure caused by the ion "dragging" some of the solvent molecules, typically water, which is called "water finger".[1] We found that the formation and break of the water finger accompany a free energy barrier, which affects the efficiency of the transfer process.[2]

A successful transfer of ion from water to oil phase requires the break of the water finger at a certain point. After the break, usually a hydrated ion cluster is formed near the interface. One of the important issues is the role of hydration on the ion transfer. Recent experiment using micropipette apparatus revealed that the efficiency of ion transfer through water-oil interface is sensitive to the trace amount of water concentration in the oil phase.[2] Since the bulk concentration of water governs the hydration state of the transferred ions, it is important to understand the effect of hydration state on the interfacial transfer mechanism.

For the purpose, the distribution of hydrated ion clusters in terms of different hydration number and location is investigated by free energy calculations. 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

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

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 distribution in bulk oil for water density $\rho_w = 130mM$, 13mM, 1.3mM and 0.13mM is shown below (Figure 1).
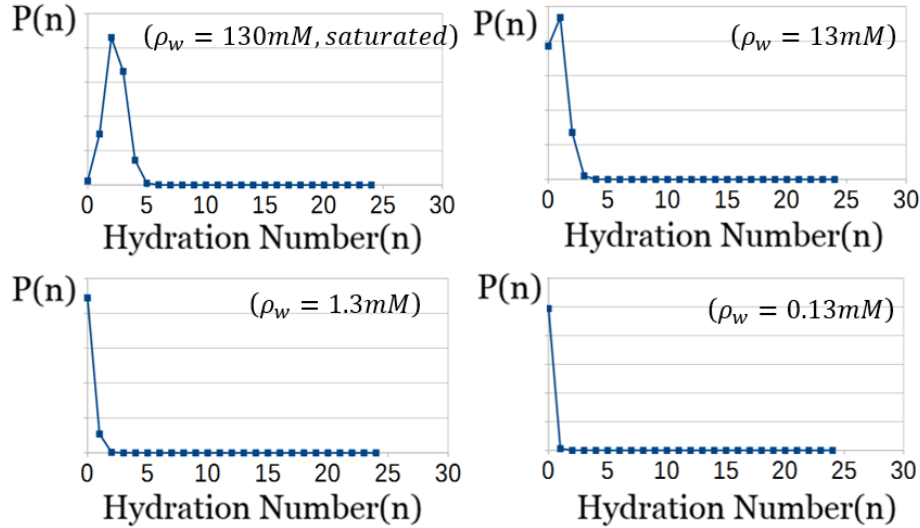

Figure 1. Distribution of hydration number around Cl- in liquid dichloromethane including water concentration ρ_w

Our result shows that the distribution of hydrated ion clusters near the interface is largely different from the distribution in the bulk oil. The much higher average hydration number near the interface[3] suggests that evaporation also plays an important role in the transfer process. The kinetics of evaporation can be affected by the relative density of water dissolved in the bulk oil. This in turn explains previous experimental observation of facilitated ion transfer process by staining oil with water.

References
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