Adsorption dynamics in Pickering emulsions

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二種類の非相溶な液体に粉体粒子やコロイド粒子を混合させると、エマルションが長時間にわたって安定化される。このようなエマルションはピッカリング・エマルションと呼ばれている。基本的に表面が均一であるようなコロイド粒子が界面活性を示し、安定なエマルションを形成することは概念的に興味深い。我々はピッカリング・エマルションにおいて、球状粒子の液液界面への吸着ダイナミクスを考察する。そこでは、主に粒子の濡れ性がダイナミクスにどのような影響を与えるかという点に注目する。

When we add solid particles such as colloidal particles to two immiscible liquids, emulsions can be stabilized for a long time. Such an emulsion is called as the Pickering emulsion. We consider the adsorption dynamics of spherical particles to liquid/liquid interfaces in Pickering emulsions. Especially, we pay attention how the particle wettability affects the dynamics.

First we consider the case where spherical particles are contained only in one of the liquids, and they adsorb to a flat liquid/liquid interface. According to the conservation of particles close to the interface, the following Ward-Tordai equation is derived [1]:

$$\phi_0(\tilde{t}) + \phi_1(\tilde{t}) = \sqrt{\frac{1}{\pi}} \left[2\phi_{\rm b}\sqrt{\tilde{t}} - \int_0^{\tilde{t}} {\rm d}\tau \, \frac{\phi_1(\tau)}{\sqrt{\tilde{t}-\tau}} \right] + 2\phi_{\rm b}, \tag{1}$$

where $\phi_0(\tilde{t})$ is the particle concentration at the interface, $\phi_1(\tilde{t})$ is the particle concentration at the sublayer adjacent to the interface, and $\phi_{\rm b}$ is the bulk concentration. We have used a dimensionless time $\tilde{t} = Dt/a^2$ where D is the diffusion constant and a is the diameter of the particle.

Next we consider the total energy as the sum of the contributions from the interface and the sublayer. Since the particle concentration at the interface is governed by the chemical potential difference between the interface and the sublayer, we obtain the following time evolution equation:

$$\frac{\partial \phi_0}{\partial \tilde{t}} = \phi_1 \left[\log \frac{\phi_1(1-\phi_0)}{\phi_0} + \frac{\alpha}{k_{\rm B}T} + \frac{\beta\phi_0}{k_{\rm B}T} \right]. \tag{2}$$

In the above, α is the particle adsorption energy, β is the interaction between the particles at the interface. Solving the above two equations simultaneously, we obtain the time dependence of $\phi_0(\tilde{t})$ and $\phi_1(\tilde{t})$. We have varied the wettability of the particle with respect to the two

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liquids, and followed the time evolution of the particle concentration at the interface. It is found that the dynamics becomes slow for a particular value of the wetting parameter. We have also confirmed that the equilibrium particle concentration at the interface is determined by the Frumkin adsorption isotherm.

As extensions of the present problem, we shall also discus the case when two different types of particles are contained in the liquid, or one type of the particles are contained in the both liquids.

References

[1] A. F. H. Ward and L. Tordai, J. Chem. Phys. **14** (1946), 453.

[2] H. Diamant and D. Andelman, J. Phys. Chem. **100** (1996) 13732.