

Diffusiophoresis of a Charged Drop[†]

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Colloids immersed in electrolyte solutions usually carry net charges on their surface due to ion adsorption, which causes a cloud of counterions surrounding the surface. This cloud, as sketched in Fig. 1, is called the “electric double layer ”(EDL). The EDL is charged with more counterions than coions, and its typical thickness is denoted by κ^{-1} .

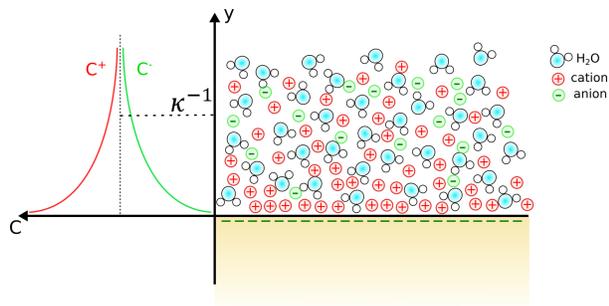


Figure 1: Electric double layer (EDL): The ratio of the number of water molecules (blue) and that of the ions is exaggerated. The former should be usually several orders of magnitude higher than the latter.

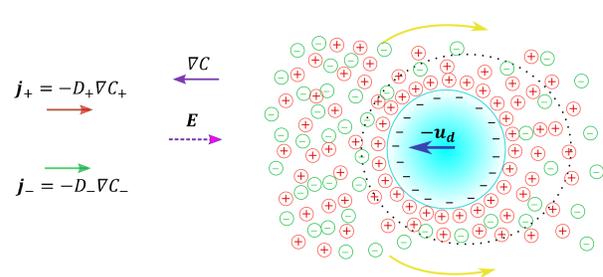


Figure 2: Mechanism of diffusiophoresis when there is an external concentration gradient ∇C : The dotted line indicates the EDL around the colloid. Due to electric forces, the counterions within the EDL move along the direction of the yellow arrows and consequently the velocity of the colloid ($-\mathbf{u}_d$) is in the opposite direction.

If the electrolyte solution has a uniform concentration gradient ∇C , the corresponding ion fluxes $\mathbf{j}_+ = -D_+\nabla C$ and $\mathbf{j}_- = -D_-\nabla C$ are different due to the difference in the diffusion coefficients of cations (D_+) and anions (D_-). Thus an electric field, which depends on the diffusion coefficient difference as well as the concentration gradient, is induced to maintain electroneutrality in solution (i.e., the net charge flux is zero), as shown in Fig. 2. The electric

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field causes motion of the charged colloids by exerting a force on the fluid inside the EDL. The solute gradient also produces an osmotic pressure gradient, which results in motion of suspended particles (chemiphoresis).

This process is called “diffusiophoresis”, first proposed by Derjaguin, et al.¹ in 1947. Most of the previous studies of diffusiophoresis have dealt with motion of rigid particles.²⁻⁴ The viscosity ratio η of the drop and the outer solution is a key factor that distinguishes drops from rigid particles.

In the literature, there are a few papers studying the diffusiophoresis and electrophoresis of drops but they report different results with respect to the dependence on η . For example, Baygents and Saville⁵ calculate the diffusiophoretic speed with respect to different η , which disagree with Lou and Lee’s⁶ calculation. In the field of electrophoresis of droplets, Booth⁷ and Jordan et al.’s⁸ results give different dependence of speed on η in the limit $\kappa a \rightarrow \infty$,⁹ where a is the radius of drops. Additionally, Ohshima and Healy¹⁰ predict that the electrophoretic speed does not depend on η only when the zeta potential on the drop is very large and $\kappa a \rightarrow \infty$, which they refer as “solidification”. However, Baygents and Saville’s¹¹ numerical results show that the “solidification” effects are more significant when κa decreases.

In this report, we study the diffusiophoresis of fluid particles analytically and experimentally. We obtain an analytical solution for the diffusiophoretic velocity of non-conductive fluid particles using perturbation methods on $\alpha = \frac{|\nabla C|a}{c_0} \ll 1$ and $\lambda = (a\kappa)^{-1} \ll 1$, where c_0 is the typical concentration. In laboratory experiments, Dr. Sangwoo Shin uses oil droplets, which are charged by adding surfactants, and measures their speed under a solute concentration gradient. The experiments show that the oil droplets move more slowly than their corresponding rigid particles. But when $\eta > 10$, the diffusiophoretic speed of oil droplets is almost the same as the rigid speed, which implies that there is no strong difference between fluid and rigid particles in a wide range of η for oil droplets. Because ζ of oil droplets can be controlled by adding surfactants, we also propose a new method to control the transport of oil droplets.

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