

Electrolyte Diffusiophoresis in One-Dimensional Salt Gradients

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October 25, 2018

Introduction: Electrolyte diffusiophoresis is the spontaneous movement of charged colloidal particles in an electrolyte gradient [4]. Since its discovery by Derjaguin et al. in 1961, novel particle behaviors due to diffusiophoresis have been observed including particle focusing [5], particle patterning [6], and enhanced particle transport in confined geometries [7, 8, 2].

Applications of diffusiophoresis include a prototype water filtration system, [3], dialysis [10], and enhanced oil recovery [11].

In 1984, Prieve et al. computed diffusiophoretic velocities of non-conducting particles in weak binary electrolyte gradients and showed that motions can be up- or down-gradient [9]. There are two components to electrolyte diffusiophoresis—chemiphoresis and electrophoresis. For chemiphoresis, particle movement is always up the gradient. The concentration gradient creates a pressure gradient in the thin electrical double layer (EDL) of the particle, causing a slip flow, and particle movement in the opposite direction. The direction of particle movement for electrophoresis depends on a diffusivity difference factor, β , and the particle surface charge.

For a symmetric (z:z) electrolyte such as NaCl, $\beta = \frac{D_+ - D_-}{D_+ + D_-}$ where D_+ is the diffusivity of the cation, and D_- is the diffusivity of the anion. When the diffusivities of the ions are different (finite β), an electric field spontaneously forms and preserves net charge neutrality in the solution. Charged colloidal particles move under the action of this electric field.

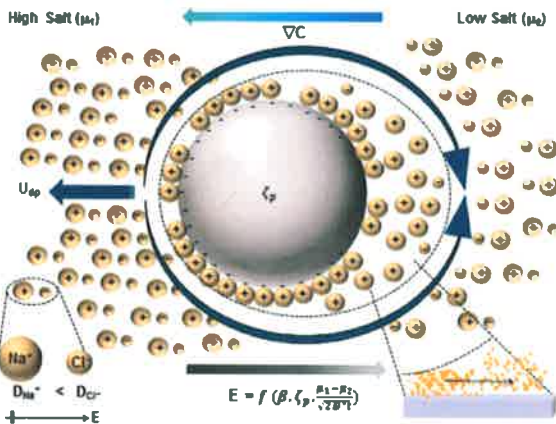


Figure 1: Electrolyte diffusiophoresis of a negatively charged particle, showing flow in the EDL induced by a pressure gradient, and an electric field generated by the different diffusivities of the ions. Picture from [1].

Research Questions: There are many fundamental questions about diffusiophoresis that have not been answered. I am studying the behavior of particles when diffusiophoresis involves ions of different valence, i.e. non-z:z electrolytes. The majority of research experiments and theory focuses on 1:1 electrolytes, which are only a subset of relevant chemistries in many applications. My findings will lay the foundation needed to tackle other questions that limit the applications of diffusiophoresis. These questions include (1) whether colloidal particles can reverse direction upon encountering concentrations high enough to affect an electrophoretic mobility reversal, (2)

whether there is a measurable difference in the diffusiophoretic behavior of constant surface potential particles (metal sols) and constant surface charge particles (latexes), and (3) what happens in the case of multiple electrolytes. Diffusiophoresis in a solution with a combination of

electrolytes is not well characterized. This is a serious omission because real world applications involve multiple chemical species. Also, multiple electrolyte diffusiophoresis is unlikely to exhibit a simple superposition of concentration gradients since ions are electrostatically coupled to each other and can be moved by the internal electric fields. The paucity of rigorous experimental work on the topic seriously limits application of diffusiophoresis-based technologies to real world problems.

I am studying the diffusiophoretic motion of negatively-charged, colloidal particles in 1D salt gradients using a well-characterized dead-end pore geometry [2]. I create salt gradients by exposing a salt solution in dead-end pores to a particle suspension in the main channel. The liquids are initially separated by a plug of air. When the plug flows downstream, the solution in the dead-end pore contacts the particle suspension in the main channel ($t = 0$), creating a concentration gradient. This gradient causes particles in the main channel to flow into the pores. I make the microfluidic channels using standard soft-lithography techniques, image the movement of the fluorescent colloidal particles into the pores using a fluorescence microscope, and extract information about the speed and displacement of the particles. I use a variety of salts to prepare electrolyte solutions: (1:1): NaCl, KNO₃, (2:1) Na₂SO₄, (1:2) CaCl₂ and MgCl₂, and CaSO₄ (2:2), which are currently under study.

Preliminary Result: In my research to date, I have found that the choice of a non z:z electrolyte significantly influences the movement of particles, and in particular the chemiphoretic component of the diffusiophoretic velocity. I plan to study the theory of these motions to rationalize these results. The ability to manipulate particles with chemical gradients will benefit water treatment, drug delivery, dialysis, enhanced oil recovery, and the drying of droplets and paint.

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