A Course in . . .

ELECTROKINETIC TRANSPORT PHENOMENA

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In the chemical engineering curriculum, both at the undergraduate and graduate levels, we spend much time teaching fluid mechanics, mass and heat transfer. Most texts approach these topics from a traditional viewpoint. The mass transferring material is assumed to be point-like molecules of negligible size, and the stationary "transferring to" surface has the usual no-slip boundary condition with no other characteristics that might affect the flow field or the mass transfer process. When dealing with a large-scale system (*e.g.,* a pipe of one millimeter diameter or larger) and with point-like particles (*e.g.,* molecules or ions), the traditional approach is quite adequate. But when dealing with sub-micron particles and with charged surfaces, the traditional approach to transport phenomena is *not* appropriate. This is simply because other forces become significant as compared to, say, viscous forces.

In this paper I give two examples to illustrate that the traditional graduate teaching of transport phenomenon is not as complete as it should be, and I will suggest a theme to cover the essentials of electrokinetic transport phenomena in order to supplement the graduate teaching of traditional transport phenomena.

► EXAMPLE 1 ◄

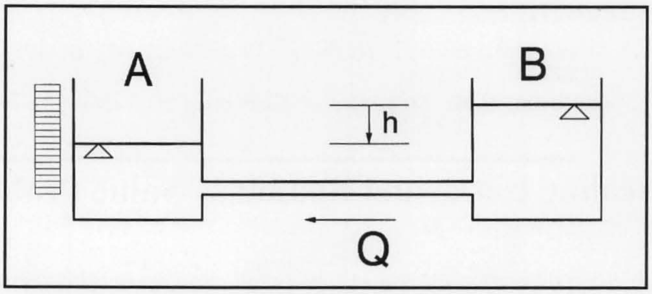

Figure 1. Capillary tube connecting two reservoirs.

Let us construct a simple thought experiment. Assume that a capillary tube of about one millimeter in diameter is attached to two reservoirs containing tap water initially held at different levels, as shown in Figure 1. Making use of a precise stopwatch and a graduated scale, we can measure the rate of change of the water level in reservoir A. From a knowledge of the cross-sectional area of reservoir A, we can evaluate the volumetric flow rate, Q, of the water in the tube. We calculate the Reynolds number in the tube and we find that it is well below 10. To a good approximation, we find that the water volumetric flow rate and the difference in the water levels, h, are governed by Poiseuille's equation.

Let us now replace the tube with a very small capillary, say one tenth of a micron in diameter, and then repeat the flow experiment. To our dismay (or surprise), we discover that Poiseuille's equation does not correlate well with our measurements. Moreover, when we replace the tap water with distilled water using the same small capillary, we obtain a different relationship between Q and h, although the viscosity and density of the two types of water are essentially the same. So why is there a deviation from Poiseuille's equation?

The deviation of our experimental data in the flow experiment is due simply to the fact that the capillary surface is charged. Most substances acquire a surface electric charge when brought into contact with an aqueous or a non-aqueous medium. Direct evidence for the existence of charge on the surface of a particle comes from the phenomenon of particle movement under an applied electric field and from experiments similar to the one suggested here. Surfaces may be-

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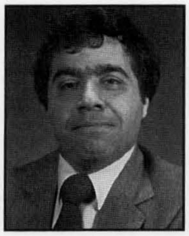

When dealing with a large-scale system . . . and with point-like particles . . ., the traditional approach is quite adequate. But when dealing with sub-micron particles and with charged surfaces, the traditional approach to transport phenomena is* not *appropriate. This is simply because other forces become significant as compared to, say, viscous forces.

come electrically charged by a variety of mechanisms. For now, let us accept that surfaces in an aqueous medium are charged. So, what if surfaces are charged? Why should tap water flow be affected by the charged capillary surface?

Water contains electrolytes (*i.e.,* ions). For our thought experiment let us assume that the capillary surface is positively charged. It is reasonable to assume that the distribution of the ions in an aqueous solution will be affected by the presence of a charged surface. Ions of opposite charge to that of the surface are attracted to the proximity of the surface, while ions of like charge are repelled from the surface. Away from the surface, one can safely assume that the charged surface has no influence on the ionic distribution. So our capillary charged surface creates an ionic concentration distribution in the radial direction of the capillary. Due to the different water levels in the reservoirs, there is a pressure difference at the capillary ends, causing the water to flow. Since the concentration of the negative ions close to the surface is higher than that of the positive ions, a fluid flow to the left reservoir would mean that a net current has to flow in the same direction. But the two reservoirs are not connected together by an "external linkage," (*i.e.,* we have an open electric circuit). Hence, physically no net current can flow. Nature must do something to prevent the current from flowing in the capillary. In order to counterbalance the convective transport of the ions in the capillary, a potential gradient is established within the capillary such that no net current can flow. This induced potential retards the motion of the ions and hence creates an additional flow resistance. That is why Poiseuille's equation is not applicable. We are dealing with additional forces not accounted for in our formulation of laminar flow in capillaries.

From a practical viewpoint, our capillary can represent a narrow pore in a sand-pack where groundwater flows within the pack under a pressure gradient. Conversely, one can make water flow through the sand-pack by imposing an electric potential gradient. In both cases, the water flow is affected by the presence of ions in the water and by the charged sand surface.

► EXAMPLE 2 ◄

A good example of the application of the Navier-Stokes equation is to solve for Stokes flow over a single sphere where we do not consider the presence of a surface charge on the sphere. We can then make use of Stokes' solution together with the boundary layer concept to solve the Levich problem of mass transfer from the sphere. Depending on the approximations used, we arrive at an equation for the dimensionless mass transfer relating Sherwood number with Peclet number:

$$\mathrm{Sh}=0.624\,\mathrm{Pe}^{1/3} \tag{1}$$

The radius of the sphere is used here as the characteristic length.

The above equation is strictly valid for mass transfer of point-like molecules or ions where only convection and diffusion interactions are present. If one is to replace the point-like particles with particles having a finite radius, would the above equation still be valid? In other words, can Eq. (1) describe particle deposition? After all, deposition of particles on a surface is simply a mass-transfer process. What happens if the particles are charged? Since we are dealing with the approach of a finite particle to a surface, surely London-van der Waals attractive forces become important when the gap between the particle and the surface is very small. How does this potential affect the mass transfer? Even a more profound question would be why we did not concern ourselves with the attractive London-van der Waals forces when we derived the mass transfer equation above for the point-like particles.

The questions raised above can be appropriately answered when we include in our analysis the electrical body force term in the momentum equation, the migration term in the convection-diffusion transport equation, and the electrostatic and London-van der Waals forces in the force balance equations. Electrokinetic transport phenomena deals with these very terms which must be added to our already established and understood transport equations.

There are many situations where the presence of a surface charge and the effect of London-van der Waals forces need to be addressed in the analysis of a transport process. Such situations may arise in groundwater flow, desalination, electroosmosis, dialysis, membrane separation, flocculation of particles, deposition of particles on surfaces within packed beds or fibre mats, movement of blood cells, oil extraction, DNA fractionation, pollution control, and rheology.

TEACHING ELECTROKINETIC PHENOMENA

Teaching electrokinetic phenomena is simply an extension of what we normally teach in our traditional transport phenomena courses. It may be clear at this stage that in order to study the two problems suggested above and the various applications previously listed, we need to expand our basic transport equations to include interaction forces other than viscous, inertial, pressure, gravitational, and Brownian interactions. The classical text in the general area of physicochemical hydrodynamics covering the various aspects of electrokinetic transport is due to Levich.[1] In the last few years, several excellent books appeared in the area of colloidal dispersions and electrokinetic phenomena. Probstein[2] gives a very good introduction to the general area of physicochemical hydrodynamics where he combines the traditional transport phenomena with the additional potentials arising from surface charge and London-van der Waals forces. In another book, Russel, *et al.,*[3] give an excellent detailed analysis on colloidal dispersions where they treat particle stabilization, capture, sedimentation, and motion under an electric potential together with a treatise on the electroviscous effects of charged colloidal particles. The mathematical demand of their book is much higher than that presented by Probstein. A comprehensive treatise on the behaviour of colloidal particles under the influence of hydrodynamic forces is given in van de Ven's text.[4]

In a recent book by Masliyah,[5] the transport equations as applied to electrokinetics are summarized with detailed analysis of electrolyte flow in a narrow capillary, motion of a single charged sphere and swarms of particles, particle capture, and deposition, and London-van der Waals dispersion forces, together with some selected applications to the electrokinetic phenomena. Books by Hiemenz[6] and Hunter[7] give good exposure to the general area of colloids and surface chemistry.

Electrokinetic phenomena can be considered as a follow-up course to fluid mechanics and mass transfer graduate courses. The student should be familiar with some of the classical solutions of the Navier-Stokes equations such as laminar flow in channels, simple and shear flows over a single sphere and a cylinder, two spheres in shear flow, and flow models for packed beds. The concept of mass transfer from single bodies for small and large Peclet numbers should also be familiar to the student.

In teaching the electrokinetic transport phenomena course I found it necessary to cover the following areas:

- ▶ Introduction to the colloidal state and its implication. Discussions center on the various forms of typical dispersions, the magnitudes of the characteristic forces as applied to a colloidal particle, and methods of preparing colloidal dispersions.
- ▶ Introduction to electrostatics as applied to a dielectric medium. The Poisson-Boltzmann equation is used to evaluate the thickness of the electric double layer near a charged surface and the electrostatic force between different surfaces within a dielectric medium. The origin of interfacial charge can also be included.
- ▶ Transport equations in electrolytic solutions:
  - Conservation of mass for an electrolyte solution
  - Conservation of ionic species
  - Conservation of current
  - Momentum equation including the electric body force term
  - Poisson equation (relating the local potential and the local charge density)
  - Nernst-Planck equation (a generalized convection-diffusion equation that contains ionic migration due to an electric potential)
  - Various relationships defining diffusivity (*e.g.,* mobility) of a particle
- ▶ Electrolyte flow in a channel. This section makes use of most of the equations discussed in the previous section.
- ▶ Motion of a single sphere under an applied electric field. This section can be expanded to include swarms of spheres.
- ▶ A brief introduction to London-van der Waals forces and their implication to colloidal stability as given by the DLVO theory.
- ▶ Coagulation of particles. Here one can introduce Brownian coagulation, effect of field forces (*e.g.,* electric and London-van der Waals forces), and the effect of shear on particle coagulation.
- ▶ Deposition of particles on surfaces. The various modes of deposition can be discussed both in the Lagrangian (applying a force balance on a particle and following its motion) and in the Eulerian (using the Nernst-Planck equation that represents the generalized convection-diffusion equation) frames of reference.

My experience in teaching this type of a course is that it enhances and sharpens the students' understanding of previously learned transport phenomena concepts. With the excellent texts now available, we have no reason to ignore this important area of the chemical engineering curriculum, especially at the graduate level.

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