Hydrodynamic Dispersion in Micro- Nano-Fluidic Systems

Emiliy K. Zholkovskiy

Institute of Bio-Colloid Chemistry of Ukrainian Academy of Sciences,
Vernadskogo,42, 03142, Kiev, Ukraine

The Hydrodynamic Dispersion (HD) is a phenomenon which is observed when a solute is transported in a hydrodynamic flow through a system of capillaries. In the simultaneous presence of both the solute macroscopic concentration gradient and a flow through capillary system, the solute is redistributed within the capillaries under the flow influence. The formed quasi-stationary concentration field of solute results in an additional portion of the macroscopic convective flux which is proportional to the concentration gradient and is directed against it. Consequently, such a portion of the convective flux behaves as an apparent diffusion flux characterized by an apparent diffusion (dispersion) coefficient being an increasing function of macroscopic velocity magnitude and a length scale parameter characterizing the non-uniformity of local hydrodynamic velocity. At sufficiently high microscopic velocities of flow, the above discussed apparent diffusion, which is referred to as the HD, becomes much stronger than usual molecular diffusion and considerably affects the substance transfer and separation.

The HD manifests itself in different analytical separation methods (electrophoresis, chromatography etc) where one observes splitting of initial portion (band) of mixed analytes into a series of bands containing individual analytes. Because of HD, the obtained bands are broadened with time, and this phenomenon negatively affects both the resolution and the productivity of device. For minimizing the HD, two important approaches are employed in modern analytical technique, namely, (i) micro- and sub-micro miniaturization of the separation column and transportation channels and (ii) the use of electroosmotic rather than pressure driven flows in analytical devices.

In our studies, we theoretically consider the HD due to (i) non- uniformity of electroosmotic flow through a long straight micro-channel and (ii) the departure from the solute adsorption equilibrium. Three types of electroosmotic velocity non-uniformity, which result in dispersion, are taken into account: (I) the non- uniformity within the double layer region and the non-uniformities due to (II) longitudinal and (III) transverse variation of electrokinetic potential. By using a thin double layer approximation, analytical expressions are obtained to address dispersion in terms of plate height for arbitrary magnitude of varying surface potential, electrolyte type and cross-section geometry. The results are presented for different cross-section geometries: parallel planes; circle; annulus; ellipse; arbitrary circumscribed polygon and rectangle. It is discussed how the predicted plate height depends on the cross-section geometry, transverse and longitudinal electrokinetic potential distributions, electrolyte content, adsorption isotherm and adsorption rate constant.

The above results are mostly related to micro-capillary systems. As for the nano-capillaries, the HD is not expected to play an important role in the band broadening there. However, the HD can be important for the processes that are observed when electric current crosses the interface between micro and nano-capillary systems, nano-micro-interfaces. It was demonstrated theoretically that HD considerably influences on the behavior of current-induced concentration polarization. The HD leads to disappearance of limiting current. At essentially “over-limiting” current densities, the time-dependent profiles of electrolyte concentration have sharp “fronts” that move away from the interface with nearly constant speed directly proportional to the imposed electric current density.