

Chemistry 4114.

Homework

30-1 Electroosmosis is the bulk flow of solution through a capillary under the influence of an electric field established along the length of the capillary. Electroosmosis is an electrokinetic phenomenon that arises from 2 electrostatic forces acting on the ions present in the electrophoretic buffer. The walls of the fused silica capillary have surface Si-OH groups present. At the appropriate pH, these groups become deprotonated, establishing a permanent negative charge on the capillary wall. This negative charge attracts cations, and forms an electrical double layer at the interface between the capillary and the buffer solution. Gouy and Chapman show that under the influence of a permanent surface charge, the concentration of ions of opposite charge decays exponentially away from the interface – generating a concentration gradient at the interface (high concentration adjacent to the silica, and the concentration decaying to the bulk value with increasing distance away from the wall).

The large electric field that is aligned along the length of the capillary induces motion of the ions present in the buffer solution (both analyte ions as well as the buffer ions). Because of the large concentration excess of cations adjacent to the capillary wall, this electrophoretic movement of the buffer cations results in frictional drag of the surrounding molecules (including the solvent molecules). This influence of this drag is so large due to the concentration enhancement of the cations at the interface, that the bulk solvent is literally forced to move along the column along with the buffer ions. This bulk flow that results from the ion drag is the electroosmotic flow.

30-3 Amino acids are amphoteric molecules – meaning that they have acidic and basic characteristics. Depending on the pH, an amino acid will exist as either a cationic species, and anionic species, or a zwitterionic species (e.g. no net charge due to cancellation of individual charges within the molecule). The pH at which an amino acid is net neutral in charge is known as the isoelectric point, and the isoelectric point is different for different amino acids. The charge state of the amino acid molecule can, therefore, be controlled by adjusting the solution pH. Because the charge can be controlled, one in principle could also alter the separation of different amino acids by adjusting the pH of the solution.

30-5 In Micellar electrokinetic chromatography, an anionic surfactant is added to the electrophoretic buffer solution at a concentration above the critical micelle concentration. The presence of the surfactant at this concentration results in the formation of micelles (surfactant aggregates that have a non-polar core). Because the micelles have a negative charge, they have a net electrophoretic migration in the direction opposite of the electroosmotic flow. The advantage of this method is that neutral species, which normally migrate only under the influence of

electroosmosis, can be separated from each other based on their different interaction with the micelle.

Organic neutrals will have a distribution equilibrium between the aqueous buffer solution and the organic core of the micelle. While the molecule is associated with the micelle, its net migration down the capillary is slowed to the velocity associated with the micelle. While the molecule is in the aqueous buffer solution, its rate of migration is equal to the electroosmotic flow. For any given neutral molecule, therefore, the time required for it to migrate the length of the capillary depends on the fraction of time spent associated the micelle – and this is given by its distribution coefficient.

The principle advantage of Micellar Electrokinetic Chromatography (MEKC) over conventional liquid chromatography is that MEKC maintains the efficiency of CZE due to the flat flow profile associated with electroosmotic flow.