Abstract

Capillary electrophoresis is a widely used separation method of analytical chemistry. Addition of a selector into the background electrolyte extends its applicability to separation of enantiomers or of compounds of similar physicochemical properties. In analytical practice, mixtures of selectors are also commonly used – either prepared intentionally to achieve better separation or because commercially available selectors may be mixtures of compounds differing in the degree of substitution and substituent positions. Mathematical description of these systems, which are highly relevant in analytical practice, can simplify search for optimal separation conditions. Also, it provides a useful insight into the separation mechanism.

In this work, a model of electromigration of an analyte interacting with a mixture of two selectors is proposed and experimentally verified. This model results from a more general description of systems with an arbitrary number of selectors. The model shows that a selector mixture can be treated as a single selector if the ratio of the respective selector concentrations is kept constant. When the mixture is prepared intentionally, this description predicts, how separation potential of the mixture changes with its composition. Thus it allows the optimal composition and total concentration of the selector mixture to be chosen.

Consequently, a generalized model of electromigration was proposed that for the first time considers analyte undergoing acid-base equilibria along with complexation with multiple selectors. The generalized model shows that the dependency of the effective mobility on the selector concentration, which was originally developed for the case of a single free form of an analyte interacting with a single selector, is generally applicable for systems with 1:1 complexation stoichiometry. The model also enables decoupling of the highly interconnected complexation and acid-base dissociation equilibria. Therefore, the most suitable perspective can be chosen for the particular system optimization. Assumptions resulting from the generalized model were experimentally verified on a system of a week monoprotic acid as an analyte and two selectors.

Determination of complexation parameters serving as input for the above mentioned models requires measurement of correct effective mobilities of analytes. Therefore, this work proposes a method enabling measurement of unbiased effective mobilities in system in which a charged selector may interact with a neutral marker of the electroosmotic flow. A procedure is also proposed for determination of correct migration time of analyte peaks deformed by the electromigration dispersion without the need of nonlinear regression.