Abstract

Mobility of the electroosmotic flow is an important quantity in capillary electrophoresis because its value is needed to determine the effective electrophoretic mobility of analytes. The effective electrophoretic mobility is used for electrophoretic determination of physico-chemical constants, such as dissociation constants or stability constants, but it is also important in analytical chemistry because identification of analytes is based on the value of the effective mobility. The most common way to measure electroosmotic flow is to add a neutral substance to the sample. However, the neutral substance can gain electrophoretic mobility due to interactions with the components of the background electrolyte. This may cause an inaccurate determination of the velocity of the electroosmotic flow.

The aim of this work was to measure the mobility of several common and less frequently used markers in the background electrolyte containing different anions and to find suitable marker – anion combinations in order to avoid major measurement errors.

Relative mobility of eight markers in the pure background electrolyte and in the background electrolyte containing a salt of the studied anion – sodium chloride, sodium perchlorate or sodium sulphate – was measured and related mobility of thiourea. Acetate buffer was used as the background electrolyte. Studied markers were: formamide, *N*-methylformamide, *N,N*-dimethylformamide, acrylamide, *N,N*-dimethylacrylamide, *N*-methylacetamide, mesityloxide, dimethylsulfoxide.

The calculated relative mobilities of the markers were different in the presence of different anions in the background electrolyte. Differences between the relative mobilities of individual markers were largest in the presence of perchlorate anions and smallest in the presence of sulphate anions. On a series of amide markers, it was observed that degree of their methylation influences their relative mobilites. It was further found out that the influence of the tested anions correlates rather well with their position in the Hofmeister's series.

In an experiment where three common food preservatives were separated – sorbic, benzoic and 4-hydroxybenzoic acid – it was found that the values of electrophoretic mobilities obtained by measurement in acetate buffer using different markers may vary by more than 10 %. This can lead to misidentification of the analytes.