Capillary zone electrophoresis (CZE) is one of the most widely used analytical methods for separation of chiral analytes. In contrast to the other common chiral separation methods, chiral complexation agent is usually added directly to the background electrolyte to create enantioselective separation environment. Thus, the type and the concentration of chiral selector can be easily varied, which results in high flexibility of separation system. The detail understanding of electrophoretic separation systems with complexation involved is the main goal of this thesis.

One of the most important advantages of capillary electrophoresis is existence of its complete mathematical model, which was implemented in several simulation programs. They can provide detail insight into the separation process or predict the separation results. However, none of the available simulators is suitable for complexing separation systems, which limits its applicability for chiral separation systems. For this reason, in the scope of this thesis we introduce the complete mathematical model of electromigration for separation systems with complexation agents. The model was implemented in our dynamic simulator Simul 5 and was verified experimentally. The new version of Simul 5 Complex provides the overall picture about the electrophoretic separation with complexation agents and allowed us to demonstrate the development of unforeseen electromigration dispersion connected with complexation. This phenomena was further elucidated using our second simulator PeakMaster 5.3 Complex, whose linearized model of electromigration was extended by complexation equilibria. The new version of PeakMaster 5.3 predicts the extent of electromigration dispersion of analyte peaks depending on concentration of complexation agent. Thus, it can be used for optimization of separation conditions to obtain symmetrical and sharp analyte peaks. Complexation agent added to the background electrolyte can interact not only with analytes but also with buffer constituents. This interaction can significantly influence the buffer properties, such as pH, ionic strength or conductivity. We showed that the value of complexation constant determined in the interacting buffers environment can be totally wrong and may provide misleading information about the strength of complexation. Therefore, the interaction of buffer constituents with the complexation agent should always be considered and tested before the very experiments, e.g. by pH measurement after adding of complexation agent to the separation buffer.