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Model-based analysis of coupled equilibrium-kinetic processes: calculation of thermodynamic and kinetic parameters from the kinetic data

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Model-based least squares fitting analysis or hard modeling is a specific part of chemometrics, which is based on mathematical relationships for describing the measurements [1]. Furthermore, model-based analysis of coupled equilibrium-kinetic processes is the computation of the concentrations of all chemical species as a function of the progress of an intertwined kinetic-equilibrium chemical process. This means equilibrium processes have been directly incorporated into the rate laws [2]. In this study, we demonstrate several models, that they can be applied to numerous chemical mechanisms. There are several different types of intertwined kinetic-equilibrium chemical processes that can be modeled; common examples, modeled in this work, include charge transfer complex formation reactions, pH_dependent degradation of chemical compounds, kinetic of complexation reaction at variable pH and Tautomerization kinetics in micellar solutions. Actually, we have restricted ourselves to chemical reactions where both equilibrium and kinetic procedures are linked with each other. The goal is to demonstrate how the concentrations of all reacting species can be computed as a function of time for any reaction mechanism using the kinetic data. It is relatively straightforward to incorporate an appropriate algorithm into a general non-linear least-squares routine for the investigated data. The calculations are based on the known initial concentrations of the components as well as all estimated rate and equilibrium constants. After the data fitting process, the optimal parameters together with an estimate of their standard deviations have been obtained. Such models allow the fitting of the rate as well as the equilibrium constants. Model-based analysis together with the possibility of calculating and incorporating the equilibrium and kinetic parameters into the fitting algorithm has allowed the complete analysis of complex reaction mechanisms. This is the first comprehensive study of all of these linked reactions, their kinetic constants, and thus their equilibrium constants. This study opens up a promising new avenue for obtaining equilibrium and kinetic constants, simultaneously, using the same kinetic data.

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[2] M. Maeder, Y. M. Neuhold, G. Puxtya, P. King, Phys. Chem. Chem. Phys., 5 (2003) 2836