Reaction equilibrium of the ω-transamination of (*S*)-Phenylethylamine: experiments and ePC-SAFT modeling

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ABSTRACT

This work focuses on the thermodynamic equilibrium of the ω-transaminase-catalyzed reaction of (S)-phenylethylamine with cyclohexanone to acetophenone and cyclohexylamine in aqueous solution. For this purpose, the equilibrium concentrations of the reaction were experimentally investigated under varying reaction conditions. It was observed that the temperature (30 and 37 °C), the pH (between pH 7 and pH 9), as well as the initial reactant concentrations (between 5 and 50 $mmol \cdot kg^{-1}$) influenced the equilibrium position of the reaction. The position of the reaction equilibrium was moderately shifted toward the product side by either decreasing temperature or decreasing pH. In contrast, the initial ratio of the reactants showed only a marginal influence on the equilibrium position. Further experiments showed that increasing the initial reactant concentrations significantly shifted the equilibrium position to the reactant side. In order to explain these effects, the activity coefficients of the reacting agents were calculated and the activity-based thermodynamic equilibrium constant K_{th} of the reaction was determined. For this purpose, the activity coefficients of the reacting agents were modeled at their respective experimental equilibrium concentrations using the equation of state electrolyte PC-SAFT (ePC-SAFT). The combination of the concentrations of the reacting agents at equilibrium and their respective activity coefficients provided the thermodynamically consistent equilibrium constant K_{th}. Unexpectedly, the experimental K_m values deviated by a factor of up to four from the thermodynamic equilibrium constant K_{th}. The observed concentration dependency of the experimental K_m values could be explained by the influence of concentration on activity coefficients. Further, these activity coefficients were found to be strongly temperature dependent, which is important for the determination of standard enthalpy of reactions, which in this work was found to be +7.7 ± 2.8 $kJ \cdot mol^{-1}$. Using the so-determined K_{th} and activity coefficients of the reacting agents (ePC-SAFT), the equilibrium concentrations of the reaction were predicted for varying initial reactant concentrations, which were found to be in good agreement with the experimental behavior. These results showed a non-negligible influence of the activity coefficients of the reacting agents on the equilibrium position and, thus, on the product yield. Experiments and ePC-SAFT predictions showed that the equilibrium position can only be described accurately by taking activity coefficients into account.

KEYWORDS

Catalyzed reactions; Equilibrium concentration; Equilibrium positions; Reactant concentrations; Reaction equilibrium; Temperature dependent; Thermodynamic equilibria; Thermodynamic equilibrium constant