Berichte aus der Verfahrenstechnik

Stefan Willersinn

Reactive Extraction Kinetics in a Membrane-based Microcontactor

D 386 (Diss. Technische Universität Kaiserslautern)

Shaker Verlag
Aachen 2017

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: Kaiserslautern, TU, Diss., 2017

Printed in Germany.

ISBN 978-3-8440-5533-7
ISSN 0945-1021

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen
Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9
Internet: www.shaker.de • e-mail: info@shaker.de

Abstract

The aim of this thesis is the fundamental investigation of mass transfer kinetics for reactive extraction processes, followed by the development of a methodology for deriving universally applicable reaction rate laws and kinetic parameters for the design and scale-up of solvent extraction equipment. This approach is not only able to identify the extraction regime, but also to quantify each individual resistance towards overall mass transfer.

The design of industrial solvent extraction equipment is time-consuming and the scale-up procedure is cost-intensive. Therefore, a predictive, model-based layout and CFD-simulations have recently become important tools for process engineers in order to skip expensive and material-consuming pilot plant experiments. Nevertheless, basic experimental investigations are (still) inevitable for a specific test system in a specific geometry to account for the manifold dynamic and interdependent phenomena. This is even more challenging and complex when considering reactive extraction processes, as a chemical reaction has to be taken additionally into account.

For this reason, a membrane-based microcontactor is developed for the examination of this intrinsic chemical reaction kinetics. Those microstructured systems are well-defined and precisely-controllable, where fundamental scientific knowledge can be derived very safely and fast at relatively low costs, as only low sample volumes are necessary. This microstructured approach additionally leads to a process intensification, which is proofed for the standard EFCE test system in solvent extraction water/acetone/toluene, yielding 10.1 transfer units per meter. The microcontactor is first validated by the well-investigated zinc extraction kinetics, resulting in a model for the reactive mass transfer. This model-based approach has several advantages over traditional methods for investigating the extraction kinetics, as for example in Lewis cells, especially for fast reactions. The implementation of liquid membrane permeation additionally shows an enhanced extraction performance.

The applicability of the methodology is also proofed for germanium extraction and different extractants, namely Kelex 100 and LIX 63. In a first step, the rate law of extraction is determined, which is an apparatus specific rate law. In the next step, all diffusional influences are subtracted and eliminated, resulting in a mass flux, which is exclusively attributed to the chemical reaction, hence the rate law of extraction is transformed into an apparatus-independent rate law of reaction. It is shown, that the chemical reaction of germanium with Kelex 100 is about 8 times faster than with LIX 63 at optimum conditions. These reaction rates and forward reaction rate constants are now easily obtainable and important parameters for the design of other reactive extraction devices.

The process intensified microcontactor has principally a high potential for difficult separation tasks, as for example the enantioselective liquid-liquid extraction. A racemate of a mandelic acid derivative as solute and a β-cyclodextrin derivative as chiral selector is applied as test system. The (S)-enantiomer is preferentially extracted yielding a higher forward extraction rate constant. However, due to the highly laminar flow and the smaller diffusion coefficients of the involved species, the diffusional resistances limit the mass transfer significantly in the microcontactor setup. The developed model needs also some adaptation to account for these homogeneous reactions.

Nevertheless, the fundamental findings as well as the developed methodology allow a future screening and kinetic quantification of potential extractants for reactive extraction systems in a fast, cheap and convenient way. Reactive extraction processes have become increasingly important recently, for example in the field of treating diluted aqueous media or secondary metal recovery from waste electric and electronical equipment, where kinetic data is inevitable for the development of innovative processes.