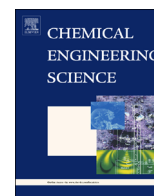




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Separation of systems forming solid solutions using counter-current crystallization

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HIGHLIGHTS

- Fractional crystallization of mixed crystals is successfully performed.
- Process configuration which avoids solid phase transport is presented.
- Mathematical description of SLE behavior and process is given.
- Experiments in lab- and pilot-scale were done.
- Applicability of model and process configuration is demonstrated.

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ABSTRACT

A multi-stage counter-current crystallization is investigated theoretically and experimentally. The process allows separating mixtures, which form complete or partial solid-solutions. An equilibrium stage model is used to describe the progress of the purification with the specific solid–liquid equilibria as main input information. Results presented in this paper concern (a) the demonstration of the process principle for two selected generic systems characterized by complete miscibility in the solid state, namely $K_2SO_4/(NH_4)_2SO_4$ and KCl/KBr , (b) the scale up from a laboratory unit to a pilot plant and (c) the evaluation of the potential of the process principle for the purification of systems characterized by partial miscibility in the solid state.

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1. Introduction

Miscibility of components in the solid state limits the applicability of commonly used crystallization processes and thus frequently complicates corresponding separation tasks. While well-known and well-studied for inorganic substances (e.g. alloys and ceramics), also for organic materials the formation and resolution of solid solutions increasingly attracts interest. The occurrence of complete or partial solid solutions has been the focus of several recent investigations directed to develop solution crystallization

processes (e.g. Kurosawa, 2004; Beckmann and Lorenz, 2006; Galland et al., 2009; Glikin et al., 2011).

In general, there are three different types of binary systems known in the field of crystallization: simple eutectic, intermediate compound-forming and solid solution systems (Mullin, 2001). The first two types represent the majority of all cases. However, also in such systems partial miscibility can occur, but it is difficult to detect and therefore often not recognized (Lorenz, 2013).

When dealing with an additional third component, e.g. a solvent, one needs to analyze ternary phase diagrams. Such a phase diagram is shown for a simple eutectic system in Fig. 1, left. Here, the tie lines, connecting compositions of solid and liquid phases in equilibrium, end at specific locations. In the two outer regions pure components (A or B) are in equilibrium with a

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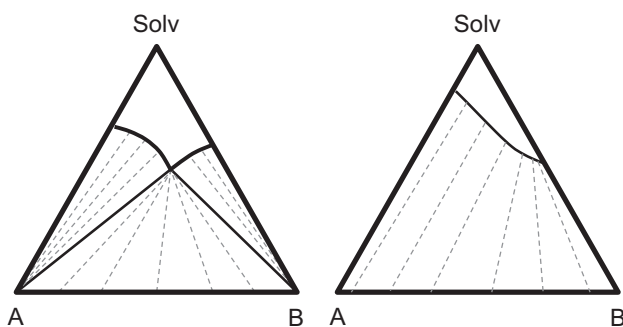


Fig. 1. Ternary phase diagrams of two components A and B in presence of a solvent including tie lines (dotted lines); simple eutectic system (left); system with full miscibility in the solid state (right).

saturated liquid phase of various compositions. In the three-phase domain in-between however, according to the initial solution composition, a saturated liquid phase of eutectic composition can be in equilibrium with variably composed mixtures of two solid phases. During a separation process, the solution composition has to be shifted (e.g. by cooling, evaporation) into the corresponding existence region of the desired product (Wibowo and Ng, 2000). Then a pure component can be obtained within a single crystallization step.

On the contrary, due to complete or partial miscibility, systems can form solid solutions. In these cases the phase diagrams (e.g. Fig. 1, right) become more complex and separations are more difficult. Two basic mechanisms can lead to solid solution formation (Desiraju, 1989; Kitaigorodsky, 1984). If the components have similar molecular shapes and sizes, molecules of a host crystal lattice can be replaced by molecules of the other component (mixed crystals of the substitutional type). Alternatively, interstitial mixed crystals are possible. Here host molecules will not be replaced. Instead, foreign molecules enter the interstices between the host molecules (Kitaigorodsky, 1984).

Due to the formation of solid solutions, the tie lines below the saturation isotherm do not end at pure component corners anymore (Fig. 1, right) and thus are characteristic for the solid–liquid equilibria (SLE) of the particular system. They connect specific compositions of saturated liquid phases and solid phases where the latter are mixed crystals of the components. As a consequence, it is impossible to purify systems with miscibility in the solid state within one crystallization step (Mullin, 2001). In such cases fractional crystallization exploiting multi-stage crystallization processes provides an opportunity for purification (Matz, 1980). This principle is used e.g. in continuously operated crystallization columns (Odagiri et al., 2007; Lin et al., 2008). These columns have some similarity with the well-known “moving beds” (Broughton and Gerhold, 1961), which have been applied successfully in the last decades to carry out chromatographic separations in a continuous manner (Rajendran et al., 2009; Schmidt-Traub et al., 2012). The operation of such crystallization columns is complicated and often not robust. Thus, the few applications are limited to specific separation problems.

A more flexible and feasible concept for fractional crystallization exploits a cascade of standard batch crystallizers. Regarding this approach, theoretical process designs are described (Lin et al., 2008) and overall concepts, based on a large number of connected unit operations, were reported (Mullin, 2001; Matz, 1980). Recently, a fractional crystallization process adapting the principle of continuous multi-column counter-current chromatography was investigated (Aumock, 2011), applying the Upjohn fractional crystallization concept (Poulos et al., 1961).

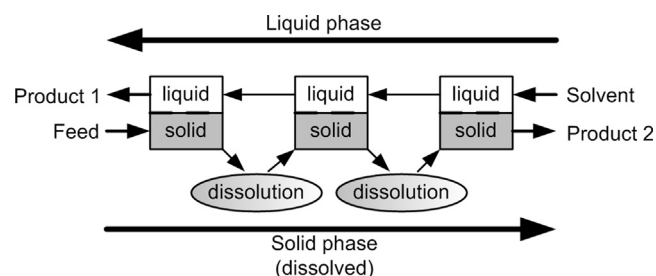


Fig. 2. Concept of the multi-stage counter-current fractional crystallization process, where a periodic dissolution of solid phases allows transporting only liquid phases.

We will describe below a widely applicable and flexible multi-stage counter-current process principle. Hereby, the challenging task of transporting solid phases between different batch crystallizers was solved by applying a new concept reported recently (HAPILA, 2009). Instead of realizing a complicated transport of solids, only liquids are moved through the stages of the process, exploiting periodically performed dissolution steps. The main principle is illustrated in Fig. 2.

Based on a first process analysis published recently (Temmel et al., 2012), we applied for this work the developed stage model of the multi-stage counter-current process, which is similar to classical equilibrium stage models frequently used in chromatography (Craig, 1944). The mass balances for all species in both phases are exploited. Incorporating concrete thermodynamic SLE data of two different salt systems into the model, experiments were planned and performed in lab- and pilot-scales. The results obtained were used to evaluate the capability and potential of the process to separate mixtures involving complete solid solutions. Finally, results of simulations will be given in order to demonstrate the possibility of using the process principle also for the separation of systems with partial solid solutions.

2. Equilibrium stage model

While the transport of liquid phases is quite simple, the transport of solid phases within a multi-stage fractional crystallization process is a more difficult task. Recently a concept was suggested, which avoids the transport of solid phases (HAPILA, 2009; Temmel et al., 2012). The general principle of the counter-current crystallization process is illustrated in Fig. 3.

Periodic realization of suitable temperature changes and arranging specific connections between the various crystallizers provides the opportunity to move the solid phases after complete dissolution as liquids in the desired direction. The individual sub-steps, i.e. transport of the liquid phases, crystallization and dissolution, are done simultaneously in the different vessels. The specific sub-steps, required for a successful separation, can be explained considering just three neighboring stages $j-1$, j and $j+1$ (Fig. 4).

The periodically repeated individual sub-steps of an overall step k can be explained beginning with the crystallization step, which may be initiated by cooling the solutions in the vessels or by evaporating the respective solvent. The crystallization leads to saturated liquid phases and corresponding solid phases in all vessels. The liquid phases are then separated from the solid phases using filters and transported two stages forward in the “liquid phase direction” towards product outlet 1 (Fig. 3), i.e. the liquid phase of stage $j+1$ is transported into stage $j-1$ (Fig. 4). The suspensions formed by the retained solid phases and the added liquid phases are then heated up in order to dissolve the solids. The formed solutions are subsequently transported to the neighboring vessels in the

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