Slope curve method for the analysis of separations in extraction columns of infinite height

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HIGHLIGHTS

- A new "slope curve method" for the conceptual design of extraction columns is described.
- The method easily finds all feasible product compositions.
- Only LLE data needed as input.
- Limitations by internal pinches can be quickly identified.

ARTICLE INFO

ABSTRACT

A new method for the conceptual design of counter-current extraction columns, the slope curve method (SCM), is presented. It is a graphical method based on the equilibrium stage model and developed here for ternary mixtures. The well-known stage-to-stage construction in the ternary phase diagram is replaced by a concise representation in the so-called slope diagram. In that diagram, the slope curve represents the tie lines and operating lines represent material balances. Infinite column height is assumed so that for given feed and solvent composition, the only remaining degree of freedom is the solvent-to-feed ratio. Varying that parameter, all feasible solutions are obtained in the slope diagram. The corresponding product compositions can be reconstructed. Using the method, it is readily shown that internal pinches only occur for certain classes of mixtures, which can be readily identified based on an analysis of the shape of the slope curve. As the SCM yields a complete survey of all feasible solutions it is particularly suited for feasibility studies in conceptual design as well as for obtaining general insights in extractive separations.

1. Introduction

In the conceptual design of chemical processes, the feasibility of flow sheet options has to be evaluated. Before starting cumbersome flow sheet simulations with commercial simulators, it is convenient to consider material balances and thermodynamic property data (e.g. chemical equilibrium or separation limitations as azeotropes) to estimate flow rates and compositions of recycles and other process streams. A number of computer-aided methods for this task have been developed. Ryll et al. (2012a, 2013, 2014) developed a framework to assess the feasibility of entire flowsheets and estimate the compositions of the process streams. The process units are assumed to achieve maximum performance, only limited by thermodynamic boundaries and material balances. A

reactor attains maximum conversion (limited by the chemical equilibrium) and the separation units attain maximum separation efficiency. Distillation columns attain the products which follow from the $\infty/\infty-$analysis (Petlyuk and Avet'yan, 1971; Serafimov et al., 1973), i.e. assuming infinite height and total reflux. The framework has been shown to be useful for the design on novel distillation-based processes, such as the production of trioxane (Grützner et al., 2007) or fuel additives (Burger and Hasse, 2013). It would be interesting to extend the framework to include other types of separation units of maximum separation efficiency as ideal crystallizers (Franke et al., 2008), absorption columns of infinite height (Burger et al., 2015) or extraction columns of infinite height (Minotti et al., 1996). In the present work this is done for the counter-current extraction columns of infinite height.

Minotti et al. (1996) were the first to study extraction columns of infinite height and systematically discuss pinch points in these columns. At the pinch points, the counter-current stream compositions are in liquid–liquid equilibrium, resulting in the absence

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of driving force for separation which leads to infinite column height. Minotti et al. (1996) distinguished two types of pinches: feed pinches that occur at the ends of the column and internal pinches (also called tangent pinches) that occur somewhere inside the column. Further, Minotti et al. (1996) proposed a geometric method for determining the minimal solvent/feed flow rate ratio and the extract composition for a given feed, solvent, and raffinate composition. Thereby, the method also determines the type of pinch that is limiting the separation. The method involves the solution of a set of non-linear equations for which a continuation method is used. It is non-iterative as long as ternary mixtures are considered. Samant and Ng (1998, 1998) showed that the method is also applicable in some reactive systems with more than three components, when the components are coupled via the reaction stoichiometry and a suitable coordinate transformation is used. Recently, Redepenning et al. (2013) mentioned an independent method for determining the minimal solvent/feed flow rate ratio and the extract composition for a given feed, solvent, and raffinate composition for mixtures with more than three components but detailed presentation of that work is still not available.

In the present work a novel geometric method for the conceptual design of extraction columns in ternary systems is introduced which is called the slope curve method (SCM). For a given solvent and feed composition, the SCM enables finding all possible raffinate and extract compositions as well as the corresponding solvent/feed flow ratios. As infinite column height is always presumed here, these ratios are the minimal solvent/feed flow ratios for the considered specifications. In the following, we will simply refer to them as (S/F). In the SCM, contrarily to previously available methods, there is no need for specifying the raffinate composition, the SCM directly yields the solutions for all feasible raffinate compositions. (Of course, here and in the above instead of specifying the raffinate composition and determining the extract composition, also the extract composition could be specified and the corresponding raffinate could be determined). As the SCM yields a complete survey of all feasible solutions it is particularly suited for feasibility studies in conceptual process design as well as for obtaining general insights in extractive separations. It is used here for a general study on the occurrence of pinches in extraction columns. The following questions are answered: under which operating conditions do internal pinches occur? Can internal pinches occur in all systems, i.e. for all solvents or only for certain ones?

It is shown that, only by analyzing the liquid–liquid equilibrium of a given system, it can be decided using the SCM whether internal pinches occur. Furthermore, it is shown here, that for certain systems only feed pinches can occur, whereas for other systems internal pinches may occur, no matter what composition the feed has. These insights are particularly useful in conceptual design. If, e.g., a system is considered in which internal pinches are never present, the design problem can be treated with much simpler methods.

2. Fundamentals

2.1. Liquid–liquid equilibria

For applying the SCM, global information on the liquid–liquid equilibrium (LLE) in the studied system is needed, which can be obtained from any thermodynamic model. We will use the UNIQUAC model (Abrams and Prausnitz, 1975) in our examples and restrict the entire discussion to ternary systems. Concentrations in ternary systems are depicted here in the non-cartesian symmetric triangular map introduced by Gibbs. Other forms like Cartesian coordinates representing concentrations of two arbitrarily selected components could also be used.

There are many methods for calculating liquid–liquid equilibria in ternary systems. We consider only the case that there are two-phase equilibria. Tie lines are used for describing them. There are many methods for determining the tie lines of liquid–liquid equilibria in ternary systems including such which were developed for determining the global behavior in the frame of conceptual process design like the convex envelope method (Ryll et al., 2012b). For the simple examples used here to illustrate the SCM, we have used standard routines based on the iso-activity criterion implemented in a process simulator to calculate the LLE.

The SCM is illustrated for a ternary system of the components A, B, C. The feed is a binary mixture of a solute (A) and a carrier (B) which are completely miscible. The solute (A) is extracted using a solvent (C) which exhibits a miscibility gap with the carrier (B).

2.2. Extraction columns of infinite height and pinches

Fig. 1 shows a simple example of an extraction column with four equilibrium stages in the system of solute (A) + carrier (B) + solvent (C) and introduces the nomenclature used in the following (feed F, solvent S, raffinate R^1, extract E^N). In the examples, we use a binary feed mixture of A + B and a pure solvent C throughout. However, in the SCM, the compositions of feed and solvent can be chosen freely.

Fig. 1 also contains the well-known graphical stage-to-stage construction introduced first by Hunter and Nash (1934). There are two "outer material balance lines", one going through F and E^N and the other through R^1 and S, while all other material balance lines
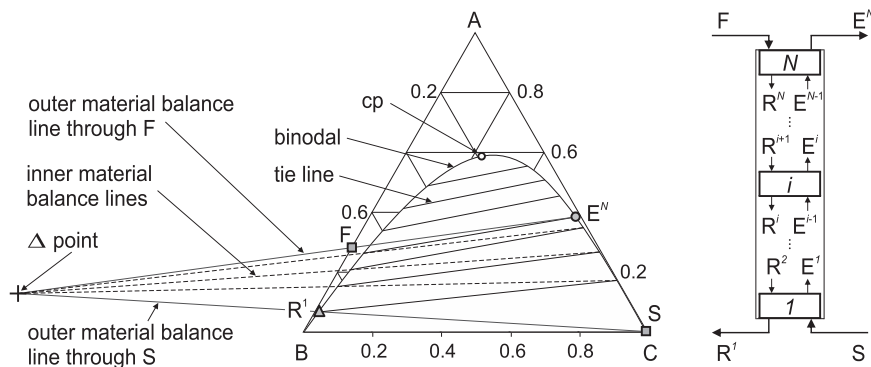

Fig. 1. Ternary phase diagram of a generalized system of solute (A), carrier (B), and solvent (C). The binodal curve and the tie lines of the liquid–liquid equilibrium are shown at constant p and T. The graphical stage-to-stage construction is shown for $N=4$ stages. The compositions are given in mole fractions. F is the composition of the feed, S the composition of the solvent, R^1 the composition of the column leaving raffinate stream, E^N the composition of the column leaving extract stream.