CHAPTER 1

INTRODUCTION

Separation processes are fundamentally important in the chemical industry. It is inevitable that during any chemical process, be it continuous or batch, the need for effective separation will arise. There are a variety of separation options available. However, distillation has proved to be the most effective and commonly used method, especially for the separation of mixtures containing compounds with relatively low molecular weights, such as organic substances. Other efficient separation techniques are absorption and liquid–liquid (solvent) extraction. In recent decades, membrane permeation has come to the fore as a successful method of separating mixtures, both gaseous and liquid.

One would like to have available a technique to select the appropriate method of separation to achieve the required product specifications. This chapter will begin to address this need, laying the foundation for the rest of the book.

Membranes have been developed for various separation applications. Examples of these include, among others, reverse osmosis, electrodialysis, pervaporation, and gas separation. Rautenbach and Albrecht (1989) discuss each of these. The aim of this book is not to reiterate what numerous texts have discussed previously. Rather, the reader is referred to this, and other texts (such as Geankoplis, 1993; Hoffman, 2003; Drioli and Giorno, 2009), which give

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more detailed appraisals of each individual membrane application. In order to demonstrate design and synthesis techniques, only diffusion membranes (e.g., gas separation and pervaporation membranes) will be considered in this book, but the method developed can be adapted and applied to the other kinds of membranes.

In diffusion membrane separation, a high-pressure fluid mixture comes into contact with a membrane, which preferentially permeates certain components of the mixture. The separation is achieved by maintaining a lower pressure (sometimes vacuum) on the downstream, or permeate, side of the membrane. The remaining high-pressure fluid is known as the retentate. Figure 1.1a,b depicts basic batch and continuous diffusion membrane separation units, respectively. A more detailed discussion of membrane process operation is given in the book where appropriate. Gas separation involves the diffusion of a gaseous mixture, whereas pervaporation is a separation process where one component in a liquid mixture is preferentially transported through the membrane and is evaporated on the downstream side, thus leaving as a vapor. These processes are discussed in more detail in Chapter 2.

The conventional way of analyzing membrane separators is to ask what permeate composition can be achieved for a particular feed, as in the experiments conducted by Van Hoof et al. (2004) and Lu et al. (2002). Furthermore, the flux of a particular component through the membrane is also reported as a function of the feed in these and similar experiments. However, it must be remembered that the flux of any of the components may not necessarily remain the same and may vary as permeation proceeds down the length of the membrane (continuous operation). Therefore, the conventional information, although accurate, is insufficient, especially when it comes to designing industrial-scale membrane separators, as well as sequencing of such equipment.

When examining how the other, more established, separation processes are analyzed, it can be seen that the methods used for membranes are somewhat ineffective. In distillation, as well as single-stage flash separations, one never reports how either the top or bottom products are related to the feed, but rather

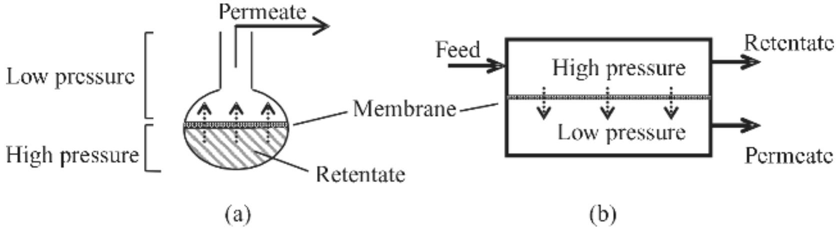

Figure 1.1. (a) Batch and (b) continuous diffusion membrane units.

how they are related to each other. A similar kind of analysis is conducted when designing solvent extraction circuits—one requires the equilibrium data that relates the aqueous phase to the organic phase.

Relating the two product streams to each other allows one to design multiple flash units, or cascades, as well as countercurrent liquid-extraction circuits and distillation columns. The design of such reflux cascades would be impossible if either one of the product compositions were related to the feed entering any of the units within the cascade. It is necessary to analyze membrane separators in a similar manner—one needs to investigate how the permeate composition is related to that of the retentate.

The relationship of the permeate to the retentate has been modeled mathematically. For example, Eliceche et al. (2002) model a pervaporation unit for a binary separation—the analysis was carried out by considering the flux of each component through the membrane and solving simultaneous mass and energy balance equations. Stephan et al. (1995), on the other hand, describe the permeation by a simple dual-mode transport model, and make use of Henry's law to relate the permeate composition to the composition of the retentate. A thermodynamic and more fundamental approach is given in the article by Wijmans and Baker (1995). In this review, the concentration and pressure gradients in the membrane are described using chemical potentials as the fundamental starting point. By appropriately modeling the chemical potentials, and by making use of Fick's law of diffusion, Wijmans and Baker (1995) are able to model the permeation for the various types of membranes, including gas separation and pervaporation. The details of the resulting equation for gas separation are discussed later in Section 2.1.1. Figure 1.2 gives a basic sketch of membrane permeation.

Although the information in these models is correct, it is somewhat difficult to interpret and utilize them for design purposes. It is therefore the aim of this book to formulate a graphical technique that can incorporate the appropriate models in order to interpret, analyze, and design membrane separators in a convenient and efficient manner.

Conventionally, it was believed that residue curve maps (RCMs), and their binary equivalent (i.e., x–y plots), were suitable only for equilibrium-based separations and could not be used for the representation of kinetically based processes (Fien and Liu, 1994). This is discussed further in Chapter 3. However, as will be shown, the differential equations that describe a residue curve are merely a combination of mass balance equations. Because of this, the inherent nature of RCMs is such that they can be used for equilibrium-based, as well as nonequilibrium-based processes. This now allows one to consider kinetically based processes, such as reactive distillation (Barbosa and Doherty, 1988; Doherty and Malone, 2001; Huang et al., 2004) as well as membrane separation processes.

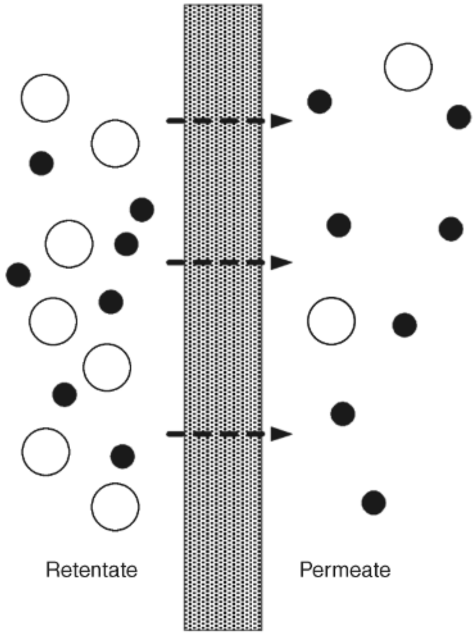

Figure 1.2. Membrane permeation. Differing permeabilities provide the driving force for separation.

This book guides the reader through the development of graphical tools for nonreacting membrane systems. It is necessary to mathematically describe the flux of material through a membrane, as detailed in Chapter 2. The models derived and discussed are used throughout the text. Chapter 3 introduces the concept of membrane plots for various systems, and from Chapter 4 onwards the various applications of these maps are explored.

The MemWorX Package

A mathematical computer program, coded in Matlab®, entitled MemWorX, was especially developed for this book. A CD-ROM containing the MemWorX program is available for the reader and is to be used to aid understanding of the material covered in this book. Throughout the book, where appropriate, references are made to MemWorX, giving basic steps on how to generate plots shown in the book and, where necessary, allow users to produce their own plots. For details on how to install and run MemWorX, the reader is referred to Appendix A, which also includes a step-by-step guide to producing plots using MemWorX.

The majority of figures displayed throughout the book can be reproduced using MemWorX, and, where appropriate, the reader is prompted to attempt to reproduce the figure being referred to (or similar) using MemWorX. The symbol, shown alongside, will indicate when MemWorX should be used. Should any problems be encountered, Table A.4 in Appendix A lists the MemWorX parameters used to produce each figure, according to the tutorial number as listed in the book. This table can be regarded as the solutions to each of the tutorials involving the MemWorX package.