ENANTIOSELECTIVE TRANSPORT OF L-PROPRANOLOL THROUGH A BULK LIQUID MEMBRANE CONTAINING COMPLEX OF (S, S)-di-n-DODECYL TARTRATE AND BORIC ACID

F. P. JIAO†‡, X. Q. CHEN†, Z. WANG and Y. H. HU‡

†School of Chemistry & Chemical Engineering.
‡School of Minerals Processing & Bioengineering, Central South University, Changsha 410083, China

jiaofp@163.com

Abstract — A method of bulk liquid membrane using complex of (S, S)-di-n-dodecyltartrate and boric acid was developed for the enantioselective transport of racemic propranolol. It was shown that l-propranolol can be effectively transported. The enantioselectivity of the complex for a specific propranolol enantiomer in BLM systems is mainly based on kinetics and is not thermodynamically driven. The effects of the concentration ratio of propranolol to chiral carrier and the buffer pH were studied, respectively. An appropriate choice for such concentration ratio and the pH in the aqueous solution result to be 1 : 20 and 5, respectively. The developed method is helpful for optimizing the transport of bulk liquid membrane systems and realizing the large-scale production of pure enantiomer.

Keywords — bulk liquid membrane, enantioselective transport, propranolol, complex of (S, S)-di-n-dodecyltartrate and boric acid.

I. INTRODUCTION

Liquid membranes are liquid phases, existing in either supported or unsupported form, serving as selective barriers between liquid or gas phases, and have shown great potential for use in chiral separations (Way et al., 1982). Bulk liquid membrane (BLM) is one of the types of liquid membranes (Ma et al., 2002, León and Guzmán, 2005). In a BLM, a relatively thick layer of immiscible fluid is used to separate the feed and strip phases; there is no means of support for the membrane phase and it is kept apart from the external phases only by means of its immiscibility. A recent development in liquid membranes is the incorporation of selective carriers within the liquid membrane phase, facilitating chemically the transport of a specific compound across the membrane. With chiral carriers, it is possible to stereoselectively transport optical isomers (Huang et al., 2006; Jiao et al., 2006; 2007a; 2007b). The type of chiral carrier is evidently a very important parameter when designing an experiment.

For resolution of racemic mixtures it is necessary to design and synthesize specific carriers with ability to recognize selectively the desired enantiomer. Hydrophobic (R, R)- and (S, S)-di-n-dodecyltartrate (DDT) have shown to have the property of forming a non polar organic soluble complex with boric acid, preferentially with the corresponding enantiomer of propranolol (PPL), which belongs to the family of β-blocker and served as a model in this study (Coelho et al., 2000). The recognition mechanism of PPL is graphically sketched in Fig. 1. The chiral carrier diffuses from the BLM phase to the feed-membrane interface, where ions PPL+ are exchanged for H+. Due to the high interfacial reactivity of DDT, a tetrahedral complex between the enantiomer of PPL, boric acid and DDT is formed. The formed complex diffuses through the membrane to the membrane-product interface, where, by reversing the described reaction, H+ ions are exchanged for PPL+ ones, which are released into the product phase. Though the presence of boric acid in the product phase, because the concentration of the PPL enantiomer in the product phase is very low, the reversibility of the transport process is very weak or impossible. So the chiral carrier is regenerated, thus beginning a new separation cycle. The enantioselective transport of l-PPL through a BLM containing complex of DDT and boric acid is illustrated in Fig. 2.

No further discussion on the enantioselective transport PPL enantiomer by complex of DDT and boric acid, through a BLM, has been carried out (Ferreira et al., 2006). Based on previous results (Coelho et al., 2000), this work presents more extensive results on the resolution method of BLM. The influence of the buffer pH and the concentration ratio of DDT to PPL were in particular investigated.

Fig. 1. Enantioselective association of l-PPL with DDT by formation of a borate.