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The development of chemically modified P84 Co-polyimide membranes as supported liquid membrane matrix for Cu(II) removal with prolonged stability

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Abstract

We have demonstrated, for the first time, P84 co-polyimide with novel chemical cross-linking modification can be effectively used as the polymeric microporous matrix for supported liquid membrane (SLM) applications. Both asymmetric and symmetric flat membranes with high tortuosity were fabricated via the phase inversion method. It is found that the symmetric membrane outperforms the asymmetric one because the former may provide (1) balanced forces exerted at two aqueous/membrane interfaces and (2) the formation of more stable stagnant layers than the latter. However, the performance of both unmodified asymmetric and symmetric flat membranes deteriorates severely after use for 20–30 h. A novel chemical modification agent, *p*-xylenediamine/water, was discovered and shows effectiveness to improve P84 membrane stability for SLM. The improved SLM stability is attributed to the reduced pore size and the enhanced hydrophobicity on the membrane surfaces. The newly developed chemically modified SLM has a similar lifetime compared with other SLM systems using commercial PTFE as the support matrix.

Keywords: Supported liquid membrane; Stability; Chemical cross-linking

1. Introduction

The use of supported liquid membrane (SLM) for the removal of metal ions from aqueous solutions is a promising separation technique (Ho and Sirkar, 1992; Juang et al., 2000) which offers an attractive alternative to conventional solvent extraction and ion exchange processes. The SLM based separation process has enjoyed many inherent advantages such as the high selectivity, the possibility to concentrate ions by coupled transport with relatively high mass transfer rates, smaller quantity of expensive extractants or solvents required, and the ability of extracting all of the solute and concentrating the extracted species in the stripping solution, which is especially economically and practically attractive when large volumes of solutions require treatment.

Although SLMs have been widely studied for the separation and concentration of a variety of compounds and present many potential advantages over other separation methods, there have been very few large scale applications of SLM due to insufficient membrane stability. Various mechanisms have been proposed for SLM instability: lose of organic phase (carrier and/or solvent) from the membrane phase by dissolution, progressive wetting of the support pores, pressure difference or osmotic pressure gradient over the membrane (Neplenbroek et al., 1992a; Kemperman et al., 1996), and emulsion formation (Neplenbroek et al., 1992b) or attrition of the organic film (Neplenbroek et al., 1992b; Dreher and Stevens, 1998) due to lateral shear forces. SLM stability can also be affected by the type of polymeric support and its pore radius (Chiarizia, 1991), organic solvent used in the liquid membranes, method of preparation (Yang and Fane, 1997), etc. The time periods of initiating instability are observed varies from few hours to several months depending on the systems (Neplenbroek et al., 1992a; Kemperman et al., 1996).

Many research groups have been working on improving the stability of SLMs by using various approaches. One effective method for SLM continuous use is the regeneration of liquid

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membranes. Different methods of regeneration techniques have been reviewed and adopted to stable the SLMs (Makoto et al., 1987). Continuous regeneration of liquid membrane works well, but feed and/or strip solutions are still polluted with the membrane liquid (Kemperman et al., 1996). Based on emulsion formation hypothesis for membrane degradation, gelation of the liquid membrane phase to stabilize SLMs was adopted (Kemperman et al., 1997; Neplenbroek et al., 1992c; Bloch et al., 1967). The major disadvantage of this technique is the poor reproducibility. In addition, the coating technique of the membrane with gel layer seems hard for hollow fibers and not suitable for practical applications (Kemperman et al., 1996). Besides the formation of barrier layers by physical deposition, interfacial polymerization was also adopted to stabilize SLMs (Wijers et al., 1998; Wang et al., 1998; Wang and Doyle, 1999). However, these approaches suffer from a number of severe limitations to their commercially viability (Kovvali and Sirkar, 2003). Normally, microporous polymeric matrix was employed as the support for SLM preparation. In Cooper et al. (2004), a novel SLM consisted of a silica layer from dip-coated colloidal silica on an alpha-alumina support and modified with dichlorodimethyl silane (DCDMS) demonstrated a good stability. But the dip-coating technique to improve stability of SLM seems not commercially viable.

In this work, P84 (BTDA-TDI/MDI, co-polyimide of 3, 3′,4, 4′-benzophenone tetracarboxylic dianhydride and 80% methylphenylene diamine+20% methylene diamine), a most recent commercially available polyimide, has been the first time used as the polymeric microporous support for SLM preparation. This aromatic polyimide was chosen because it possesses a number of attractive mechanical and physicochemical properties (Ohya et al., 1996; Qiao et al., 2005). Because of its superior chemical resistance, it may have potential to serve as the polymeric support matrix for organic carrier immobilization and then to separate two aqueous solutions in harsh chemical environments. To prove our hypothesis, both symmetric and asymmetric membranes were fabricated by both casting and solution spinning using the phase inversion method. Chemical modifications with the aid of *p*-xylenediamine were conducted in order to enhance chemical resistance, surface hydrophobicity and SLM stability. It was found that the SLM with symmetric membrane support had much higher stability than that of the asymmetric one. In addition, in our previous study (Yang and Kocherginsky, 2006) we found when the feed copper concentration is low and the strip acidity is high enough, only transport from the feed solution through the membrane phase is important. We further concluded that in this case the copper transmembrane flux is determined by total of three resistances, that is, the resistance in the feed aqueous solution, the resistance of the chemical reaction and the resistance in the organic membrane phase. Obviously the configuration of membrane itself serving as the support matrix for an SLM system will influence the resistance in the membrane phase, thus changing the flux: the higher porosity, thinner membrane thickness and lower tortuosity of membrane matrix will provide a higher flux; while the membrane with a thin and less tortuous structure is not favorable in terms of stability.

Therefore, the objectives of this paper aim to summarize our studies on (1) the science and engineering of solution spinning of flat P84 microporous membranes for SLM system with reasonable high flux and stability, (2) the effects of *p*-xylenediamine chemical modification on P84 membranes stability and their separation performance for SLM applications.

2. Experimental

2.1. Materials

Fig. 1 shows the chemical structure of P84. It was purchased from HP Polymer GmbH, Austria. The polymer was dried at 120 °C in a vacuum oven overnight before use. The solvent for P84 was *N*-methyl-2-pyrrolidinone (NMP) purchased from Merck. Non-solvent ethanol was purchased from Fisher Scientific. Methanol and *n*-hexane from Merck were used to conduct solvent exchange. *p*-xylenediamine purchased from Tokyo Kasei Kogyo Co. Ltd., Japan, was employed as the crosslink agent. All these chemicals were used as received without further purification. Technical grade isopropanol purchased locally after filtration was mixed with NMP as the coagulation bath for symmetric membrane spinning. LIX54 was supplied by Cognis Corporation, USA and was diluted in kerosene from Aldrich in 33 v/v% as a carrier in liquid membrane phase. LIX54 is recommended as a carrier for selective removal of copper from alkaline solutions with ammonia (LIX 54, 1975).

2.2. Preparation of asymmetric membranes

The dried P84 powder was dispersed slowly into a chilled NMP and ethanol mixture at predetermined weight ratio of P84/NMP/ethanol (25/65/10). According to the phase diagram of this ternary system (Qiao et al., 2005), this composition may produce membranes with reasonably high porosity. The mixture solution was stirred until it became homogeneous, then it was cast onto a glass plate with a casting knife at a thickness about 200 μm. The nascent films were immediately immersed into a coagulation bath of 60/40 wt% NMP/ethanol at 60 °C for half an hour. The specific composition of the coagulant was chosen to reduce the difference in solubility parameter between the polymer solution and the coagulant, thus slowing down the precipitation rate in a hot bath and forming spongy-like cross-section morphology.

The as-cast asymmetric polyimide membranes were solvent exchanged and dried according to the following procedure: the membranes were immersed into water overnight. Low surface tension liquids (methanol and followed by hexane) were employed to remove water and residual solvents.

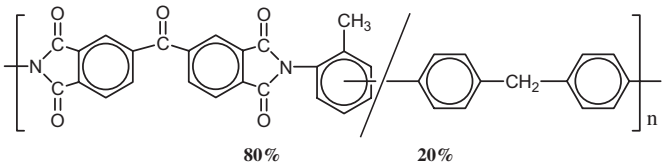

Fig. 1. The chemical structure of P84 co-polyimide.