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Pervaporative recovery of N-methyl-2-pyrrolidone from dilute aqueous solution by using polyurethaneurea membranes

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Abstract

Hydroxyterminated polybutadiene (HTPB)-based polyurethaneurea membranes were synthesized and used for pervaporative recovery of N-methyl-2-pyrrolidone (NMP) from dilute aqueous solution. The sorption of NMP in cross-linked polyurethaneurea membranes was found to vary with feed NMP concentration and soft segment content of the membrane. A linear sorption isotherm was observed. The effects of membrane soft segment content, feed NMP concentration, operating temperature and membrane thickness on the pervaporation performance of the synthesized polyurethaneurea membranes were studied. With decrease in soft segment content of the membrane, the permeation flux was observed to decrease slightly but the separation factor increased to some extent. With the increase in concentration of NMP in feed solution, permeation flux was found to improve significantly. Both the permeation flux and the separation factor for NMP were found to increase with increase in operating temperature. The activation energy for pervaporation of both NMP and water calculated from Arrhenius plot indicated that an increase in hard segment content imposed a restriction to the transport of the components through the membrane.
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1. Introduction

Traditional methods for the separation, purification and concentration of various chemicals often involve a phase change as in distillation or extraction followed by distillation. These techniques are energy intensive. Separations of the chemicals are often unattainable to a satisfactory level through conventional separation based on adsorption. Therefore, it is desirable to develop a low energy separation process. Pervaporation (PV) is an efficient membrane-based separation process, which is widely considered as an alternative method due to its beneficial advantages over conventional energy intensive separation processes such as high selectivity, low energy consumption, moderate operating temperature, physical separation mechanism and no additives requirements [1]. PV is used for the economical separation of liquid mixtures; especially,

aqueous–organic azeotropes, close-boiling mixtures, isomers, heat sensitive and hazardous chemicals [2–4]. Separation by pervaporation is almost independent of the vapor–liquid equilibrium, because the transport resistance depends on the sorption equilibrium and mobility of the permeant components in the membrane.

N-Methyl-2-pyrrolidone (NMP) is a powerful, aprotic solvent with high solvency, and low volatility. NMP has high chemical and thermal stability and is completely miscible with water at all temperatures. NMP is a versatile solvent for use in numerous applications including graffiti removal, automotive and industrial cleaning, water borne coatings, and photoresist stripping. NMP is used as a solvent in synthesis of pharmaceuticals because of its broad solvency. NMP has been shown to have a selective affinity for unsaturated hydrocarbons, aromatics and sulfur-bearing gases and hence it is widely used as a solvent in petroleum refining and petrochemical industries. Due to its relative non-reactivity and high solvency, NMP finds wide applications as an extraction solvent in lube oil processing as well as in natural and synthetic gas purifications. Many monomers and polymers are soluble in NMP. NMP is also

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used in the microelectronics fabrication industry. In agriculture, NMP is used as a solvent-carrier in pesticides. Hence, separation of NMP from wastewater from the above-mentioned industries dealing with NMP is very challenging and rewarding. PV could be a better alternative to separate NMP from wastewater than other traditional processes.

According to the solution–diffusion model describing the transport of molecules through pervaporation membranes [5], the permeation process consists of the three consecutive steps: (i) sorption from the liquid phase into the membrane which comprises the partitioning of the mixture components between the separated mixture and the swollen layer of the membrane; (ii) diffusion of the sorbed components through the membrane; (iii) desorption from the polymer into the vapor phase at the permeate side of the membrane. The separation effect of pervaporation is based on different permeabilities of the compounds to be separated and combines the influences of both sorption and diffusion steps. The separation performance of the membrane is determined to a great extent by the sorption step in the pervaporation process. The sorption coefficient gives information about the selectivity of a polymer membrane towards one of the components of the feed mixture since the component in the feed with the lowest energy requirement is preferentially sorbed in the membrane polymer. In order to understand and describe the separation of NMP from aqueous streams by pervaporation through polyurethaneurea membrane, the sorption and diffusion properties of permeating components are, therefore, to be studied first.

In this communication, the prepared hydroxyterminated polybutadiene (HTPB)-based polyurethaneurea (PUU) membranes were used to effect separation of *N*-methyl-2-pyrrolidone (NMP) from synthetic wastewater by pervaporation. The effect of sorption of NMP on permeation flux and separation factor was studied. Moreover, the influences of process parameters such as the feed composition, operating temperature, membrane thickness and soft segment content of the membrane on the separation performance of the membranes were studied.

2. Experimental

2.1. Materials

HTPB (functionality = 2.4, hydroxyl value = 43.2 mg of KOH g^{-1}) with a number average molecular weight of 2580 (M_n, in g mol^{-1}) was received from VSSC (India) and was used as received. 2,4-Toluylene diisocyanate (TDI) (Fluka AG) was used without further purification. 4,4′-Diaminodiphenylsulfone (DADPS) was first dehydrated under vacuum overnight and then was sublimed. The catalyst dibutyltindilaurate (DBTDL) (Fluka AG) was used as received. *N*-Methyl-2-pyrrolidone (NMP) was procured from Merck (India).

2.2. Synthesis of polyurethaneurea membranes

Prepolyurethane (PPU) was prepared by the reaction of HTPB and TDI in THF at 30 °C in presence of 0.5 wt.% DBTDL as catalyst maintaining NCO:OH mole ratio of 2:1. The degassed polymer solution was cast on a petridish for obtaining PPU membrane. For the synthesis of polyurethaneurea (PUU), diamine chain extender (DADPS) solution in THF of required concentration was added slowly to the reaction mixture containing prepolyurethane with constant stirring after 55 min of reaction between HTPB and TDI. The reaction was continued for further 30 min. The excess solvent and entrapped bubbles were removed from the viscous solution by evacuation. The PUU film was cast on a clean petridish. The cast films of PPU and PUU having thickness of about 0.18 and 0.35 mm were left overnight at room temperature for moisture curing followed by thermal curing at 80 °C for 5 h.

2.3. Sorption experiment

Sorption experiments were performed to determine the mass sorption coefficient by immersing the membrane in feed NMP solution for 48 h. After the experiment, the feed solution was analyzed for NMP content by UV spectroscopic analysis. The amount of feed components sorbed in the membrane was determined by mass balance.

Mass of the solution and the mass of NMP in the solution was measured before sorption experiment. The gain in mass by the membrane due to sorption was calculated by taking mass of the membrane sample before and after the sorption experiment using a weighing balance. The concentration of NMP in the solution after sorption experiment was analyzed by UV spectroscopic analysis. The change in solution mass was due to the sorption of feed components in polymer matrix. Mass of NMP in the solution after the sorption was obtained from the product of mass of solution after sorption and concentration of NMP in solution after sorption. This gives change in mass of NMP in the solution due to sorption. This much NMP was sorbed in the membrane and thus the concentration of NMP in the membrane was obtained. The decrease in solution weight due to sorption onto the membrane was also found to match exactly with the membrane weight gain.

2.4. Measurement of diffusion coefficient

The diffusion coefficients of NMP and water (D_{NMP} and D_{water}) in polyurethaneurea were measured at different temperatures and at different NMP concentration by keeping the membranes immersed in aqueous NMP solution and noting the change in relative weight gain (m_t/m_α) with time. Thicker membranes were preferred in order to nullify the error due to vaporization of liquid from surface. The value of average diffusion coefficient was calculated from the slope of a plot of relative weight gain (m_t/m_α) against t following the equation [6]:

$$\ln\left(1 - \frac{m_t}{m_\alpha}\right) = -\frac{\pi^2 D}{l^2}t + \ln\left(\frac{8}{\pi^2}\right) \tag{1}$$

where, m_t and m_α are fractional weight gain of membrane at time t and at equilibrium swelling, respectively. D and l are diffusion coefficient and thickness of the membrane, respectively.