

Dehydration of isopropanol and its comparison with dehydration of butanol isomers from thermodynamic and molecular aspects

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Abstract

By examining the dehydration of aqueous isopropanol (IPA) systems using two Sulzer commercially available polyvinyl alcohol (PVA)/polyacrylonitrile (PAN) membranes which were prepared from different cross-linking agents, we have (1) investigated the membrane performance from the standpoints of flux versus permeance and separation factor versus selectivity plots and (2) determined the effects of membrane properties such as degrees of cross-linking and hydrophilicity on water and IPA flux and permeance and their separation factor and membrane selectivity. PERVAP 2201 has higher degrees of cross-linking and chain packing than PERVAP 2510, while PERVAP 2510 has stronger hydrophilicity than PERVAP 2201. For PERVAP 2510, water permeance increases sharply with feed water concentration, but shows little dependence on temperature. For PERVAP 2201, water permeance shows flat relationship with feed water concentration, but increases with increasing temperature. Both IPA flux and permeance increase with increasing feed water concentration and their relationship with feed water content can be mathematically explained. It is noticed that the separation factor versus feed water content plots may mislead the analysis of water influence on membrane performance and exaggerate the plasticization phenomenon. Coupled transport has been observed between IPA and water. However, the degree of coupled transport is dependent on the membrane properties, such as the degree of cross-linking, affinity to water and structure responses on temperature rise. Compared with the dehydration of butanol systems, we found that the degree of coupled transport follows the order of 1-butanol > 2-butanol > IPA \geq *tert*-butanol. After examining many physicochemical properties of penetrants and membrane materials, it is concluded that the molecular linearity (or the aspect ratio) of penetrant molecules and their solubility parameters (as well as polarity parameter) determine the magnitude of coupled transport, while the effects of other physicochemical properties seem to be not so important if coupled transports become dominant in the dehydration process.

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1. Introduction

Presently, isopropanol (IPA) is drawing attention as an important solvent in pharmaceutical and electronic industries. Most of the applications require high purity, i.e. 99.5% of IPA content [1–2]. However, IPA forms an azeotrope with water at 88 wt.% [3] and this makes it difficult to be separated from water by conventional processes. Compared to conventional processes such as distillation or adsorption, pervaporation

is very promising because of its interesting energy saving aspect [4] and effectiveness for azeotropic separation and solvent recovery. Pervaporation uses a dense membrane as a barrier to separate liquid mixtures. The solution–diffusion model is generally accepted [5,6] to describe the transportation of pervaporation membranes. Besides the driving force difference, the separation can also be achieved by the differences in diffusivity and solubility of each component through the membrane. However, the preferential sorption contributes more to the selectivity of pervaporation membranes than gas separation membranes. Generally, the transport phenomenon in pervaporation is more complicated than many other mem-

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brane processes, such as microfiltration and air separation. This makes the analysis of experimental data very difficult. The feed side of a pervaporation membrane is in contact with a liquid mixture, and hence the degree of swelling and plasticization are strongly affected by the composition of feed liquid mixture. As a result, the permeability of each component is also affected. Moreover, mutual interaction between liquid molecules is much stronger than gas molecules, thus increases the complexity of the pervaporation transport. Mulder and Smolders [7] and Huang and many other workers have laid the foundation of the solution–diffusion model based on the free volume theory and the modified Flory-Huggins thermodynamics [8–11]. The Flory-Huggins interaction parameters were employed to describe the interactions between permeants as well as between permeants and the membrane [7,8,10,11].

Coupling effects have often been reported in pervaporation [7–17]. This phenomenon arises from the complicated coupled transport of the penetrants across the membrane. One component may flow without or even against its own driving force because of the influence of the other component and the membrane. The origins of coupling may be derived from two aspects; namely, thermodynamics and kinetics [7,8]. Thermodynamically, interactions between the penetrants molecules always exist depending on their chemistry. Kinetically, diffusion with the aid of thermodynamic interactions induces kinetic coupling. Kedem considered this type of coupling as a mutual drag [12]. Wessling et al. reported the extent of coupling depends on the difference in the permeabilities of the pure components [13]. In addition, the physicochemical interactions between the penetrants and the membrane material may result in membrane swelling or plasticization, thus change the thermodynamics of the sorption of penetrant components in the membrane and the dynamics of diffusion jumps between the interstitial chain spaces. Drioli et al. believed the orientation of the dissolved penetrant molecules also alter the configuration of the microvoids among the polymer chains and results in the facilitation or inhibition of transport of the other component through the membrane [15]. Schaetzel et al. investigated dehydration of aqueous ethanol solution through a PVA based membrane and concluded that coupling phenomenon is more exhibited for the flux of ethanol (the slow permeant) than for the flux of water (the fast permeant) [17].

Ethanol separation by pervaporation has received most attention during the last several decades [7,9,11,18–20], while intensive research on IPA separation by pervaporation just started about from 10 years ago [2–4,21–27]. Most of published works focus on the dehydration of IPA. Among the polymeric materials being investigated, PVA based membranes are the most popular one. This is probably because PVA is a highly hydrophilic polymer and has unique film-forming characteristics. Controllable hydrophilicity and good chemical-resistant properties make it very effective for pervaporation dehydration. However, the performance of PVA membranes for ethanol and IPA is often interpreted using

flux and separation factor. It is worth noting that these two parameters traditionally used to characterize pervaporation membrane performance are a complex combination of the effect of driving forces, the effect of interaction between permeants, and the intrinsic property of the membrane. Wijmans and Baker [28,29] proposed using the normalized permeation flux (permeance) to exclude the effect of operating conditions and to reveal the intrinsic property of the membrane. We have studied the dehydration of aqueous butanol solutions and compared flux versus permeance and separation factor versus selectivity [30] and found that normalizing the flux with respect to the driving force would make the comparison much more meaningful and explainable. In other words, using permeance and selectivity can significantly decouple the effect of operating conditions on performance evaluation, therefore clarify and quantify the contribution by the nature of the membrane to separation performance. By doing so, it also brings new insights to the factors that truly govern mass transport in pervaporation. However, such comparison of using permeance and selectivity rather than flux and separation factor is still fairly scarce in the literature.

In order to confirm our previous observation on other systems and to facilitate the understanding of the complicated relationship between permeance/permeability and plasticization/swelling, we choose the dehydration of IPA systems using two different commercial PVA/PAN composite membranes in this study. We also try to compare the pervaporation of IPA systems with a series of butanol isomer systems by using permeance to elucidate the influence of permeants interaction, their molecular shapes and sizes on the performance.

2. Experimental

2.1. Materials

PERVAP 2510 and PERVAP 2201 membranes were purchased from Sulzer Chemtech, Germany. Both membranes have a cross-linked PVA selective layer and a porous PAN supporting layer cast on a polyphenylene sulfide (PPS) non-woven fabric. HPLC grade IPA was supplied from Fisher Scientific Singapore. IPA has a boiling point of 82.5 °C.

Fig. 1 shows the SEM pictures of PERVAP 2510. The PPS non-woven fabric was carefully removed before fracturing the membrane in liquid nitrogen. The total thickness of the membrane is about 87 μm , where the dense selective PVA layer is about 0.7 μm .

2.2. Pervaporation experiments

A lab scale Sulzer pervaporation unit was purchased to carry out the pervaporation experiments and its design has been described elsewhere [30,31]. Briefly, a testing membrane was placed in a stainless steel permeation cell with an inner diameter of 15.24 cm and an estimated surface area of

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