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Coupled concentration-dependent diffusivities of ethanol/water mixtures through a polymeric membrane: Effect on pervaporative flux and diffusivity profiles

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ABSTRACT

The partial pervaporative (PV) fluxes of ethanol/water mixtures in polydimethylsiloxane (PDMS) were predicted using Fick's first law and modified Maxwell–Stefan equation. The sorption levels were predicted using UNIQUAV-HB and the experimental solvent diffusion coefficients of the mixtures were expressed in terms of their sorption concentrations according to Long's model. Both permeant diffusion coefficients were found to vary with the ethanol concentration alone. The predicted partial fluxes and the PV separation factor agreed well with the experimental data by integrating Fick's law over the ethanol concentration. The modified Maxwell–Stefan equation was employed to estimate the partial fluxes by taking into account both permeant concentration gradients. The modified Maxwell–Stefan equation rendered similar partial permeant flux and ethanol-over-water separation factor as in Fick's law. The agreement between the predicted PV performance and the experimental data indicates that the unsteady-state permeant diffusion coefficients reflect the diffusion behavior in the steady-state PV operation. The concentration and diffusivity profiles for the permeants in the PDMS were illustrated along the trans-membrane direction. These diffusivity profiles can be explained using the Vrentas–Duda free volume theory.

1. Introduction

Pervaporation (PV) is a membrane-based separation process. It has applications in the separation of a wide range of aqueous and organic mixtures [1–3] and may offer an energy-saving advantage. Many researchers found that PV can effectively separates ethanol from aqueous mixtures at a low operational cost [2,4,5]. Polydimethylsiloxane (PDMS) is a suitable polymer film for pervaporatively separating ethanol mixtures [5–7]. The solution–diffusion mechanism [8–10] and Fick's law [11,12] are often used to describe the mass transfer behavior for permeants through the non-porous membrane phase. The sorption and diffusion selectivities of the permeants in the membrane are the main factors governing the PV performance [1,13–20].

The sorption behavior of the permeants in membranes is the first differentiation factor in a PV separation process. Although the sorption level of some ideal mixtures, such as xylene isomers in a polyurethane-based membrane [1], demonstrate a linear relationship with the feed composition, most aqueous alcohol solutions exhibit a more complex sorption pattern. Polymer plasticization upon solvation [21] and intra-molecular hydrogen bonding [22] among the permeants significantly influence the solubilities and permeabilities of the mixtures in membranes. Perhaps these phenomena explain the significant deviations of the permeation selectivities from the sorption selectivities for ethanol/water mixtures in hydrophobic membranes even after the concentration-dependent Flory–Huggins interaction parameters were introduced to account for the coupled sorption effect [13]. In our previous work, we have described the sorption behavior of ethanol/water mixtures in PDMS using the Flory–Huggins equation [23] and UNIversal QUAsi Chemical (UNIQUAC) models [22]. It was found that the UNIQUAC-hydrogen bond (UNIQUAC-HB) model is advantageous over the classic UNIQUAC model and the Flory–Huggins equation for the ternary ethanol/water/PDMS system [22]. Only the binary interaction parameters (e.g., parameters obtained from the pure solvent sorption data) are needed to adequately estimate the sorption levels of the mixtures in the PDMS using the UNIQUAC-HB model. In contrast, in the Flory–Huggins model, the interaction parameter between the solvent and the polymer was concentration-dependent and must be determined experimentally for the ternary component system [13,23]. The UNIQUAC model offers the same advantage as the UNIQUAC-HB model, but the synergistic water solubility due to the presence of ethanol was better captured using the UNIQUAC-HB equation [22].

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The permeant diffusivity in the membrane provides the second screening mechanism in a PV process. Organic and water vapors have been report to diffuse independently in a PDMS membrane; the single vapor diffusivity is the same as that in a binary gas mixture of organic and water molecules at the same sorption concentration [24]. For liquid mixtures, however, the diffusion parameters are hardly available from single-solvent experiments because the solvent diffusion coefficients often depend on the other sorbed penetrant concentration. In the PDMS film, we found that both water and ethanol permeants exhibited similar diffusivities [25].This indicates a strong coupling effect between the permeants. The diffusion selectivities from mixtures are significantly different from the ideal diffusion selectivity based on the pure solvents in PDMS [25].

In light of the complicity of coupled diffusion between non-ideal ethanol and water permeants, most approaches involve experimentally determined solubilities and pervaporative fluxes from the mixtures and derive the diffusion behaviors from these data. [13]. In this process, a certain diffusion–solution relationship assumption is used, such as Long's model or free-volume theory [26,27]. In our previous paper [25], we employed the sorption method on ethanol/water mixtures into PDMS and determined the individual solvent uptake history as a function of the elapsed time. The diffusion coefficient of each penetrant was derived in the presence of the other co-permeant. These diffusivity data were based on the unsteady state of the sorption experiment and it is ultimately important to evaluate these data for the applicability in predicting steady-state PV flux.

The objective of this study was to predict the PV fluxes for water and ethanol using the sorption and diffusion data of ethanol/water mixtures in the PDMS membrane at 298 K. The UNIQUAC-HB model was employed to describe the sorption behavior of the ternary system. The permeant diffusivities were expressed as a function of the solvent sorption levels in a membrane matrix. Fick's first law and the modified Maxwell–Stefan equations were employed to build mathematical expressions for the partial fluxes of the ethanol and water components through the PDMS membrane. The predicted fluxes were compared with the experimental data to verify the validity of the permeant diffusivity based on the unsteady state (i.e. sorption experiments) reflects the actual diffusion behavior during a steady-state PV operation. In addition, once the concentration-dependent diffusivity was determined, the permeant concentration and diffusivity profiles along the trans-membrane axis were illustrated for the permeant when the mixtures were fed to the PV process.

2. Experimental

2.1. Materials

Pure ethanol (absolute ethanol) was obtained from Sigma-Aldrich Inc., St. Louis, MO, USA and water was purified using the Elix 5/Milli-Q Gradient system (Millipore Corp., Bedford, MA, USA). The densities for ethanol and water were 0.785 and 0.997 g/cm^3, respectively, at 298 K. The toluene solvent was purchased from Mallinckrodt Baker Inc., Phillipsburg, NJ, USA. A two-component PDMS recipe was obtained from Shin-Etsu Chemical Co. Ltd., Tokyo, Japan.

2.2. Membrane preparation

The PDMS membrane was prepared as described by our previous study [28]. The PDMS prepolymer (KET 3001) was dissolved in 1.5 times its weight in toluene. After mixing for 2 h, the cross-linker (CAT 3001) was added to the solution at an amount equal to one-tenth of the PDMS prepolymer and mixed for an additional 30 min. The solution was then placed in an ultrasonic bath (model DC-300H, Delta New Instrument Co. Ltd., Taipei, Taiwan) at 283 ± 1 K for 3 h to remove air bubbles. The homogeneous solution was cast onto a Teflon plate (Taiwan Shang Da Fiber Plate Co. Ltd., Taoyuan, Taiwan), and an applicator knife (model 3580, Elcometer Instrument Ltd., Edge Lane, England) was used to achieve a uniform film thickness. The film was dried in a vacuum oven at 353 K for 6 h. The film was then peeled off and stored in a desiccator until use [28].

A thickness gauge (model 7331, Mitutoyo Co. Ltd., Kawasaki, Japan) was used to measure the membrane thickness at 10 random locations. The average thickness of the membrane for the PV test was 200 ± 15 μm with a membrane density of 1.090 ± 0.051 g/cm^3 measured using the pycnometer (model Accupyc II 1340, Micromeritics Inc. Co., Norcross, Georgia, USA). The characterization of the PDMS membrane has been shown in previous studies [29,29]. The molecular weights of the prepolymer and cross-linker were determined using gel permeation chromatography (GPC) and found to be 73,700 and 2800, respectively. The polydispersity indices (M_w/M_n) of the prepolymer and cross-linker were 1.57 and 1.39, respectively [29]. The X-ray photoelectron spectroscopy (XPS) analysis of the PDMS membrane showed the presence of silicon, carbon, and oxygen. The Si/C ratio was approximately 0.398 [29]. This PDMS membrane had a glass-transition temperature (T_g) of −94.9 °C, as measured utilizing a differential scanning calorimeter (DSC) [20,28]. The degree of cross-linking (%) of the PDMS membrane was approximately 9.37%, as estimated by the Fourier-transform infrared (FTIR) spectrometer [29]. The free volume of polymer was found to be 20.49–21.66% using conventional positron annihilation lifetime spectroscopy (PALS) [29,30].

2.3. Solvent sorption levels and diffusion coefficients in the membranes

The solvent sorption levels and diffusion coefficients were determined using the gravimetric method [31]. The membrane dry weights were first determined using a microbalance (model BP211D, Sartorius AG, Goettingen, Germany). The dry membranes were immersed in double-jacked containers filled with 0–100% ethanol solutions at 298 K. After a fixed time interval, the membrane was removed from the solvent and wiped with tissue paper as soon as possible. The weight of the wet membrane was then recorded. The total sorbed solution weight was the wet membrane weight less the dry film weight. The composition of the remaining solution was measured using a density/specific gravity meter (model DA-130N, Kyoto Electronics Manufacturing Co. Ltd., Kyoto, Japan). After the composition and the individual solvent weights in the remaining solution were determined, the solvent uptake in the membrane was calculated from the difference between the original solvent weight and the remaining solvent weight. In this way, the solvent uptake from a mixture was partitioned into individual water and ethanol uptakes. A new dry membrane was immersed in a mixture with the same composition for sorption over a longer time. These steps were repeated until the sorption in the membrane reached equilibrium. The transient relative sorption data as a function of time of the individual permeants were used to calculate the diffusion coefficients during the sorption process [25] and the equilibrium sorption levels (in kg/kg) were employed in establishing the sorption isotherms [22,23].

2.4. Model building

The following assumptions were made when building the model:

(i) The mass transport takes place due to the solution–diffusion mechanism.
(ii) The PV process is isothermal.