Pervaporation dehydration of binary and ternary mixtures of acetone, isopropanol and water using polyvinyl alcohol/zeolite membranes

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A B S T R A C T

Mixed matrix membranes were prepared by uniformly dispersing of zeolite particles in a polyvinyl alcohol matrix. After membrane characterization, the ability of the prepared membranes was examined toward pervaporation dehydration of binary and ternary mixtures of acetone, isopropanol and water because of their industrial importance. The effect of different parameters on the membrane performance was investigated and the best conditions were obtained. The results showed that, NaA zeolite particles significantly improved the separation performance of the membranes. The selectivity was increased with an increase of zeolite loading up to 5% wt. The best results were obtained for dehydration of isopropyl alcohol where the separation factor was calculated as 1881. Based on the findings of the research, the incorporation of NaA zeolites into the polymer matrix can be very effective for dehydration of acetone and isopropanol. The results show that the prepared membrane can be a good candidate for removal of water in acetone production from isopropyl alcohol.

1. Introduction

Acetone (ACE) is one of the most important solvents that is mainly used as a solvent and as a raw material for the production of methyl methacrylate and bisphenol A. This compound may be produced by several methods. One of the common methods is its production from isopropyl alcohol (IPA) by catalytic oxidation or dehydrogenation of isopropyl alcohol. In most cases, regardless of the process used for its preparation, manufactured acetone contains a substantial amount of water. Therefore, dehydration of acetone still remains a critical issue. Although acetone and water do not form an azeotrope, a strong reflux, a large column and high energy cost are required during the distillation process to obtain high purity acetone. On the other hand, dehydrogenation of IPA is a very important process for producing of ACE in Western Europe. A ternary system ACE/IPA/Water is formed in the reactor container during the dehydrogenation process of IPA [1]. The separation of IPA and water is difficult due to the formation of an azeotropic mixture between IPA and water (at the mole fraction of water: $0.3167 \, mol \, mol^{-1}$ and the boiling temperature of 353.55 K at atmospheric pressure) [2].

The membrane technology can be used in the acetone production industries through two methods: in the selective removal of water from the water/ACE or ACE/IPA/Water mixtures by pervaporation processes and in the membrane reactor manufactured using appropriate membranes for simultaneous removal of water along the acetone production.

Pervaporation is a membrane separation technique which has a significant ability for removing water from liquid mixtures [3]. In the conventional distillation processes, the separation depends on the vapor–liquid equilibrium, but in the pervaporation, separation of the liquid mixtures can perform based on the difference in diffusivity of each liquid component in a membrane [4]. In this technique, the separation of mixtures is achieved by a partial vaporization of components through a suitable membrane. Due to the vaporization of permeating components, pervaporation is the most economical one when the concentration in the feed mixture is low for the favorable permeating components [5,6]. In the case of pervaporation, the difference in fugacity between feed and permeate side of the membrane, can be expressed as driving force for transferring the components through the membrane matrix [7].

One of the most important applications of pervaporation is separation of close boiling mixtures [8,9]. Because of requiring no additional chemicals and operating at moderate pressures and temperatures, pervaporation is reported as eco-friendly, economical and safe method [10–12]. Pervaporation is an economical separation technology and also an environmentally clean technology in which potential pollution sources for azeotropic distillation are not needed [13].

A hydrophilic membrane might be used to separate water from water/organic mixtures. Recent trends in membrane separation involve the development of composite membranes by incorporating zeolites as the reinforcing fillers. A mixed-matrix membrane might be useful for

Nomenclature		M	Molar (mol/L)
		NaA	Zeolite 4A
α	Separation factor	PV	Pervaporation
A	Membrane surface (m^2)	PVA	Polyvinyl alcohol
AC	Acetone	R	Gas constant
E	Activation energy (kJ/mol)	SEM	Scanning electron microscopy
FT-IR	Fourier transform infrared	T	Temperature (k)
GA	Glutaraldehyde	TCD	Thermal conductively detector
GC	Gas chromatography	w	Permeate mass (kg)
IPA	Isopropyl alcohol	W_d	Dry membrane weight
J	Permeation flux ($kg/m^2.h$)	W_s	Swollen membrane weight
$??_0$	Pre-exponential factor of permeation	Wt%	Weight percent

water pervaporation since it shows not only molecular sieve effects, but also good thermal, chemical and mechanical stabilities [14,15].

Polyvinyl alcohol (PVA) is a proper candidate as a bulk of membranes because of its excellent membrane-forming properties, convenient physical properties, low cost, high hydrophilicity, process ability and suitable chemical resistance in many pervaporation separation processes [16–18]. Nevertheless, especially when the membrane is operated under high fraction of water in feed mixtures, the –OH groups along PVA main-chains make the PVA-based membranes suffered from an excessive swelling [19].

Among the zeolites, NaA zeolite has appropriate molecular sieving action, high selective adsorption capacity and strong hydrophilic nature [20,21]. The molecular sieving effect is provided by the porous structure of the embedded-zeolite, with 0.4 nm pore diameter. The zeolite NaA allows water molecules with a kinetic diameter of 0.296 nm to diffuse easily through its apertures, but excludes larger organic molecules such as ACE and IPA [22] (kinetic diameters of ACE and IPA are 0.46 and 0.47 nm respectively). Incorporating the zeolite NaA with the PVA membranes will enhance the water permeation flux while reducing the membrane swelling and giving a higher degree of water selectivity. In addition, zeolites have a high mechanical strength, good thermal and chemical stability and the membranes incorporated with these fillers can be used over a wide range of operating conditions.

The aim of this paper is pervaporation separation of the binary ACE/Water, IPA/Water and ternary ACE/IPA/water solutions using high efficiency PVA/NaA composite membrane. The effects of some parameters such as zeolite contents and feed temperature on pervaporation performance were also investigated.

2. Materials and methods

2.1. Materials

PVA (98%, molecular weight = 72000, Applichem) was used as a dense membrane material. Glutaraldehyde (GA, 25 wt%, Merck) was used as cross-linking agent. HCl (Merck) as a 0.1 M solution was used for hydrolyzing the polymer during the cross linking process. ACE and IPA were supplied with purity > 0.998 kg kg^{-1} and used without any further purification. The following chemicals were utilized to synthesize the NaA zeolite particles: sodium hydroxide (NaOH, 1.0 mol/L) as a Na source, aluminum chloride with a content of 98 wt% as an Al source, silica gel as a Si source. Commercially available NaA zeolite (code: 233668, molecular sieve, powder, < 5 μm) and isobutanol (GC grade 99.5%) were purchased from Merck.

For the calibration of GC (in the analytical step for ternary mixtures) the chemicals (ACE, IPA and isobutanol) were obtained from Merck with a guaranteed purity of ≥0.999. Double distilled water was used throughout the research work.

2.2. Synthesis and characterization of NaA zeolite particles

The hydrothermal synthesis of NaA zeolite particles was performed as follows: an aluminate solution was prepared by dissolving sodium hydroxide (4.04 g) and aluminum chloride (4.04 g) in distilled water (16 mL). A silica solution was prepared by dissolving 2.30 g sodium hydroxide and 1.63 g silica gel in 18 mL distilled water. Then aluminate solution was immediately added to the silica solution, and then it was stirred vigorously for 14 min. The prepared gel was hydrothermally treated for 3 h at 100 °C. The molar composition of the resulting gel was: 3.165 Na_2O: Al_2O_3:1.926 SiO_2: 128 H_2O [23]. The crystal structure of the synthesized zeolite particles was examined with a thin-film X-ray diffraction using Cu k_α radiation (XRD, Bruker, AXS Co., Germany, 30 kW). The XRD pattern of the synthesized NaA particles was compared to the standard NaA zeolite crystals. The surface morphology of the zeolite particles was observed using TESCAN Scanning Electron Microscopy (SEM).

2.3. Membrane preparation

The PVA/NaA composite membrane was prepared by uniformly dispersing NaA particles into the polymer matrix. Because of hydrophilic properties of PVA and NaA zeolite particles, water is a favored permeating component. The integrated flat sheet membrane (4 cm in diameter) was placed in a test cell built of polyethylene and had an effective area of 50.24 cm^2.

In a typical synthesis, a polymeric solution was prepared with dissolving proper portions of dry PVA powder (solvent = 90 wt.% and polymer = 10 wt.%) in double distilled water at 100 °C to obtain a clear solution. This solution was mixed with different amounts of zeolite particles to reach final contents of 0, 2.5, 5, 7, 10, 12 wt fractions. The PVA-zeolite dispersion was stirred at 70 °C for 12 h to allow the cross linking reaction of the gel to proceed and propagation of particles become complete, followed by the addition of 0.5 mL GA cross linking agent [24,25]. After rigorous stirring for 2 h the prepared solution was sonicated for 15 min and immediately was cast on the plate. A thin film with about 60–70 μm thickness was formed after water evaporation at room temperature for 24 h.

2.4. Characterization

The surface morphology of the cast composite membrane was observed by scanning electron microscopy (SEM). The samples were prepared by fracturing in liquid N_2 and coated with a conductive layer of sputtered gold. Moreover, the FT-IR spectra of the composite membrane was obtained from Jasco, 6300 FT-IR Spectrometer, operating in the range of 4000–750 cm^{-1}.

The swelling tests were performed for the membranes containing different amount of zeolite (0, 2.5, 5, 7, 10, and 12) after they were dried in vacuum at room temperature for 12 h. The dried membranes were weighted (w_d) and immersed in the ternary mixture for 20 days.