



Preparation and Characterization of Dense Membranes Based Zeolitic Imidazolate Framework (ZIF-8) For Separation: Aromatic—Aliphatic Mixture

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Received. June 11, 2017. Accepted. July 12, 2017. Published. December 02, 2017.

DOI: <https://doi.org/10.58681/ajrt.17010105>

Abstract. Separation of organic–organic liquid mixtures using membranes has been investigated extensively over the past several decades due to its great significance in the chemical 2- industry, with aromatic-alkane and alkane-alkene systems among the most studied. The latter is one of the most difficult to separate using a membrane process, but promising results have already been obtained for the former. However, even for these highly studied systems, pervaporation (PV) has not yet been attempted as an economical and simple alternative to organic-organic separation technologies. These liquid-liquid separations are still carried out by energy-consuming processes, such as rectification, azeotropic distillation or liquid-liquid separation. To overcome this problem, we decided to investigate the potential of mixed matrix membranes based on a low-cost technical polymer. Polyvinyl chloride (PVC)-based mixed matrix membranes were prepared with zeolitic imidazolate framework (ZIF-8) particles, and the composite membranes were studied for the separation of toluene-heptane mixtures. It was found that the PVC transport properties could be significantly modified both by the amount and by the type of ZIF-8 incorporated.

Keywords. Membrane, Composite, Separation, Polyvinyl chloride, ZIF 8.

INTRODUCTION

Separation of the aromatic-aliphatic fractions of industrial cuts, such as ethane-ethylene or benzene-cyclohexane, is an important goal in the petrochemical industry. Unfortunately, because the physical properties of the saturated and unsaturated compounds are similar, the conventional industrially used separation methods, i.e., adsorption, distillation, and liquid-liquid extraction, are not very efficient and can even be energy demanding because of the

formation of azeotropes or the lack of significant volatility differences of the close boiling components (Aouinti et al., 2015a; Sánchez, 2008).

Metal-organic frameworks (MOFs) are a relatively new family of nanoporous materials which are produced from metal ions or clusters linked by organic molecules. (Li et al., 2009; Tian et al., 2011) Many MOF-type materials with diverse framework architectures and functional properties have been synthesised to date (Sumida et al., 2011; Betard et al., 2011). Zeolitic imidazolate frameworks (ZIFs) are a sub-family of MOFs that have tuneable pore sizes and chemical functionality, coupled with exceptional chemical stability, and exhibit versatile structures analogous to that of inorganic zeolites (Hayashi et al., 2007). Particularly, several ZIFs have been successfully prepared as membranes and have demonstrated the molecular sieving effect needed for gas separation (Venna et al., 2010; Thomson et al., 2013).

For example, ZIF-8 is made from linking of zinc(II) cations and 2-methylimidazole anions, giving a sodalite topology with a pore cavity of 11.6 Å and a theoretical pore aperture of 3.4 Å (Park et al., 2006).

Recently, ZIFs gained attention as fillers for mixed matrix membranes because of their molecular sieving effect, facile synthesis and good compatibility with polymers. (Bae et al., 2010) synthesised ZIF-90 particles with sub-micrometer size and incorporated them into several polyimide polymers (Ultem polyetherimide Matrimid, and 6FDA-DAM).

In this study, poly (vinyl chloride) (PVC), a low-cost polymer, was used as a highly selective hosting matrix. Improvement of its pervaporation properties was achieved by incorporating aromatic-selective inorganic fillers into the organic network.

PVC is a glassy polymer ($T_g = 82^\circ\text{C}$) with low transport properties for hydrocarbons. PVC was primarily chosen because of its medium polarity. The solubility parameter of PVC (δ_{PVC}) is $19.2 \text{ MPa}^{1/2}$, close to that of aromatics (e.g., $\delta_{\text{Benzene}} = 18.8 \text{ MPa}^{1/2}$ and $\delta_{\text{Toluene}} = 18.2 \text{ MPa}^{1/2}$) and significantly higher than the solubility parameters of aliphatic compounds, e.g., $\delta_{\text{hexane}} = 14.9 \text{ MPa}^{1/2}$ and $\delta_{\text{heptane}} = 15.1 \text{ MPa}^{1/2}$ (Okamoto et al., 1999). This indicates that PVC will have a high affinity for aromatic structures and a relatively low affinity for nonpolar aliphatic structures (Kwei, 1990; Neel et al., 1985).

The aim of the present work is to develop a novel and high-performance mixed matrix membrane for the separation of organic molecules using PVC and ZIF-8. ZIF-8 particles were chosen for their higher affinity for toluene versus heptane. The structures and morphologies of the nanocomposite membranes were characterized.

EXPERIMENTAL

Reagents.

The PVC, graciously provided by ENIP of Skikda (ALGERIA), has an average molecular mass of approximately 149.1 kg/mol. The IR characteristics of the PVC are in agreement with those previously reported.

Synthesis of ZIF-8

The ZIF-8 nanocrystals were synthesised following the rapid room temperature synthesis method reported by (Cravillon et al., 2009).

In a typical synthesis, a solution of 3 g (10 mmol) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of methanol and another solution of 6.6 g (80 mmol) of 2-methylimidazole in 100 mL of methanol were prepared and then mixed by vigorously stirring for 1 h at room temperature. After 1 h stirring, the resulting ZIF-8 nanocrystals were separated by centrifugation, washed three times with fresh solvent.

Preparation of pure and nanocomposite membranes

With thicknesses between ($80 \cdot 10^{-6}$ and $200 \cdot 10^{-6}$ m) was performed from THF polymer solutions (12 wt%) by dispensing samples into 6×10^{-2} -m-diameter molds at a stirring speed of 280 tr/min. For nanocomposite films, particular attention was given to proper dispersion of the inorganic particles in the polymer matrix in order to ensure good contact with the polymer phase. Hence, a suspension of ZIF-8 in 7 ml of THF were stirred for 24 h and was slowly added to the polymer solution and then stirred for 24 h before casting into the glass molds. The membranes were allowed to dry slowly at room temperature, and composite films up to 40 wt% of ZIF-8 were prepared. The pure PVC films were colorless, whereas the composite films were white.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectral measurements were performed using a Nicolet spectrophotometer scanning from 400 to 4000 cm^{-1} .

X-ray diffraction measurements (XRD)

Have been performed using advanced diffractometer (PANalytical, XPERT-PRO) equipped with a $\text{CuK}\alpha$ radiation source ($\lambda = 0.154 \text{ nm}$). The diffraction data were collected in the range of $2\theta = 3\text{--}60^\circ$.

Scanning electron microscopy (SEM)

The membrane surface cross section images were recorded with SEM using a high-resolution Jeol JMS – 7001 F apparatus.

Sorption measurements

Sorption measurements of the PVC films was performed by immersion in pure liquids (toluene, n-heptane) at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$). The samples, weighing at least 5×10^{-4} kg each, were submerged in the liquids until the sorption equilibrium was reached, approximately 24 h. Before each measurement, the samples were rapidly blotted, and the weight increase was recorded using a hermetically sealed flask. The measurements were repeated several times (relative error: $\pm 3\%$). The degree of swelling (S_w) was calculated for each sample using the following equation:

$$S_w (\%) = 100 \times (W_w - W_d) / W_d \quad (1)$$

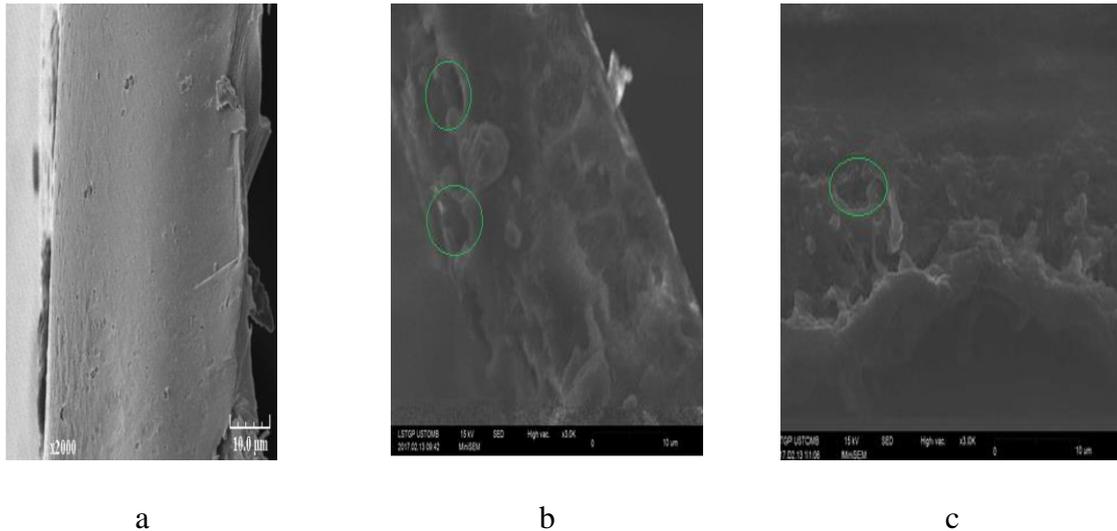
Where W_w and W_d are the weights of the membrane in the wet and dry states, respectively.

RESULTS AND DISCUSSION

Membrane characterizations

Membrane morphology

The SEM images of the homogeneous and composite membranes are shown in figure 1(a–c). A major difference in the microstructure. SEM pictures were obtained to determine whether the effect of the filler at the microscopic level could be seen (Fig.1). The PVC view can be considered as a reference for a fully dense cross section of the glassy polymer (Fig. 1a); with a magnification of 2000, the cross section appears neat and homogenous, and only some small defects can be seen. Conversely, all other pictures show heterogeneous surfaces. The micron-sized cavities and pores are visible in the SEM images.



a-PVC, b-c PVC membranes loaded with 10.20 wt% of ZIF-8 respectively
Fig. 1. SEM images of membrane cross-section

X-ray diffraction of ZIF-8 and membranes

It is well known that a stable dispersion at the nanometer scale level is essential to achieving high-quality coatings nanohybrids X-ray diffraction was used to determine whether ZIF-8 was well represented as individuals in nanohybrids are presented (Feng et al.1997). The diffraction patterns of 1-X-rays, PVC, ZIF-8, and PVC- ZIF-8- nanohybrids are shown in the figure 2. After the incorporation of ZIF-8 into the PVC matrix, the first two characteristic X-ray diffraction peaks of ZIF8 disappeared in the spectrum of the PVC-15% ZIF 8 membrane and the PVC-30% ZIF-8 membrane.

Other new peaks with different intensities and reticular distances appeared

- The formation of a crystalline phase for PVC-15% ZIF-8
- Good dispersion and good adhesion between ZIF8 nanoparticles and PVC.
- Membranes are nanocomposites.

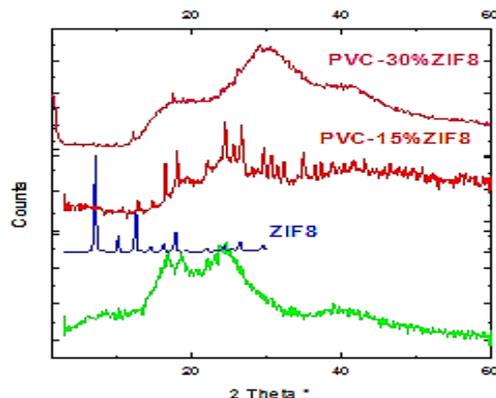
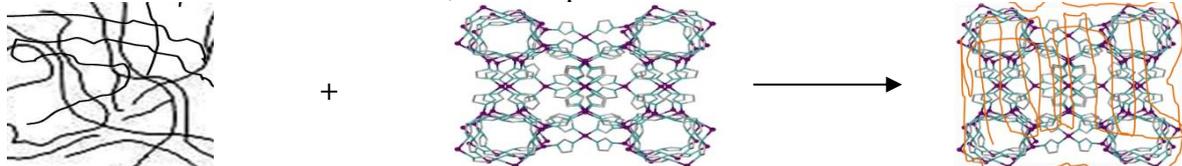


Fig.2. Membranes ZIF-8 and PVC X-ray.

The results of diffractometer XRD, there is provided two structures:



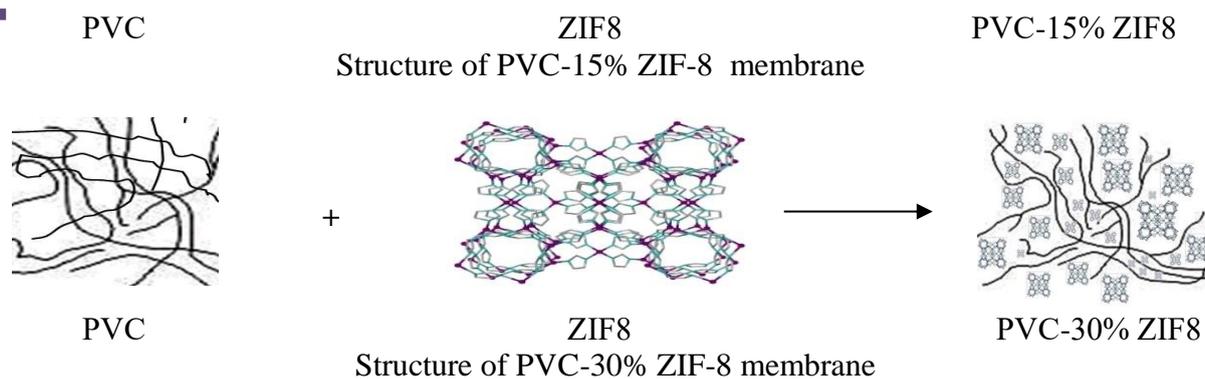


Fig. 3. Possibility of different intercalation structures between PVC and ZIF-8.

Fourier transform infrared spectroscopy

Infrared spectroscopy has been used to complement the structural information, this method allows to characterize the presence of chemical functions molecular interaction between PVC and ZIF-8 in the membranes is investigated by FTIR.

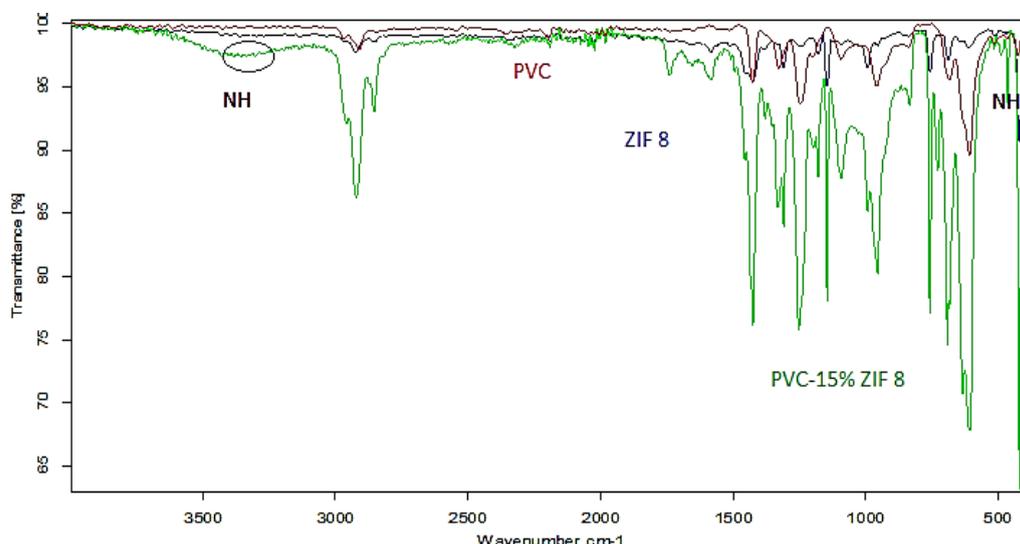


Fig.4. FTIR spectra of PVC, ZIF-8, PVC-15% ZIF8.membrane.

Comparison of three bands of spectra gives the appearance of a new band at 3354.35 cm^{-1} is attributed to the formation of hydrogen bonding between the ZIF-8 and the PVC is the N-H bond for nanocomposite membranes.

Sorption properties

The mass transfer of homogenous polymeric membranes in pervaporation can be described by the well-accepted sorption–diffusion model. For a single component, the permeability P of a dense film can be expressed according to equation (2), where D is the diffusion coefficient of the permeant, and S is the sorption coefficient.

$$P = S \times D \quad (2)$$

However, in the pervaporation (PV) process, the permeability is rarely constant and can vary significantly with the concentration or the activity of the species of the partially vaporized species. When a given species has a good affinity for the polymer, the degree of sorption increases exponentially manner with the increase of the species activity and can be modeled by the Flory–Huggins equation (Wijmans and Baker, 2006).

Quantification of the sorption behavior characterizes the amplitude of the interactions between the small molecules and the PV film and makes it possible to predict the selectivity expected with a given binary mixture (Swaddle, 1997).

For mixed-matrix films, such as those prepared with ZIF-8 and PVC, it should be emphasized that the two matrices do not interact with the small molecules in a similar manner, and thus the sorption properties are not governed by the same laws. For the polymer matrix, the absorption interactions occur within the entire mass of the organic matrix. For ZIF-8, the absorption interactions are limited to specific fixed sites on the surface created by the inorganic matrix. One of the simplest models used to describe adsorption is the Langmuir model, which uses a perfectly planar surface and a single molecule adsorption per site (Lombardo and Bell, 1991).

The adsorption capacity was also measured for a 1/1 mixture of toluene and n-heptane at 25 °C. The results obtained after a long period remained consistent, as shown in Fig.5; they correspond to an average value of the two pure values, i.e., $S_w = 37\text{wt}\%$.

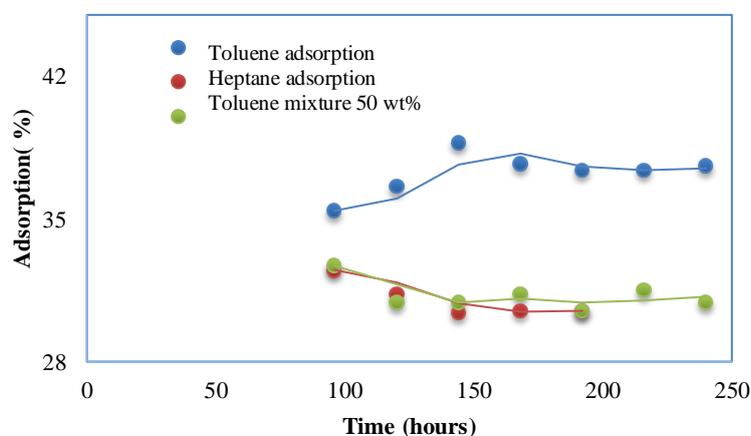


Fig.5. Adsorption characteristics of ZIF 8 measured in pure toluene vapor, pure n-heptane vapor and a 1/1 mixture of toluene/n-heptane vapor.

This result clearly indicates that there is no adsorption competition between toluene and heptane and that the ZIF 8 selectivity remains the same.

It was observed that ZIF-8 had a strong affinity for toluene and exhibited a clear preferential sorption for toluene (1.2 times higher than that for heptane).

The sorption properties of the composite PVC–ZIF 8 membranes were registered with a 50–50 wt% toluene/n-heptane mixture (Fig.6). Compared with the initial PVC swelling degrees, the results show a strong increase in the solvent sorption with the composite membranes, which significantly varies with the ZIF 8 content, as expected.

To gain a better insight, the composition of the liquid sorbed at equilibrium was determined for the composite membrane having the higher ZIF 8 content, i.e., 40 wt% of ZIF 8, to obtain a reliable value and to check that the enhanced swelling degree was not just an artefact due to membrane defect (cracks) or to inadequate measurements.

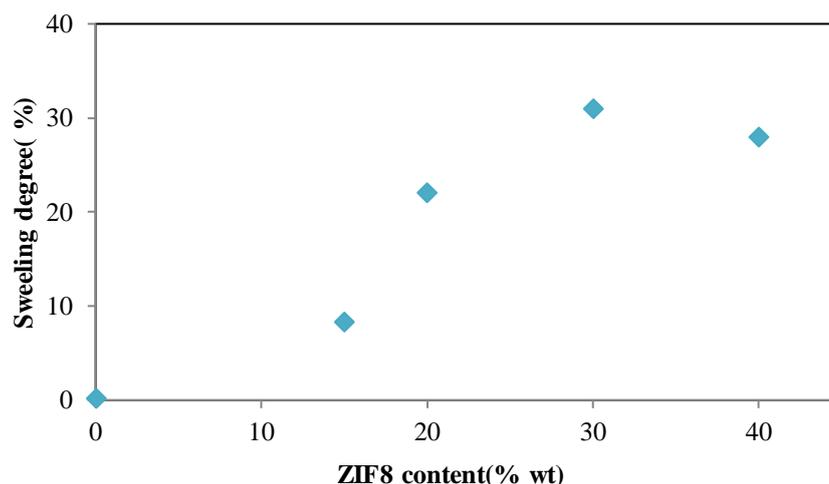


Fig.6. Effect of ZIF8 content on the swelling degrees of the mixed matrix membranes in the toluene/n-heptane mixture (50/50 wt%) at 25 °C.

Comparison of the degree swelling S_w (%)

The comparison of our swelling results with previously reported data in the literature is not a straight forward task (Aouinti et al., 2015a, Aouinti et al., 2009b). A tentative comparison between the swelling results of the nanocomposite membranes prepared in this study and those reported in the literature (Aouinti et al., 2015c) was made and is listed in Table 1. It can be observed that the PVC-20% ZIF 8 membrane prepared in this research showed good performances compared with the other composite membranes investigated for the removal of aromatic compounds from their mixtures.

Table. 1. Comparison of sorption for 50-50 wt % Feed Mixture.

Membrane Material	T (°C)	Separation mixture	Degree swelling S_w (%)	Ref
PVC	20	Toluene-n-heptane	0.2	Aouinti et al., 2015a
PVC-20% Activated carbon	20	Toluene –n-heptane	10	Aouinti et al., 2015a
PVC-20% Nanocor	20	Toluene –n-heptane	15	Aouinti et al., 2009b
PVC-20% Magh H	20	Toluene –n-heptane	3	Aouinti et al., 2015c
PVC-20% ZIF 8	25	Tolu3ene –n-heptane	22	This study

CONCLUSION

In this study, several nanocomposite membranes were produced using PVC and ZIF-8 nanoparticles, a filler material with a higher affinity for toluene than for heptane. The sorption studies of the membranes revealed that the incorporation of filler significantly increases the extent of swelling of the nanocomposite PVC membranes.

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