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Separation of gases by using pristine, composite and nanocomposite polymeric membranes: A molecular dynamics simulation study

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ABSTRACT

In this study, the separation of acid gases H_2S and CO_2 from N_2 and CH_4 by pristine polymeric membranes including poly(amide-b-ethyleneoxide) (Pebax-1657), poly(acrylonitrile) (PAN) and poly(trimethylsilyl)propyne (PTMSP) have been studied by utilizing molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulation methods. The results indicated that, while the selectivity of the pristine Pebax membrane, for these gases, was higher than those of pristine PAN and PTMSP membranes, its permeability was lower. To obtain polymeric membrane with higher permeability, composite polymeric membranes (CPMs) consisting of [Pebax-1657 + PAN] and [Pebax-1657 + PTMSP + PAN] were constructed. However, the results indicated that the CPMs had low selectivity, in comparison to pristine Pebax membrane, for the binary gas mixtures. Therefore, to increase the CPMs' selectivity along with their permeability, the nano-filler zeolitic imidazole framework (ZIF-7) were added to the Pebax-1657 matrix of CPM with the optimum amount of 22 wt%, where the resulting nanocomposite polymeric membranes (NCPMs) indicated more significant separation efficiency (higher; diffusivity, solubility, permeability and selectivity). The physical properties of the simulated polymeric membranes such as density, glass transition temperature and fractional free volume were evaluated and the mechanisms involved in the gas separation, by the studied polymeric membranes, were discussed in the light of the obtained results, where their agreement with the available experimental data validated the simulation procedures as utilized in this study.

1. Introduction

In present days, energy consumption for domestic applications and industrial utilization is a major concern. Natural gas is widely used for energy production in comparison with other energy resources [1–3]. However, hydrogen sulfide (H_2S) and carbon dioxide (CO_2) as the most pollutant gases should be separated from the natural gas since H_2S is harmful to the environment and corrosive to the industrial equipment whereas, CO_2 as a greenhouse gas can cause climate change in the atmosphere [2,4–6].

There are various methods for separation of these gases (H_2S and CO_2) from natural gas which include: absorption [7–9], adsorption [10,11], cryogenic distillation [12,13] and membrane techniques [1,4–6,14–23]. The separations based on the membrane techniques are more favorable, since in comparison with the other separation methods are more economical, operationally simple and less harmful to the environment [22,24,25].

The two types of membranes which are generally used in gas separation include; polymeric and inorganic membranes [3,21,26–36]. The polymeric membranes have the following advantages: favorable mechanical flexibility, simple processing ability and economical cost productivity as well as having effective separation properties such as diffusivity, solubility and permeability for various gas mixtures [3,21,31,32,35]. However, the major disadvantage of polymeric membranes is their low selectivity for gases which their molecular size, are close to each other such as H_2S, CO_2, N_2 and CH_4 [18,22,37]. In application of polymeric membranes, there is a trade-off between two major factors, selectivity and permeability, which govern the separation processes [6,22,38]. To improve the selectivity of polymeric membranes, inorganic and organic fillers with porous structure (such as zeolites and carbon nanotubes) and nonporous structure (such as silica) are mixed with the polymeric matrix [17,23,39–41]. The resulting

Abbreviations: PAN, Poly(acrylonitrile); PA6, Polyamide 6; Pebax-1657 or Pebax, Poly(amide-b-ethyleneoxide); PEO, Poly(ethyleneoxide); PTMSP, Poly(trimethylsilyl)propyne; CPM, Composite polymeric membrane; CPM2, [Pebax + PAN]; CPM3, [Pebax + PTMSP + PAN]; MMM, Mixed matrix membrane; NCPM, Nanocomposite polymeric membrane; NCPM3/ZIF8%, [Pebax/ZIF(8 wt%) + PTMSP + PAN]; NCPM3/ZIF22%, [Pebax/ZIF(22 wt%) + PTMSP + PAN]; NCPM3/ZIF34%, [Pebax/ZIF(34 wt%) + PTMSP + PAN]; ZIF-7 or ZIF, Zeolitic imidazolate frameworks

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Nomenclature

a	Simulation cell length in x-direction (Å)
b	Simulation cell length in y-direction (Å)
b	Langmuir hole affinity parameter (1/bar)
c	Simulation cell length in z-direction (Å)
C	Concentration of gas molecules in the simulation cell (cm^3 gas (STP)/cm^3 polymer)
C_D	Gas concentration based on Henry's law sorption (cm^3 gas (STP)/cm^3 polymer)
C_H	Gas concentration based on Langmuir sorption (cm^3 gas (STP)/cm^3 polymer)
C'_H	Langmuir hole capacity parameter (cm^3 gas (STP)/cm^3 polymer)
D	Diffusivity (cm^2/s)
E	Energy of configuration (kcal/mol)
FFV	Fractional free volume
f_i	Fugacity of component i in the gas phase (bar)
k_B	Boltzmann constant (bar m^3/K)
k_D	Henry's law coefficient (cm^3 gas (STP)/cm^3 polymer bar)
n	Proportionality coefficient
n_A	Proportionality coefficient at anomalous diffusion regime
n_E	Proportionality coefficient at Einstein diffusion regime
N_i	Current number of component i molecules in the membrane cell
p	Total pressure (bar)
P	Permeability (Barrer, 1 Barrer $=10^{-10}$ cm^3(STP) cm/cm^2 s cmHg)
P_{acc}	Acceptance probability
$\boldsymbol{r}(t)_z$	Final position vectors of the center of mass of the gas molecules over the time interval t (Å)
$\boldsymbol{r}(0)_z$	Initial position vectors of the center of mass of the gas molecules (Å)
S	Solubility (cm^3 gas (STP)/cm^3 polymer bar)
t	Simulation time (ps)
t_m	Membrane thickness (Å)
T	Temperature (K)
T_c	Critical temperature (K)
T_g	Glass transition temperature (K)
V	Volume of membrane cell (Å^3)
V_m	Volume of membrane region (Å^3)
V_O	Occupied volume of the polymer chains (Å^3)
V_{vdW}	van der Waals volume of the polymer chains (Å^3)
V_F	Free volume (Å^3)
V_{feed}	Volume of feed region (Å^3)

Greek variables

α_{AB}	Selectivity
ε/k_B	Lenard-Jones interaction parameter (K)
σ	Kinetic diameter of gases (Å)

membranes are known as the mixed matrix membranes (MMMs) [42–44]. The utilization of MMMs compensates the selectivity of polymeric membranes and also can improve the inherent inflexibility of the added, inorganic and organic, constituents to the membranes, such as zeolites, carbon nanotubes and silica particles [4,42,44–46].

Many MMMs have been made experimentally with efficient separation properties, but unfortunately without industrial applications [23,43], which can be due to their difficult manufacturing. Also, the detailed molecular structure of polymeric membranes which can be helpful in understanding their behavior in the gas separation has not been yet properly elucidated [47,48].

The experimental works on the polymeric membranes were mostly aimed at enhancing H_2S and CO_2 separation performance of the pristine membranes by addition of different nano-fillers such as Mordenite [49–52], POSS [41,53], silica [19,34,54], carbon nanotube [47,55–57], ceramics [58,59] and metal organic frameworks (MOFs) [60–62] into the matrix of the pristine membranes.

Among the above mentioned nano-fillers, the MOFs and their subclass zeolitic imidazolate frameworks (ZIFs) with porous structure, good wetting properties and superior chemical and thermal stability, have been broadly investigated both as the pristine inorganic membranes and as the mixed matrix membranes, where positive results have been obtained for their application in gas separation [17,23,39,40,43,44,48,63,64]. Several experimental studies have been performed on ZIFs as the porous nano-filler particles to be mixed with various polymers to form MMMs [44,46,48], for application in gas separation, where the resulting MMMs indicated more efficient gas permeability and selectivity [40,42].

In this work, zeolitic imidazole framework (ZIF-7, hereafter abbreviated to ZIF) with various compositions was used as a nano-filler to construct the MMM, [Pebax/ZIF + PTMSP + PAN], and to examine the transport properties and selectivity of the resulting membranes. Poly (amide-b-ethyleneoxide) with trade name of Pebax-1657 (hereafter abbreviated to Pebax) is a thermoplastic elastomer which is known as a multi-block copolymer because of having both polyamide 6 (PA6) and polyethyleneoxide (PEO) segments with the (PA6/PEO) segment ratio of (40/60 wt%) [43,65,66]. The resulting membrane has flexibility and high permeability as well as mechanical strength due to presence of PEO (as a soft segment) and PA6 (as a hard segment), respectively [65,66]. In the present work, Pebax was used as the base polymer, with high chain mobility and rubbery behavior to give flexibility to the membrane and to interact with the added nano-filler ZIF particles to improve the mechanical strength of the resulting membrane by promoting adhesion between its constituents and also, to increase its selectivity for separating the gas molecules with molecular size close to each other such as H_2S, CO_2, N_2 and CH_4 [43,65,66].

A MMM with a good separation performance, should have a film thickness as thin as possible. But the MMM with thin film thickness has low mechanical strength which causes difficulties in its applications. Therefore, the thin membrane film should be placed on a support such as the microporous poly(acrylonitrile), PAN [21,67–69].

Penetration of the selective layer consisting of Pebax into the pores of the supporting layer (PAN), may impose a negative effect on the membrane efficiency by blocking the PAN's pores and making the gas molecules to pass through the low-permeable selective layer (Pebax), instead of penetrating through the high permeable PAN's pores [70]. Therefore, the gas molecules would diffuse through a longer path into the selective and support layers of the composite membrane. To overcome this problem, poly(trimethylsilyl)propyne (PTMSP) is used as an intermediate coating layer on the PAN's surface [19,43]. PTMSP with nanoporous structure is a glassy polymer ($T_g > 600$ K) with extremely high free volume fraction (up to 35%) and high gas permeability [19,68]. Therefore, it is expected that using composite polymeric membranes (CPMs) consisting of [Pebax + PAN] abbreviated as (CPM2) and [Pebax + PTMSP + PAN] abbreviated as (CPM3) would present higher diffusivity, solubility and permeability but unfortunately in practice, they indicate low selectivity. To increase the selectivity of CPMs, the nano-filler ZIF particles are added into the selective layer of CPMs. The resulting nanocomposite polymeric membranes (NCPMs) would consist of three layers PAN (as the support layer), PTMSP (as the intermediate layer) and Pebax/ZIF (as the selective top-layer).

In this work, the performance of pristine polymeric membranes (Pebax, PAN and PTMSP), composite polymeric membranes CPM2 (with two layers, [Pebax + PAN]) and CPM3 (with three layers, [Pebax