
FEATURES OF THE NON-POLAR AND ACID GASES TRANSPORT ACROSS THE SUPPORTED IONIC LIQUID MEMBRANES

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Introduction

In recent decades, acidic gases have drawn considerable attention owing to their contribution to global warming and other negative impacts on global climate change [1]. The stringent environmental requirements and improvement in the quality of natural gas for customers necessitates the complete removal of acidic impurities from gas streams. Apart from the traditional removal techniques, a novel class of absorbents based on ionic liquids (IL) has been given a great deal of attention by scientists and commercial organizations [2] in recent years. It should be noted that the majority of ILs characterized by the highest sorption properties toward the acidic gases contains fluorinated anions. The notable feature of fluorinated ILs is the chemical degradation in the presence of water at high temperatures accompanied by the formation of volatile, toxic and aggressive HF. For this reason, much attention should be given to the creation of novel environmentally benign ILs for the acidic gases removal. One of the promising approaches for the replacement of fluorinated ILs is based on the introduction of flexible moieties, such as the ether groups, which enable dipole–quadrupole interactions between the oxygen atoms of functional group and CO₂, leading to the increase of the free volume.

With these factors in mind, we have synthesized two ILs based on amphiphilic bis(2-ethylhexyl) sulfosuccinate anion and imidazolium cations. The goals of this study sought to establish the gas transport properties of acidic and non-polar gases across the SILMs impregnated by the aforementioned ILs.

Experiments

The novel ILs N-methylimidazolium bis(2-ethylhexyl) sulfosuccinate (mim[doc]) and 1-butyl-3-methylimidazolium bis(2-ethylhexyl) sulfosuccinate (bmim[doc]) were prepared via anion exchange reaction [3]. All reagents were purchased from Sigma-Aldrich and used without any further purification. As polymeric supports, commercially available microfiltration composite membranes supplied by Vladipor JSC (Vladimir, Russian Federation) were used. The membranes were composed of tetrafluoroethylene–vinylidene fluoride copolymer of F42L (upper layer) and the non-woven polypropylene bottom layer. For the preparation of supported ionic liquid membranes, a vacuum method was used.

Permeability coefficients (P) ($1 \text{ Barrer} = 3.348 \cdot 10^{-16} \text{ mol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$) were calculated according to the method, using the experimental set-up with the automation of the permeability measurement process, which was calculated through the use of programming logic controller (Unitronix, Airport City, Israel) according to the following equation:

$$\frac{1}{\beta} \ln \left(\frac{|p_{feed} - p_{perm}|_0}{|p_{feed} - p_{perm}|} \right) = \frac{1}{\beta} \ln \left(\frac{\Delta p_0}{\Delta p} \right) = P \frac{t}{l} \quad (1)$$

where p_{feed} is the feed pressure in compartments (Pa), p_{perm} is the pressure in permeate compartments (Pa), P is the calculated permeability ($\text{m}^2 \text{ s}^{-1}$), t is the time (s), l is the membrane thickness (m), and β is the geometric parameter of the cell (m^{-1}).

The solubility measurement experiments were based on the pressure drop method.

Results and Discussion

The transport of gases through the SILMs containing 1-butyl-3-methylimidazolium hexafluorophosphate (bmim[PF₆]), 1-butyl-3-ethylimidazolium tetrafluoroborate (bmim[BF₄]), 1-methylimidazolium docusate (mim[doc]) and 1-butyl-3-methylimidazolium docusate (bmim[doc]) are explained by the solution-diffusion mechanism, according to which the concentration gradient between the feed and receiving phase is the driving force for dissolution of gases in ILs and their diffusion through the liquid phase. According to the solution-diffusion model, SILM permeability is predicted by the solubility coefficient and the diffusion coefficient, whereas the gas dissolution is based on Henry's law where the concentration of the gas in the membrane was directly proportional to the applied gas pressure. The high viscosity of ILs leads to mass transfer diminishing through the liquid phase; on the other hand, there can be more interactions between the penetrant and absorbent owing to a slower transition rate, and as a consequence, an increase in the solubility occurs.

It can be observed for all the SILMs that the permeability of non-polar gases (methane and nitrogen) was much lower in comparison to the acidic gases (hydrogen sulfide and carbon dioxide) (Figure 1 and 2). Nitrogen permeability values through SILMs range from 6.9 to 18.9 Barrer and generally do not depend on the ionic liquid present or the pore size of the support. A similar tendency is observed for methane transport through SILMs with bmim[PF₆], bmim[BF₄], bmim[doc], but for mim[doc], CH₄ permeability increases almost 2-fold compared with conventional ILs. The CO₂ permeability across SILMs depends on the nature of IL and varies from 68.9 to 205.0 Barrer. When mim[doc] is used as IL, the permeability of CO₂ is near 70 Barrer, whereas the data for bmim[BF₄] are the highest among the SILMs tested. The results for bmim[doc] and bmim[PF₆] were comparable. The H₂S permeability through the SILMs was in accordance with CO₂ permeability results. Briefly, the permeability data can be ranged as follows: mim[doc] < bmim[doc] < bmim[PF₆] < bmim[BF₄]. The highest values of permeability for all ILs with mixed gases were found for hydrogen sulfide as compared with carbon dioxide, due to stronger dipole-ion interactions between H₂S and IL, than the quadrupole-ion interactions for CO₂.

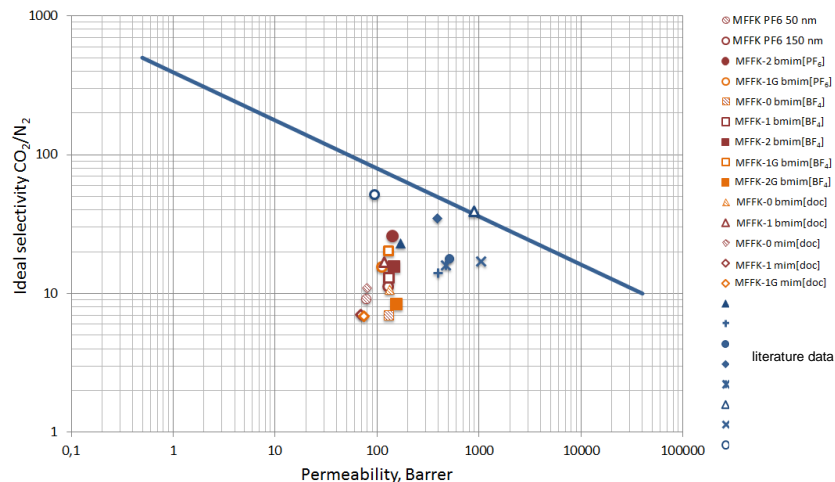


Figure 1. – The Robeson plot for separation carbon dioxide from nitrogen

The results obtained for SILMs with immobilized bmim[Tf₂N] points to the instability of those membranes, and desorption of the liquid phase at 1 bar of transmembrane pressure. For bmim[PF₆], the loss of IL occurs in the case of polymeric supports with pore dimensions greater or equal to 250 nm. The distinctions between the calculated capillary pressures and experimentally determined stability of membranes under pressure, most probably, are associated with the composite structure of the membrane composed of the upper fluorinated polymeric layer and the non-woven polypropylene bottom layer. The space between the threads of the non-

woven layer is larger than the pore size of the upper layer, which can lead to a significant decrease in capillary pressures.

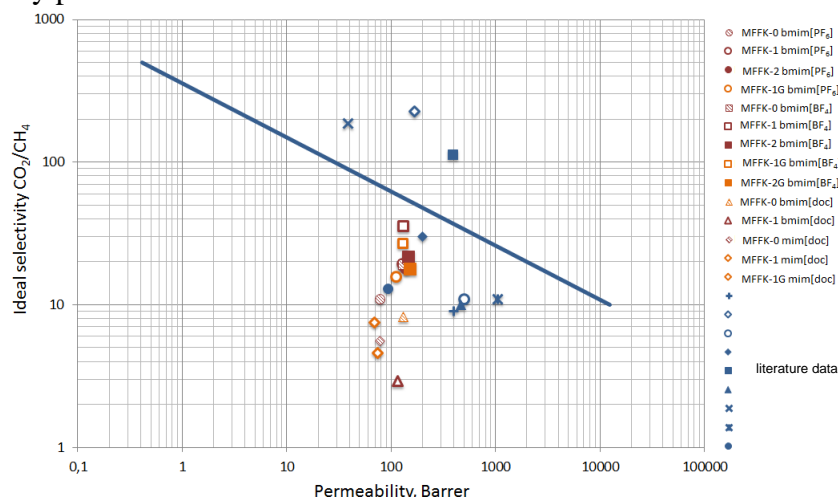


Figure 2. – The Robeson plot for separation carbon dioxide from methane

It should also be noticed that the low viscosity of the liquid phase decreases membrane stability. Although higher viscosities of ILs limit the mass transfer in the membrane and decrease the permeability, it can be expected that more viscous ILs lead to stabilization of the liquid phase within the pores of the support. The viscosity of ILs increases in following anion order: $[\text{Tf}_2\text{N}] < [\text{BF}_4] < [\text{PF}_6]$; arising from this, the stability of membranes also follows this trend. The ILs with $[\text{doc}]$ anion were characterized by the highest viscosity values, but lower surface tension, leading to relatively low values of capillary pressure. This observation explains the instability of SILMs with $[\text{doc}]$ anion immobilized into MFFK-2 and MFFK-2G support with a pore size equal 250 nm.

The experimental results show that the most promising liquid phase of SILMs for the separation of CO_2 among the tested materials is based on the 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium bis(2-ethylhexyl) sulfosuccinate, providing selectivities of 20.3 ± 0.01 , 26.1 ± 0.01 and 16.9 ± 0.01 , respectively. The synthesized 1-butyl-3-methylimidazolium bis(2-ethylhexyl) sulfosuccinate (bmim[doc]) and aforementioned ILs have exhibited a quite high ideal selectivity value regarding $\text{H}_2\text{S}/\text{N}_2$ and $\text{H}_2\text{S}/\text{CH}_4$ separations. A more detailed examination of bmim[doc] gas transport properties revealed that the key factor leading to the relatively high separation of H_2S is the solubility component. We found that the Henry's law constant of H_2S in bmim[doc] at 303.2 K was 2.9 bar and exceeded the corresponding values for conventional ILs. Concerning to removal of CO_2 , the most effective separation was observed in case of 1-butyl-3-methylimidazolium tetrafluoroborate.

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