Effect of monoethylene glycol and triethylene glycol contamination on CO_2/CH_4 separation of a facilitated transport membrane for natural gas sweetening

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ABSTRACT

A CO_2-facilitated transport composite membrane made of PVAm/PVA blend was exposed to a humid synthetic natural gas mixture with monoethylene glycol (MEG) and triethylene glycol (TEG). The effects of different parameters such as relative humidity, types of impurities, exposure temperature were analyzed to understand the real mechanism of interaction and their effects on the CO_2/CH_4 separation performance. Both the CO_2 and CH_4 permeances were increased after the exposure of hygroscopic MEG and TEG, except in one case. The CO_2/CH_4 selectivity was slightly reduced by the exposure to MEG since MEG plasticized the membrane a little bit, whereas the selectivity was slightly increased by the exposure to TEG. Water plays a significant role in the overall performance. For this facilitated transport PVAm/PVA blend membrane, the high relative humidity helps the facilitated transport of CO_2 through the PVAm/PVA blend composite membrane to maintain its permeation properties to a value very close to that of a fresh membrane. This study reports the effect of MEG and TEG on the CO_2/CH_4 separation of a PVAm/PVA blend composite membrane, and documents a positive step forward for using this membrane in a rigorous environment of natural gas sweetening where entrained glycol is considered as a potential threat to the membrane.

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1. Introduction

The importance of removing acid gases such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from natural gas is well known. Membrane technology for removal of CO_2 from natural gas was introduced already around 30 years ago, and is expected to take more shares from other conventional capture processes in upcoming years. Even for the unconventional source like shale gas where the reserve is thought to be more than five times the proven amount of conventional natural gas, membranes are now going to be used to remove CO_2 from shale gas in British Columbia, Canada [1]. However, the performances of a CO_2 removal membrane may be reduced by different components which are present in the gas. Most of these components are originally present in the geological reservoirs (water, heavy hydrocarbons, etc) but others may also come from the units/ chemicals used in the natural gas pre-treatment chains either accidentally (glycols, compressor oils) or intentionally (well additives, corrosion inhibitors).

Natural gas generally coexists with water in the geological reservoir. Water in the liquid phase causes corrosion or erosion problems in pipelines and equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas—this may cause the formation of hydrates with hydrocarbons [2–3]. Dehydration with glycol is a widely used absorption technology in natural gas processing to meet pipeline specifications [4]. Glycol dehydrators and chillers are typically used upstream of membrane modules to prevent hydrate formation or freeze-up [5]. However, glycol dehydrators may also pose a potential hazard to membrane systems: for instance, an upset in dehydrator operation may flood the membrane modules with triethylene glycol (TEG), commonly used as the working fluid [6]. Glycol dehydrators are not well suited for use on small gas stream or on offshore platforms, increasingly common source of natural gas [7]. Instead, glycols can be added to the well stream as antifreeze to inhibit the formation of hydrates before the raw natural gas is being transported through long distance pipelines, quite common for offshore fields. For instance, monoethylene glycol (MEG) is used as the antifreeze in the Statoil operated Snøhvit field in Barents Sea with 145 km multiphase-flow pipeline running to the LNG plant in Hammerfest, Norway [8,9]. Though the glycol–water mixture is separated, a trace amount of glycol may be carried by the natural gas. A recent simulation study on the MEG and TEG

injection to the natural gas shows that most of the glycol lost is associated with the vaporization of the glycols into the processed natural gas [10]. However, almost no study is found in the literature which describes the effects of these carried-over glycols on the CO_2/CH_4 separation performance of a membrane.

Most of the CO_2/CH_4 separation studies with membranes deal with either pure gas permeation experiments or binary mixed-gas experiments [11]. For application in industry, it is important to examine multiple mixed-gas environments and interactions with the components not only present geologically in natural gas wells but also the components added artificially or accidentally in natural gas streams such as glycols. Among the three common varieties of glycols, diethylene glycol (DEG) is the most toxic. TEG is the most commonly used glycol to dehydrate natural gas by glycol dehydration unit, whereas MEG is popular for being injected into raw natural gas as antifreeze (inhibitor to gas hydrate and ice formation). In this study, MEG and TEG are chosen as the model impurities to study the effects of these two glycols on the performance of a polymeric blend composite membrane in CO_2/CH_4 separation.

The PVAm/PVA blend composite membrane acts as a CO_2 facilitated transport membrane in the presence of water and shows impressive permeation performance in CO_2/CH_4 separation as reported earlier in [12,13]. The study of the effects of hydrogen sulfide and hydrocarbons on this membrane is being reported separately in parallel. In the current article, the effects of MEG and TEG on membrane permeation properties in presence of water are reported. Static durability experiments of the PVAm/PVA blend membrane under the exposure of MEG and TEG were performed, and the CO_2 permeation properties of the membrane were compared before and after different exposure conditions. The term static exposure is used since the membrane is kept in a durability chamber filled with the test gases during the entire exposure. The impurity gases are hence not forced to pass through the membrane as they do in a standard permeation module. The performance of the membrane is checked before and after exposure. The support of this blend composite membrane is polysulfone (PSf), a well-known glassy polymer, on a non-woven polypropylene (PP). The rigidity and highly ordered structure of the PSf glassy polymer might make them more susceptible to the harmful effects of condensable impurities [11]. MEG and TEG are highly condensable, and have very low vapor pressure. Hence, the effects of these condensable additives in natural gas were studied on the performance of the composite PVAm/PVA–PSf membrane.

The need to study the impacts of entrained glycol impurities of natural gas streams on the performance of a membrane was mentioned almost a decade ago by Vu et al. [11], however, very few studies were found in the literature. TEG is reported by Ito et al. [14–16] to be used in liquid membranes to separate out volatile organic compound (VOC), while the dehydration behaviour of ethylene glycol (MEG) water mix in different pervaporation membranes is documented by several researchers [17–22]. Polyethylene glycol (PEG) is introduced in numerous blends to make different membranes. The early reverse osmosis cellulose diacetate or triacetate membranes [23,24] were treated with glycerol as a conditioning agent, which allows easy rewetting with water and physically holds open the pores of the asymmetric microporous membrane structure; however, for gas separation membranes glycerol is not an option since it may physically inhibit the passage of gases [6]. The effects of CO_2 on glassy polymer are documented by several researchers in [25–30]. A number of studies describing the effects of H_2S, hydrocarbons, water, and both condensable and non-condensable impurities on different membranes are likewise found in the literature [31–44]. However, no such studies are found on the effects of MEG or TEG in CO_2/CH_4 separation membrane. Glycols are well known as hygroscopic compounds and are also used as plasticizers [45–46].

Since the transport behaviour of gases like CO_2, CH_4 in PVAm/PVA blend membrane are strongly correlated with relative humidity, it was expected that MEG and TEG should have some effects on the permeation behaviors of this facilitated transport membrane in presence of H_2O. One of the most important findings of this research was that the permeation behaviors of the membrane were found to be dependent on the type of glycols, temperature and more profoundly on relative humidity. Moreover, the effects of MEG and TEG on the CO_2, CH_4 transports were studied with respect to relative humidity and hydrophilicity of the membrane. The hydrophilicity of the membrane was increased by the exposure in both cases, but the separation performances of the membrane were affected differently by MEG and TEG. The study also gave an indication about the potential operational relative humidity range where the CO_2 selective PVAm/PVA blend membrane may perform best in presence of these glycols in natural gas sweetening.

2. Experimental

2.1. Membrane preparation, characterization and permeation experiment

The composite membrane is composed of a thin selective layer of PVAm/PVA blend on a polysulfone (PSf) on non-woven polypropylene (PP) support membrane (Alfa Laval, MWCO 50,000). The membrane was prepared the same way as reported earlier in [12,47,48], with the exception that a high molecular weight PVAm (BASF, MW 340,000) was used after successive purification steps as described in [49]. The membrane was characterized by a field emission scanning electron microscope (FESEM, Zeiss Ultra 55 Limited Edition) and water contact angle on the membrane was measured by a CAM 200 (KSV Instruments Ltd. Finland) equipped with a high speed camera. All permeation experiments reported here were carried out at temperature of 25 °C, feed pressure at 2 bars, with 10.0% CO_2 and 90.0% CH_4 (from YaraPraxair) as feed and with nitrogen as sweep in a permeation set-up as described in [47]. The sweep was saturated with water, while the relative humidity of the feed was controlled in a range of 20–92%.

2.2. Static exposure experiments with impurities

The pre-mix gas used in this study was supplied by YaraPraxair at 100 bars and the compositions is 10.0 mol% of CO_2 and 90.0 mol% of CH_4. The static exposure of the blend membrane is done with this gas mixture saturated with water and MEG/TEG (one at a time) and kept at 2 bars and 10 bars each for 1 week in durability chambers made of stainless steel of a volume of 0.60 L. Both the MEG (Purity grade, $\geq 99.5\%$) and TEG (Bioultra grade, anhydrous, $\geq 99.0\%$) used are from Sigma Aldrich. The schematic structures of MEG [50] and TEG [51] are shown in Fig. 1.

Fig. 2 shows a schematic diagram of the set-up used for the static exposure experiments. The system was first evacuated and then the exposure gas was passed through the water humidifier to become saturated before being fed to the durability chamber. Since MEG and TEG are very hygroscopic in nature a special procedure is followed to ensure that the feed gas is saturated with
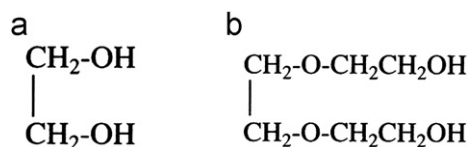
a

$CH_2\text{-}OH$
$|$
$CH_2\text{-}OH$

b

$CH_2\text{-}O\text{-}CH_2CH_2OH$
$|$
$CH_2\text{-}O\text{-}CH_2CH_2OH$

Fig. 1. Schematic structure of (a) MEG and (b) TEG.