



Facilitated transport of ethylene through the polyethylene-graft-sulfonated polystyrene membranes. The role of humidity



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ABSTRACT

The possibility of ethane/ethylene mixture separation at the passing these gases through polyethylene-graft-sulfonated polystyrene membranes in silver and hydrogen forms has been shown. The results showed that the permeability of ethylene and the value of the separation coefficient increased significantly with increasing relative humidity of the separated gases. It was concluded that in both cases the transfer of ethylene occurred in the form of a positively charged complex. The patterns of change in the permeability and separation factor were explained on the basis of the structure of the initial membranes and the solubility of the separated gases in the “phases” forming the membrane.

1. Introduction

The constant growth of the interest in the processes associated with refinery gases and their components (ethane, propane, butane) is observed [1]. These gases are known as not only a fuel, but also as a raw material for the synthesis of valuable products having olefins as the products of the first stage of the processing. One of the problems along this path is the separation of saturated and unsaturated hydrocarbons mixtures [2]. Industrially, this separation is carried out by cryogenic distillation, which is highly energy-intensive [3,4]. The membrane separation has some advantages in comparison with distillation and adsorption methods due to its low energy consumption, moderate cost and compact design [5–7].

However, ethylene/ethane separation using conventional membranes has some difficulties caused by the similar structure and sizes of their molecules [8–11]. This problem can be solved with the use of membranes in which the facilitated transport mechanism is realized [12]. The significant attention to such materials and processes is determined by their high efficiency [13–20]. One of the examples is the process of facilitated olefin transport via the selective formation of complexes with silver and copper ions contained in the membranes. The advantages of these systems are high olefin permeability coefficients and selectivity of the gas mixture separation processes [21–24]. The disadvantage of these membranes can be considered the gradual loss of

selectivity owing to Ag^+ ions, which are easily reduced under exposure to light [25]. In [26], the effect of the facilitated ethylene transport through membranes in a hydrogen form was observed. In light of the above, the ion exchange membranes in H^+ or Ag^+ form can be suggested as the most promising solution. The membranes based on polyethylene with radiation chemically grafted sulfonated polystyrene (SPS) were chosen because of the possibility to obtain membranes with a wide range of carrier concentrations by varying the polystyrene grafting degree and its sulfonation [26–28]. The difference in the gas permeability of the initial membranes by ethane and ethylene is relatively small, but in the H^+ -form these differences can be substantially increased by changing the humidity of the gases above the membrane [28–30].

In this paper, the dependence of the transport processes selectivity of ethylene/ethane mixture components on the pressure and the gas stream humidity in membranes based on polyethylene with radiation chemically grafted SPS in hydrogen and silver forms was studied.

2. Materials and methods

2.1. Materials

The sulfocathionite membranes obtained by post-radiation graft polymerization of styrene on a low density polyethylene (PE) film with

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a thickness of 20 μm were studied, followed by sulfonation of the grafted polystyrene (PS) by the procedure described in [26]. The membranes with different grafting degrees were studied (0–122%). The grafting degree of polystyrene (G) was calculated as the weight gain of the film, referred to the original film mass.

2.2. Preparation of the Ag^+ -form membrane

Before carrying out the experiments, the membranes were transferred to the H^+ or Ag^+ -form. The modification of the membrane into the hydrogen form was carried out by dipping the membranes in a 0.1 N hydrochloric acid solution, which was replaced three times with a new one. To obtain the Ag^+ -form, the membrane was sequentially treated with 0.1 N solutions of NaOH and AgNO_3 in a dark box to prevent the reduction of silver ions. After this, the membranes were washed with distilled water and dried.

2.3. Atomic absorption spectrometry (AAS) studies

The silver content was determined by flame atomic absorption spectrometry using an AAnalyst 400 device from Perkin Elmer. The samples were previously dissolved in mineral acid after burning in a muffle furnace at 450 $^\circ\text{C}$.

2.4. Mixed-gas permeation experiments

The permeability measurements of the polymeric membranes based on polyethylene grafted with sulfonated polystyrene for the ethylene/ethane mixture separation (the ratio $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 = 6:94$) were carried out in a stainless steel flow-through diffusion cell divided by a membrane with an area of 3.46 cm^2 into two non-communicating chambers. The studied gas mixture was introduced into one of the chambers, while helium was introduced into another chamber and acted as a carrier gas. Both gas streams were moistened by passing through the bubbler. The relative humidity level (from 30 to 80%) was created by changing the temperature of the bubblers with distilled water. Before each experiment, the membrane was pre-moistened with a stream of moistened gases for two hours. Humidity of gases was determined at the outlet from the membrane cell.

The permeability coefficients of ethylene and ethane (P) were determined as the individual gases fluxes through the membrane at room temperature and expressed in Barrers [$1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s cm Hg})$]. The separation factor of ethylene and ethane was determined as the ratio of the permeability coefficients of these gases.

3. Results

The data on the silver content were obtained by atomic absorption spectrometry. The silver sorption even exceeded the calculated for 100% protons substitution for membranes aged in AgNO_3 solution. This is determined by the nonspecific overequivalent sorption of the silver nitrate solution in the membrane pores. The degree of sodium ions substitution with silver ions decreased from 90 to 70% after removing excess silver nitrate by membrane washing.

The transformation of the membranes into the silver form, as expected, led to a significant increase of the membrane permeability for ethylene (Table 1). At the same time, ethane permeability also increased, although its growth occurs at slower rates. Considering obtained values, the increase of the separation factors for a gas mixture of ethane and ethylene is expected that was confirmed by data in Table 1. The separation factors of ethylene and ethane mixture of this composition were even higher and reached the values of 70–80 indicating a competitive sorption of gases. There is no doubt that when using a membrane in silver form, facilitated transport of ethylene forming complexes with silver is observed. This can also be confirmed by the fact that the coefficient of ethylene permeability increases with

Table 1

Data on the permeability of gases and separation factors for membranes with a grafting degree of 50 and 122% in H^+ – and Ag^+ – forms. F is the gas separation factor of the mixture, which is calculated by the formula: $F = P(\text{C}_2\text{H}_4)/P(\text{C}_2\text{H}_6)$.

Humidity	H^+			Ag^+		
	$P(\text{C}_2\text{H}_4)$	$P(\text{C}_2\text{H}_6)$	F	$P(\text{C}_2\text{H}_4)$	$P(\text{C}_2\text{H}_6)$	F
G = 122%						
30	400	10	40	980	20	49
50	425	10	45	1100	19	58
65	510	9	57	1300	18	72
80	445	8	59	1000	16	63
G = 50%						
30	435	25	18	960	33	29
50	530	24	22	1100	30	37
65	610	20	31	1350	30	45
80	570	19	30	1270	28	45

increasing gases humidity. Since the ethylene transfer occurs in the form of a positively charged complex, it takes place in a system of pores and channels, and the carriers mobility increases with increasing moisture content. On the contrary, the ethane permeability, which does not form complexes and is insoluble in water, decreases with increasing moisture content (Table 1). At the same time, the disadvantage of this approach is a significant decrease in permeability in time due to the reduction of silver.

The significant difference in the permeability of the membranes for the studied gases was also observed in the hydrogen form. The changes in the permeability of ethane and ethylene through the membranes with different PS grafting degree in H^+ -form, depending on the humidity of these gases are shown in Figs. 1 and 2. It can be noted that, at low humidity, an increase of the PS grafting degree leads to a decrease in the permeability of both gases. We assume that this was caused by lower solubility of gases in SPS compared to PE. For ethane this dependence was kept even at increased the supplied gases humidity values (Fig. 2) due to a significant growth of membrane pore and channels volume containing water in which ethane was insoluble. At the same time, the permeability of ethylene increased significantly for the intermediate PS grafting degree (Fig. 1), although at the highest PS grafting degree the permeability of ethylene decreased again. In addition, the ethylene permeability increase with increasing moisture content should be noted. These patterns allow us to conclude that in this case the transfer of ethylene, as well as in the silver form, occurs in the form of a positively charged complex in concentration raising with an increase of the PS grafting degree owing to the increase of the carrier concentration.

Unexpected data can be understood taking into account the features of these membranes structure. At higher gas humidity values, the increase of the sulfonated polystyrene content led to an increase in the

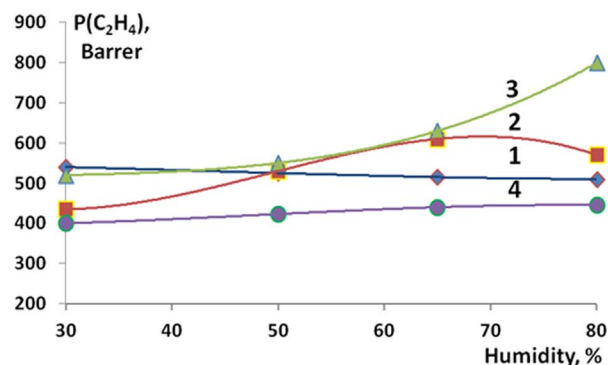


Fig. 1. The dependence of the ethylene permeability coefficient on humidity for the membrane films in hydrogen form with a different PS grafting degree: 1 – 36%; 2 – 50%; 3 – 74%; 4 – 122%.

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