ISSN 0965-5441, Petroleum Chemistry, 2015, Vol. 55, No. 9, pp. 693–702. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © E.M. Erdni-Goryaev, A.Yu. Alentiev, G.N. Bondarenko, A.B. Yaroslavtsev, E.Yu. Safronova, Yu.P. Yampolskii, 2015, published in Membrany i Membrannye Tekhnologii, 2015, Vol. 5, No. 3, pp. 167–177.

Facilitated Transport of Gases in Polymer Hybrid Materials Containing Ionic Liquid Additives

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Received February 16, 2015

Abstract—Gas permeation characteristics (permeability (P), diffusion (D), and solubility (S) coefficients for CH_4, C_2H_4, C_2H_6, C_3H_8, CO_2, O_2, N_2, and Ar and gas separation selectivities) for hybrid materials based on ionic-liquid (IL) saturated MF-4SC membranes in H^+ and Ag^+ forms and in presence of AgCl nanoparticles have been studied. It has been shown that, in the IL-impregnated MF-4SC membranes in H^+ and Ag^+ forms, the permeation of CO_2 and C_2H_4 occurs by the facilitated transport mechanism. At the same time, in the presence of AgCl nanoparticles, the facilitated transport mechanism is implemented only for CO_2. Diffusion coefficients in the polymer matrix, effective diffusion coefficients between “fixed” carriers, sorption Henry constants in the polymer matrix, and effective interaction constants of CO_2 and C_2H_4 with the membrane material have been determined in terms of the dual-mode sorption model formalism for CO_2 and C_2H_4. It has been shown that the most effective material for the separation of CO_2 and C_2H_4 is an IL-impregnated MF-4SC membrane in a hydrogen form. Using model approaches, it has been shown that the main cause of the facilitated transport of ethylene in these membranes is the interaction between the double bond of the ethylene and the IL cation.

Keywords: membranes, permeability, selectivity, facilitated transport, ionic liquids

DOI: 10.1134/S0965544115090029

INTRODUCTION

Facilitated transport phenomena for the membrane separation of gases have been known for over 40 years [1, 2]. Advantages of this approach in the implementation with mobile carriers (impregnated liquid membranes) or fixed sites are attributed to the fact that this approach makes it possible to increase the selectivity of sorption and permeability with respect to certain types of penetrants, while maintaining the diffusion and permeability coefficient values unchanged (particularly in the case of impregnated liquid membranes). The problems that are tackled using the facilitated transport method include the extraction of oxygen from the air [3], the separation of propylene/propane or ethylene/ethane mixtures [4], and the extraction of CO_2 from mixtures thereof [5]. New problems are arising, such as the separation of CH_4/C_2H_4 mixtures. This mixture is formed during the oxidative dimerization of methane, which is a promising method for producing petrochemical feedstocks from natural gas [6]. At the same time, the separation of this mixture by means of polymer membranes operating on the principle of passive transport is hindered because of the close permeability coefficients of methane and ethylene in polymers. However, the implementation of facilitated transport processes encounters great difficulties, the most important of which is the removal of the liquid phase from the membrane pores containing a solution of the complexing agent.

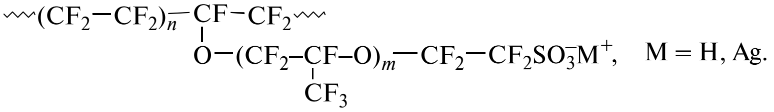
This difficulty can be overcome using ionic liquids (ILs) as the liquid phase [7]. In particular, some ILs have shown interesting results in the separation of olefins and paraffins [8]. Ag^+ ions can be used as the complexing agent, particularly in IL-containing composites. A large number of studies addressing membranes containing ILs in combination with Ag^+ ions have been published [8–11], although there are examples [12] that show that individual ILs are capable of operating in facilitated transport systems. The introduction of nanoparticles can lead to an increase in the permeability coefficients and selectivities of separation of olefin/paraffin mixtures. However, in the vast majority of these studies, the object of research was the propylene/propane pair.

In this study, transport of various gases, primarily CO_2, CH_4, and C_2H_4, in IL-impregnated MF-4SC perfluorinated sulfonated cation-exchange membranes has been examined. The effect of the counterion upon switching from a proton (H^+) to silver form (Ag^+) of the polymer has been studied; the effect of the presence of AgCl nanoparticles in the film has been analyzed. Apparently, the ethylene/methane pair, which is important in the applied aspect, has been first studied for these membranes.

EXPERIMENTAL

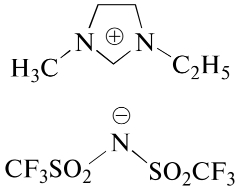
Membrane Preparation

Perfluorinated sulfonated membranes (films) based on MF-4SC (Plastpolimer, St. Petersburg) in proton and silver ionic forms were used in the study. The structural formulas of the two forms are shown below:



$$\sim(CF_2-CF_2)_n-\underset{\displaystyle O-(CF_2-\underset{\displaystyle CF_3}{CF}-O)_m-CF_2-CF_2SO_3^-M^+}{CF}-CF_2\sim, \quad M = H, Ag.$$

In addition, an MF-4SC membrane in a silver form doped with AgCl nanoparticles was prepared and studied. The membranes of all the three types were impregnated the $[(MeEtIm)^+(CF_3SO_2)_2N^-]$ IL, which has the following structural formula



To standardize the conditions, the membrane was subjected to conditioning as described in [13]. To convert the membrane into a silver form, the original sulfonic acid sample was held in a 2 M silver nitrate solution under constant stirring for 72 h and then repeatedly washed in deionized water to remove nitrate ions. To provide the formation of silver chloride in the membrane pores, the membranes were sequentially exposed to 2 M solutions of silver nitrate and sodium chloride. To convert the functional groups into a silver form, at the last stage, the membrane was again exposed to a 2 M silver nitrate solution and washed with water. During this treatment, AgCl nanoparticles are formed in the hydrophilic pores of the membranes [14]. In all the membrane samples, the aqueous phase was replaced by the IL. To this end, the membranes were washed in methanol for 1 day and then placed in the IL. The impregnation of the membranes with the IL was conducted to constant sample weight. The IL content in the membranes was calculated from measurements of the initial and final density of the membranes by hydrostatic weighing.

Transport parameters of the membranes (80-μm-thick films of membrane materials) were determined by mass spectrometric methods [15] for the following gases: O_2, N_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, and Ar. A Balzers QMG-420 mass spectrometer was used to measure the partial pressure of the penetrant that has penetrated into the calibrated-volume receiving chamber through the polymer film. Permeability coefficient was calculated using the formula

$$P = Jl/(A\Delta p), \tag{1}$$

where J is the penetrant flux across the membrane, l is the membrane thickness, A is the membrane surface across which the mass transfer occurs, and Δp is the pressure difference across the membrane. Experiments were conducted at room temperature, an upstream pressure in a range of 0.1–1 atm, and a downstream pressure of about 10^{-3} mm Hg. Permeability coefficient (P) was calculated from the time variation of the ion current for a given ion (typically, the most intensive one) in the mass spectrum of a given gas after the stabilization of the diffusion process. Diffusion coefficients (D) were determined from time lag θ using the Daynes–Barrer formula

$$D = l^2/6\theta. \tag{2}$$

The measurement error for P and D is 5 and 10%, respectively. The P and D values were used to determine solubility coefficient S:

$$P = DS. \tag{3}$$

RESULTS AND DISCUSSION

Table 1 lists the values of the gas transport characteristics of the studied materials. Analyze the effect of the introduction of the IL into the MF-4SC films on gas permeability. Note that there are a great number of literature data on the permeability of Nafion membranes with respect to various gases [16, 17]; however, data on the permeability of MF-4SC are scarce. In addition, gas permeability can significantly depend on humidity. The authors of [18] compare the MF-4SC and Nafion-117 membranes. At room temperature and humidity, the two membranes have approximately the same permeability coefficients with respect to hydrogen of about 20 Barrer. The effect of humidity on permeability with respect to hydrogen and oxygen has been studied in [17]. An increase in humidity to 80–100% leads to an increase in the permeability by no more than a factor of 1.5. Comparison of the results of these studies [16, 17] suggests that the permeability coefficients of the MF-4SC membrane for different gases must have values listed in Table 2. Comparison of the data in Tables 1 and 2 reveals that the introduction of the IL into the MF-4SC membrane leads to a sev-

Table 1. Transport parameters of the test membranes

Gas	MF-4SC–H^+–IL			MF-4SC–Ag^+–IL			MF-4SC–Ag^+–IL–AgCl		
	P^1	D^2	S^3	P	D	S	P	D	S
O_2	4.3	24	1.8	7.1	97	0.73	2.1	13	1.6
N_2	2.0	14	1.4	3.5	38	0.93	0.89	7.9	1.1
Ar	5.8	34	1.8	6.8	52	1.3	2.0	9.1	2.2
CH_4	2.0	7.9	2.5	3.6	20	1.9	0.92	3.4	2.7
C_2H_6	1.9	2.8	6.9	3.4	5.4	6.2	0.77	1.4	5.4
C_3H_8	1.5	0.90	17	2.4	1.7	14	0.53	0.40	13
CO_2	31	12	27	50	35	16	9.4	6.6	14
C_2H_4	4.4	0.89	50	7.3	1.4	54	0.63	1.6	4.0

[1] P [Barrer]. 1 Barrer = 10^{-10} cm^3(STP) cm/(cm^2 s cmHg); [2] $D \times 10^8$, cm^2/s; [3] $S \times 10^3$, cm^3(STP)/(cm^3 cmHg).

Table 2. Permeability coefficients of the MF-4SC membrane

Gas	O_2	Ar	N_2	CH_4	CO_2
P [Barrer]	1.1–1.6	0.5–0.7	0.26–0.4	0.1–0.15	2.4–3.6

eral-fold increase in the permeability (to different degrees for the different gases).

On the other hand, the data on the permeability of ethane and ethylene in the Nafion-117 membranes at high humidity [19, 20] significantly differ from the experimental data obtained in this study for the IL-impregnated membranes. For the Nafion-117 membranes—both saturated with silver ions and in a Na form— $P(C_2H_6) = 2$ Barrer; this value is close to the results obtained in this study; however, it is but substantially higher than the value that would be expected from the data for neutral gases (Table 2). For the Nafion-117 membranes in a Na form in [19, 20], the permeability of ethylene $P(C_2H_4)$ was 2 Barrer, which is close to the results of our study. At the same time, for the Nafion-117 membrane in an Ag form, the authors obtained a permeability coefficient of $P(C_2H_4) =$ 1000 Barrer, which is more than two orders of magnitude higher than the value obtained in this study. Apparently, this effect is associated with significant differences in the diffusion coefficients of ethylene in the water filling the nanochannels in a wet Nafion-117 membrane and the significantly more viscous IL: according to [19], the diffusion coefficient of ethylene was 330 cm^2/s, which is more than two orders of magnitude higher than the value determined in our experiments.

As in the case of any polymer material filled with an IL [21–23], all the membranes based on MF-4SC (Table 1) have high permeability and solubility coefficients with respect to CO_2. The first two membranes also exhibit high permeability and solubility coefficients with respect to ethylene. The diffusion coefficients of ethylene in these materials are relatively low; these values are comparable with the D value for propane and much lower than that of ethane. In addition, according to [24, 25], the kinetic diameter for ethylene is significantly lower than that of propane.

This behavior of the diffusion properties of facilitated transport systems has been described in considerable detail in the literature. Thus, the authors of [10–12] have shown that, in Ag^+ ion containing systems, the diffusion coefficient of propylene is significantly low than that of propane; this fact is attributed to the partial immobilization of ethylene during complexation. In our case, the effective diffusion coefficient can also decrease owing to the specific interaction of ethylene with the membrane material and the transfer of the “interacting” gas by the facilitated transport mechanism. In this case, in terms of various models [4], the effective diffusion coefficient is determined by a combination of two transport processes: the nonspecific diffusion of the gas in the polymer matrix and the facilitated transport during complexation with the specific carriers (silver ions). In addition, the diffusion coefficient of the complex involving silver ions is substantially lower than the nonspecific diffusion coefficient in the matrix; this feature leads to a decrease in the effective diffusion coefficient. According to [19], in the Nafion-117 membranes saturated with silver ions, the diffusion coefficient of ethylene is 16.5 times higher than that of an ethylene–silver complex.

Table 3. Ideal gas separation selectivities (α), diffusion selectivities (α^D), and solubility selectivities (α^S) of the test membranes

	MF-4SC–H$^+$–IL			MF-4SC–Ag$^+$–IL			MF-4SC–Ag$^+$–IL–AgCl		
Gas pair	α	α^D	α^S	α	α^D	α^S	α	α^D	α^S
α (O_2/N_2)	2.2	1.8	1.2	2.0	2.6	0.78	2.3	1.6	1.5
α (CO_2/N_2)	15	0.86	18	14	0.92	17	10	0.84	13
α (CO_2/O_2)	7.1	0.50	15	7.0	0.36	22	4.5	0.51	8.8
α (C_2H_4/CH_4)	2.2	0.11	20	2.0	0.070	28	0.68	0.47	1.5
α (C_2H_4/C_2H_6)	2.3	0.32	7.3	2.1	0.26	8.7	0.82	1.1	0.74
α (C_2H_4/C_3H_8)	2.9	0.99	2.9	3.0	0.82	3.7	1.2	4.0	0.31

The observation of a significant decrease in all the three parameters— *P*, *D*, and *S*—in the membrane with additives of AgCl nanoparticles is unexpected. It is known that the introduction of nanoparticles into polymers (production of hybrid polymer membranes) typically leads to an increase in permeability, which is commonly accompanied by an increase in diffusion coefficients [26, 27]. At the same time, according to [18], the introduction of modifying additives into MF-4SC membranes resulted in a decrease in the permeability with respect to hydrogen. The hypothesis that the resulting AgCl particles can have micrometer sizes (i.e., that the case in hand is the classical case of filled polymers, where the introduction of an additive leads to an increase in the diffusion path lengths and thereby to a decrease in the diffusion and permeability coefficients [28]) seems to be hardly plausible because the size of the pores in which the particles are formed is as low as 4–6 nm. At the same time, this fact can be reasonably explained in terms of the model of limited elasticity [29]. According to this model, the nanoparticles are formed in the pore volume and displace the "free solution" in which the gases mostly undergo dissolution. However, according to the results of [9], the introduction of AgBr nanoparticles leads to an increase in selectivity $\alpha(C_3H_6/C_3H_8)$ and permeability with respect to propylene; in addition, this effect is particularly strong in the presence of an IL.

As noted above, one of the aims of this study was to explore the possibility of separating ethylene-containing mixtures. Table 1 shows that the substitution of a silver ion for the proton in the acid form of the membrane leads to a certain increase, albeit not very large, in $P(C_2H_4)$, while the solubility coefficient remains almost unchanged. This observation apparently suggests that the complexation with the Ag$^+$ ion is not the determining factor in IL-impregnated MF-4SC membranes.

At the same time, it is worth noting that the absolute value of the solubility coefficient of ethylene in the MF-4SC–H$^+$–IL and MF-4SC–Ag$^+$–IL samples is high. Typically, in polymers, the solubility coefficients of gases correlate with the critical temperatures thereof. This feature is responsible for the fact that the solubility coefficient of CO_2 ($T_c = 304$ K) in polymers is generally higher than the solubility coefficient of ethylene ($T_c = 283$ K) [30]. However, it is evident from Table 1 that, for the first two samples, $S(C_2H_4) > S(CO_2)$. At the same time, for the third sample, for which the facilitated transport phenomena are not observed, for the solubility coefficients, $S(C_2H_4) < S(CO_2)$, as for conventional polymers.

Table 3 shows that permeability selectivities $\alpha(C_2H_4/CH_4)$ and $\alpha(C_2H_4/C_2H_6)$ vary only slightly after the introduction of the Ag$^+$ ion. The separation selectivities of presumably noninteracting gases $\alpha(O_2/N_2)$ differ only slightly from the separation selectivity in rubber resins [31]. At the same time, for the gases interacting with the membrane material, such as CO_2 and C_2H_4, the solubility selectivities (α^S) are significantly higher than the diffusion selectivity (α^D) and determine the separation selectivity (except for the MF-4SC–Ag$^+$–IL–AgCl membrane for which the α^S value of ethylene-containing gas pairs is not high).

The selectivity α values listed in Table 3 are relatively low. However, the α values observed for the C_3H_6/C_3H_8 pair are typically also low [9, 12]. This feature is attributed to a few factors: (i) the introduction of a complexing agent leads to an increase in *S* and a decrease in *D* so that the two components of the permeability coefficient— $P = SD$—act in opposite directions and (ii) along with the facilitated transport, a less selective passive transport of the studied gases across the polymer matrix is observed.

Since diffusion (*D*) and solubility coefficients (*S*) of various gases were determined for three membranes of different compositions, it is of interest to consider the classical correlations [25], i.e., the correlations of log *S* with Lennard-Jones potential energy parameter ε/k and the correlations of $\log D$ with squared effective gas-kinetic diameter of diffusant molecules d^2. In the case of the passive transport of gases in a polymer matrix, these correlations are linear; deviations of these correlations can indicate the occurrence of specific interactions.

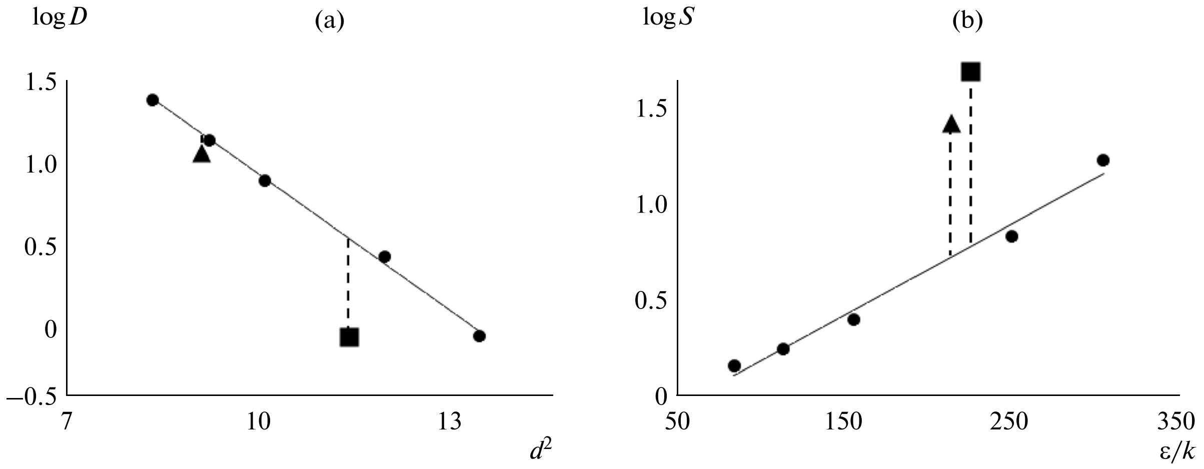


Fig. 1. (a) Log$D$–d^2 and (b) log$S$–ε/k correlation plots for the MF-4SC–H$^+$–IL membrane: (▲) CO_2 and (■) C_2H_4.

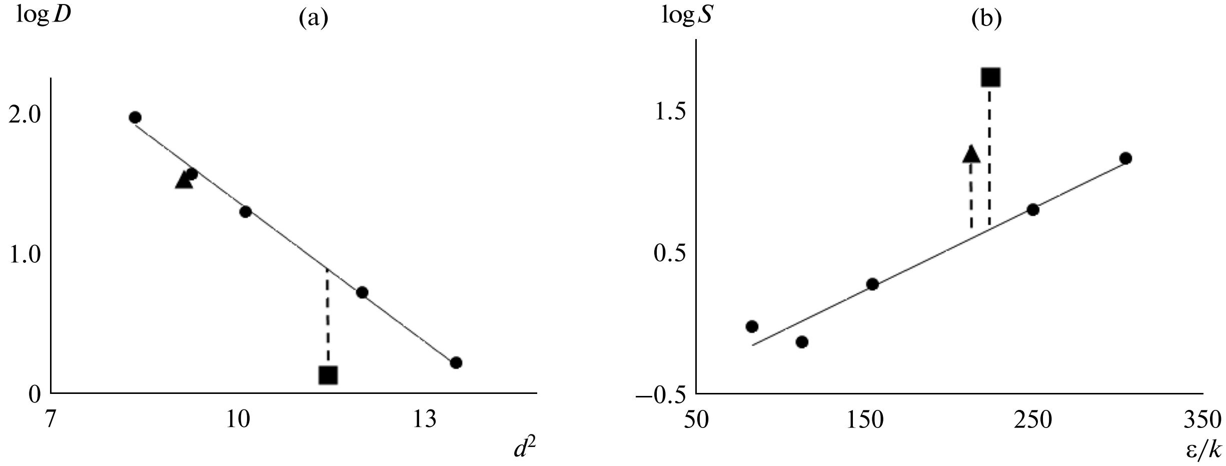


Fig. 2. (a) Log$D$–d^2 and (b) log S–ε/k correlation plots for the MF-4SC–Ag$^+$–IL membrane: (▲) CO_2 and (■) C_2H_4.

Figures 1–3 show the log$D$–d^2 and log$S$–ε/k dependences for all the three materials and the following gases: O_2, N_2, CH_4, CO_2, C_2H_4, C_2H_6, and C_3H_8.

It is evident from Figs. 1b–3b that, for the MF-4SC–H$^+$–IL and MF-4SC–Ag$^+$–IL membranes, the S values for CO_2 and C_2H_4 are significantly higher than the values that would be expected from the linear dependences of the correlation for noninteracting gases. At the same time, for the MF-4SC–Ag$^+$–IL–AgCl membrane, only the S values for CO_2 deviate from the above linear correlation.

In the correlations for the diffusion coefficients of ethylene in the case of the MF-4SC–H$^+$–IL and MF-4SC–Ag$^+$–IL membranes (Figs. 1a, 2a), significant negative deviations (reduced diffusion coefficients) are observed, while in the case of the MF-4SC–Ag$^+$–IL–AgCl membrane (Fig. 3a), $D(C_2H_4)$ is in the linear dependence for noninteracting gases. For all the membranes, the diffusion coefficients of CO_2 slightly deviate from the linear dependence toward a decrease in D (Figs. 1a–3a). As noted above, this decrease in the effective diffusion coefficient can indicate the occurrence of the facilitated transport mechanism for interacting gases. Thus, analysis of the correlations shown in Figs. 1–3 suggests that, for all the materials, the permeation of CO_2 occurs by the facilitated transport mechanism. In the case of ethylene, the conclusion about the occurrence of the facilitated transport mechanism can be made only for the MF-4SC–H$^+$–IL and MF-4SC–Ag$^+$–IL membranes.

Hence, in interpreting the results for interacting gases, it is necessary to use equations to describe the facilitated transport, one of the versions of which can the formal application of the dual-mode sorption model. Thus, it is known that, in the case of facilitated transport, the sorption isotherms of olefins in fixed site carrier systems are similar to the sorption isotherms of gases in glassy polymers. This feature has made it possible to use the formalism well-developed for the dual-mode sorption model to consider the facilitated trans-

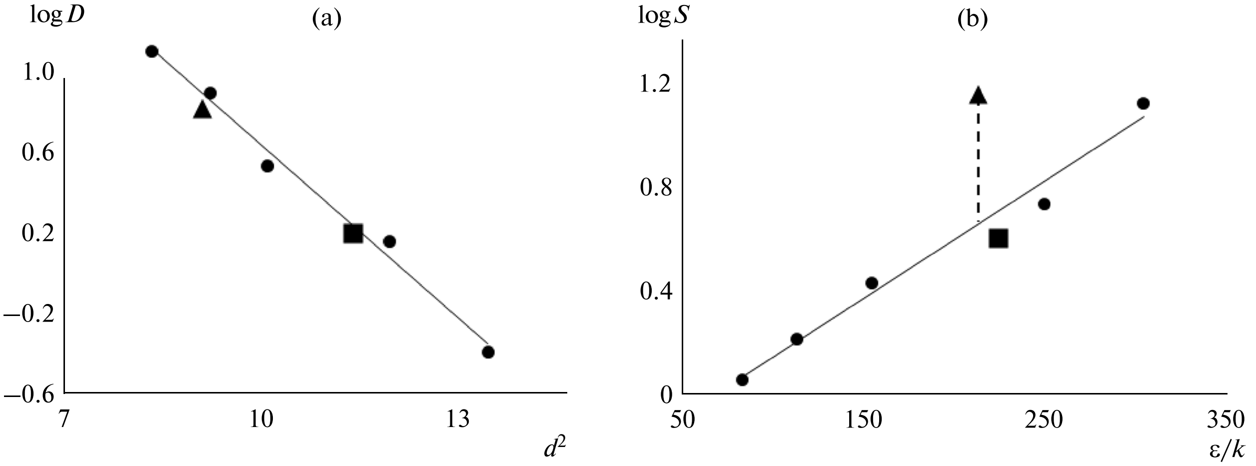


Fig. 3. (a) Log$D$–d^2 and (b) log$S$–ε/k correlation plots for the MF-4SC–Ag^+–IL–AgCl membrane: (▲) CO_2 and (■) C_2H_4.

port [4]. In particular, for permeability coefficients, it has been proposed [32] to use a formula similar to that used in the dual-mode sorption model in glassy polymers:

$$P = k_D D_D + D_C C'_C K/(1 + Kp). \quad (4)$$

Here, k_D is the solubility coefficient for the Henry sorbate molecule "population" in a polymer matrix, D_D is the diffusion coefficient of passive transport corresponding to this population in the matrix, D_C is the effective diffusion coefficient between the complexing carriers, C'_C is the limiting gas concentration reversibly coupled with the complexing agent, K is the equilibrium constant of this interaction between the gas and the complexing agent, and p is the gas pressure.

At minimum pressures or pressure differences (the version used in this study), i.e., at $p \to 0$, expression (4) is simplified:

$$P = k_D D_D + D_C C'_C K. \quad (5)$$

The effective diffusion coefficient observed in the material, which is experimentally measured using the Daynes–Barrer equation, at $p \to 0$, is defined by the formula [33]

$$D = D_D(1 + C'_C K D_C/k_D D_D)/(1 + C'_C K/k_D). \quad (6)$$

The solubility coefficient of the gas observed at $p \to 0$ is as follows:

$$S = k_D + C'_C K. \quad (7)$$

In the case of IL-containing materials that presumably transfer CO_2 and C_2H_4 by the facilitated transport mechanism, it can be assumed that the mobility of these gases is much higher than that of the IL in the material and, therefore, can be described to a first approximation in terms of the mathematical model of facilitated transport for a fixed carrier in a polymer matrix (4).

Thus, determining the P and D values in one experiment at $p \to 0$, finding the gas solubility by the expression $S = P/D$, and using the data for the so-called noninteracting gases, i.e., for O_2, N_2, CH_4, C_2H_6, and C_3H_8, it is possible to determine coefficients a and b from the linear correlation relationship $\log S = a(\varepsilon/k) + b$ (Figs. 1b–3b) and then calculate the respective value of Henry constant k_D for presumably interacting gases CO_2 and C_2H_4. If this value is significantly lower than the experimentally determined S value, which means that the specific interaction takes place, then the $C'_C K$ value can be calculated using expression (7). Knowing the IL concentration in the material, it is possible to estimate the equilibrium constant of interaction between the gas and the carrier.

Nonspecific diffusion coefficient D_D for the gas in the material can also be estimated from the linear correlations of diffusion coefficient versus squared kinetic diameter of the gas $\log D$–d^2 known from the literature (Figs. 1a–3a) via determining the parameters of this correlation for noninteracting gases and calculating the D_D value. Next, effective diffusion coefficient D_C between the "active" carries can be estimated according to equation (6).

Table 4 lists the coefficients of the $\log D$–d^2 and $\log S$–ε/k linear dependences. These dependences hold true with high correlation coefficients, which can be used to calculate the respective data for nonspecific diffusion coefficient in the polymer matrix D_D and Henry sorption constant in the polymeric matrix k_D, while neglecting specific interactions.

Hence, the coefficients of these dependences can be used to calculate the respective data for nonspecific diffusion coefficient in the polymer matrix D_D and Henry sorption constant in the polymeric matrix k_D, while neglecting specific interactions between CO_2 and the IL; these data can be used to calculate the interaction efficiency between CO_2 and the IL ($C'_C K$) and effective diffusion coefficient D_C between the fixed

Table 4. Data on the $\log D–d^2$ and $\log S–\varepsilon/k$ correlations of the test membranes for noninteracting gases

Membrane	Relation	a	b	R^2
MF-4SC–H$^+$–IL	$\log D–d^2$	–0.275	3.69	0.99
	$\log S–\varepsilon/k$	0.005	–0.29	0.98
MF-4SC–Ag$^+$–IL	$\log D–d^2$	–0.335	4.72	0.99
	$\log S–\varepsilon/k$	0.006	–0.64	0.97
MF-4SC–Ag$^+$–IL–AgCl	$\log D–d^2$	–0.288	3.52	0.99
	$\log S–\varepsilon/k$	0.005	–0.31	0.98

Table 5. Parameters calculated in terms of the dual-mode sorption model

Membrane	Gas	$D_D \times 10^8$, cm^2/s	$D_C \times 10^8$, cm^2/s	$k_D \times 10^3$, cm^3(STP)/(cm^3 cmHg)	$C'_C K \times 10^3$, cm^3(STP)/(cm^3 cmHg)	C'_C (IL) cm^3(STP)/cm^3	K*
MF-4SC–H$^+$–IL	CO_2	15	11	5.4	22	0.18	120
	C_2H_4	3.5	0.5	6.2	44		240
MF-4SC–Ag$^+$–IL	CO_2	47	31	4	12	0.22	54
	C_2H_4	7.9	0.7	4.6	49		230
MF-4SC–Ag$^+$–IL–AgCl	CO_2	7.9	6	4.4	9.9	0.14	69

carriers. All data on the calculation by equations (6) and (7) are shown in Table 5.

Table 5 shows that nonspecific diffusion coefficient D_D and effective diffusion coefficient D_C between the active carriers for CO_2 in the studied membranes differ only slightly: D_C decreases with respect to D_D by a factor of 1.3–1.5. At the same time, the effective diffusion coefficients of nonspecific diffusion and facilitated transport for ethylene differ significantly: by 7 and 11 times in the case of the MF-4SC–H$^+$–IL and MF-4SC–Ag$^+$–IL membranes, respectively. Thus, the diffusion of ethylene in the material is substantially limited to the diffusion of the ethylene–carrier complex; it is this feature that contributes to the significant decrease in the experimentally determined diffusion coefficient (Figs. 1a, 2a). At the same time, the diffusion coefficients of ethylene calculated in terms of the dual-mode sorption model for the studied membranes are a few tens lower than the values determined in [19] for a wet Nafion-117 membrane saturated with silver ions: $D_D = 300$ and $D_C = 20 \times 10^{-8}$ cm^2/s, respectively. Apparently, an increase in the viscosity of the medium upon switching from water to the IL affects the substantial decrease in the mobility of the ethylene–carrier complex. However, according to theD_C and D_D values, the mobility of the CO_2–IL complex differs only slightly from the mobility of CO_2.

It is of interest that Henry sorption constants in the polymer matrix k_D are almost identical for CO_2 and C_2H_4 and vary in a range of 4×10^3 to 4.6×10^3 cm^3 (STP)/(cm^3 cmHg) for the silver-saturated membranes. For the MF-4SC–H$^+$–IL membrane, this value is 35% higher for both CO_2 and C_2H_4.

Calculation of interaction efficiency $C'_C K$ between the gas and the carrier also confirms the above conclusion that, in the IL-impregnated MF-4SC membranes, the complexation with the Ag$^+$ ion is not a determining factor in the transport of ethylene in the material because this parameter differs only slightly for the membranes in hydrogen and silver forms (Table 5). This finding confirms the previous observation (although for another IL) that facilitated transport phenomena and specific interactions can occur involving an olefin and an IL, i.e., in the absence of Ag$^+$ ions [12]. Moreover, the IL content in the MF-4SC–Ag$^+$–IL membrane (C'_C) is 20% higher than that in the MF-4SC–H$^+$–IL membrane (Table 5). Thus, to a first approximation, we can assume that the carrier concentration in the membrane material for interacting gases is associated with the IL concentration.

Assuming that the carrier concentration in the IL-containing material is close to the IL concentration in the material with an accuracy to a constant factor, we can estimate effective interaction constant K* between the IL and the interacting gases in the material, which can characterize the efficiency of application of the material for the separation of interacting gases from

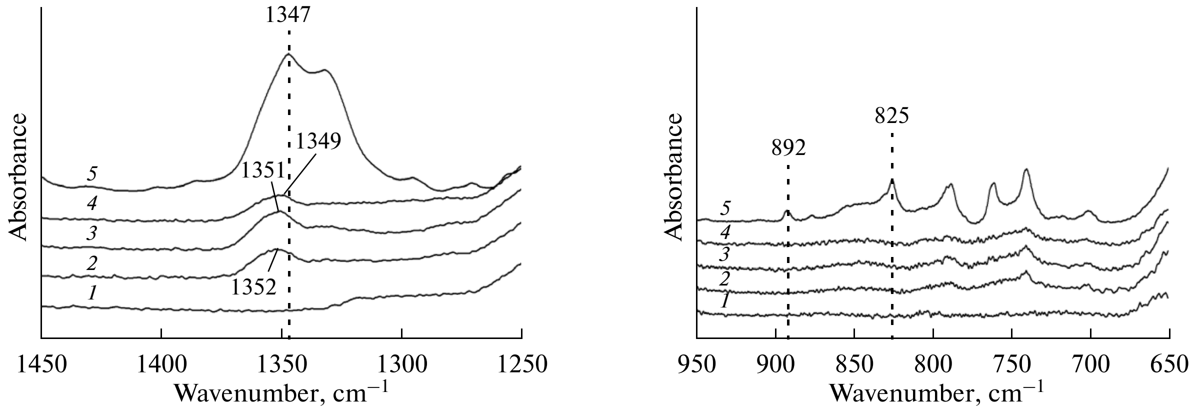


Fig. 4. ATR IR spectra of (*1*) MF-4SC, (*2*) MF-4SC–H$^+$–IL, (*3*) MF-4SC–Ag$^+$–IL, (*4*) MF-4SC–Ag$^+$–IL–AgCl, and (*5*) IL.

mixtures thereof. This estimate shows that the most effective material for the separation of CO_2 is the IL-impregnated MF-4SC–H$^+$ membrane. Against the background of a general increase in permeability, with respect to this parameter, the MF-4SC–Ag$^+$–IL membrane is more than 2 times less effective for the separation of CO_2 despite the higher IL content in the sample. This finding is consistent with the extreme dependences of the permeability and solubility of CO_2 on the IL concentration in the hybrid material sample in [34].

For ethylene, this parameter is also the highest for the MF-4SC–H$^+$ membrane. The AgCl nanoparticle-containing MF-4SC–Ag$^+$–IL–AgCl membrane is the least effective of the three studied membranes with respect to the separation of ethylene from hydrocarbon mixtures.

Comparison of the K^* value (Table 5) with the effective interaction constant of ethylene for a wet Nafion-117 membrane saturated with silver ions of 1.7 atm^{-1} from [19] with the data for the MF-4SC–H$^+$–IL and MF-4SC–Ag$^+$–IL membranes of 3.2 and 3.0 atm^{-1}, respectively, shows that the interaction of ethylene with the carrier in the case of our membranes is thermodynamically more advantageous than the interaction of ethylene with silver ions in the case of the wet Nafion-117 membrane. The significantly lower permeability coefficients of ethylene in our membranes are determined by the diffusion limitations of gas transport in the IL.

Thus, analysis of the gas transport data suggests that, in the IL-impregnated MF-4SC membranes, the IL, rather than the silver cation, acts as a carrier. To confirm this assumption, IR spectroscopic studies of the IL-impregnated membranes were conducted.

Figure 4 shows ATR IR spectra for the three test membranes, the pure IL, and the pure MF-4SC membrane without the ionic filler. In a region of 1350 cm^{-1}, the pure MF-4SC membrane does not have any absorption band, while the IL exhibits a characteristic absorption band for the cation. Different shifts of the absorption band are observed in the spectra of the IL-impregnated films. The smallest and largest shifts are detected in the MF-4SC–Ag$^+$–IL–AgCl and MF-4SC–H$^+$–IL films, respectively. In a region of 825 cm^{-1}, the IL exhibits an absorption band responsible for the out-of-plane bending vibrations of the CH bonds in the IL cation ring. In the spectra of all the IL-containing MF-4SC membranes, this absorption band disappears. It is obvious that, in the membranes, the IL interacts with the membrane material; the largest shifts are observed in the MF-4SC–H$^+$–IL membrane, which is the most efficient in the separation of both carbon dioxide and ethylene. In addition, the IL concentration in the sample of this membrane is less than that in the MF-4SC–Ag$^+$–IL membrane. Apparently, the interaction between the IL cation and the MF-4SC sulfocationite group contributes to the specific interactions of the gases with the membrane material.

However, the issue of the interaction between the IL cation and the double bond of ethylene remains open. To clarify the possibility of occurrence of this interaction, model studies of the interaction between the IL and liquid unsaturated hydrocarbon heptene-1 were conducted. The IR transmission spectra of the IL, heptene-1 (this olefin was selected as a model sample for the experiment), and a mixture thereof were recorded (Fig. 5).

Under the action of heptene-1, the spectrum of the mixture exhibits the broadening of the absorption bands of the IL in a region of 1350 cm^{-1} and a variation in the intensity ratio, which indicates a change in the electron distribution in the cyclic cation. This band is characteristic of the IL cation with respect to the region of skeletal vibrations in the imidazole ring. At the same time, a shift of the absorption band of heptene-1 in a region of 910 cm^{-1} can be observed; this absorption band is attributed to the out-of-plane deformation of the hydrogen atoms at the double bond in heptene-1.

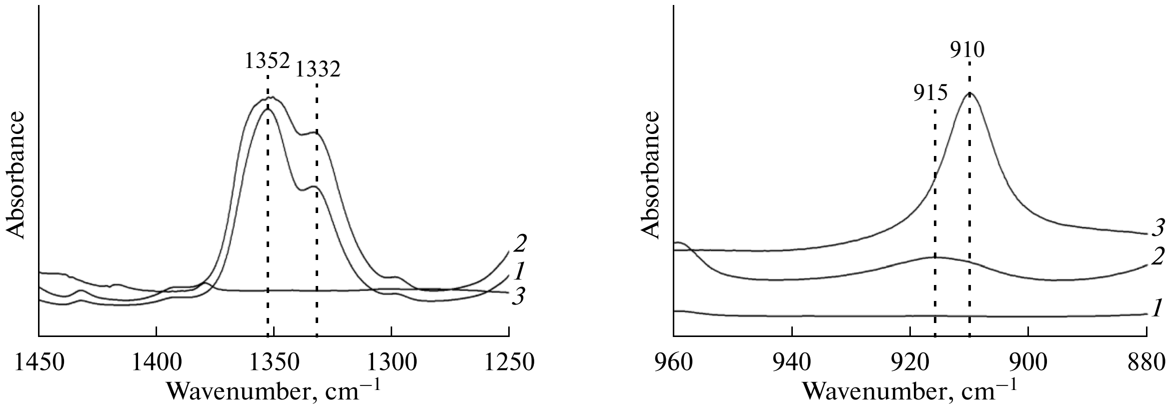


Fig. 5. IR transmission spectra of (*1*) the IL, (*2*) IL + heptene-1, and (*3*) heptene-1.

Thus, we can state that the IL cation reacts with ethylene and thus determines the selectivity of the MF-4SC membrane; apparently, it is an active carrier. Hence, it is appropriate to search for novel ILs for the impregnation ion exchange membranes to contribute to the separation of lower paraffin–ethylene mixtures.

CONCLUSIONS

(i) Based on analysis of the permeation characteristics of gases that do and do not interact with the membrane material, it has been shown that, in the IL-impregnated MF-4SC membranes in hydrogen and silver forms, the permeation of CO_2 and C_2H_4 occurs by the facilitated transport mechanism.

(ii) Nonspecific diffusion coefficient in the polymer matrix D_D and Henry sorption constant in the polymeric matrix k_D, while neglecting specific interactions of CO_2 and C_2H_4 with the membrane material, have been determined; effective interaction constant K^* of CO_2 and C_2H_4 with the membrane material and effective diffusion coefficient D_C of CO_2 and C_2H_4 by the facilitated transport mechanism have been estimated.

(iii) It has been shown that the most effective material for the separation of CO_2 and C_2H_4 is the IL-impregnated MF-4SC membrane in a hydrogen form.

(iv) It has been revealed that the main cause of the facilitated transport of ethylene in these membranes is the interaction between the double bond of ethylene and the IL cation.

ACKNOWLEDGMENTS

We thank Yu.V. Kostina for assistance in the measurements of IR spectra.

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Translated by M. Timoshinina