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Facilitated Transport of Ethylene in Poly (Amide 12-Block Tetramethylenoxide) Copolymer/AgBF₄ Membranes Containing Silver (I) and Copper (I) Ions as Carriers

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Abstract: Metal-incorporated poly(amide 12-block-tetramethylenoxide) (PA12-co-PTMO) copolymer was used for studying facilitated transport of olefines through new composite membranes. The metals incorporated were silver {Ag(I)} and copper {Cu(I)}. Tests were carried out at room temperature (25±2°C) to determine the selectivity and permeability of these membranes to ethylene and ethane gas. The membranes prepared by mixing in solution the copolymer with silver (AgBF₄) or copper (CuBF₄) salt show a ethylene/ethane selectivity much higher than that of pure PA12-co-PTMO. The membranes were also characterized by Fourier Transform Infra Red (FTIR) spectroscopy and Scanning Electron Microscopy (SEM) in order to understand the structural feature responsible for the observed behaviour. The IRFT spectrum indicate that Ag⁺ and Cu⁺ ions are developing interactions with the copolymer. The permeation results obtained with copper containing membranes show that CuBF₄ salt introduction in the copolymer tends to reduce ethane permeability. This phenomenon is explained by a diminution of the free volume caused by a decrease of the interchain distance due to the formation of metal ions-polymer matrix complexes. At the same time, for ethylene, the decrease in permeability observed at low salt content is recouped rapidly, when the salt content increases, by a dramatic increase of the permeability which attains 10 times that of the pure PA12-co-PTMO. This behaviour is attributed to the facilitated transport mechanism of the ethylene molecules able to develop specific interactions with the incorporated metal ions. It results from these two antagonistic phenomena a multiplication by 18 of the ethylene/ethane selectivity of the pure copolymer when the CuBF₄ content of the composite attains 60%.

Key words: Ethane-ethylene separation, silver salt membranes, cuprous salt membranes, PA12-co-PTMO copolymer membranes, PebaxTM, facilitated transport

INTRODUCTION

Olefin/paraffin separation represents a class of most important and also most costly processes in the petrochemical industry. Cryogenic distillation has been used for over 60 years for this separation (Keller *et al.*, 1992). It continues to be the most energy-intensive method because of the close relative volatilities of the compounds to separate (Humphrey *et al.*, 1991). The most important olefin/paraffin separations are for the binary mixtures of ethane/ethylene and propane/propylene. A number of alternatives have been investigated (Eldridge, 1993). The most promising is separation based on π -complexation. The metal-olefin bonding described by the Dewar-Chatt model is commonly known as π -bond complexation. The

Dewar-Chatt description, as applied to Cu(I)- or Ag(I)-ethylene complexes, is shown in Fig. 1. The complex is formed by double bonding of a Cu(I) or Ag(I) atom with the olefin (Quinn, 1971; Long, 1972; Herberhold, 1974; Bochmann, 1977; Yamamoto, 1986). Both the metal and alkene act as an electron donor and acceptor in the complexation interaction. A σ component of the bond results from overlap of the vacant outermost s atomic orbital of the metal with the full π (bonding) molecular orbital of the olefin. This new molecular orbital, formed by donation of electrons from olefin to metal, has electron density concentrated between the bond members. In Cu(I) and Ag(I) ions, the outermost s orbital is empty because the single electron present in the metal is lost upon ionization to a+1 valence. In nonionizing facilitators, the metal is often bound to an electronegative

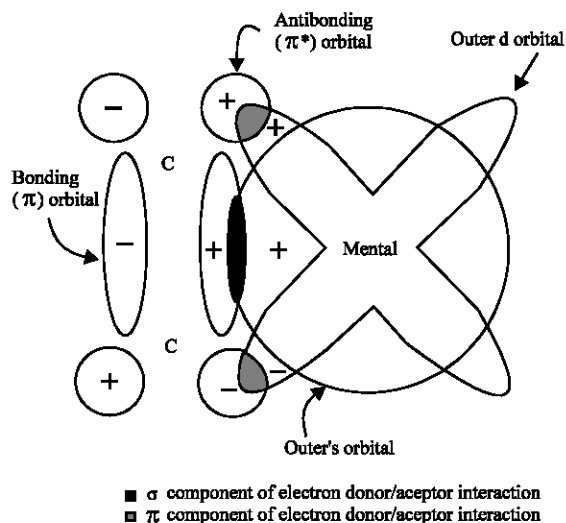


Fig. 1: Dewar-Chart model of π -bond complexation

atom (as oxygen atom in ether bond). These electronegative atoms withdraw electron density from the metal, resulting in a partial positive charge and a substantially vacant outermost s orbital. A π component of the metal-olefin bond is formed by backdonation of electrons from the full outer d atomic orbital of the metal to the vacant π^* (antibonding) molecular orbital of the olefin. This new molecular orbital has a nodal plane of electron density between the members of the bond.

The effects of metal ions and weight percentage of metal salts on the ethylene/ethane selectivity of PA12-co-PTMO based membrane were studied. The gas permeation properties and gas sorption properties of PA12-PTMO/AgBF₄ and PA12-PTMO/CuBF₄ membranes were compared.

MATERIALS AND METHODS

Chemicals: The PA12-PTMO granulates (Pebax™ 2533) were kindly provided by Arkema Corp. Its density as measured with a Micrometrics Accupyc 1330 instrument was 1.01 g cm⁻³ and its Shore D hardness was 25. This Pebax™ grade contains 25 wt. % of PA12 blocks and 75 wt. % of PTMO blocks. All other chemicals were purchased from Aldrich and used without further purification.

Ethylene and ethane N. 35 quality gases were purchased from Air liquide/Alphagaz Company.

Membranes: The membranes were prepared by dissolving first the copolymer in ethanol at 75°C to obtain a 9 wt. % solution. Then appropriate mass of AgBF₄ or CuBF₄ was dissolved in the Pebax™ solution and the obtained dopes

were cast onto a glass plate with a Gardner knife and the membranes were slowly dried in ambient air first, then under vacuum. The flat membrane samples were used shortly after their preparation, as the membrane darkens in long storage.

The resulting membranes contain 35% wt. of silver salt and 32, 43, 50, 57 and 60% wt. of copper salt in the polymer matrix. The thickness of the membranes obtained was about 100 μ m.

Gas permeation measurements: Ethane and ethylene permeation properties of films were determined using the time-lag permeation apparatus previously described (Joly *et al.*, 1999). Before measurement, the air present in the permeation cell was completely evacuated by applying a vacuum on both sides of the film for one night. Thus, the pressure in the permeation cell had a constant value $< 5 \times 10^{-3}$ mbar. Then the upstream side was exposed to the gas under test.

The upstream pressure applied to the samples $p_1 = 1$ bar was chosen in order to make measurements in a reasonable time allowing comparisons between the different films. The increase of pressure p_2 , in the calibrated downstream volume, was measured using a sensitive pressure gauge (0-10 mbar, Effa AW-10-T4) linked to a data acquisition system.

The permeability coefficient, P, was calculated using the variable pressure method (Glatz *et al.*, 1994) assuming $p_1 \gg p_2$:

$$P = J_{st} \cdot \frac{L}{p_1} \quad (1)$$

with J_{st} the steady-state gas flux obtained from the slope of the steady-state part of the curve p_2 versus time t :

$$J_{st} = \frac{dQ}{A \cdot dt} \quad (2)$$

where, dQ is the quantity of gas permeated at STP in a time interval dt in the steady state of gas flow, A is the effective film area for gas permeation.

The accuracy on p-values (cm³ (STP) cm⁻² sec⁻¹ cmHg⁻¹) is about 6%.

A time-lag diffusion coefficient, D , was calculated from the time-lag, t_L , given by the extrapolation of the steady-state asymptote to the time axis: $D = L^2/6t_L$. A solubility coefficient S , which links at equilibrium gas concentration in the material to its pressure, is given by the ratio $S = P/D$.

The ethylene/ethane permeation selectivity coefficient α was determined from $P_{C_2H_4}$ and $P_{C_2H_6}$, the

permeability coefficients of ethylene and ethane respectively: $\alpha_{C_2H_4}^{C_2H_6} = P_{C_2H_4} / P_{C_2H_6}$.

This coefficient can be expressed as the product of the diffusion selectivity coefficient by the solubility selectivity coefficient:

$$\alpha_{C_2H_4}^{C_2H_6} = \alpha D_{C_2H_4}^{C_2H_6} / \alpha S_{C_2H_4}^{C_2H_6} \quad (3)$$

with $\alpha D_{C_2H_4}^{C_2H_6} = D_{C_2H_4} / D_{C_2H_6}$ and $\alpha S_{C_2H_4}^{C_2H_6} = S_{C_2H_4} / S_{C_2H_6}$

IR spectrometry: FTIR spectra were recorded in Attenuated Total Reflectance mode on a Nicolet Avatar 360 instrument equipped with a germanium crystal. 64 scans were accumulated with a resolution of 4 cm⁻¹ for each spectrum and IR spectra present absorbance from 3800 to 900 cm⁻¹.

RESULTS AND DISCUSSION

From appearance point of view, PA12-co-PTMO membranes were colourless whereas the metal incorporated polymer membranes obtained were coloured, the colour differing for different metals and were also transparent. The colour indicates that the metals are certainly incorporated in the ionic form making charge transfer type complexes with the polymer structure. Scanning electron microscopy (SEM) was then performed to detect particles in the materials. The SEM micrographs show crystal-like particles (20 lm needles, Fig. 2).

Membrane structure IR characterization: FTIR spectra of pure PA12-co-PTMO and metal salt-PA12-co-PTMO composite membranes with low salt contents are shown in Fig. 3. It can be observed that all the metal-copolymer samples show only a slight change in the overall FTIR picture compared to the pure PA12-co-PTMO. This could be probably due to the large number of polymer repeat units which suppress the

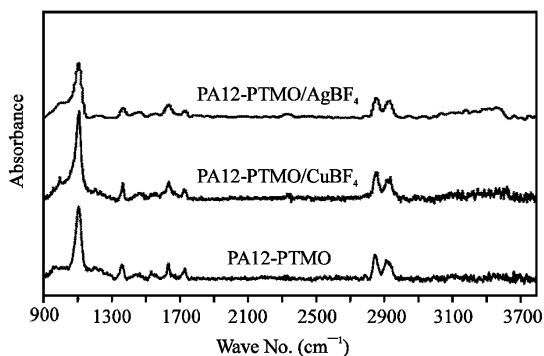


Fig. 2: SEM photograph of the Pebax films with 32 wt. % of CuBF₄

vibrational effects shown by the low concentration of the metal incorporated in the copolymer.

Permeability and selectivity of PA12-co-PTMO-Salt membranes: The permeation properties of ethylene/ethane gases in CuBF₄-PA12-co-PTMO complex membranes are shown in Table 1 as a function of the copper salt content (32, 43, 50, 57 and 60 wt. % salt in the polymer matrix).

Pure PA12-co-PTMO membrane exhibits a poor performance for ethylene/ethane separation; its ethylene/ethane selectivity is only 1.25. Composite membranes containing up to 32 wt. % CuBF₄ also has poor olefin/paraffin separation properties. However when the CuBF₄ concentration exceeds 43 wt. %, the complexation effect of the copper ions in the polymer membrane is clearly evident. The ethylene flux now increases dramatically with increasing copper salt concentration.

The ethylene permeability of membranes containing 60 wt. % copper salt are 18 times higher than those of pure PA12-co-PTMO membrane and 13 times higher than PA12-co-PTMO membranes containing 32 wt. % CuBF₄. These results give direct indications on the transport mechanism occurring in the PA12-co-PTMO based composite membranes under test. Based on the pure-gas

Table 1: Effect of CuBF₄ salt concentration on the permeation of pure ethylene and ethane in PA12-co-PTMO/ CuBF₄ composite membranes (p₁ = 1 Atm. and T = 25°C)

CuBF ₄ content	Permeability coefficient (Barrer)		Pure gas selectivity
Wt. %	C ₂ H ₄	C ₂ H ₆	$\alpha_{C_2H_4}^{C_2H_6}$
0	79	63	1.25
32	48	28	1.71
43	360	19	19.00
50	500	26	19.23
57	630	32	19.70
60	810	48	22.50

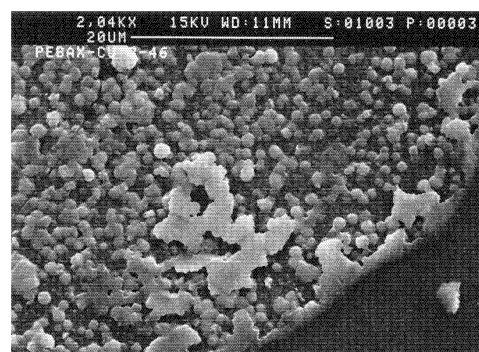


Fig. 3: FTIR spectra of PA12-co-PTMO (Pebax) membranes loaded with AgBF₄ and CuBF₄ at low salts contents

permeation properties, facilitated ethylene transport occurred only in membranes containing at least 50 wt. % dissolved CuBF₄. That suggests that the copper ions are not freely mobile in the polymer matrix and that therefore the facilitated transport in this kind of solid polymer electrolyte membrane is likely to occur by a hopping mechanism. In this hypothesis olefin molecules move from copper-ether site to site across the membrane, similar to that suggested for fixed-site carrier membrane (Cussler *et al.*, 1989; Noble, 1990). Based on this mechanism, the copper ions must be close enough to allow olefin molecules to diffuse from site to site. Accordingly, a threshold concentration of copper ions exists, below which no facilitation of olefin molecules occurs. This hypothesis is supported by our pure-gas permeation data in Table 1 which show that the ethylene fluxes increased dramatically for PA12-co-PTMO membranes containing more than 43 wt. % CuBF₄.

The composite membrane containing Ag⁺ ions shows a higher ethylene/ethane ideal selectivity than the membranes containing Cu⁺ ions (Hsiue and Yang, 1996). The ethylene/ethane selectivity is obviously enhanced by the incorporation of the metal ion, such as Ag⁺ and Cu⁺. Though the PA12-PTMO/AgBF₄ membranes were accompanied with a lower permeability coefficient. This is due to the fact that the high crystallinity of the PA12 matrix reduces the effective permeating area as well as the permeability of the film (Yang and Hsiue, 1991; Hsiue and Yang, 1993, 1994).

Effect of solubility and diffusivity: Membrane selectivity is related to the ideal separation factor which is partitioned between the preferential sorption, expressed by $S_{olefin}/S_{paraffin}$ and the ratio of diffusivities, $D_{olefin}/D_{paraffin}$. Therefore, the olefin/paraffin selectivity (α) can be analyzed by the former solubility selectivity (α_s) and latter diffusivity selectivity or mobility selectivity (α_D) as follows (Nakagawa, 1992):

$$\alpha = \frac{P_{olefin}}{P_{paraffin}} = \frac{D_{olefin}}{D_{paraffin}} \cdot \frac{S_{olefin}}{S_{paraffin}} = \alpha_D \cdot \alpha_S \quad (4)$$

The effects of S and D for various complex membranes and the corresponding non-Ag membranes are shown in Table 2. The gas diffusivity in complex membranes are decreased as compared with the non-Ag membranes. The α_s and α_D are increased as compared with the corresponding non-Ag membranes since membrane modification not only increases the affinity of olefin, but also increases the sieving effect. As compared with PA12-PTMO membrane, higher olefin/paraffin selectivity in PA12-PTMO/Ag⁺ membrane

Table 2: The solubility, diffusivity and their corresponding selectivity in complex membranes at 1 atm and 25°C

Sample	S (cm ³ /cm ³ cm Hg)		D (cm ² sec ⁻¹)		α_s	α_D	(Wt. %)
	S_{olefin}	S_{ethane}	D_{olefin}	D_{ethane}			
Pebax	3.8×10^{-4}	3.43×10^{-4}	2.35×10^{-7}	1.02×10^{-7}	1.10	2.19	-
Ag-Pebax	6.15×10^{-4}	2.48×10^{-4}	7.49×10^{-4}	1.02×10^{-7}	2.48	4.30	35
Cu-Pebax	5.54×10^{-4}	2.75×10^{-4}	4.40×10^{-7}	2.28×10^{-7}	2.02	1.93	35

Table 3: Gas permeability coefficients, ideal selectivities and % metal-content of ordinary and metal incorporated Pebax membranes

Polymer	Permeability coefficient		Ideal selectivity	Metal content (Wt. %)
	$P \times 10^5 \left(\frac{cc \cdot cm}{cm^2 \cdot s \cdot cm \cdot Hg} \right)$	P_{ethane}		
Pebax	14.9	6.7	2.2	-
Ag-Pebax	7.8	7.2	10.8	35
Cu-Pebax	23.4	7.6	3.1	32

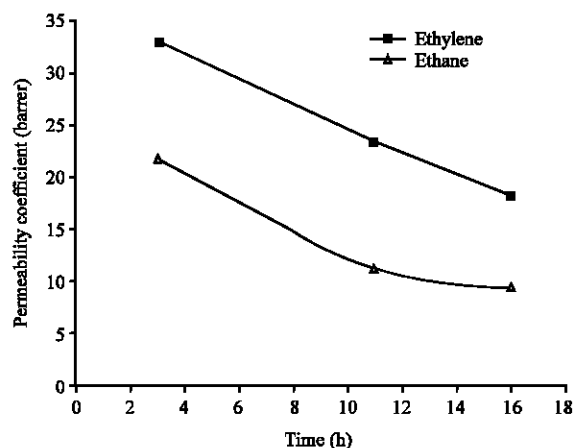


Fig. 4: Pure-gas permeation properties a PA12-co-PTMO (Pebax)/CuBF₄ composite membrane (60 wt. % CuBF₄) as a function of permeation time: ethylene and ethane permeability coefficient

is mainly due to the contribution of α_D that was caused by the molecular sieving effect.

Both the S and D values are important for olefin/paraffin transport through PA12-PTMO/AgBF₄ membrane since α_s and α_D are higher than those in PA12-PTMO/CuBF₄ membrane. The lower D in silver complex membrane as compared with copper complex membrane also indicates that the relative amounts of gas transport by diffusion in PA12-PTMO/AgBF₄ membrane are lesser than that in PA12-PTMO/CuBF₄ membrane. It means that the diffusivity determined PA12-PTMO membrane ($\alpha_D > \alpha_s$) can be altered to solubility determined PA12-PTMO/AgBF₄ membrane ($\alpha_s > \alpha_D$).

Gas permeability coefficients, ideal selectivities and % metal-content of ordinary and metal incorporated Pebax membranes are shown in Table 3.

Stability of pure-gas permeation properties: Mechanical and chemical instability are major concerns with conventional facilitated transport membranes. Therefore, the pure-gas permeation properties of a PA12-co-PTMO/60 wt. % CuBF_4 composite membrane were evaluated continuously for 16 h with ethylene and ethane gases at a feed pressure of 3 atm as a function of operating time. The results are shown in Fig. 4. Although the ethylene and ethane permeabilities decrease over time, the ethylene/ethane selectivity of near 2 is essentially constant over the permeation period.

During 16 h of continuous permeation, both ethylene and ethane permeabilities decreased to 50% of their original values. This loss may be a result of slow crystallization of the copper salt in the polymer electrolyte. In future work, we will investigate this hypothesis further using X-ray diffraction and FTIR.

CONCLUSION

The dense complex membranes of PA12-co-PTMO/ AgBF_4 and PA12-co-PTMO/ CuBF_4 with homogeneous Ag^+ and Cu^+ distribution were developed for olefin/paraffin separation. The two ions are coordinated onto the carbonyl of the PA12 and behave as fixed carriers for facilitating olefin transport.

The High-flux, solid polymer electrolyte composite membranes were prepared by coating a solution containing PA12-PTMO, silver and copper tetrafluoroborate onto a microporous poly(ether imide) support. Formation of a polyether/silver, copper salts complex resulted in the formation of a solid polymer electrolyte membrane. Permeation tests with pure gases showed a significant increase in ethylene and propylene permeance of PA12-PTMO- AgBF_4 membranes with a silver salt concentration of more than 43 wt. % over those of the pure PA12-PTMO membrane, confirming that olefin transport results from interaction of the olefin with metal ions. In addition, the high carrier concentration also hinders paraffin transport. An increase in metal salt concentration in the polymer matrix increases the olefin permeance and olefin/paraffin selectivity. A Pebax-based electrolyte membrane containing 60 wt. % CuBF_4 had a pure-gas ethylene permeance of about 810 barrer and an ethylene/ethane selectivity of 22.5.

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