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Gas separation investigations on polyaniline composite membranes

Summary — Composite homogeneous polyaniline (PANI)/(5%) polystyrene (PS) membranes cast from benzene solutions and composite laminar membranes were studied to determine the permeability coefficients of hydrogen, nitrogen and air, and hence to evaluate the selectivity coefficients in the O_2/N_2 and H_2/N_2 systems (Tables 1, 2). The thickness of PANI layer did not affect the permeability coefficients. With PS as carrier substrate, the resulting membranes could not be made less than 5 μm thick in active layer; they had permeation properties close to those of pure PANI membranes and were mechanically stable over a pressure range of 0.3—0.5 MPa; such membranes correspond to pure PANI membranes 25 μm thick; pure PANI membranes 5 μm thick were entirely unsuitable for permeation studies at the pressures applied. In the homogeneous membranes prepared by emulsion polymerization, PANI 40—65 μm/PS 35 μm, the permeability coefficients decreased as the PANI content was increased. The gas molecules permeated along pathways offering the least resistance to flow, *i.e.*, as in a composite with PANI content equal to zero; the permeation coefficients of such membranes are close to those of polystyrene membranes. Likewise permeability, the selectivity coefficients were only slightly affected by active layer thickness.

Key words: polyaniline-based composites, composite homogeneous polyaniline/polystyrene membranes, composite laminar membranes, permeability coefficients, separation of gases.

Polyaniline (PANI) is the most stable conducting polymer. It is highly resistant both to air and to high temperatures and can be cast in the form of films which are resistant to most organic and inorganic solvents [1, 2]. An important feature of this polymer is its ability to undergo a reversible and controllable reaction of protonation—deprotonation. The degree of protonation can be easily controlled by changing pH of the acid solution in which protonation is carried out. These advantages have recently focused attention on PANI as a potential membrane material. Gas separation on PANI membranes has been reported [3, 4]. Pure PANI membranes have shown a satisfactory selectivity and low permeability. Some data, scarce as yet, indicate that there exists a possibility of changing the selectivity coefficient by doping the conductive polymer [5].

In this study, possibilities of using composite membranes are explored, involving PANI as an active gas separating constituent and polystyrene as a carrier substrate, the latter enabling good mechanical properties of the membrane to be obtained at a reduced content of the active constituent. Two type of membranes were used in the study: composite homogeneous polyaniline/polystyrene (PANI/PS) membranes obtained by emulsion polymerization [6] and composite laminar membranes obtained by casting a polystyrene layer onto a previously prepared PANI membrane.

EXPERIMENTAL

Preparation of laminar membranes

PANI was obtained by oxidative polymerization in an acid solution. The reaction was conducted in aqueous 1 M sulfuric acid at temperatures of -5°C to -3°C [4]. An oxidizing agent, a 1.5 M solution of ammonium persulfate in 1 M sulfuric acid, was added dropwise into the reaction mixture. The resulting precipitate was washed with water until the pH was neutral and then deprotonated by keeping in 1 M ammonia for 20 hours. The resulting navy blue polymer was washed with water until the pH was neutral and dried at reduced pressure to constant weight (~50 hrs).

PANI membranes were prepared by casting from 1-methyl-2-pyrrolidinone (NMP) solutions. The PANI concentration enabling homogeneous membranes of uniform thickness to be prepared was determined to be 5 wt %. The solvent was evaporated in a dryer for 4—10 days at 70—90°C.

To prepare laminar membranes composed of PANI and PS, first PANI membranes of appropriate thickness were prepared and then coated with a 3 wt % polystyrene solution in benzene. Benzene was evaporated at ambient temperature. The resulting films were 40 to 65 μm thick with the polystyrene layer 35 μm thick in each case. The thickness of each membrane was measured by using a TGL-682 thickness gage at 30 randomly selected places. The membranes scattering in thickness less than 0.2% were taken for testing.

Preparation of homogeneous membranes

PANI/PS composites were obtained by emulsion polymerization of aniline. The aqueous solution of sodium salt of dodecylbenzenesulfonic acid and the solution of aniline and polystyrene in benzene were the continuous and the dispersed phases, respectively. Aniline was polymerized by adding the oxidizing agent, *viz.*, ammonium persulfate dissolved in 1 M hydrochloric acid, with vigorous stirring of the emulsion. Composites were precipitated from the mixture by adding methanol. The PANI content in the composites was determined by elemental analysis, based on the work of Ruckenstein *et al.* [6].

In the case of PANI/PS composites, membranes were obtained by casting benzene solutions and subsequently evaporating the solvent at ambient temperature. Optimum concentration of the composite solution was found to be 5% of PS. The resulting membranes were 30—40 μm thick.

Gas permeability tests

An APG-1 tester [7] was used to measure gas permeability of the membranes. The tester enables permeant flow rates to be measured by the volumetric method. The flow rate can be determined by connecting a gas-buret with the stub pipe outlet from the tester's permeation chamber.

Measurements were performed under the following conditions: pressure difference on the two sides of the membrane, Δp = 4 kG/cm^2 and Δp = 6 kG/cm^2; atmospheric pressure, p = 730—755 mmHg; ambient temperature, T = 19—24°C.

Permeability coefficients were determined for H_2, N_2, and O_2. The permeability coefficients were ratioed to obtain the ideal gas-transport selectivity coefficient, $\alpha_{g_1/g_2} = P_{g_1}/P_{g_2}$.

Indirect determination of the permeability coefficient

For safety reasons, the apparatus described cannot be used to measure the permeability of oxygen under elevated pressure. Therefore, it was decided to calculate the oxygen permeability by using the results for air.

RESULTS AND DISCUSSION

PANI exhibits an interesting gas-separating selectivity for oxygen and nitrogen and therefore efforts were made to use PANI composites to increase the permeability coefficient of the membranes, while keeping the gas-separating selectivity of the membrane unaffected. Polystyrene was a carrier substrate because of its satisfactory mechanical properties and because thin films could be cast from solutions prepared in common solvents. Again, the much higher permeability coefficients justifieds the assumption that gas separation would take place on the PANI layer. The use of polystyrene allowed membranes to be prepared having permeation properties similar to those made of PANI only, but with the active layer 5 μm thick, whereas the membranes made solely of PANI, still suitable for permeability determinations within the pressure range tested, were at least 25 μm thick.

Permeation properties of the membranes prepared were determined for selected gases, *viz.*, H_2, N_2, and air. These results allowed to determine the selectivity in the systems H_2/N_2 and O_2/N_2. Air permeability data were used in the calculations of the approximate values of the O_2 permeation coefficients.

It was assumed that (i) permeability coefficients of nitrogen and oxygen are identical both for pure gases and for mixtures (air), (ii) the compositions of the gas feeding the diffusion and the permeate chambers are identical.

These assumptions proved the more true, the higher was the pressure difference on the two sides of the membrane and the lower was the membrane selectivity.

By the equation:

$$J_{sN_2} = \frac{P_{N_2} \cdot \Delta p}{\delta} \tag{1}$$

where: J — *gas stream (cm^3/s)*, P — *permeability coefficient (barrer)*, δ — *effective membrane thickness (mm) and* Δp — *pressures on two sides of the membrane (mmHg)*,

and by the assumptions (2, 3):

$$J_{sp} = J_{N_2} + J_{O_2} \tag{2}$$

$$J_{sp} \equiv X_{N_2} P_{N_2} \left(\frac{\Delta p}{\delta}\right) + X_{O_2} P_{O_2} \left(\frac{\Delta p}{\delta}\right) \tag{3}$$

where: J_{sp} — *air stream under standard conditions and* X_{O_2}, X_{N_2} — *mole fractions of nitrogen and oxygen in air*, the following relationship is obtained:

$$P_{O_2} = \frac{J_{sp} - X_{N_2} \cdot P_{N_2}\left(\frac{\Delta p}{\delta}\right)}{X_{O_2}\left(\frac{\Delta p}{\delta}\right)} \tag{4}$$

The experimental permeability and selectivity coefficients are presented in relation to PANI (active constituent) content or to active layer thickness in the composite membranes and to PANI content in the homogeneous membranes. As the active layer thickness was decreased, the permeability coefficients of the gases slightly increased. In the composite laminar membranes the polystyrene carrier layer did not affect the permeability coefficients significantly. In the case of a membrane having a PANI layer practically as thick as the non-protonated PANI layer, the permeabilities were approximately identical (Table 1).

T a b l e 1. **Permeability and selectivity coefficients in relation to polyaniline layer thickness in composite membranes**

Polyaniline layer thickness µm	Permeability coefficient P, barrer*)			Selectivity coefficient, α	
	H_2	N_2	O_2	H_2/N_2	O_2/N_2
30	2.21	0.62	0.20	3.57	0.32
20	2.69	0.59	0.27	4.57	0.45
15	2.68	0.55	0.23	4.88	0.42
5	2.76	0.57	0.24	4.84	0.41
0	35.0	2.96	7.21	11.8	2.43
polyaniline only	2.12	0.66	0.30	3.23	0.45

*) 1 barrer = 10^{-10}cm^3(STP) · cm/(cm^2 · s · cmHg)

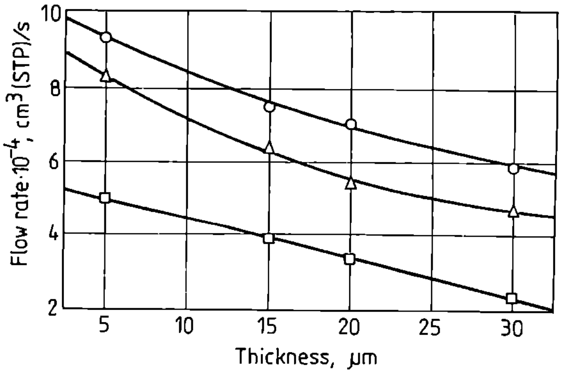

Fig. 1. Gas flow rate through the membrane vs. polyaniline layer thickness in composite membranes: □ air, △ nitrogen, ○ hydrogen

As the PANI layer is increased in thickness, the permeability is seen to increase but slightly. The selectivity coefficients in the O_2/N_2 and H_2/N_2 gas systems also rose but slightly. The lower layer thickness and consequently the higher gas flow rate through the membrane (Fig. 1) result in only slightly changed or even increased selectivity coefficients, which is an unquestionable advantage of these membrane. An additional advantage is the enhanced mechanical strength. The membrane having a 5 µm thick active layer was stable within a pressure range of 0.3 to 1.5 MPa, which corresponds to a 30 µm thick membrane made of PANI only; the PANI membranes 5 µm thick were unsuitable for tests whatsoever. The present method did not allow an active layer thinner than 5 µm to be obtained; it can be presumed that composite membranes may prove satisfactory in gas separation applications also with PANI layers less than 5 µm thick.

In the homogeneous composite membranes prepared by emulsion polymerization, any increase in PANI content in the composite led to a decrease in the permeability coefficients for the gases tested (Table 2). This result could be explained by the fact that the gas molecules permeate along the pathways offering the lowest resistance to flow, *i.e.*, such as when the PANI content in the composite is zero. As a result, the permeation coefficients for such composite membranes are proportional and similar to those of the polystyrene membranes. Similarly as for the permeabilities, an increase in the active layer thickness did not affect the selectivity coefficients significantly.

T a b l e 2. **Permeability and selectivity coefficients in relation to polyaniline (active constituent) content in homogeneous membranes**

Polyaniline content wt %	Permeability coefficient P, barrer*)			Selectivity coefficient, α	
	H_2	N_2	O_2	H_2/N_2	O_2/N_2
0	35.0	2.96	7.21	12.00	2.43
3	34.3	2.90	7.00	11.8	2.47
5	33.5	2.85	6.86	11.7	2.41
10	31.8	2.73	6.52	11.6	2.38
100	2.12	0.66	0.30	3.23	0.45

*) 1 barrer = 10^{-10}cm^3(STP) · cm/(cm^2 · s · cmHg)

CONCLUSIONS

Laminar membranes exhibit the permeation and mechanical strength properties within a wide range of pressures similar to those of PANI. Such membranes prepared with an active layer 5 µm thick can operate at 1.5 MPa of pressure difference. PANI membrane must be 30 µm thick to be of the same strength. In the membranes the active PANI layer is responsible for the permeability and selectivity coefficients of gas transport of the gases tested. A decrease in the active layer thickness in laminar membranes leads to a slight increase in the permeability coefficients as compared with the membrane made of PANI only, whereas in homogeneous membranes an increase in the PANI content in the composite leads to a decrease in the permeation coefficients of the gases tested. The explanation of the results obtained is that, in the homogeneous membranes, the gas molecules permeate along pathways offering the lowest resistance to flow, just as in the case of zero PANI percentage in a composite, so the permeation coefficients of such a type of membranes are proportional and similar to those of polystyrene membranes.

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Received 8 X 1999.

WYNALAZKI

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Sposób polimeryzacji akryloamidu w środowisku wodnym (Zgłoszenie nr 329 650, Politechnika Wrocławska)

Inicjowaną promieniowaniem polimeryzację prowadzi się w wodnym, zakwaszonym (pH = 1,2—4,0) roztworze akryloamidu o stężeniu 40—50% mas., w obecności cząstek ciała stałego o wymiarach 10—10^4 nm z odsłoniętymi powierzchniowymi grupami Si-OH i/lub Al-OH (wg Biul. Urz. Pat. 2000, nr 11, 36).

Sposób wytwarzania statystycznych kopolimerów glikolidu z laktydem i/lub z laktonami (Zgłoszenie nr 329 628, Centrum Chemii Polimerów PAN, Zabrze)

Sposób wytwarzania ww. bioresorbowalnych kopolimerów polega na prowadzeniu kopolimeryzacji z udziałem alkilów, alkiloalkoholanów lub acetyloacetonianów Li, Ca i Mg w środowisku rozpuszczalnika organicznego lub bez niego w zakresie temp. od -20°C do 250°C. Kopolimery te można wykorzystywać jako materiał do wyrobu biodegradowalnych implantów stosowanych w chirurgii i biodegradowalnych mikrosfer napełnianych lekiem, wprowadzanych bezpośrednio do organizmu. Kopolimery nie wymagają usuwania zawartego w nich metalu, ponieważ stosowane jako katalizatory ww. związki Li, Ca i Mg są małotoksyczne i dobrze tolerowane przez organizm człowieka (wg Biul. Urz. Pat. 2000, nr 11, 37).

Sposób wytwarzania żywic węglowodorowych (Zgłoszenie nr 329 829, Instytut Chemii Przemysłowej, Warszawa)

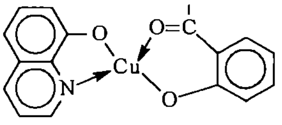
Sposób polega na wygrzewaniu frakcji węglowodorowej zawierającej dicyklopentadien, dimery izoprenu oraz *cis-* i *trans*-piperylenu jak również ich kodimery z cyklopentadienem w temp. 200—300°C w ciągu 0,5—12 h i na następnym destylacyjnym wyodrębnieniu żywicy (wg Biul. Urz. Pat. 2000, nr 12, 38).

Termoplastyczna kompozycja kauczukowa (Zgłoszenie nr 329 980, Zakłady Tworzyw Sztucznych Nitron SA, Krupski Młyn)

Na 100 cz. mas. blokowego kopolimeru styren/butadien/styren (SBS) i/lub terpolimeru styren/etylen/butylen/styren (SEBS) kompozycja zawiera (w cz. mas.) 5—70 polistyrenu, 5—70 oleju parafinowo-naftenowego, 0—50 syndiotaktycznego poli(1,2-butadienu), 0—5 modyfikatorów płynięcia, 0—2 środków przeciwstarzeniowych, 0—2 poroforów fizycznych, chemicznych lub ich mieszanin oraz, korzystnie, 5—60 kopolimeru etylen/okten, 5—45 homo- lub kopolimeru propylenu i 0,01—2 cz. mas. esencji zapachowych (wg Biul. Urz. Pat. 2000, nr 12, 39).

Termo- i światłostabilizowane poliamidowe tworzywa konstrukcyjne (Zgłoszenie nr 329 987, Zakłady Włókien Chemicznych Stilon SA, Gorzów Wlkp.)

Ww. tworzywa, uodpornione na działanie podwyższonej temperatury i światła, zawierają jako podstawowy polimer wielkocząsteczkowe poliamidy termoplastyczne (PA6 i/lub PA 66) i/lub kopolimery, komodyfikatory oraz stabilizator, którego substancję czynną stanowi sól kompleksowa 8-hydroksychinolinianu miedziowego z kwasem salicylowym o wzorze (I) oraz, korzystnie, chlorek magnezowo-potasowy. Zawartość tego stabilizatora wynosi od 1:15 do 1:30 cz. mas. w stosunku do polimeru podstawowego i komodyfikatorów (wg Biul. Urz. Pat. 2000, nr 12, 39).



(I)

J. F.