Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Effect of Feed Composition on the Performance of Polymer-Zeolite Mixed Matrix Gas Separation Membranes

Turgut Battal[a]; Nurcan Baç[a]; Levent Yilmaz[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, MIDDLE EAST TECHNICAL UNIVERSITY, ANKARA, TURKEY

To cite this Article Battal, Turgut , Baç, Nurcan and Yilmaz, Levent(1995) 'Effect of Feed Composition on the Performance of Polymer-Zeolite Mixed Matrix Gas Separation Membranes', Separation Science and Technology, 30: 11, 2365 — 2384
To link to this Article: DOI: 10.1080/01496399508013117
URL: http://dx.doi.org/10.1080/01496399508013117

SEPARATION SCIENCE AND TECHNOLOGY, **30**(11), pp. 2365–2384, 1995

Effect of Feed Composition on the Performance of Polymer–Zeolite Mixed Matrix Gas Separation Membranes

TURGUT BATTAL, NURCAN BAÇ, and LEVENT YILMAZ*
DEPARTMENT OF CHEMICAL ENGINEERING
MIDDLE EAST TECHNICAL UNIVERSITY
06531 ANKARA, TURKEY

ABSTRACT

An emerging membrane morphology with future potential is mixed matrix membranes composed of two interpenetrating matrices of different materials. In this study, mixed matrix membranes of an amorphous glassy polymer (polyethersulfone) and hydrophilic zeolite (4A) were prepared. An elaborate membrane preparation technique that enables incorporation of high zeolite loading into the membrane was developed. Performance of membranes was tested by using a laboratory-scale gas separation apparatus. The permeation rates of N_2, CH_4, Ar, O_2, CO_2, and H_2 were evaluated through a dense homogeneous PES membrane and a PES-4A mixed matrix membrane. For the mixed matrix membrane, gas permeabilities were either not changed or significantly improved. The ideal separation factors of economically important gas pairs were substantially increased due to the faster permeation of H_2 and CO_2 through the mixed matrix membrane. In order to understand their interaction with each other and with membrane matrices, permeabilities and selectivities of CO_2/CH_4, CO_2/Ar, and H_2/CH_4 binaries as a function of gas composition were measured through a dense homogeneous PES membrane and a PES-4A mixed matrix membrane. Observed selectivity independence with respect to gas composition for a dense homogeneous PES membrane indicates that ternary interactions and factors like plasticization and gas fugacity do not affect the gas permeation mechanism appreciably for this type of membrane. However, selectivities demonstrated a strong concentration dependency through a PES-4A mixed matrix membrane. For CO_2/CH_4 and CO_2/Ar systems, when the CO_2 concentration in the feed increased, selectivity decreased linearly. In the case of H_2/CH_4 binaries, unlike the cases with CO_2 binaries, a higher H_2

---

* To whom correspondence should be addressed.

concentration in the feed caused higher selectivity values. The trend was also linear with H_2 concentration in the feed. This indicates that, for mixed matrix membranes, the existence of a third component causes the gas molecules to interact with the heterogeneous membrane matrix, affecting selectivities. Selectivity dependency indicates the importance of gas–membrane matrix and gas–gas–membrane matrix interactions.

Key Words. Gas separations; Mixed matrix membrane; Polyethersulfone membrane; Zeolite; Membrane morphology

INTRODUCTION

Membrane gas separation has become quite attractive for the purification of gases based on selective permeation through asymmetric, composite, or mixed matrix membranes (1–11). Although the concept of separating gases with polymeric membranes was developed a long time ago, the widespread use of gas separation membranes has occurred only within the past 10 to 15 years. The primary reason for this was that the early membranes were insufficiently permselective and exhibited insufficient fluxes so that the cost of membrane processes never successfully competed with the cost of conventional processes such as cryogenics, scrubbing, absorption, and adsorption. However, modifications in the physical and chemical structures of membranes have enhanced separation characteristics. Recently, interest has focused on novel polymer–zeolite mixed matrix membranes composed of two interpenetrating matrices of different materials because the interaction of materials in the membrane matrix and the shape and size selective properties of zeolites may enhance membrane performances (1–11).

Tsujita (1) investigated the effects of additives on polymeric membranes. His conclusion was that the polymer–filler system often raises its glass transition temperatures, indicative of restricted segmental motion of the polymer itself because of strong polymer–filler interaction. Therefore, the permeability and diffusivity coefficients decrease with filler content. In the case of weak polymer–filler interaction the filler may form a void in the interface between the polymer and filler. Then the permeability coefficient increases considerably, indicating hydrodynamic permeation through the void or pore in the membrane matrix. These findings point to the need for the investigation of different polymer–filler combinations in order to create membranes with widely differing permeabilities and selectivities.

Hennepe et al. (2) reported improved permselectivities for the separation of various alcohols from water by way of pervaporation using silicone rubber membranes filled with a hydrophobic zeolite, namely silicalite.

Gürkan and coworkers (3) focused on the separation of O_2/N_2 and H_2/N_2 gas pairs using a zeolite 13X-filled polysulfone membrane made by extrusion. They reported a substantial increase in the selectivities of the H_2/N_2 gas pair over the pure polysulfone membranes.

Okumuş and coworkers (4, 5) studied the separation of water–alcohol mixtures by pervaporation using a mixed-matrix membrane composed of cellulose acetate and either zeolite 13X or 3A. Their results showed that the addition of zeolites to the matrix improved the fluxes substantially, with some loss in selectivities. Electron micrographs reported in this study showed that introduction of zeolites created a complex morphology in which zeolites placed themselves in tiny cavities through the partial incompatibility of zeolite and polymer.

Jia et al. (6) studied the permeation of N_2, O_2, CO_2, and nC_4 by using a membrane composed of polydimethylsiloxane (PDMS), a rubbery polymer, and silicalite-1, a hydrophobic zeolite. In this study, a couple of very high zeolite loadings were investigated. They concluded that silicalite plays the role of a molecular sieve in the membrane by facilitating the permeation of smaller molecules but hindering the permeation of larger ones.

The effect of the introduction of specific adsorbents on the gas separation of polymeric membranes was studied by Duval and coworkers (7). For this purpose, both carbon molecular sieves and zeolites were considered. The results showed that zeolites such as silicalite-1, 13X, and KY improve the separation properties of poorly selective rubbery polymers for a mixture of CO_2/CH_4 to some extent, but zeolite 5A leads to a decrease in permeability with unchanged selectivity. Also they observed that active carbon fillers are not effective as mixed matrix membrane materials.

Goldman and coworkers (8) prepared an effective novel membrane for pervaporation by combining zeolite NaA and PVC modified by 2-(2 butoxyethoxy) ethyl thiolate. They modified the polymer by grafting it with suitable hydrophilic side chains and added zeolites to the polymers in different weight percentages (0 to 70 wt%). According to this study, when the amount of zeolite was below a certain limit, then the membrane behaves as a pure modified PVC membrane. When the amount of zeolite filler exceeded a certain critical point, the rate-determining step in the overall transport was passage through the zeolite/modified PVC interface.

In our previous studies (9–11) we focused on the effect of type of zeolites and their amounts introduced into a glassy polymer (PES), and the effect of membrane preparation procedure on the transport properties of membranes. Permeability measurements of single gases (N_2, O_2, Ar, CO_2, and H_2) were carried out with a variety of membranes prepared at different zeolite loadings. It was concluded that the type of membrane preparation procedure and the type of zeolite strongly affect the transport properties of membranes. Significant changes in the membrane morphologies of PES-13X and PES-4A matrices were observed, implying the importance of zeolite type. SEM studies showed that the addition of zeolite particles induced a microporous cavity and channeling system, demonstrating polymer–zeolite interactions and partial incompatibility. The permeabilities of all the gases studied showed a slight minimum, then an increase with increasing zeolite loading. For both zeolites 13X and 4A, the permeabilities and ideal separation factors were enhanced at high zeolite loadings for certain commercially important gas pairs due to faster permeation of H_2 and CO_2 through the membrane matrix. It was concluded that the increasing selectivities with increasing filler content could not be solely due to a molecular sieving mechanism. Shape selective properties of zeolites, the polarities of gases, and the microstructures of membranes might play roles in increasing permselectivities.

Studies investigating the dependence of permeabilities and selectivities on such operating conditions as temperature, pressure, and feed composition are limited in the literature (12). The effect of feed composition on the separation performance of homogeneous and mixed matrix membranes has not been substantially studied, even though interactions between components in the feed stream and the membrane can substantially alter membrane performance. However, the concentration-dependent transport of gases and vapors in glassy polymers has been described (13), and it was reported that the separation of a multicomponent mixture depends on the composition of the mixture, even under the condition that the dissolved penetrants do not interact with each other, and that maximum separation can be achieved by adjusting the total pressure.

The dependence of permeabilities and selectivities on the temperature, pressure, and feed composition was reported when an asymmetric membrane was employed [14–17]. This behavior suggests that if constant values of the permeabilities are assumed in the design calculations, a serious error may occur, resulting in either under- or overdesign of the separation system.

Donohue et al. (14, 15) used an asymmetric cellulose acetate membrane and observed that the separation factors were functions of the feed composition and operating pressure. An increase in pressure resulted in a lower separation factor for the same feed composition whereas separation factors obtained from pure gas permeability data increased with operating pressure. Higher concentration of CO_2 in the feed gave a lower separation factor for the same pressure. They developed mathematical models based on solution–diffusion theories to explain this behavior. Their models take into account membrane plasticization through an exponential dependence of diffusivities on penetrant gas concentrations.

Minhas et al. (16) studied asymmetric cellulose acetate membranes for the separation of CO_2/CH_4 gas mixtures and concluded that the permeation rate increases with an increase of CO_2 concentration in the feed. In general, variation of the separation factor was found to be negligible, which contradicts their previously mentioned findings (14, 15), although they used similar types of membranes. This demonstrates the importance of the membrane preparation procedure and the resulting morphology.

Li et al. (17) studied the variation in the permeabilities of CO_2 and N_2 with the pressure and the feed composition through cellulose acetate membranes. They found that in the case of pure CO_2, an increase in the feed pressure results in a similar increase in the permeability. However, the permeability of pure component N_2 remains unchanged with increasing feed pressures. At the same time, the presence of CO_2 in the feed stream actually results in an increase in N_2 permeability by a factor of nearly 3 at a pressure ratio of 23 and with a feed composition of 50% CO_2.

Koros et al. (18) studied the performance of mixtures such as CO_2/CH_4 which interact relatively strongly with membrane materials compared with O_2/N_2 which interacts weakly. They concluded that the results obtained by using mixtures are different from the permeability and selectivity results obtained by single gas measurements. Gas-phase fugacity effects in the mixed gas were used in order to explain the differences between pure and mixed gas results. In the absence of actual mobility and solubility data for mixtures, they concluded that the behavior of mixed feeds compared to the ratios of pure gas permeabilities must be somewhat tentative.

Mixed gas separation properties of phosphazene-based polymers were reported by Peterson et al. (19, 20). The mixed gas transport behavior of the polyphosphazene was examined at several temperatures, and they found that permeabilities and selectivities generally increase with increasing temperature. They concluded that the transport of these gases is a sorption-controlled process since these gases significantly deviated from the diffusion-controlled permeability size correlation.

Using gas sorption and transport data in polyethersulfone, accompanied by bulk physical and mechanical properties of the polymer in the presence and absence of penetrant, plastization of the polymer matrix was examined by Sanders (12). According to Sanders, sorption kinetics, T_g depression measurements, and mechanical properties of the CO_2/polyethersulfone system indicate the polymer is highly plasticized. Although the polymer is plasticized, the permeability of PES to CO_2 at 25°C decreases by 54% as feed pressure is increased from 0 to 27 atm CO_2. He concluded that plasticization of the polymer matrix alone is not a sufficient condition for the permeability to increase with feed pressure. The presence of large side groups on the polymer backbone is also required.

Membrane literature does not include many studies about the effect of feed composition on the separation performance of homogeneous and mixed matrix membranes. In particular, zeolite-filled mixed matrix membranes which show future potential for commercial applications have to be examined. Therefore, in order to verify performance improvements of zeolite-filled mixed matrix membranes, this study enlarges the limited variable operating parameter studies and observes the selectivity and permeability dependences on gas compositions in binary mixtures.

EXPERIMENTAL

Materials

The polymeric material used was commercial polyethersulfone (PES) which were kindly supplied by BASF (BASF-E2010). The solvent used was dimethylformamide (DMF) which was purchased from Merck. Zeolite 4A was used as the adsorptive filler, and it was supplied by Alfa Products. Since the zeolites used were highly hydrophilic, they were dried at 400°C for 4 hours before each membrane preparation. PES was also dried at 60°C for 12 hours before each casting.

Membrane Preparation Procedure

Dense homogeneous membranes of an amorphous glassy polymer (polyethersulfone, 70% wet basis) and mixed matrix membranes of polyethersulfone and hydrophilic zeolite 4A (42% dry basis) were prepared.

During this study, an elaborate membrane preparation technique that enables incorporation of high zeolite loading into the membrane was developed (Fig. 1). The membranes were prepared by dissolving PES and zeolite 4A in DMF at the desired percentages and thoroughly mixing them until a homogeneous paste formed. The paste was then automatically cast on a glass plate as a 300-μm thick film. The cast film was allowed to dry at partial vacuum ($P = 0.2$ atm) with nitrogen circulation at 60°C for 8 hours. Quenching by water (only in the case of homogeneous membranes) was followed by annealing at 80°C for 24 hours at atmospheric pressure. The final thickness of dry membranes was in the 40 to 50 μm range.

Differential scanning calorimetry (DSC) was used to detect the glass transition temperatures of membranes and polymers. A Thermal Analyst 2000, DSC 910S type thermal analyzer was used. The DSC cell was heated at a rate of 10°C/min under N_2 circulation.

Gas Separation Measurements

The apparatus used in the determination of permeability coefficients of single and binary gases has been designated as ASTM D1435-82 (Fig.

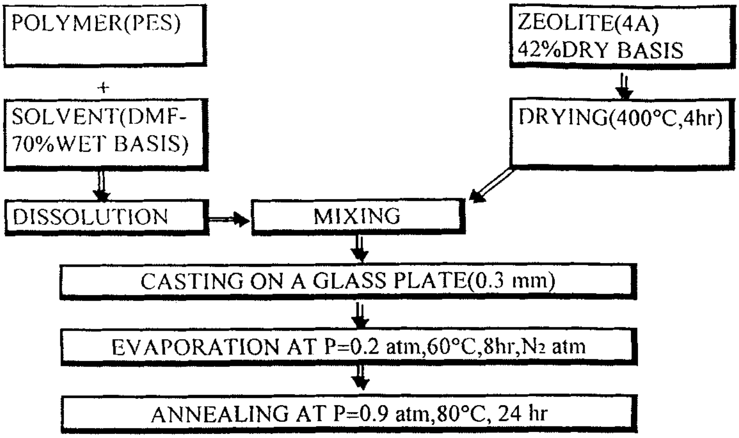

FIG. 1 Membrane preparation procedure.

2). Measurements are done using a constant volume, variable pressure technique in a permeation cell. The penetrant gas taken from the gas cylinder is allowed into the gas chamber and sustained at 100 psig while the low pressure side is at atmospheric pressure. In the case of a binary system, the gas mixtures are prepared in the gas chamber by using the

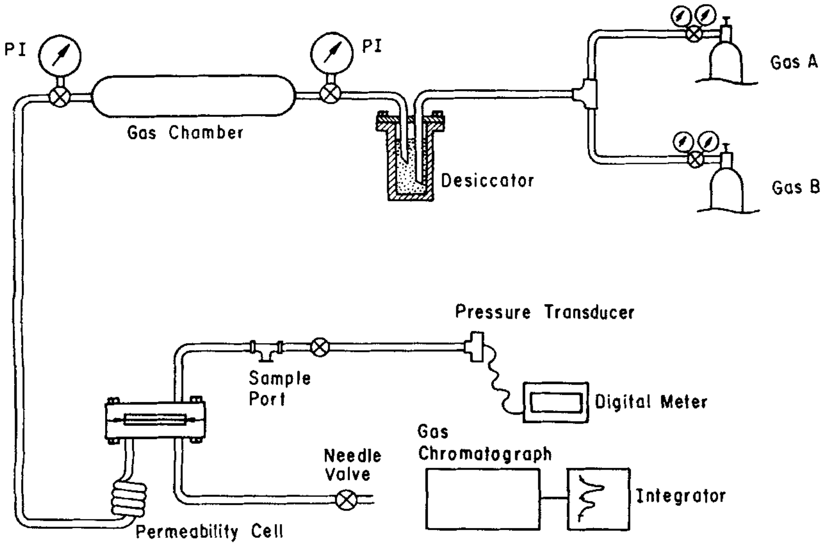

FIG. 2 Experimental set-up.

pressure gauge at the inlet. The permeation rates of N_2, CH_4, Ar, O_2, CO_2, and H_2 and of CO_2/CH_4, CO_2/Ar, and H_2/CH_4 binaries are evaluated by measuring the rate of increase of pressure in the permeate side by using a pressure transducer (Data Instruments, Model SA). Purge lines are used to take samples with a gas-tight syringe. Then the binary gas samples are analyzed with a HP chromatograph using a TCD detector. Prior to binary gas mixture experiments, feed gases were injected and analyzed at least three times in the gas chromatograph. When a run was completed, the feed and permeate sides were analyzed the same way. During these measurements it was observed that the feed side gas compositions remained constant throughout the run. After the permeation of any gas or gas mixture through a membrane, the membrane should be degasified prior to the next experiment in order to return the membrane material to its virgin state.

Permeabilities of gas(es) were evaluated using Eq. (1), which is a combination of Fick's and Henry's law. The mean permeability coefficient of any component can be expressed as

$$P = J\delta/(P_h/P_l) \tag{1}$$

where δ is the membrane thickness and P_h and P_l are the pressures of the high and low pressure sides, respectively.

The ideal separation factor α_{ij} is determined by dividing by the individual permeation rates of single gases, expressed as

$$\alpha_{ij} = P_i/P_j \tag{2}$$

For a binary system, the selectivity is defined (21) in terms of the downstream and upstream mole fractions of Components i and j:

$$\alpha_{ij} = ((x_i/x_j)_{\mathrm{permeate}}/(x_i/x_j)_{\mathrm{feed}})(\Delta P_j/P_{j2})/(\Delta P_i/P_{i2}) \tag{3}$$

where ΔP_i and ΔP_j are the partial pressure differences taken as arithmetic averages across the membrane for Components i and j, respectively. P_{i2} and P_{j2} are the partial pressures of the components at the high pressure side. The pressure control factor in the right-hand side of the equation compensates for nonzero downstream pressures in the calculation of intrinsic (material) selectivity.

RESULTS AND DISCUSSION

Material Characterization

A polymer–filler system often has an elevated glass transition temperature (T_g), indicative of the restricted segmental motion of the polymer itself because of strong polymer–filler interaction. In the case of weak polymer–filler interaction, the filler may form a void in the interface between the polymer and the filler (1). In this case, the glass transition temperature should not be affected. Therefore, polymeric materials and cast membranes were analyzed thermally to observe the type of polymer–zeolite interaction in the membrane matrix.

The results of DSC measurements show that the PES polymer and PES-4A mixed matrix membrane have almost the same glass transition temperatures (222 and 221°C, respectively). This indicates that the zeolite-filled membrane has a weak polymer–zeolite interaction, verifying the partial incompatibility.

Single Gas Permeabilities

The permeabilities of single gases through homogeneous dense PES and PES-4A mixed matrix membranes and the ideal separation factors calculated from individual gas permeabilities are given in Figs. 3 and 4, respectively.

From Fig. 3 it can be observed that for this zeolite loading, gas permeabilities are either not changed or for most cases significantly improved.

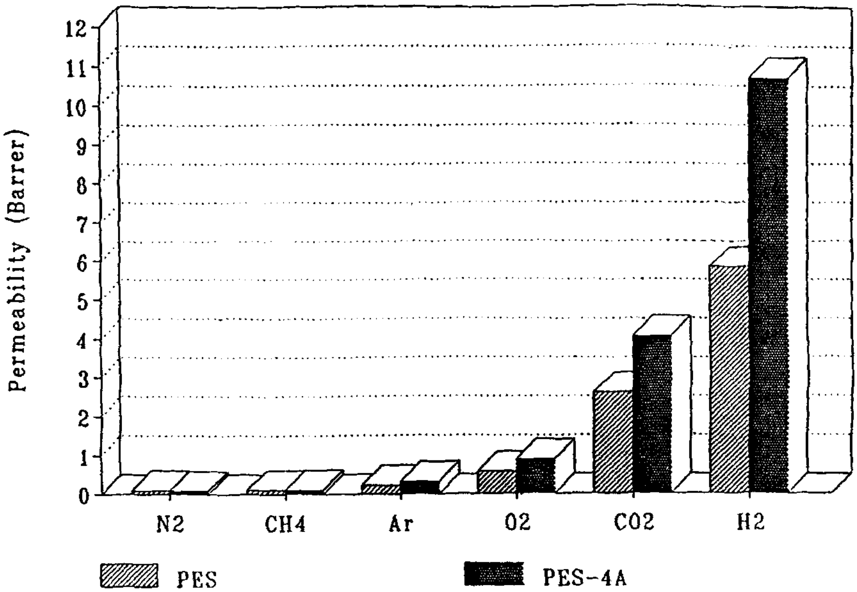

FIG. 3 Permeabilities of single gases.

As mentioned in the literature survey, this result is expected and is in line with our previous studies (9–11).

Figure 4 indicates that the PES-4A mixed matrix membrane possesses better separation characteristics than zeolite-free membranes. The selectivities of economically important gas pairs are substantially increased due to faster permeation of H_2 and CO_2 through the membrane matrix. Increases in both permeabilities and selectivities indicate the possible potential of PES-4A mixed matrix membranes for commercial applications.

The increase of separation factors is not explained only by using the molecular sieving effect of zeolites since all gas molecules are able to pass through the windows of zeolite 4A (22). On the other hand, the shape selective properties of zeolites and the microstructure of membranes may play a role when there is a homogeneous distribution in the matrix (11). Substantial increases of H_2 and CO_2 permeabilities due to zeolite loading may be attributed to polarity and the adsorption properties of gases (for CO_2) within the membrane matrix in addition to diffusional aspects, which imply faster permeation of smaller molecules (for H_2) (10, 11).

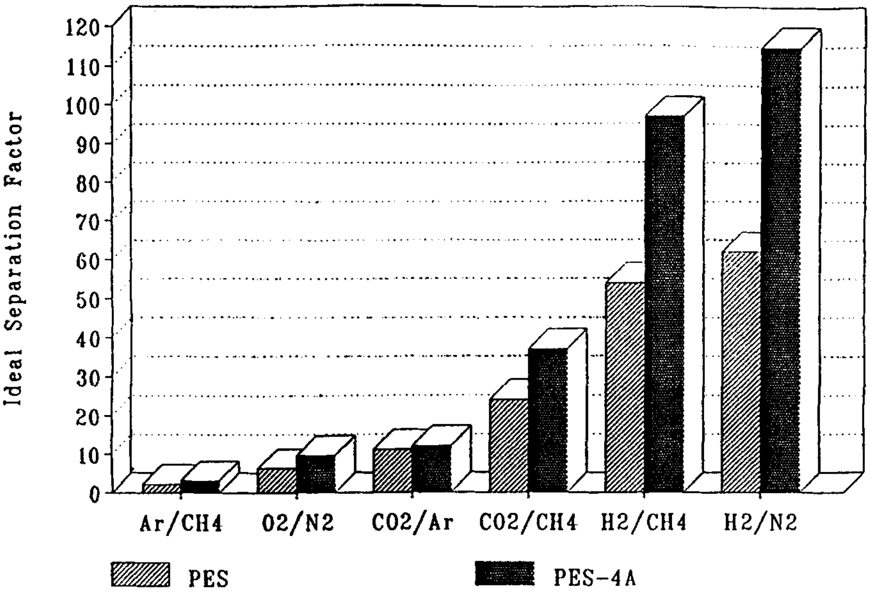

FIG. 4 Ideal separation factors for some gas pairs.

Binary Gas Studies

It was observed that the duration of the degasification step by applying vacuum to return the membrane material to its virgin state was important, especially for mixed matrix membranes. As indicated by the exemplary case given in Table 1, long periods of vacuum should be applied to obtain steady-state selectivities. For dense homogeneous membranes, a much shorter degasification period (less than 1 hour) was sufficient. The complicated micromorphology of mixed matrix membranes could be the reason for this observation.

Binary Gas Studies through Dense Homogeneous PES Membrane

Most studies about the separation performance of homogeneous membranes were restricted to single gas measurements. Ideal separation factors were reported as selectivities, implicitly assuming that the composition variation of binary gas mixtures will not affect the separation performance of homogeneous polymeric membranes. In our study, this presumption was explicitly investigated.

In order to observe the effect of feed composition on dense homogeneous PES membrane performance, CO_2/CH_4, CO_2/Ar, and H_2/CH_4 binaries were used as gas systems (Tables 2–4, Figs. 5–7). A composition range as wide as possible was employed for all gas pairs.

Tables 2–4 show that, as expected, when the composition of gases with higher single gas permeabilities (CO_2, H_2) increases, so does the permeability of the mixture. Meanwhile, the measured selectivities stay constant (Figs. 5–7) around the ideal separation factor value. In the literature (14, 15, 17, 18), the composition dependency of selectivities for gas separation membranes was explained based on chemical interactions (either in the membrane phase based on plasticization, or in the upstream gas phase based on nonlinear fugacities). In this study it was observed that for dense homogeneous PES membranes, selectivity does not depend on composition. Thus, ternary interactions and factors like plasticization of the membrane polymer, interaction with CO_2, and the composition dependency of

TABLE 1

Degasification Results (Membrane: PES-4A. Feed: 50% H_2–50% CH_4)

Time in vacuum (hours)	1	3	5	12
Measured selectivities	54	65	78	78

TABLE 2
Permeability[a] and Selectivity of CO_2–CH_4 (through PES[b])

	Percent CO_2 in feed								
	0	6.7	24.0	27.4	51.5	52.0	72.5	73.5	100
Permeability	0.109	0.10	0.34	0.36	0.54	0.65	0.90	1.10	2.61
Selectivity	—	24.0	23.0	24.0	25.0	24.0	25.0	24.0	—

[a] In barrer (10^{-10} $cm^3STP \cdot cm/cm^2 \cdot cmHg \cdot s$).
[b] Dense homogeneous polyethersulfone membrane.

TABLE 3
Permeability[a] and Selectivity of CO_2–Ar (through PES[b])

	Percent CO_2 in feed									
	0	20.5	21.5	43.8	43.9	60.9	63.6	76.9	81.7	100
Permeability	0.234	0.49	0.47	0.90	0.86	1.20	1.20	2.00	2.00	2.61
Selectivity	—	10.7	10.4	10.8	10.4	10.3	10.9	9.8	10.6	—

[a] In barrer (10^{-10} $cm^3STP \cdot cm/cm^2 \cdot cmHg \cdot s$).
[b] Dense homogeneous polyethersulfone membrane.

TABLE 4
Permeability[a] and Selectivity of H_2–CH_4 (through PES[b])

	Percent H_2 in feed							
	0	10.1	10.1	27.6	30.6	49.3	55.9	100
Permeability	0.109	0.22	0.19	0.78	0.71	2.06	2.17	5.85
Selectivity	—	52.0	51.0	52.0	51.0	52.0	53.0	—

[a] In barrer (10^{-10} $cm^3STP \cdot cm/cm^2 \cdot cmHg \cdot s$).
[b] Dense homogeneous polyethersulfone membrane.

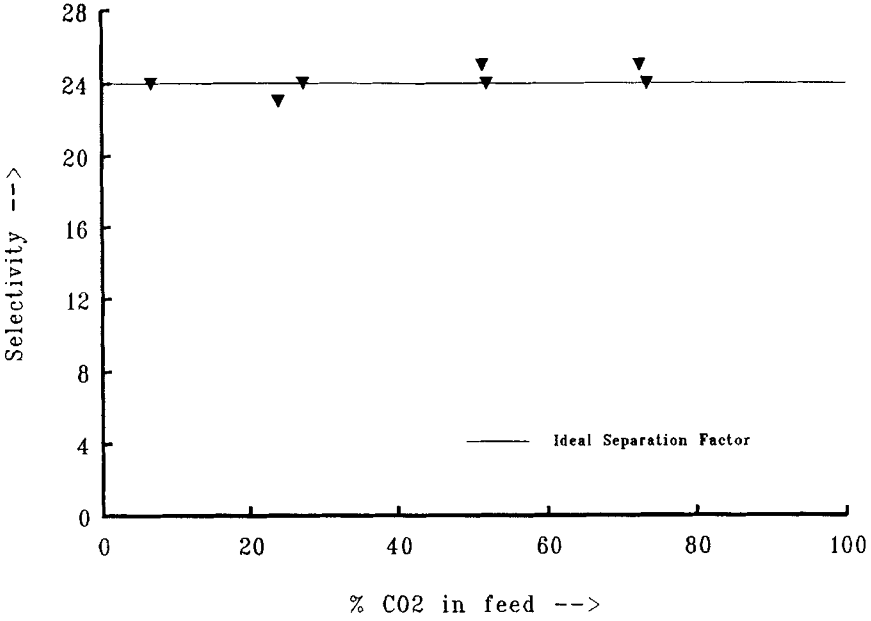

FIG. 5 Effect of composition on selectivity for CO_2/CH_4 through PES membrane.

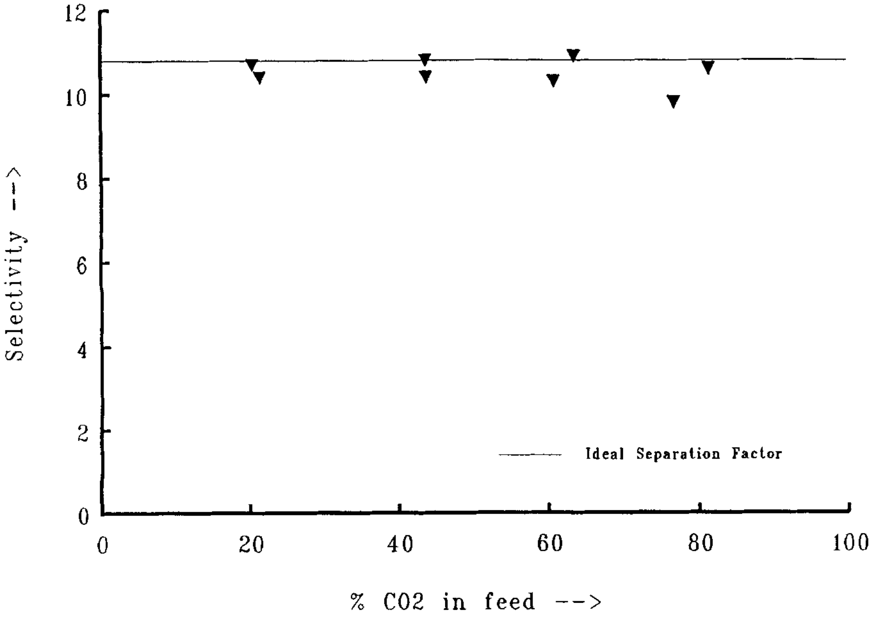

FIG. 6 Effect of composition on selectivity for CO_2/Ar through PES membrane.

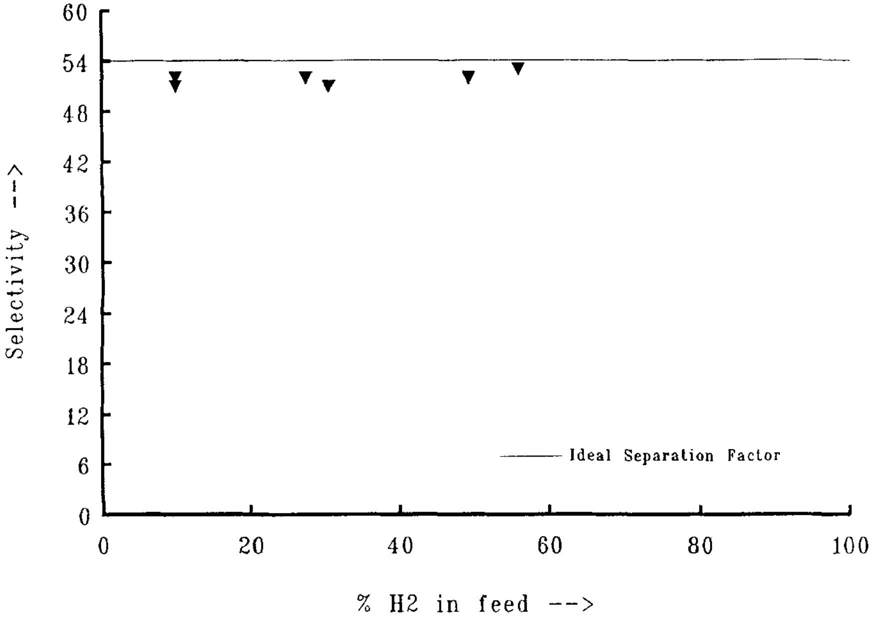

FIG. 7 Effect of composition on selectivity for H_2/CH_4 through PES membrane.

gas-phase fugacities cannot affect gas permeation mechanism appreciably. Therefore, in our opinion, the explanation of the composition dependency of selectivities for asymmetric membranes may be based on the micromorphology of these membranes rather than on the chemical interaction of gases with the membrane polymer and/or with each other.

Binary Gas Studies through PES-4A Mixed Matrix Membranes

In order to investigate the effect of feed composition on the transport properties of the PES-4A mixed matrix membrane and to verify the improved separation characteristics of this type of membrane, a wide composition range has been investigated by using CO_2/CH_4, CO_2/Ar, and H_2/CH_4 binaries (Tables 5–7, Figs. 8–10).

For all binaries, the effect of feed composition on the permeability of the mixtures showed a similar trend with dense homogeneous PES membranes, but selectivity demonstrated a strong concentration dependency.

For CO_2/CH_4 and CO_2/Ar binaries (Tables 5 and 6, Figs. 8 and 9), the concentration dependences of selectivities are very similar. Higher CO_2

TABLE 5

Permeability[a] and Selectivity of CO_2–CH_4 (through PES-4A[b])

	Percent CO_2 in feed										
	0	9.2	12.3	25.1	29.5	41.5	47.3	59.2	70.6	85.2	100
Permeability	0.11	0.17	0.38	0.32	0.79	0.75	1.40	2.05	1.50	2.23	4.07
Selectivity	—	35.0	34.7	29.8	30.4	28.0	25.0	22.0	19.0	15.3	—

[a] In barrer (10^{-10} cm^{3}STP·cm/cm^2·cmHg·s).

[b] Polyethersulfone-zeolite 4A (42% dry basis) mixed matrix membrane.

TABLE 6

Permeability[a] and Selectivity of CO_2–Ar (through PES-4A[b])

	Percent CO_2 in feed											
	0	9.7	9.7	23.9	25.1	47.0	47.1	68.3	70.0	85.0	85.7	100
Permeability	0.335	0.50	0.50	0.95	0.86	1.68	1.70	2.00	2.15	2.85	2.65	4.07
Selectivity	—	11.5	11.4	9.8	9.9	7.7	8.0	5.9	5.9	4.7	4.4	—

[a] In barrer (10^{-10} cm^{3}STP·cm/cm^2·cmHg·s).

[b] Polyethersulfone-zeolite 4A (42% dry basis) mixed matrix membrane.

TABLE 7

Permeability[a] and Selectivity of H_2–CH_4 (through PES-4A[b])

	Percent H_2 in feed											
	0	1.4	8.6	10.0	11.4	28.8	29.0	50.6	55.0	70.7	71.5	100
Permeability	0.11	0.12	0.35	0.43	0.45	1.39	1.41	4.15	4.60	7.27	7.00	10.71
Selectivity	—	40.0	45.0	46.0	47.0	58.0	57.0	78.0	81.0	95.0	92.0	—

[a] In barrer (10^{-10} cm^{3}STP·cm/cm^2·cmHg·s).

[b] Polyethersulfone-zeolite 4A (42% dry basis) mixed matrix membrane.

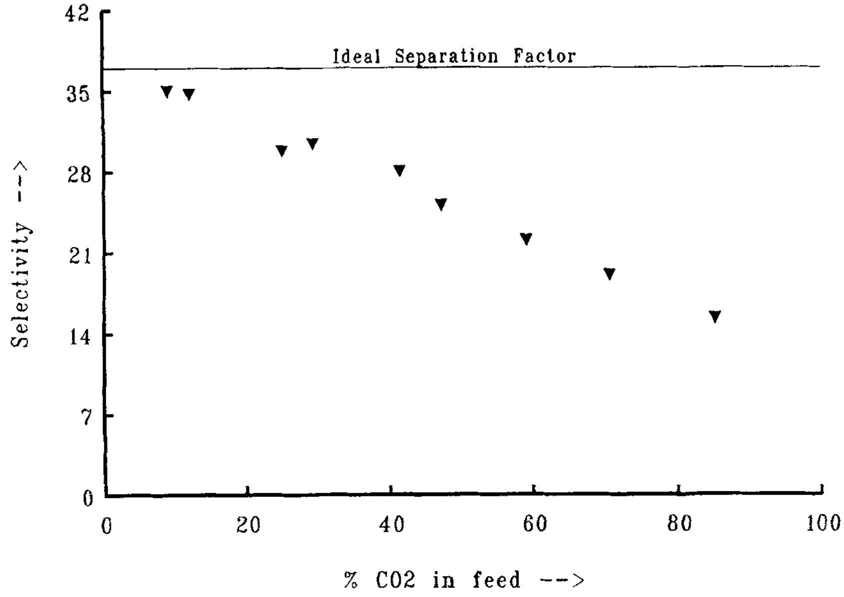

FIG. 8 Effect of composition on selectivity for CO_2/CH_4 through PES-4A mixed matrix membrane.

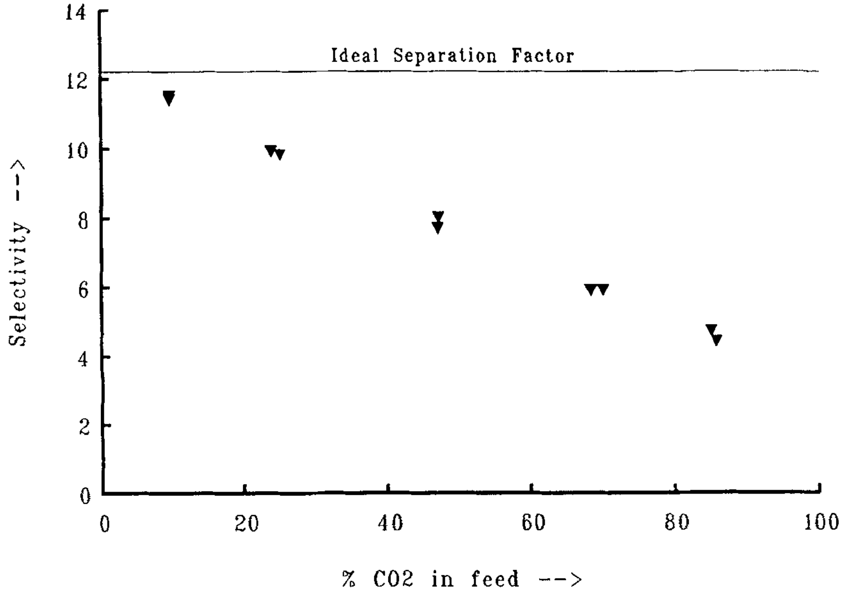

FIG. 9 Effect of composition on selectivity for CO_2/Ar through PES-4A mixed matrix membrane.

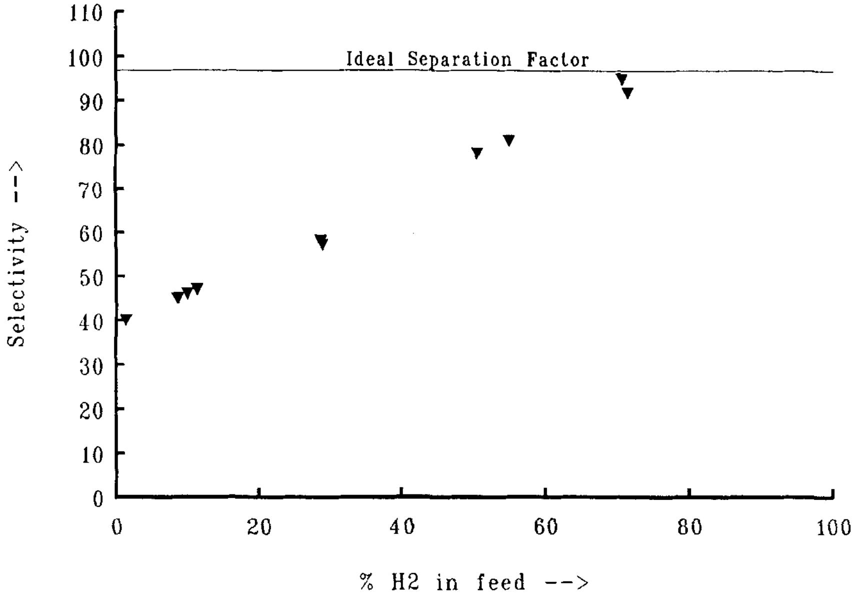

FIG. 10 Effect of composition on selectivity for H_2/CH_4 through PES-4A mixed matrix membrane.

concentrations in the feed caused appreciably lower selectivity values which are below the ideal separation factor, and the trend is linear with CO_2 concentration. For the CO_2/Ar system, the same order of magnitude decreases in selectivities are also observed. Therefore, one may conclude that when the faster permeating component has a possibility of interaction with the membrane matrix, selectivities decrease with increasing composition.

In the case of H_2/CH_4 binaries (Table 7, Fig. 10), unlike the cases with CO_2, higher H_2 concentrations in the feed cause higher selectivity values which are below the ideal separation factor. The trend was linear with H_2 concentration in the feed. Therefore, when the component with a high permeability is transported faster because of its size, selectivities increase with increasing composition.

The reasons for selectivity dependence on gas composition are not very clear. In the case of mixtures containing CO_2, there are some reasons, such as plasticization, given in the literature for asymmetric cellulose acetate membranes for concentration dependency (14, 15). It was claimed that plasticization occurs at high penetrant activities, the actual selectivity begins to fall significantly below the ideal selectivity, and previously glassy material starts to behave in a less selective, rubberlike fashion. Explanations such as plasticization of polymer by one of the gases cannot be valid for mixed matrix membranes, since similar observations would also have arisen with homogeneous membranes. DSC studies showed that the glass transition temperature of the mixed matrix membrane is equal to that of pure PES. Thus, the molecular configuration of polymer within the bulk of the membrane matrix is not affected, and it may not be an explanation of composition dependency. Interaction of the internal surfaces, which are created by introduction of zeolites, with feed gases and plasticization of this surfaces by components of gas mixtures still remains a possibility.

Previous SEM studies (9) showed that introduction of zeolites creates a very complicated micromorphology. Zeolite particles induce a cave-like porous structure into which they may fit. At high zeolite loadings, as in the case of this study, the channel network created may mature and connect separate cave-like voids to provide an alternate path for smaller molecules. Therefore, any speculation about the composition dependency of selectivities should consider the existence of this complicated physical structure.

In this morphology, three alternative transport pathways for gas molecules may exist. First, they may pass through the polymer matrix by a solution diffusion mechanism, similar to the transport mechanism in homogeneous membranes. Second, they may flow through the microvoid network created. Third, they may be transported through zeolitic surfaces by interacting with it. For each species, the dominant mechanism may depend mainly on the molecular size, polarity, and interactive potential. The availability and dominance of one of these pathways for a specific gas can be strongly affected by the existence of another gaseous component by means of ternary interactions, gas–gas interactions, or the interaction of molecules of the second gas with the membrane matrix. By considering this qualitative analysis, the following arguments can be made for the observed composition dependency of selectivities.

For CO_2 systems, the CO_2 molecules may saturate the active sites of zeolites at high CO_2 concentrations. This may lead to self-inhibition of CO_2. As CO_2 saturates the active sites of zeolites, the priority for CO_2 to permeate through the membrane may no longer be effective, since its interaction potential is reduced. Thus, selectivities are decreased. Since the introduction of high zeolite loading creates a large amount of internal surfaces, as observed by SEM micrographs (9), surface plasticization by CO_2 at high CO_2 concentrations could also be a contributing factor.

In order to explain selectivity dependence to the feed composition for the H_2–CH_4 system, the microcavity network created by high zeolite loading may be considered. CH_4, as a relatively larger molecule, may hinder the permeation of H_2 by blocking the narrow regions of the network, resulting in lower selectivities for CH_4-rich feed mixtures.

CONCLUSIONS

1. Membranes containing zeolitic filler 4A show a better separation performance than zeolite-free membranes due to the enhancement in permeabilities and selectivities. The increasing selectivities with the filler cannot be solely due to a molecular sieving mechanism. The shape-selective properties of zeolites, the interactive potentials and adsorptive capacities of zeolites, and the induced microstructure of membranes may all play roles in increasing permselectivities.
2. Transport properties of dense homogeneous PES membranes show an ideal behavior. The independence of selectivity from feed composition indicates that ternary interactions and factors like plasticization do not affect the gas permeation mechanism appreciably for this type of membrane.
3. For mixed matrix membranes, selectivities demonstrated a strong concentration dependency. This indicates that the existence of a third component strongly affects the interaction of gas molecules with the heterogeneous membrane matrix, and this appreciably modifies selectivities. Also, the importance of gas–membrane matrix and gas–gas–membrane matrix interactions are demonstrated. The strong concentration dependency of selectivities on gas composition also strengthens our opinion that the effect of zeolitic fillers cannot depend solely on a molecular sieving mechanism. They act as morphology modifiers as well. In our opinion, the composition dependency of separation performance can be explained by a transport model based on the microstructure of the membrane matrix.
4. The dependence of permeability and selectivity on process conditions, such as feed composition, must be taken into account in designing membrane separation systems. Different type of membranes may have better performance characteristics at different feed concentration ranges. Therefore, great care must be exercised in using pure permeabilities to predict the separation properties of gas separation membranes for mixtures.

ACKNOWLEDGMENTS

The authors acknowledge financial supports from The Scientific and Research Council of Turkey through Grant TBAG-1166 and from METU Research Fund Grant AFP-94-03-04-07.

REFERENCES

1. Y. Tsujita, in *Membrane Science and Technology* (Y. Osada and T. Nakagawo, Eds.), Dekker, New York, 1992, pp. 3–57.
2. H. J. Hennepe, C. A. Smolders, D. Bargeman, and M. H. V. Mulder, *Sep. Sci. Technol.*, *26*, 585 (1991).
3. T. Gürkan, N. Baç, G. Kiran, and T. Gür, *A New Composite Membrane for Selective Transport of Gases*, Paper Presented at 6th International Symposium on Synthetic Membranes in Science and Industry, Tubingen, Germany, August 1989.
4. E. Okumuş, T. Gürkan, and L. Yilmaz, *Development of a Zeolite–Polymer Membrane for Pervaporation*, Paper Presented in Chromatographic and Membrane Processes in Biotechnology, Azores, Portugal, July 1990.
5. E. Okumuş, L. Yilmaz, and T. Gürkan, *Sep. Sci. Technol.*, *29*, 2451 (1994).
6. M. Jia, K. V. Peinemann, and R. D. Behling, *J. Membr. Sci.*, *57*, 289 (1991).
7. J. M. Duval, B. Folkers, M. H. V. Mulder, and C. A. Smolders, *Ibid.*, *80*, 189 (1993).
8. M. Goldman, D. Fraenkel, and G. Levin, *J. Appl. Polym. Sci.*, *37*, 1791 (1989).
9. M. G. Süer, "Gas Permeation Studies with Novel Polymer–Zeolite Membranes," Chemical Engineering M.S. Thesis, Middle East Technical University, Ankara, Turkey, 1993.
10. M. G. Süer, N. Baç, L. Yilmaz, T. Gürkan, and A. Sacco Jr., *Sep. Technol.*, (E. F. Vansant, Ed), Elsevier, Amsterdam p. 661 (1994).
11. M. G. Süer, N. Baç, and L. Yilmaz, *J. Membr. Sci.*, *91*, 77 (1994).
12. E. S. Sanders, *Ibid.*, *63*, 37 (1988).
13. S. A. Stern and V. Saxena, *Ibid.*, *7*, 47 (1980).
14. M. D. Donohue, B. S. Minhas, and S. Y. Lee, *Ibid.*, *42*, 197 (1989).
15. M. D. Donohue, B. S. Minhas, and S. Y. Lee, *Membrane Materials and Processes* (AIChE Symp. Ser. 261), 1988, p. 84.
16. B. S. Minhas, T. Matsuura, and S. Sourirajan, *Ind. Eng. Chem. Res.*, *26*, 2344 (1987).
17. K. Li, D. R. Acharya, and R. Hughes, *AIChE J.*, *36*(10), 1610 (1990).
18. W. J. Koros and D. R. B. Walker, *Polym. J.*, *23*, 481 (1991).
19. E. S. Peterson and M. L. Stone, *J. Membr. Sci.*, *86*, 57 (1994).
20. E. S. Peterson, M. L. Stone, R. R. McCaffrey, and D. G. Cummings, *Sep. Sci. Technol.*, *28*, 423 (1993).
21. W. J. Koros and G. K. Fleming, *J. Membr. Sci.*, *83*, 1 (1993).
22. D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974.

Received by editor September 19, 1994