

A Manuscript Submitted

to

Journal of Membrane Science

Ms. No. K0479n (Final Version)

**Separation of Dilute Organic/Water Mixtures
with
Asymmetric Poly(vinylidene fluoride) Membranes**

1993

K. Jian, P.N. Pintauro*, and R. Ponangi
Department of Chemical Engineering
Tulane University
New Orleans, LA 70118

* To whom all correspondence should be sent; Telephone: (504) 865-5872,
FAX: (504) 865-6744; E-mail: peter@che.che.tulane.edu

Keywords: asymmetric membrane, membrane preparation and structure, pervaporation,
polyvinylidene fluoride, water treatment.

19960315 059

DTIC QUALITY INSPECTED 1

Abstract

An in-depth investigation of integral asymmetric poly(vinylidene fluoride) (PVDF) membranes has been carried out for the extraction of polar and non-polar organic compounds from dilute organic-in-water feed solutions. Membrane performance for low and high-boiling non-polar organic feed components was excellent, with separation factors as high as 4900 and high organic transmembrane fluxes. Polar organic feed components such as ethanol and acetone were also separated effectively from water but the separation factors were lower than non-polar organics. There was no change in membrane performance when either the dense or porous face of a PVDF membrane contacted the feed solution as long as the feed solution flow rate was sufficiently high. The effect of membrane preparation conditions, such as casting solution composition, air humidity and temperature during film drying, and the molecular weight of PVDF, on membrane performance was quantified. Although the water flux through the resulting films changed significantly, the organic (benzene) flux was essentially independent of the fabrication method. Variations in casting conditions also changed the mean diameter of a small number of pores in the dense layer of PVDF membranes. Transmembrane water fluxes during benzene/water separations correlated with increasing pore size, indicating that such pores were providing pathways for water movement across the hydrophobic PVDF dense layer. Based on benzene swelling and diffusivity measurements in homogeneous PVDF films, pores in the dense layer of an asymmetric membrane control permeate enrichment by either a membrane distillation, pore flow, or capillary condensation mechanism. The total time for asymmetric membrane casting was reduced from 69-72 minutes to 7 minutes, while maintaining a high organic (benzene) separation factor with only a small drop in transmembrane benzene flux.

Introduction

Membrane pervaporation is an attractive and potentially cost-competitive alternative to traditional methods (e.g., air stripping, carbon adsorption, and biotreatment) for removing low concentrations of organic solvents from waste water [1]. In such a pervaporation (PV) process, water/organic separation is achieved by the difference in membrane solubility and permeability of the feed solution components. Much of the prior work on the PV extraction of organics from water has focused on the use of elastomeric (rubbery) polymers, including polydimethylsiloxane (PDMS) and copolymers thereof, copolymers of styrene and styrene derivatives [2], and soft segment elastomers such as polyether block amides [3], nitrile butadiene and styrene-butadiene rubbers [4], and poly(acrylic acid ester-co-acrylic acid) [5]. A comprehensive review of the PV literature dealing with the selective removal of organics from water can be found in Reference 3. The membranes mentioned above were found to remove selectively a number of organic components including chloroform, benzene, toluene, ethanol, 1,1,2-trichloroethane, and acetone from dilute aqueous feed solutions. In order to improve organic transport rates, composite membranes were fabricated, where a thin permselective elastomeric polymer top-layer was coated on a microporous backing which offered little or no resistance against the permeating organic species. Examples of such composite-coated PV membranes are the MTR-100 and MTR-200 membranes manufactured by Membrane Technology Research, Inc. [6] where a silicone rubber (PDMS) rejecting layer is coated on an inert (non-elastomeric) polymeric support.

An attractive alternative to homogeneous and composite-coated PV membranes, in terms of mechanical stability and simplicity of fabrication, is a one-component (integral) asymmetric film where the dense and support layers are formed from a single casting solution. Such membranes are normally prepared by a phase inversion technique where a homogeneous polymer solution is cast as a thin film or spun as a hollow fiber, partially air dried, and then immersed in a non-solvent bath. Recently, Jian and Pintauro [7] reported on preliminary PV tests of an integral asymmetric poly(vinylidene fluoride) (PVDF) membrane. The hydrophobic nature of PVDF was exploited to promote the selective absorption and transport of the organic component of an organic/water feed solution. Transmembrane organic fluxes were maximized by the relatively thin dense layer of the asymmetric films. The formation of an asymmetric microstructure proceeded via an unusual phase inversion process where a dense polymer layer was created at the membrane/casting surface interface and a microporous structure formed at the membrane/air interface. For the removal of low concentrations of benzene from water, the asymmetric PVDF membranes performed remarkably well, with benzene separations factors as high as 1,530 and benzene fluxes as high as 105 g/m²-hr, for an 890 ppm benzene-in-water feed solution at 25°C and a downstream pressure of 0.025 atm.

In this paper we report, in detail, on additional separation studies with asymmetric PVDF membranes, where a variety of polar and non-polar organic feed components (at ppm feed concentrations) were selectively removed from water. Flux and selectivity data are presented to show the effects of operating conditions (feed composition, temperature, and

pressure), film orientation (dense vs. porous layer facing the feed solution), and variations in casting conditions on membrane performance. For benzene/water feed solutions, water fluxes were found to correlate well with the mean diameter of pores in the membrane's dense layer, whereas the benzene flux remained constant and essentially independent of pore size.

Experimental

Membrane preparation: The PVDF membranes used in this study were prepared using a phase inversion process that was first reported in Reference 7. A mixed solvent consisting of acetone (a low boiling point component) and dimethylacetamide (which has a high boiling point and a strong affinity for water) was used to dissolve PVDF polymer. In the majority of the experiments, Aldrich Chemical Co., Inc. PVDF polymer (530,000 average molecular weight) was used to cast the films. Asymmetric films were also fabricated from Kynar 761 (350,000 molecular weight) and Kynar 461 (572,000 molecular weight) manufactured by Elf Autochem North America, Inc. and Solef 1015 (210,000 molecular weight) and Solef 1012 (152,000 molecular weight) supplied by Solvay Polymers, Inc. Casting solutions were prepared using PVDF (between 10 and 16 wt%), dimethylacetamide (8-35 wt%), and acetone (55-78 wt%), which were heated to 50°C for a period of 30-60 minutes and then kept at room temperature for about 24 hours to remove gas bubbles. The mixture was then spread uniformly on a glass plate (wetted with a 85 wt% dimethylacetamide/water solution) to a thickness of approximately 0.3 mm. The resulting film was air dried under controlled temperature and humidity conditions (by use of a Tenney Engineering Inc. Versa Tenn II constant temperature/humidity environmental chamber) for 9-12 minutes. The membrane and

glass plate were then immersed in two precipitation baths (15 minutes immersion in each bath). The first bath was a solution of 50 vol% water, 40 vol% acetone and 10 vol% DMAc maintained at 15°C and the second bath was composed of 60 vol% water and 40 vol% acetone at 15°C (the membrane separated from the glass plate in the first bath). The membrane was then submerged for 30 minutes in a third bath containing distilled water at 15°C and allowed to air dry at room temperature. A total of 24 different casting methods were examined in this study; the various casting solution compositions and fabrication conditions are listed in Table 1. All of the membranes had a dry thickness of approximately 60 μm . As discussed previously [7], the dense layer forms at the membrane/glass plate interface, and thus distinguishes the present casting method from other phase inversion fabrication processes.

The structure of the asymmetric PVDF films was investigated by transmission electron microscopy (JOEL Model 1210) of frozen slices (0.06 μm in thickness) microtomed parallel to the membrane surface. As a representative example, Figure 1(a-d) shows four micrographs of slices at various depths from the dense layer surface, for a membrane fabricated using method no. 3 from Table 1. The membrane structure is similar at depths of 0.06 μm (top layer of the membrane) and 0.18 μm , with pores < 300 Å in diameter and a low porosity (estimated to be < 1%). We believe these two micrographs show the membrane dense layer. At greater depths into the membrane, the porosity and pore size (diameter) increase from 10% and ~500 Å (at 0.36 μm) to 25% and ~1000 Å (at 0.84 μm). The porosity continues to increase beyond 0.84 μm until a high porosity support layer (micron-size pores) is reached 10

μm from the dense layer surface. These results suggest that the dense layer of the asymmetric PVDF membranes is approximately $0.3 \mu\text{m}$ in thickness, with a transition layer $\sim 10 \mu\text{m}$ in depth followed by a microporous support layer of thickness $50 \mu\text{m}$. As will be discussed below, pores in the dense layer of the PVDF membranes play a critical role in transporting (and separating) organic and water feed components. The measurement of N_2 gas flux through asymmetric PVDF membranes provided additional evidence of dense layer micropores, with gas permeabilities of between 9.01×10^{-3} and 1.05×10^{-1} (m^3 (STP)- m/m^2 -hr-bar) depending on the casting method, as compared to 8.1×10^{-7} (m^3 (STP)- m/m^2 hr-bar) for a homogeneous (and nonporous) PDMS membrane [8].

Pervaporation experiments: Pervaporation experiments were conducted using the flat sheet membrane apparatus shown schematically in Figure 2. An organic/water feed solution of known composition was pumped from a sealed and thermostatted tank (4.0 l volume) to the stainless steel membrane test cells at a controlled and monitored flow rate. A cross flow fluid pattern delivered feed solution to the upstream side of the membrane (225 cm^2 membrane area per cell). The feed channel for each of the two cells had cross sectional dimensions in the flow direction of 0.7 mm (depth) \times 15 cm (width) and was fitted with a nylon screen turbulence promoter. Feed solutions were prepared using reagent-grade organic chemicals and deionized and distilled water. Transmembrane fluxes were generated by a downstream vacuum pump. The downstream pressure was controlled by a vent valve and measured by a digital pressure transducer (Omega Engineering Inc. Model DP204). The permeate was condensed and collected in two liquid nitrogen cold traps positioned between the membrane

cells and vacuum pump. In a typical pervaporation experiment, membrane fluxes were allowed to stabilize for approximately one hour before permeate samples were collected over a period of between 15 and 30 minutes. The total transmembrane flux was determined from the weight of sample in the cold traps. The organic species concentration in the condensed permeate liquid was determined by gas chromatography (Perkin-Elmer Model Sigma 115). For low water solubility (non-polar) feed components, the collected permeate was diluted with an excess of acetone in order to produce a single phase sample for GC analysis. Membrane performance was assessed from the organic and solvent fluxes and from the organic separation factor, which is defined as

$$\text{Separation Factor} = \frac{[C_o/C_w]^P}{[C_o/C_w]^F} \quad (1)$$

where C_o and C_w are the concentration of organic and water species, respectively, and the superscripts P and F designate the permeate and feed solutions. All PV experiments were repeated several times to insure reproducibility; the measured separation factor and flux normally varied by no more than $\pm 5\%$.

Results and Discussion

Effects of Feed Flow Rate and Membrane Orientation on Flux and Separation Factor -

Preliminary separation experiments were performed to determine the effects of membrane orientation (dense rejecting layer vs. porous support layer in contact with the feed solution)

on benzene separation factor and flux. The asymmetric PVDF membranes used in these experiments were fabricated from a casting solution composed of 14 wt% Aldrich PVDF, 13 wt% DMAc, and 73 wt% acetone polymer with a 12 minute air dry time (preparation method No. 14 in Table 1). The upstream feed solution was composed of 150 ± 7 ppm benzene in water. Separations were carried out at 25°C , with a downstream pressure of 0.025 atm. As shown in Figures 3a and 3b, the benzene separation factor and flux are strongly dependent on upstream fluid flow conditions for feed solution flow rates < 0.85 l/min, due to concentration polarization effects that cause a drop in the benzene concentration at the upstream membrane/solution interface. At low feed flow rates, concentration polarization was more severe when the porous sublayer contacted the feed solution, as would be expected if the porous polymer layer were part of an extended stagnant boundary layer on the upstream side of the dense layer (where benzene/water separation presumably occurs). The most interesting finding from these experiments was that the asymmetric PVDF membranes worked equally well with either the dense rejecting layer or porous support facing the feed solution, as long the feed flow rate was sufficiently high. This result has important implications for possible large-scale fabrication and use of these membranes. In principle, asymmetric PVDF films could be cast on a nonwoven backing structure, as opposed to the glass plate used in the present study, in which case the dense rejecting layer would form at the PVDF polymer/backing layer interface. Extraction of organic(s) from an organic(s)/water feed solution could be achieved using such membranes with the microporous layer of PVDF in contact with a well-stirred feed solution. In the present study, the asymmetric PVDF films were always positioned with the dense polymer layer upstream and the feed flow rate

maintained at 1.4 l/min to eliminate concentration polarization. Periodically over the course of our study, the effect of flow rate on organic flux was checked to insure that concentration polarization was not affecting membrane performance as the various PVDF membranes in Table 1 were examined and the type and concentration of organic solute in the feed solution was changed.

Organic/Water Separation Experiments - Measured organic permeate concentrations and organic membrane fluxes are plotted against the organic feed solution concentration in Figures 4 and 5, respectively, for a series of sparingly soluble non-polar (benzene, toluene), moderately polar (chloroform), and polar (ethylacetate, acetone, ethanol, and dioxane) organic solutes in water. All experiments were performed at a feed solution temperature of 25°C and a downstream pressure of 0.025 atm. The asymmetric PVDF membranes used in these experiments were cast using Method No. 14 of Table 1. Additional examples of PVDF membrane performance for organic/water separations are given in Table 2 for styrene/water separations at 25°C and 45°C and Table 3 for feed solutions containing various ppm mixtures of benzene, toluene, and xylene in water. Typically, in our PV tests, a membrane was exposed to a given organic feed component (of various concentrations) for up to eight hours and the same membrane was used many times for different organic feeds. Some membranes were used for a total of 100 hours; in no case did we observe a decline in membrane performance due to membrane degradation.

For all of the organic feed components and concentrations examined, the PVDF membranes were remarkably efficient at extracting selectively organic species from the aqueous feed solution. The membranes worked best for non-polar feed components (even those with boiling points greater than that of water), as would be expected since these chemicals have a stronger affinity to the organophilic PVDF polymer than water-soluble solutes. For example, when the feed solution was composed of 570 ppm toluene in water the downstream permeate was nearly 49 wt% toluene (corresponding to a toluene separation factor, as defined by Equation 1, of 1,685) and the toluene flux was 75 g/m²-hr. In general, we found that asymmetric PVDF membrane performance was characterized by reasonably high organic separation factors and very high organic fluxes, as compared to other pervaporation membranes. The PVDF membranes out-performed MTR-100 and MTR-200 composite-coated PDMS membranes (in terms of organic separation factor) for benzene/water and chloroform/water separations (at a temperature and downstream pressure similar but not identical to those used in the present study) [6]. Some PDMS membranes were more selective than the asymmetric PVDF membranes, but the transmembrane organic flux through these membranes was always very low. For example, when a 5.1 ppm toluene/water feed solution was separated at 25°C and a 0.0012 atm. downstream pressure with a composite-coated PDMS hollow fiber membrane, the toluene separation factor (as defined by Equation 1) was very high (16,772) but the toluene flux was quite low (0.8 g/m²-hr) [9]. Ethanol removal from an ethanol/water feed solution with the asymmetric PVDF membranes, on the other hand, was substantially better than that reported for PDMS films. For a 5.3 wt% ethanol/water feed, the PVDF ethanol separation factor and flux at 25°C and 0.025 atm

downstream pressure were 22.3 and 50 g/m²-hr, as compared to a separation factor and flux of 11.0 and 18.5 g/m²-hr for PDMS with a 5 wt% ethanol feed solution at 30°C and a downstream pressure of 9 mbar [3]. Even the separation results with acetone, a strong PVDF swelling agent, are reasonably good with acetone permeate concentrations ranging from 3.0 wt% to 17.1 wt% and acetone fluxes between 3.0 and 24.1 g/m²-hr, when the acetone feed concentration was varied from 1500 ppm to 5900 ppm.

Representative examples of the effects of feed concentration, downstream pressure, and operating temperature on asymmetric PVDF membrane performance (organic separation factor and flux) are shown in Figures 6-8, respectively, for a benzene/water feed solution. The behavior of the asymmetric PVDF films is similar to that observed during organic/water pervaporation separations with elastomeric membranes. As the benzene concentration in the feed increases, there is an increase in the transmembrane benzene flux and a decrease in the benzene separation factor due to increased water transport rates across the membrane (see Figure 6). These results are consistent with prior organic/water separation experiments [10] where the organic feed component was plasticizing and swelling the membrane, which, for a solution-diffusion transport model would allow for higher water permeation rates. When the downstream pressure in a PVDF membrane separation experiment was increased, both the benzene and water fluxes declined because the pressure gradient driving force across the membrane was reduced. The flux of that feed component with the lower solubility in the membrane (water for the data in Figure 7) decreases more rapidly with pressure, resulting in higher organic separation factors. An increase in feed temperature during a PV separation

normally results in increased permeation rates of the water and organic species [11]. This phenomenon was observed with the asymmetric PVDF membranes, as shown by the results in Figure 8. When the feed stream temperature was increased from 25°C to 60°C, there was nearly a 4-fold increase in benzene flux. The pronounced decrease in benzene separation factor (from 1400 to 50) was due to high water fluxes at the elevated feed temperatures, suggesting that the activation energy for water permeation is much smaller than that for benzene.

Effects of Casting Conditions on Membrane Performance - The effects of PVDF membrane preparation conditions (air temperature and humidity during membrane drying and the DMAc/acetone composition of the casting solution) on the fluxes of benzene and water are shown in Figures 9-11. The feed solution contained benzene in water at a fixed benzene concentration between 120 and 150 ppm. For these PV separation experiments, the temperature was 25°C and the downstream pressure was fixed at 0.025 atm. Our interest in examining transport in only asymmetric PVDF films limited the range over which a given casting condition could be varied. The asymmetric structure of the PVDF membranes in Figures 9-11 was essentially the same, as determined from transmission electron micrographs, with a dense layer porosity <1% and a thickness of ~0.3 μm .

The amount of water which absorbs into the PVDF/acetone/DMAc casting solution during asymmetric film fabrication appears to be an important variable that regulates the overall permselectivity of the membrane. Figures 9 and 10 show a substantial increase in

water flux and an essentially constant benzene flux with increasing water content in the air during film drying (i.e., with increasing air dry temperature at a constant relative humidity or by increasing relative humidity at a constant air temperature). A similar trend in the water and benzene flux was observed when the amount of DMAc (which has a strong affinity to water) in the casting solution was increased from 8% to 19% (Figure 11). It should be noted that the measured benzene fluxes in Figures 9-11 did not change as the feed solution flow rate was increase from 1.4 to 2.5 l/min, thus ruling out the possibility that upstream liquid boundary-layer resistance (concentration polarization) was controlling benzene transport.

The results in Figures 9-11 can be explained by a simplified description of the membrane formation mechanism, where the increase in water flux is associated with an increase in the dense layer porosity. During the air drying step, a porous microstructure forms due to instantaneous liquid-liquid demixing at the top surface of the cast film as acetone rapidly evaporates and water is absorbed from the air. A dense layer is created at the polymer film/glass plate interface by the delayed onset of liquid-liquid demixing, followed by gelation. High air drying temperatures and air humidities increase the exchange rates of solvents (acetone and DMAc) and/or nonsolvent water, causing rapid liquid-liquid demixing and a more porous dense layer. The porosity of the dense layer also increases when the concentration of PVDF in the film at the start of gelation is low (or equivalently the DMAc concentration is high).

To investigate the role of dense layer pores (observed in Figure 1) on water permeability, we first sought to determine the effect of casting conditions on pore size and then correlate water flux with our calculated pore diameters. Both mean and maximum pore diameters were determined experimentally using the gas permeation method of Yasuda and Tsai [12] and standard bubble point measurements [13] (with 2-propanol as the wetting liquid). A Millipore stainless steel membrane holder, which accommodated a 12.4 cm² membrane specimen, was used in these experiments. For the mean pore size measurements, pressurized nitrogen gas was supplied to one side of the membrane and the downstream steady-state gas flow rate was measured using a Manostat flowmeter. The pressure difference across the membrane was continuously monitored using digital pressure transducers. The nitrogen gas permeability coefficient (β) in a PVDF film was computed from the ratio of the measured gas flux (N , with units of g/cm²-s) and pressure difference across the membrane,

$$\beta = \frac{N}{P_{up} - P_{down}} \quad (2)$$

The mean pore diameter (d , with units of cm) in the dense layer of a PVDF membrane (i.e., that part of the film which controls the flux of N₂) was computed using the following relationship,

$$d = \left[\frac{B\eta}{A} \right] \left[\frac{16}{3} \right] \left[\frac{4RT}{\pi M} \right]^{1/2} \quad (3)$$

where the constants A and B are the slope and intercept of a linear plot of β vs. mean pressure ($P_{up}+P_{down}/2$), η is the viscosity of nitrogen gas, T is absolute temperature, and M is the molecular weight of N_2 . This experimental technique was highly reproducible (3% error) and gave linear nitrogen permeability vs. mean pressure plots.

Representative examples of the mean and maximum (bubble point) pore diameters for eight different asymmetric PVDF membranes are listed in Table 4. Mean pore diameters in the dense layer range from 58 Å to 882 Å depending on the membrane casting technique. Bubble point measurements could not be made when the mean pore diameter was less than 162 Å due to the pressure limitations of our equipment. As would be expected, the mean pore diameters in Table 4 were always less than those determined from the bubble point measurements. The relative difference between the two diameters, a very qualitative measure of pore size distribution, is not large, especially for pores with large diameters. We also found that entirely different casting methods produced an asymmetric film with dense layer pores of similar size (e.g., casting methods nos. 1 and 18 or methods nos. 15 and 24)

In Figures 12 and 13, the water flux and benzene/water separation factor are plotted vs. the dense layer's mean pore diameter for 19 different membrane casting methods (the numbers associated with each data point in these figures correspond to the casting methods in Table 1). The upstream benzene concentration for all PV experiments was fixed at 120 ± 10 ppm, the temperature was 25°C, and the downstream pressure was 0.025 atm. Water fluxes correlated well with mean pore diameter, suggesting strongly that the dense layer pores seen in Figure 1

and listed in Table 4 are providing pathways for water movement across asymmetric PVDF membranes. The correlation of benzene separation factors with pore diameter, shown in Figure 13, is a consequence of the pore size dependence on water flux and the constant benzene flux data in Figures 9-11.

In Figure 14, we focus more closely on the pore size dependence of water fluxes for those membranes with a mean pore diameter $< 400 \text{ \AA}$ and feed solutions of 120 ppm and 800 ppm benzene in water. The data show that the water flux for an 800 ppm benzene feed, at a given pore size, is approximately twice that observed with an upstream benzene concentration of 120 ppm. The data also show that the water fluxes do not correlate precisely with the square of the pore diameter, as would be the case for a simple pore-flow transport mechanism, indicating that the various membranes are differing by more than just their mean pore diameter. The best-fit correlations of the water flux data (shown by the solid lines in Figure 14) were found to be $N_w = 5.5 \times 10^{-6} (\text{Diameter})^{2.5}$ for the 120 ppm benzene feed solution and $N_w = 3.3 \times 10^{-6} (\text{Diameter})^{2.7}$ for the 800 ppm benzene feed, where the units for flux are $\text{g/m}^2\text{-hr}$ and the units for pore diameter are \AA . Since there was no observable difference in the dense layer thickness among the various membranes in Figure 14, there may have been an increase in the dense layer porosity, a change in the number of pores wetted by the feed solution, and/or a decrease in the pore tortuosity as the mean pore diameter increased.

To further clarify the role of the dense layer pores on water transport across an asymmetric PVDF membrane, the convective flux of liquid benzene/water solutions through

asymmetric PVDF membranes with different dense layer mean pore sizes was measured for a transmembrane pressure drop of 0.975 atm (i.e., the same ΔP as in the pervaporation experiments). The steady-state convective fluxes of liquid water containing 120 and 800 ppm benzene through five different asymmetric PVDF membranes (with mean pore diameters between 164 Å and 409 Å) are listed in Table 5 for an upstream pressure of 1.975 atm and a downstream pressure of 1.0 atm. For comparison purposes, the measured water fluxes from pervaporation experiments are also listed in this table. The liquid flux was found to increase with increasing pore diameter and increasing benzene concentration. The fluxes were always less than the water fluxes measured in the benzene/water PV separation experiments and the relative difference between the two fluxes was small, especially for large mean pore size membranes. We were unable to force pure liquid water through any of the asymmetric PVDF membranes at $\Delta P=0.975$ atm, because water with no benzene could not wet the hydrophobic PVDF pores. For a 120 ppm benzene in water solution, liquid could not be forced through membranes with a mean pore size less than 125 Å. This lower-limit pore diameter for liquid intrusion decreased to 98 Å when the liquid water contained 800 ppm benzene. Thus, the increase in convective flux for the 800 ppm benzene feed solution, as compared to the 120 ppm benzene case in Table 5, appears to be due to wetting and liquid flow through an increased number of the smaller pores in the dense layer.

We next turned our attention to the benzene transport across an asymmetric PVDF membrane. The possibility of a solution-diffusion mechanism was investigated by measuring the degree of membrane swelling by benzene and the membrane-phase benzene diffusion

coefficient in a 45 μm thick homogeneous dense PVDF film (which was assumed to be identical to a pore-free dense layer in an asymmetric PVDF membrane). Experiments were performed using a McBain sorption apparatus [14]. The equilibrium swelling of a homogeneous PVDF film at 25°C by benzene vapor (at an activity of 0.92) was found to be only 6.5 vol% (for comparison purposes, volume changes due to water vapor sorption, at an activity of 0.94, was even lower, at 0.13 vol%). The benzene vapor diffusion coefficient through the pore-free film (as determined by analyzing the rate of benzene vapor sorption and desorption [15]) was $1.4 \times 10^{-10} \text{ cm}^2/\text{s}$. Both the membrane swelling and benzene diffusivity results are significantly smaller than those reported for elastomeric polymer membranes, such as natural rubber where the benzene vapor swelling was reported to be 20% and the benzene diffusivity was $1.0 \times 10^{-7} \text{ cm}^2/\text{s}$ [16]. When we carried out the microbalance measurements on a homogeneous PDMS membrane (supplied by Specialty Silicone Products, Inc.), both the equilibrium benzene swelling and benzene diffusivity were found to be high, 34 vol% and $2.0 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. From the results of these experiments and the transmission electron micrographs in Figure 1 (indicating a 0.3 μm dense layer thickness), we concluded that a solution-diffusion mechanism was highly improbable and could not have produced the observed high benzene fluxes.

Based on the experimental data described above, we are proposing the following pore-flow mechanism for both water and organic (benzene) transport across an asymmetric PVDF membrane. The benzene/water liquid feed mixture will always wet and pass through large pores in the dense rejecting layer. There will be complete downstream evaporation of liquid

from these pores and the benzene/water separation factor will be unity. Since the pore liquid contains ppm concentrations of benzene, the benzene flux through the large pores must be nearly zero. Benzene/water feed will not wet small pores in the PVDF dense layer, in which case benzene/water separation occurs by either a membrane distillation [17], a pore flow (partial pore wetting) [18], or a capillary condensation [19] mechanism, where benzene vapor is selectively removed from the feed solution. For example, in a membrane distillation process the concentration of benzene vapor in the small pores at the upstream membrane/solution interface is governed by the downstream pressure which is drawing vapor out of the pore and by vapor-liquid equilibrium considerations that are dependent on the feed composition and temperature. Using liquid-phase activity coefficients from the UNIQUAC group contribution method [20], the equilibrium benzene vapor composition is 53.6 wt% at a pressure of 0.039 atm for a 120 ppm benzene-in-water feed and is 88.4 wt% at 0.087 atm for an 800 ppm benzene/water feed mixture. These benzene concentrations (which correspond to a benzene separation factor of $\approx 9,600$) are considerably higher than those observed in our PV experiments because the benzene permeate vapor is eventually diluted by benzene/water feed penetrating through the large pores via convective liquid transport. There is also a finite water vapor flux through the small pores (the pores contain 12-45 wt% water vapor), which is necessary to reconcile the PV and liquid convective fluxes in Table 5. The near constant benzene flux with membranes of different mean pore size suggests that the size and/or number of non-wetted pores in the PVDF dense layer (where organic/water separation is occurring) is essentially independent of membrane casting conditions. Additional experiments

as well as modeling studies are presently being carried out to validate this transport mechanism; the results of these studies will be the subject of a future publication.

Accelerated Casting Conditions - In an effort to demonstrate that the total time required for asymmetric PVDF membrane casting can be reduced significantly from that listed in Table 1, preliminary studies were conducted to accelerate membrane fabrication time. In these experiments, the casting solution composition (14 wt% Aldrich PVDF, 13 wt% DMAc, and 73 wt% acetone), air dry temperature (25°C), and air humidity (50% RH) were held constant. The air dry time was varied between 2 and 6 minutes and the three bath immersion times were varied between 1 and 30 minutes. Each of the accelerated-cast membranes was examined by transmission and scanning electron microscopy to insure an asymmetric microstructure; a dense layer thickness of $\sim 0.3 \mu\text{m}$ was observed for all of the membranes. The membranes were tested for their ability to separate a 115 ppm benzene/water feed solution at 25°C and a downstream pressure of 0.025 atm. The results of these experiments (total flux, benzene flux, and benzene separation factor) are listed in Table 6. In general, we found that the total casting time can be shortened to as little as 7 minutes while maintaining an asymmetric membrane structure and acceptable fluxes. If the air dry time and immersion times in the first two precipitation bath were shortened to under 2 minutes, unacceptable shrinkage of the membrane occurred. We presume that the depletion of DMAc from the casting solution and the resulting precipitation of polymer (to form the dense layer) was too rapid under those conditions where membrane shrinkage was observed. Also, a soak time less than one minute in the final water bath produced a membrane with poor mechanical

strength. The data in Table 6 also show a general trend of lower water fluxes and higher benzene separation factors as the membrane fabrication time was shortened. When the mean size of pores in the dense layer of the accelerated-cast membranes was determined by N_2 permeation rates, we found a water flux vs. pore size correlation essentially identical to that shown in Figure 12. The modest decrease in benzene flux for the accelerated casting methods can not be fully explained at this time but may be due to a small increase in the dense layer thickness. The results in Table 6 show clearly that asymmetric PVDF membranes can be cast quickly. We are currently attempting to reduce the air dry time below 2 minutes and the total casting time below 7 minutes by designing proper experiments for the examination of all casting variables, including casting solution composition, air dry temperature, and air humidity (which were not varied in Table 6).

Conclusions

Asymmetric PVDF pervaporation membranes were fabricated by a new phase-inversion technique involving an air drying step followed by immersion of the film in three precipitation baths. A thin dense layer (approximately 0.3 μm in thickness) formed at the membrane/casting surface (glass plate) interface, the remainder of the film being a thick microporous support layer. The membranes were highly efficient in removing both low and high boiling non-polar organic feed components from water (e.g., benzene, toluene, styrene, xylene, and chloroform) and performed as good or better than composite-coated PDMS membranes in terms of both a high organic separation factor and a high organic flux. Lower separation factors were observed when the aqueous feed solution contained a water-soluble

polar organic, such as acetone, ethanol, ethyl acetate, and dioxane, however, the separation factors and transmembrane organic fluxes were comparable to or greater than those reported in the literature for silicone rubber PV membranes. With sufficient upstream stirring to eliminate concentration polarization effects, the membranes were found to perform equally well with either the dense or porous layers in contact with the feed solution. The benzene flux increased and its separation factor decreased with increasing feed concentration, due presumably to plasticization of PVDF; in this regard the behavior of the asymmetric PVDF films was similar to that of elastomeric polymer membranes.

The effects of variations in asymmetric membrane fabrication conditions on benzene/water separation were investigated, where the PVDF molecular weight, casting solution composition, and air dry temperature and humidity were varied. The magnitude of the water flux through the PVDF films was found to be strongly dependent on the membrane preparation technique, whereas the benzene flux remained essentially unchanged. N₂ gas permeability measurements of the mean pore diameter in the membranes' dense layer revealed that: (i) pore sizes varied from 58 Å to 850 Å depending on the casting conditions and (ii) water fluxes and benzene separation factors correlated well with increasing mean pore size for both low and high benzene feed concentrations (i.e., different casting methods which produced the same benzene separation factor and water flux were found to have the same mean pore diameter). Dilute benzene/water liquid solutions could pass through the asymmetric PVDF membranes with a modest pressure driving force (0.975 atm). The results suggest that organic/water feeds pass through the membrane as liquid via a small number of

large pores in the dense layer. Benzene/water mixtures can not wet small pores and permeate enrichment in organic occurs by either a membrane distillation, pore flow, or capillary condensation mechanism.

In an effort to demonstrate that the total time required for asymmetric film casting could be shortened, PVDF membranes were prepared with 2-6 minute air dry times and a total immersion time in the three precipitation baths between 5 and 60 minutes. The air dry temperature and humidity and the casting solution composition were held constant for all of these accelerated-casting experiments. The resulting asymmetric membranes were used to remove benzene from a 115 ppm benzene in water feed solution at 25°C and 0.025 atm downstream pressure. For an asymmetric membrane fabricated completely in 7 minutes, the measured benzene separation factor was high (5184), but the benzene flux ($4.9 \text{ g/m}^2\text{-hr}$) was somewhat lower than that observed using a more time-consuming casting method.

Unacceptable film shrinkage was observed when the air dry time was reduced to below 2 minutes and the immersion times in each of the first two precipitation baths were shortened to under 2 minutes. Adjustments in the polymer composition and/or the temperature and humidity of the air drying step were not investigated in the present study but will be examined to shorten further the time required for asymmetric membrane casting.

Acknowledgment - This work was supported by the Office of Naval Research and by the Defense Nuclear Agency of The Department of Defense, through Tulane University's Center for Bioenvironmental Research. The styrene separation experiments were performed by Ms.

Julia Taravella. The authors also wish to thank Dr. Richard Wycisk for his helpful suggestions during the preparation of this paper.

References

1. R. W. Baker, Pervaporation, in R. W. Baker, E. L. Cussler, W. Eykamp, W. J. Koros, R. L. Riley, and H. Strathmann (Eds.), Membrane Separation Systems, Recent Developments and Future Directions, Noyes Data Corp., Park Ridge, NJ, 1991, pp. 151-188.
2. M. Yoshikawa, T. Ohsawa, M. Tanigaki, and W. Eguchi, Application and Development of Synthetic Polymer Membranes. I. Separation of Aqueous Ethanol Mixtures by Pervaporation Through Common Polymer Membranes Containing Methacrylic Esters, J. Polym. Sci. Polym Lett., 26 (1988) pp. 89-94.
3. K. W. Boddeker and G. Bengtson, Selective Pervaporation of Organics From Water, in R. Y. M. Huang (Ed.), Pervaporation Membrane Separation Processes, Elsevier, Amsterdam, 1991, pp.437-456.
4. J. P. Brun, C. Larchet, G. Bulvestre, and B. Auclair, Sorption and Pervaporation of Dilute Aqueous Solution of Organic Compounds Through Polymer Membrane, J. Membr. Sci., 25 (1985) pp.55-100.

5. T. Nakagamma , M. Hoshi, and A. Higuchi, Separation of Aqueous Organic Solvents Through Poly(Acrylic acid ester-co acrylic acid) Membranes by Pervaporation, in R. Bakish (Ed.), Proceedings of the Fifth Conference on Pervaporation in the Chemical Industry, Bakish Materials Corp., Englewood, NJ, 1991, pp.88-97.
6. J. G. Wijmans, J. Kaschemekat, J. E. Davidson and R. W. Baker, Treatment of Organic Contaminated Wastewater Streams by Pervaporation, Environ. Progress, 9 (1990) pp.262-268.
7. K. Jian and P. N. Pintauro, Integral Asymmetric Poly(vinylidene fluoride) (PVDF) Pervaporation Membranes, J. Membr. Sci., 85 (1993) pp.301-309.
8. H. Paul, C. Hilpsen, F. J. Gerner, and H. Strathmann, Removal of Organic Vapor from Air by Selective Membrane Pervaporation, J. Memb. Sci., 36 (1992) pp. 363-72.
9. P. Côté, C. Lipski, and H. Campbell, A Cross-Flow Pervaporation System for Removal of VOCs from Contaminated Wastewater, U.S. EPA Final Report No. EPA/540/R-94/512, May 1994.
10. G. Bengtson and K. W. Boddeker, Pervaporation of Low Volatiles from Water, in R. Bakish (Ed.), Proceedings of the Third Conference on Pervaporation in the Chemical Industry, Bakish Materials Corp., Englewood, NJ, 1989, p.439-448.

11. R. Y. M. Huang and J. W. Rhim, Separation Characteristics of Pervaporation Membrane Separation Processes, in R. Y. M. Huang (Ed.), Pervaporation Membrane Separation Processes, Elsevier, Amsterdam, 1991, pp.165.
12. H. Yasuda and J. T. Tsai, Pore Size of Microporous Polymer Membranes, J. Appl. Polymer Sci., 18 (1974) pp.805-819.
13. M. C. Porter, Handbook of Industrial Membrane Technology, Noyes Publications, NJ, 1990, pp.72-73.
14. R. M. Felder and G. S. Huvard, Permeation, Diffusion and Sorption of Gases and Vapors, in R.A. Fava (Ed.), Methods of Experimental Physics, Academic Press, New York, 1980, pp. 315-377.
15. G.S. Park, Transport Principles-Solution, Diffusion and Permeation in Polymer Membranes, in P.M. Bungay and H.K. Lonsdale (Eds.), Synthetic Membranes: Science, Engineering and Applications, D. Reidel Publishing Co., Boston, 1986, pp. 57-107.
16. J. Kärger and D.M. Ruthven, Diffusion in Zeolites and Other Micropore Solids, John Wiley and Sons, Inc. New York, 1992, pp.563-585.

17. V. Calabro, E. Drioli, and F. Matera, Membrane Distillation in The Textile Wastewater Treatment, Desalination, 83 (1991) pp.209-224.
18. T. Okada and T. Matsuura, Theoretical and Experimental Study of Pervaporation on The Basis of Pore Flow Mechanism, in R. Bakish (Ed.), Proceedings of the Sixth Conference on Pervaporation in the Chemical Industry, Bakish Materials Corp., Englewood, NJ, 1992, pp.137-152.
19. K.-H. Lee and S.-T. Hwang, The Transport of Condensable Vapors Through a Microporous Vycor Glass Membrane, J. Colloid Interface Sci., 110 (1986) pp. 544-555.
20. J.M. Prausnitz, R.N. Lichtenthaler, and E.G.de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd Edition, Prentice-Hall Inc., Englewood Cliffs, NJ, 1986, pp.233-244.

Table 1
Casting Methods for Asymmetric PVDF Membranes

Method No.	Casting Solution Composition			Air Drying Conditions		
	PVDF ¹ (Type/wt%)	DMAc (wt%)	Acetone (wt%)	Humidity (%RH)	Temp. (°C)	Time (min.)
1	1/14	13	73	45	25	9
2	1/14	13	73	55	25	9
3	1/14	13	73	65	25	9
4	1/14	13	73	75	25	9
5	1/14	13	73	85	25	9
6	1/14	13	73	90	25	9
7	1/14	13	73	65	20	9
8	1/14	13	73	65	35	9
9	1/14	13	73	65	45	9
10	1/14	13	73	65	50	9
11	1/11	16	73	50	25	12
12	1/12	15	73	50	25	12
13	1/13	14	73	50	25	12
14	1/14	13	73	50	25	12
15	1/16	11	73	50	25	12
16	1/14	8	78	50	25	12
17	1/14	9	77	50	25	12
18	1/14	11	75	50	25	12
19	1/14	15	71	50	25	12
20	1/14	19	67	50	25	12
21	2/14	13	73	60	25	12
22	3/14	13	73	60	25	12
23	4/10	35	55	80	25	12
24	5/10	35	55	80	25	12

1 - PVDF: Type 1 - Aldrich Chemical Co., Inc. (530,000 MW); Type 2 - Elf Autochem North America, Inc. (Kynar 461, 572,000 MW); Type 3 - Elf Autochem North America, Inc. (Kynar 761, 350,000 MW); Type 4 - Solvay Polymers, Inc. (Solef 1015, 210,000 MW); Type 5 - Solvay Polymers, Inc. (Solef 1012, 152,000 MW).

Precipitation Bath Conditions For All Methods: 15 minutes in 50 vol% water/40 vol% acetone/10 vol% DMAc; 15 minutes in 60 vol% water/40 vol% acetone; 30 minutes in distilled water.

Table 2

Styrene/Water Separations with Asymmetric PVDF Membranes

PVDF membrane casting method No. 14 (from Table 1)

Downstream pressure - 0.025 atm.

Feed Conditions		wt% Styrene in Permeate	Flux (g/m²-hr)		Separation Factor
Temp (°C)	wt% Styrene		Total	Styrene	
25	0.0078	6.3	32.2	2.0	862
	0.0093	7.6	33.2	2.5	884
	0.0113	8.7	33.3	2.9	843
	0.0138	10.5	36.2	3.8	850
	0.0179	13.9	33.3	4.6	901
	0.0223	16.5	37.8	6.2	886
45	0.0076	5.9	60.0	3.5	825
	0.0089	7.3	57.3	4.2	885
	0.0114	11.2	49.6	5.6	1106
	0.0146	14.3	51.9	7.4	1143
	0.0195	16.2	60.0	9.7	992
	0.0243	20.3	62.1	12.6	1048

Table 3
Separation of BTX/Water Mixtures with Asymmetric PVDF Membranes

PVDF Membranes made by Casting Method No. 14 (Table 1)

Temperature = 25°C

Downstream Pressure = 0.025 atm.

Feed Composition (ppm)	Permeate Composition (wt%) ¹	Total Flux (g/m ² -hr)	Organic Flux (g/m ² -hr)	Organic Separation Factor
Benzene: 62 Toluene: 68 Xylene: 15	B: 8.2 T: 12.2 X: 2.2	47.2	B: 3.7 T: 5.8 X: 1.0	B: 1437 T: 2043 X: 1499
Benzene: 158 Toluene: 150 Xylene: 15	B: 16.1 T: 22.3 X: 1.32	78.7	B: 21.7 T: 17.5 X: 1.0	B: 1217 T: 1910 X: 891
Benzene: 214 Toluene: 211 Xylene: 15	B: 20.3 T: 27.5 X: 1.1	96.6	B: 19.6 T: 26.6 X: 1.0	B: 1188 T: 1796 X: 721
Benzene: 300 Toluene: 312 Xylene: 20	B: 26.2 T: 34.8 X: 1.65	121.1	B: 31.7 T: 42.1 X: 2.0	B: 1182 T: 1708 X: 838

1 - 100 ppm = 0.01 wt%

Table 4

**Comparison of Mean and Maximum (Bubble Point) Pore Diameters
in the Dense Layer of
Asymmetric PVDF Membranes**

Casting Method Number (From Table 1)	Mean Pore Diameter (Å)	Bubble Point Pore Diameter (Å)
16	58	--
17	98	--
24	117	--
15	125	--
18	162	388
1	164	397
14	208	480
2	235	504
4	409	664
20	475	685
9	580	751
5	641	765
11	882	974

Table 5

**Measured Convective Benzene/Water Mixture Liquid Fluxes
and Pervaporation Water Fluxes
in Asymmetric PVDF Membranes with Different Mean Pore Diameters**

Mean Pore Diameter (Å)	120 ppm benzene/water feed		800 ppm benzene/water feed	
	Convective Flux (g/m ² -hr)	PV Water Flux (g/m ² -hr)	Convective Flux (g/m ² -hr)	PV Water Flux (g/m ² -hr)
58	no flow	4.9	no flow	8.8
98	no flow	12.7	4.7	29.9
125	8.3	15.4	23.1	34.7
164	17.0	24.3	30.7	43.3
235	35.6	44.5	66.0	81.5
304	85.3	97.0	179.1	199.0
409	121.7	135.0	344.1	374.0

Table 6**Accelerated Casting Conditions for Asymmetric PVDF Membranes**

air dry time (min.)	1st bath immersion time (min.)	2nd bath immersion time (min.)	3rd bath immersion time (min.)	flux (g/m ² -hr) ¹		separation factor ¹
				total	benzene	
12 ²	15	15	30	46.8	9.3	2159
6	15	15	30	38.1	10.7	3736
2	15	15	30	17.8	6.2	4969
2	6	15	30	15.4	5.9	5411
2	2	15	30	14.1	5.3	5230
2	2	6	30	13.5	5.1	5292
2	2	2	30	13.0	4.9	5280
2	2	2	6	13.6	5.2	5364
2	2	2	1	13.1	4.9	5184

1 - Fluxes and separation factors for a 115 ppm benzene-in-water feed solution at 25 °C and 0.025 atm downstream pressure.

2 - Base-line case (casting method No. 14 in Table 1).

Figure Captions

- Figure 1** Transmission electron micrographs of PVDF membrane slices (0.06 μm in thickness) parallel to the dense layer surface. Asymmetric membrane fabrication method no. 3 from Table 1. Depth from the dense layer surface: (a) 0.06 μm (top layer of membrane); (b) 0.18 μm ; (c) 0.36 μm ; (d) 0.84 μm .
- Figure 2** Schematic diagram of membrane pervaporation test cell apparatus. (1) constant temperature feed tank, (2) feed pump, (3) feed sample collection valve, (4) temperature transducers, (5) feed flowmeter, (6) membrane cells, (7) pressure transducers, (8) switch valves, (9) liquid nitrogen cold traps, (10) pressure meter, (11) vacuum pump, (12) vent valve.
- Figure 3** The effect of feed flow rate on asymmetric PVDF membrane performance with either the dense or porous layer contacting the feed solution. Membrane casting methods No. 14 (Table 1); feed composition 150 \pm 7 ppm benzene in water; temperature = 25°C; downstream pressure = 0.025 atm. (a) benzene separation factor vs. flow rate, (b) benzene flux vs. flow rate.

Figure 4 Organic permeate concentration vs. feed concentration for non-polar and polar organic solutes in water. Asymmetric membrane casting method No. 14 (Table 1); temperature = 25°C; downstream pressure = 0.025 atm. ○ benzene; ▲ toluene; ● chloroform; ▼ ethyl acetate; ◆ acetone; ■ ethanol; ◇ dioxane.

Figure 5 Organic flux vs. feed concentration for non-polar and polar organic solutes in water. Asymmetric membrane casting method No. 14 (Table 1); temperature = 25°C; downstream pressure = 0.025 atm. ○ benzene; ▲ toluene; ● chloroform; ▼ ethyl acetate; ◆ acetone; ■ ethanol; ◇ dioxane.

Figure 6 Effect of benzene feed concentration on benzene separation factor and flux. Asymmetric membrane casting method no. 14 (Table 1); temperature = 25°C; downstream pressure = 0.025 atm.

Figure 7 Effect of downstream pressure on benzene separation factor and flux. Asymmetric membrane casting method no. 12 (Table 1); benzene feed concentration = 85 ± 3 ppm; temperature = 25°C; downstream pressure = 0.025 atm.

Figure 8 Effect of operating temperature on benzene separation factor and flux.
Asymmetric membrane casting method No. 13 (Table 1); benzene feed concentration = 80 ± 2 ppm; temperature = 25°C ; downstream pressure = 0.025 atm.

Figure 9 Effect of air dry temperature during film casting on benzene and water fluxes.
Asymmetric membrane casting methods nos. 3, 7, 8, 9, and 10 (Table 1); benzene feed concentration 120 ± 10 ppm; temperature = 25°C ; downstream pressure = 0.025 atm.

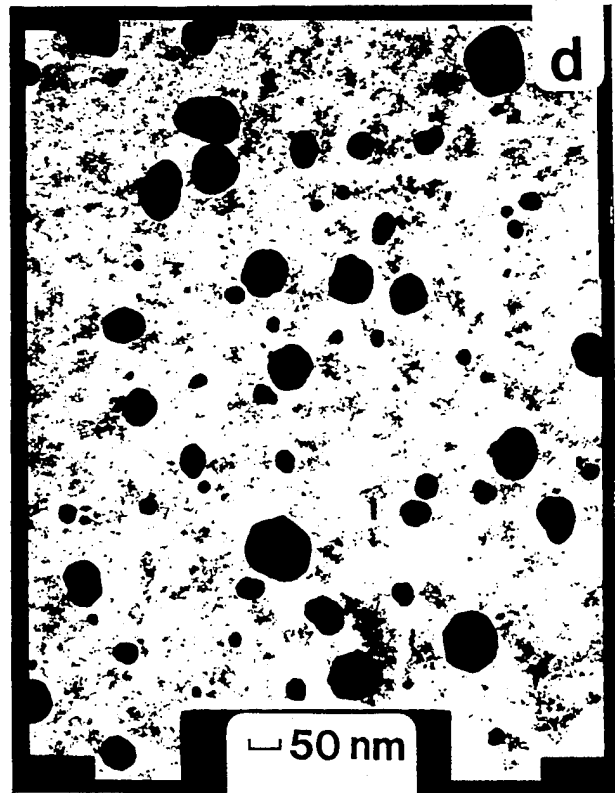
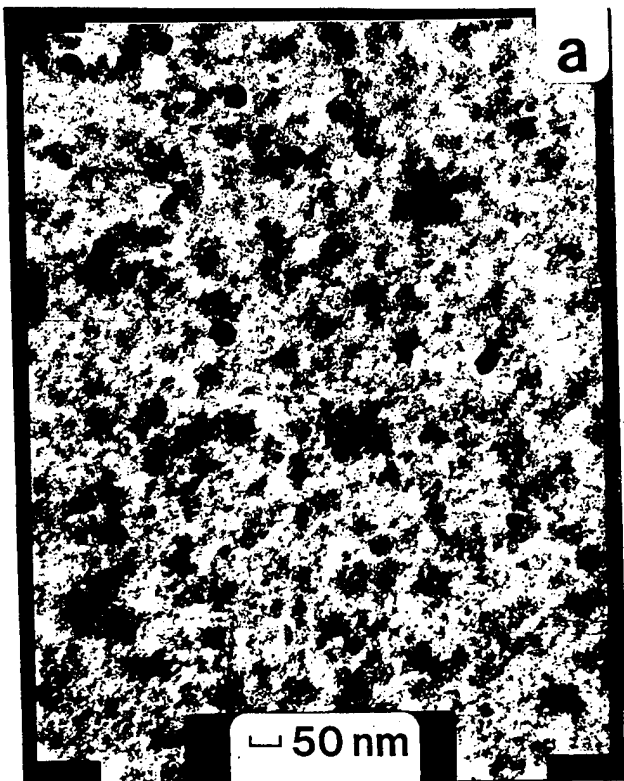
Figure 10 Effect of air humidity during film casting on benzene and water fluxes.
Asymmetric membrane casting methods nos. 1-6 (Table 1); benzene feed concentration 120 ± 10 ppm; temperature = 25°C ; downstream pressure = 0.025 atm.

Figure 11 Effect of DMAc concentration in the membrane casting solution on benzene and water fluxes. Asymmetric membrane casting methods nos. 14, 16, 17, 18, 19, and 20 (Table 1); benzene feed concentration 150 ± 5 ppm; temperature = 25°C ; downstream pressure = 0.025 atm.

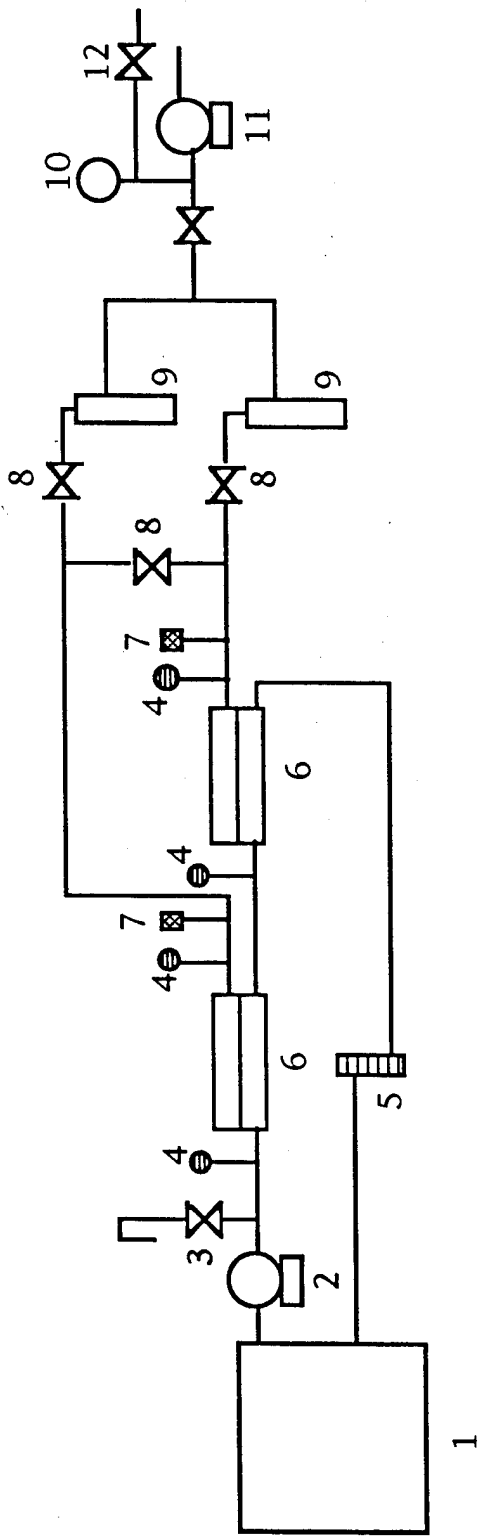
Figure 12 Increase in water flux with the measured mean diameter of pores in the dense layer of asymmetric PVDF membranes. Benzene feed concentration 120 ± 10 ppm; temperature = 25°C ; downstream pressure = 0.025 atm. Numbers associated with each data point identify the casting method in Table 1.

Figure 13 Interdependence of benzene separation factor and the measured mean diameter of pores in the dense layer of asymmetric PVDF membranes. Benzene feed concentration 120 ± 10 ppm; temperature = 25°C ; downstream pressure = 0.025 atm. Numbers associated with each data point identify the casting method in Table 1.

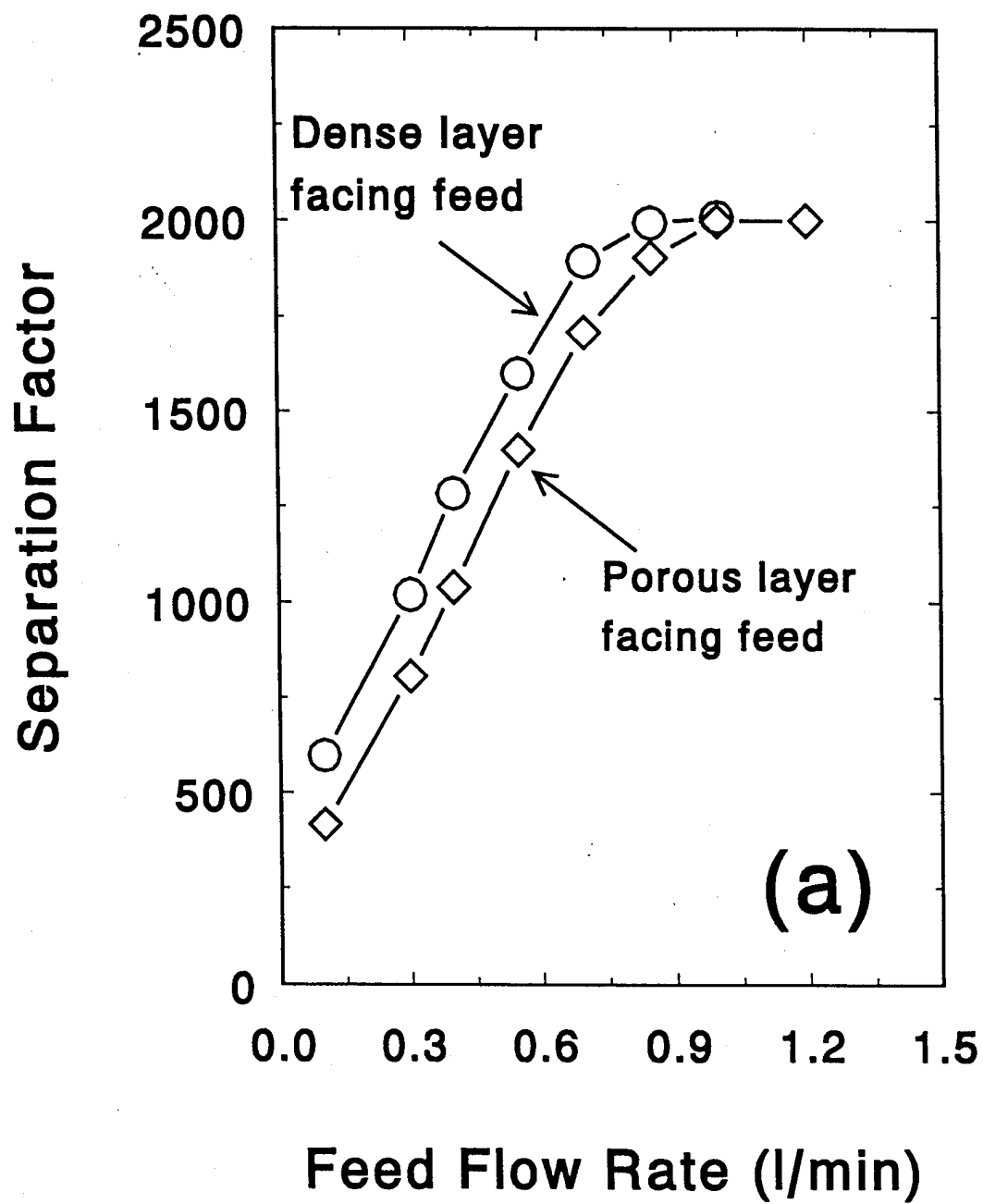
Figure 14 The effects of mean pore size and benzene feed concentration on water flux. Temperature = 25°C ; downstream pressure = 0.025 atm. Numbers associated with each data point identify the casting method in Table 1. \blacktriangledown 800 ± 7 ppm benzene in water feed solution; \bigcirc 120 ± 10 ppm benzene in water feed solution.



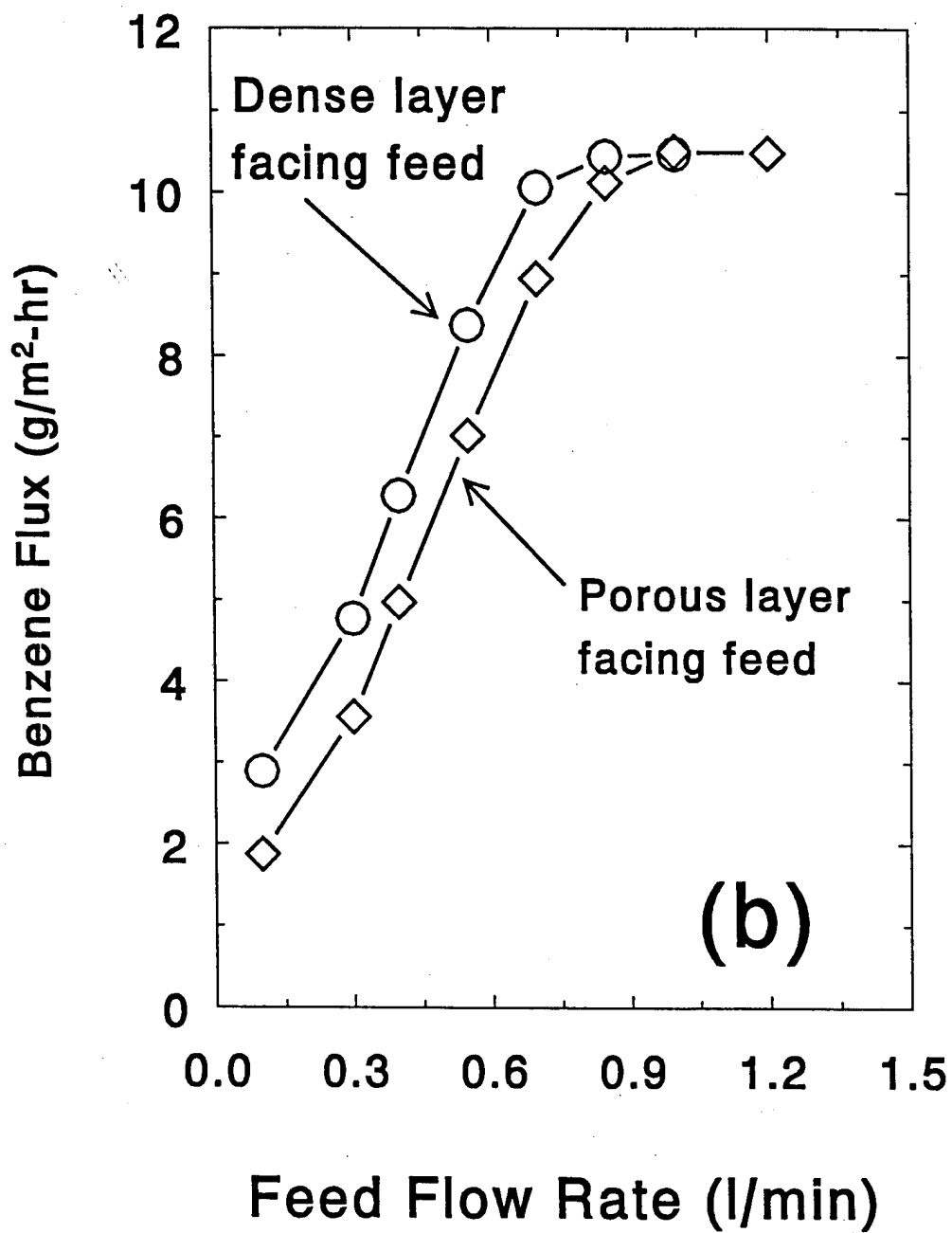
Jian and Pintauro
Figure 1



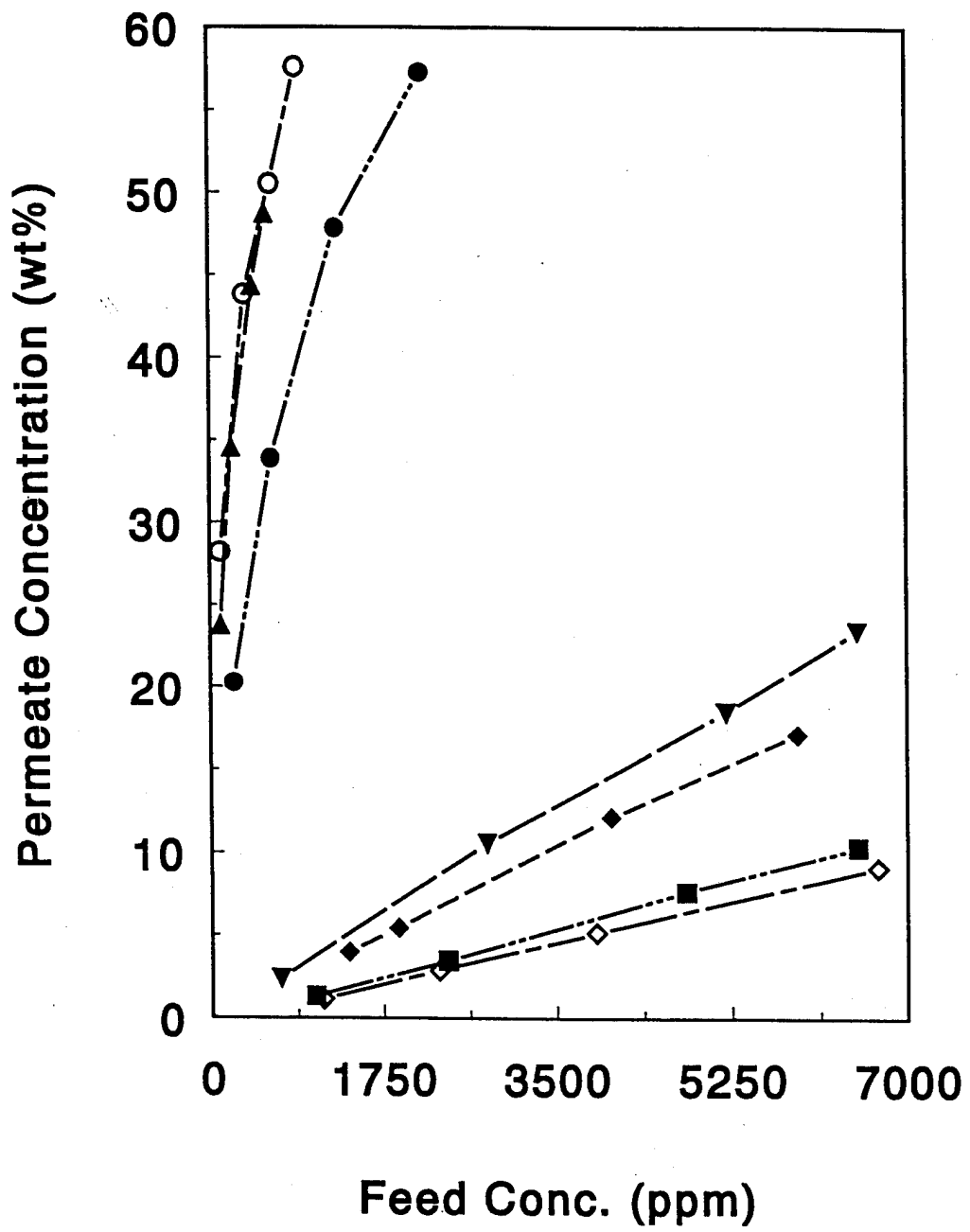
Jian and Pintauro
Figure 2



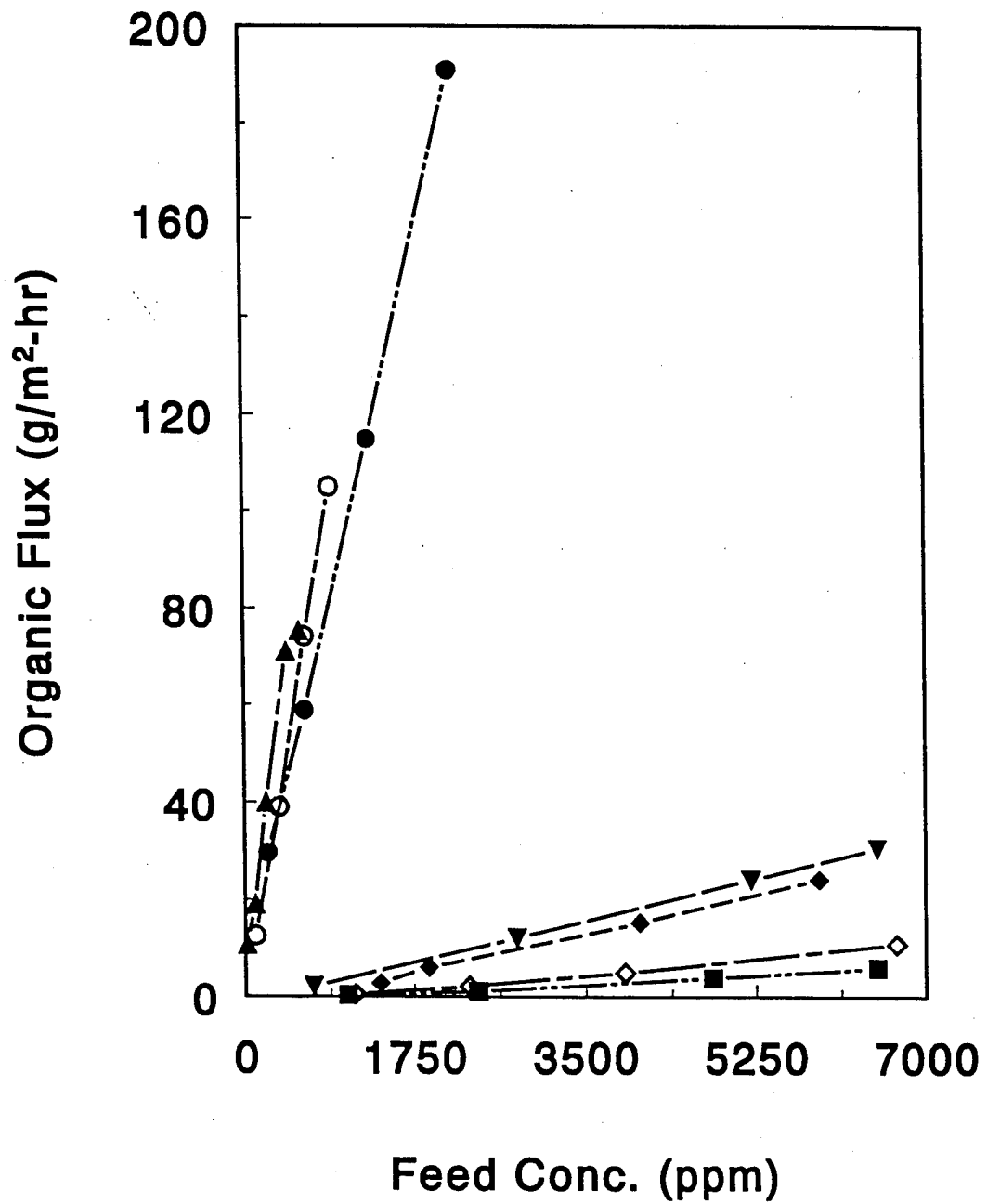
Jian and Piutauro
Figure 3a



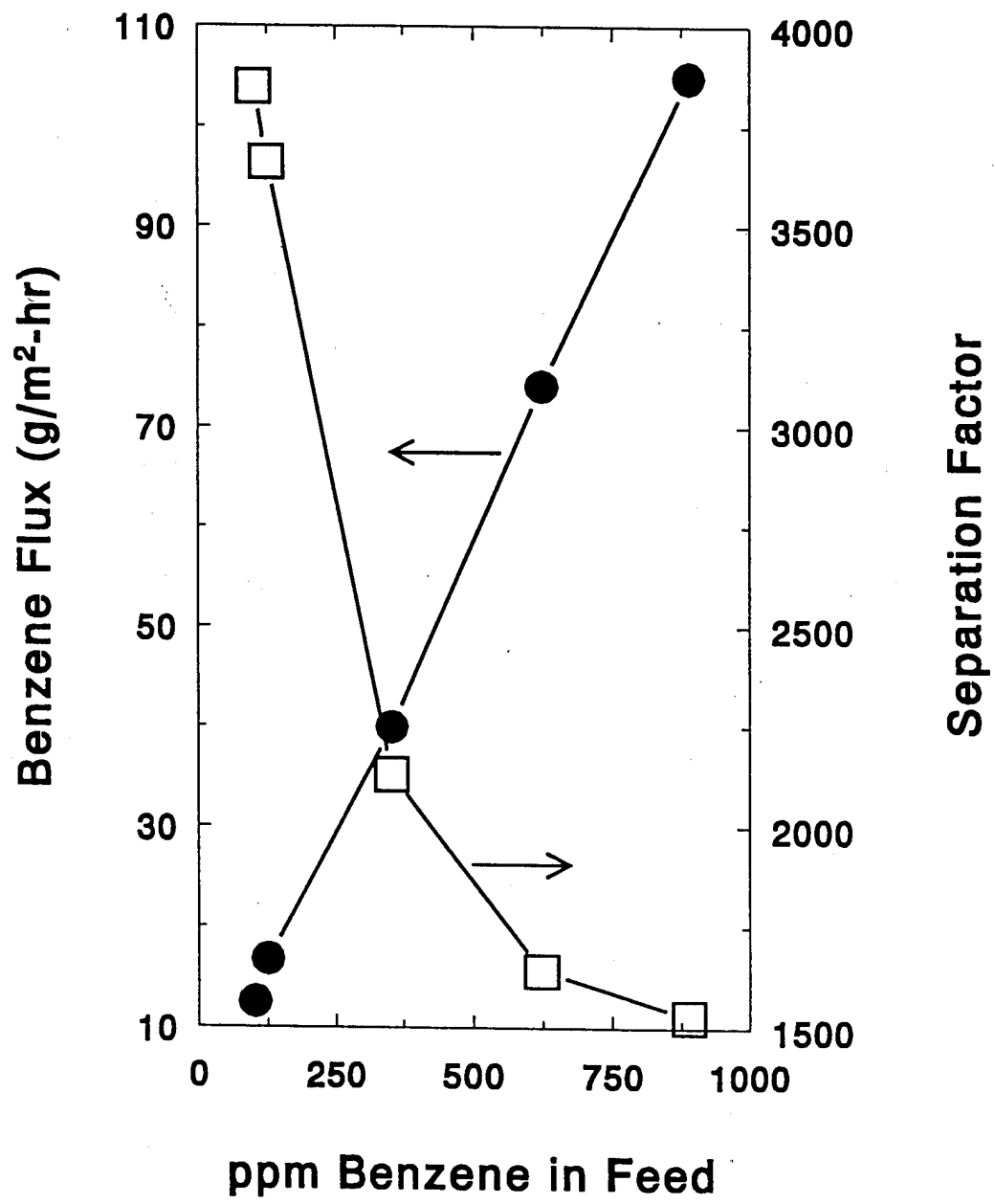
Jian and Pintauro
Figure 3b



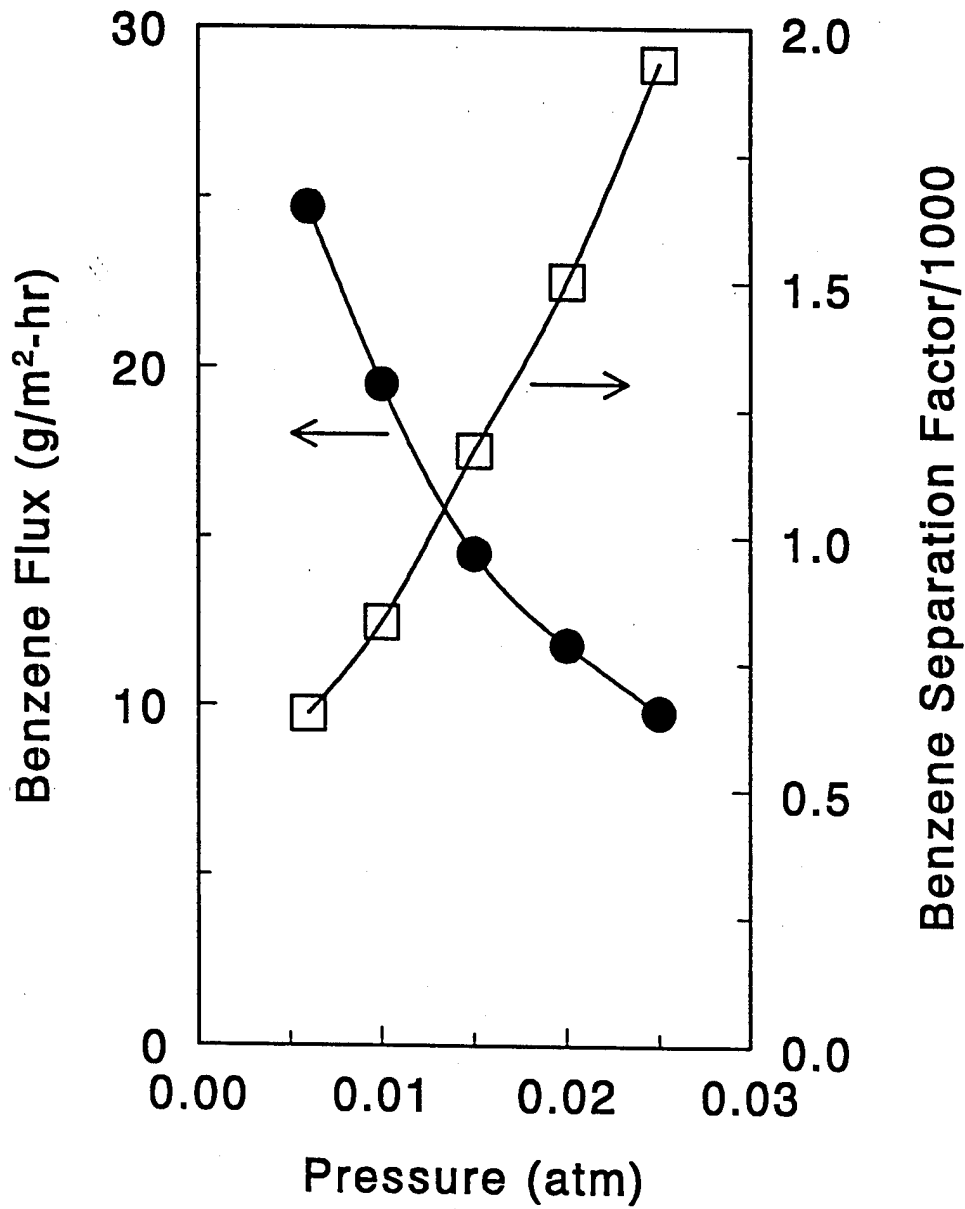
Jian and Pintauro
Figure 4



Jian and Pintauro
Figure 5

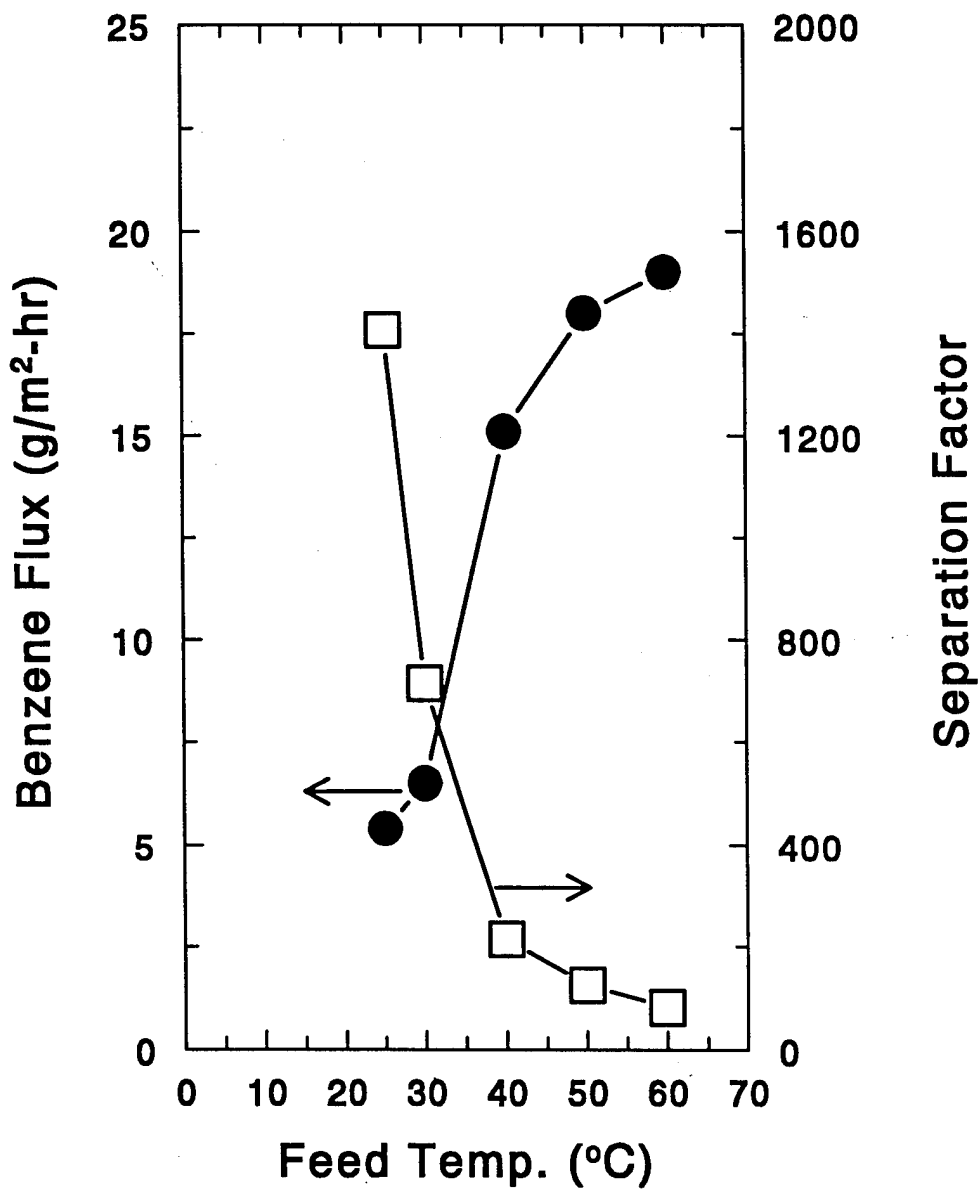


Jian and Pintauro
Figure 6

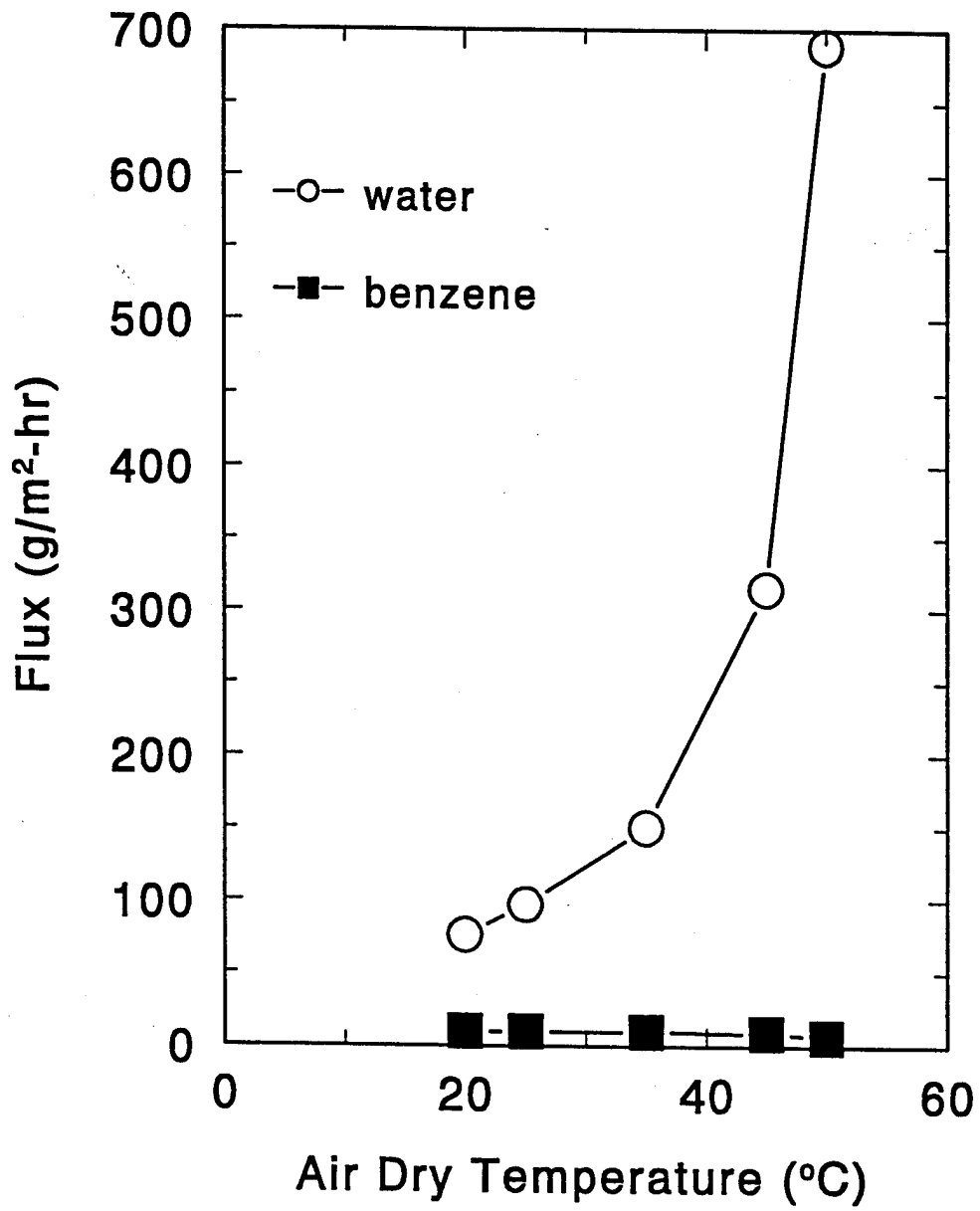


Jian and Pintauro

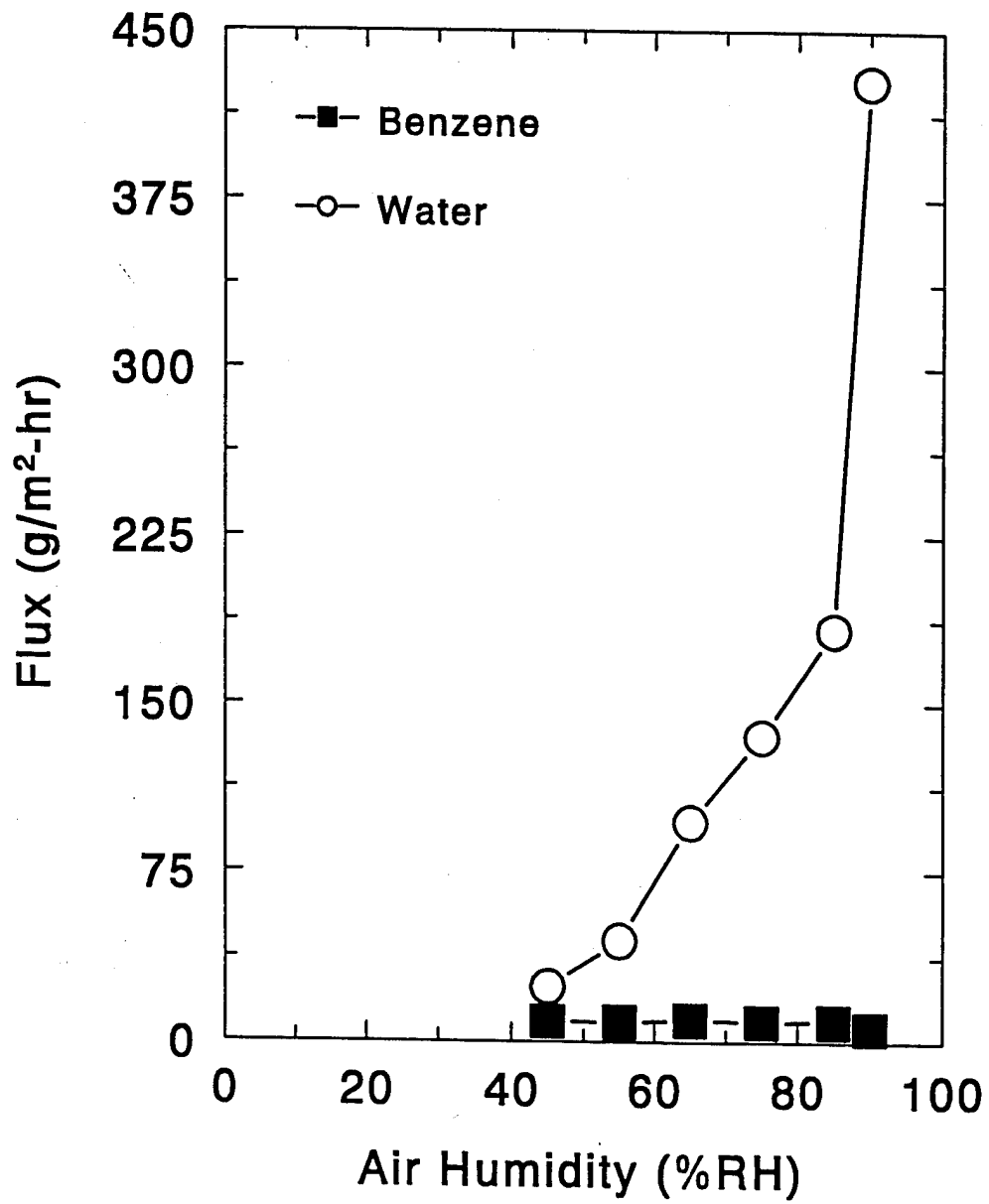
Figure 7



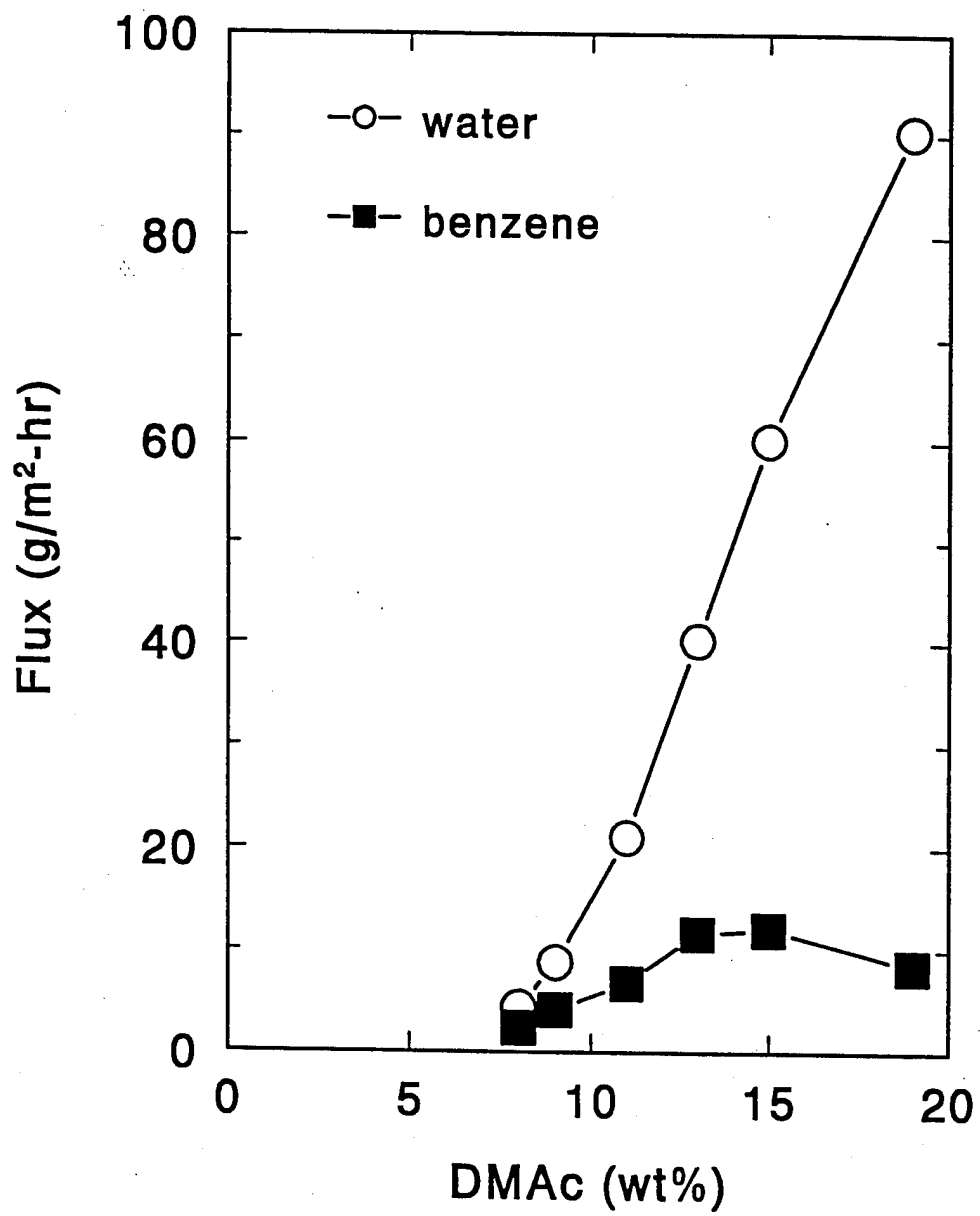
Tian and Pintauro
Figure 8



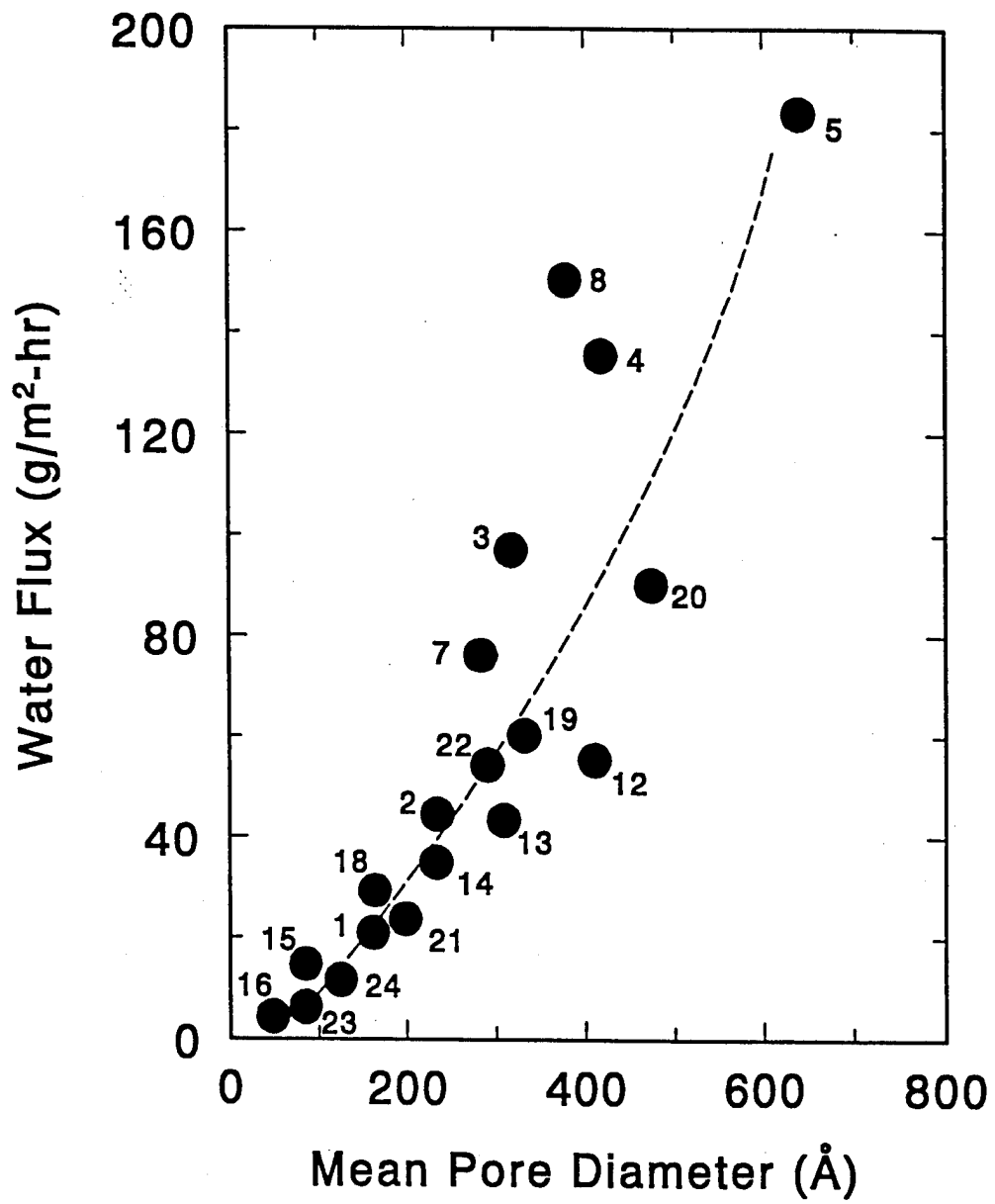
Jian and Pintau
Figure 9



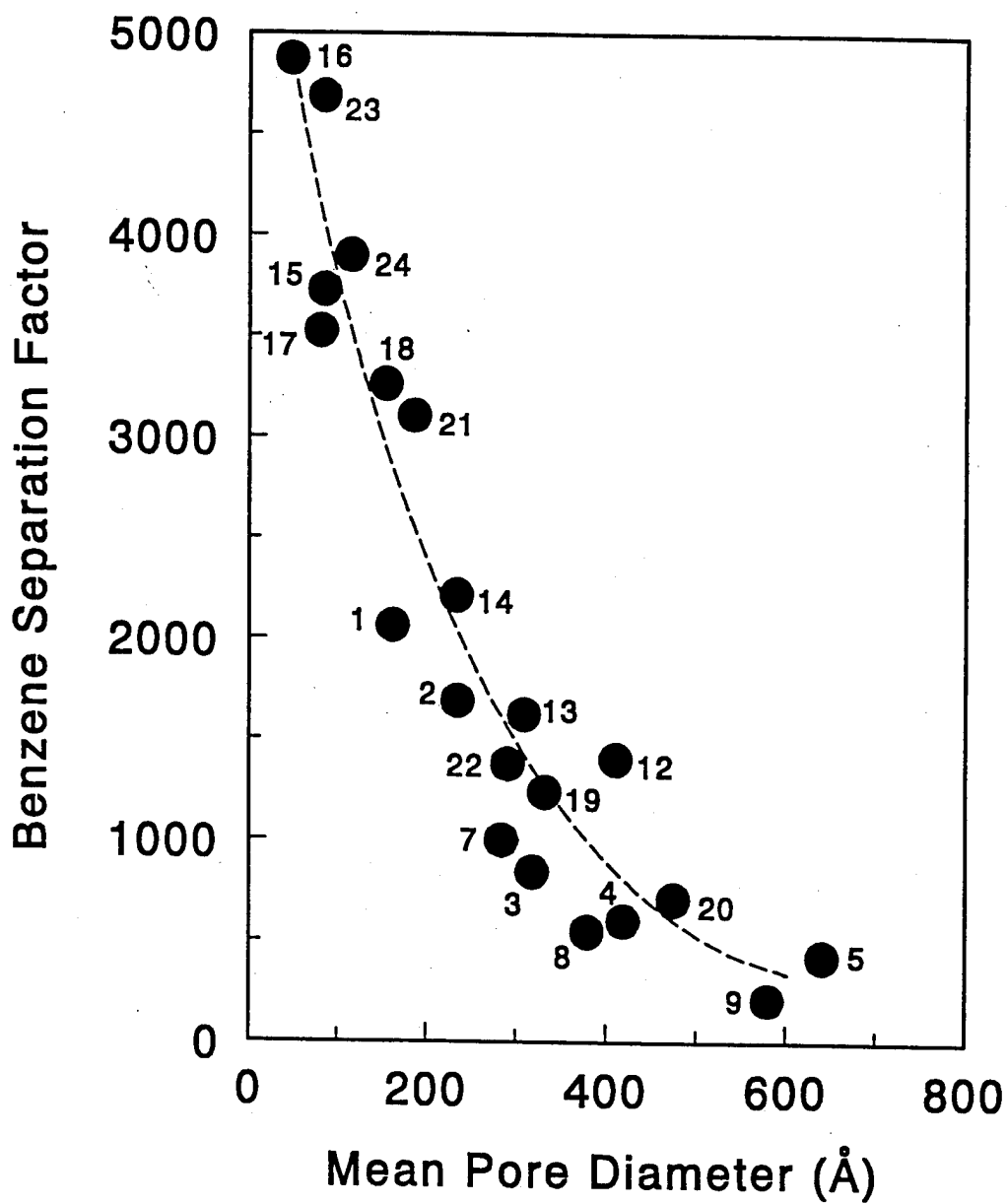
Jian and Pintau
Figure 10



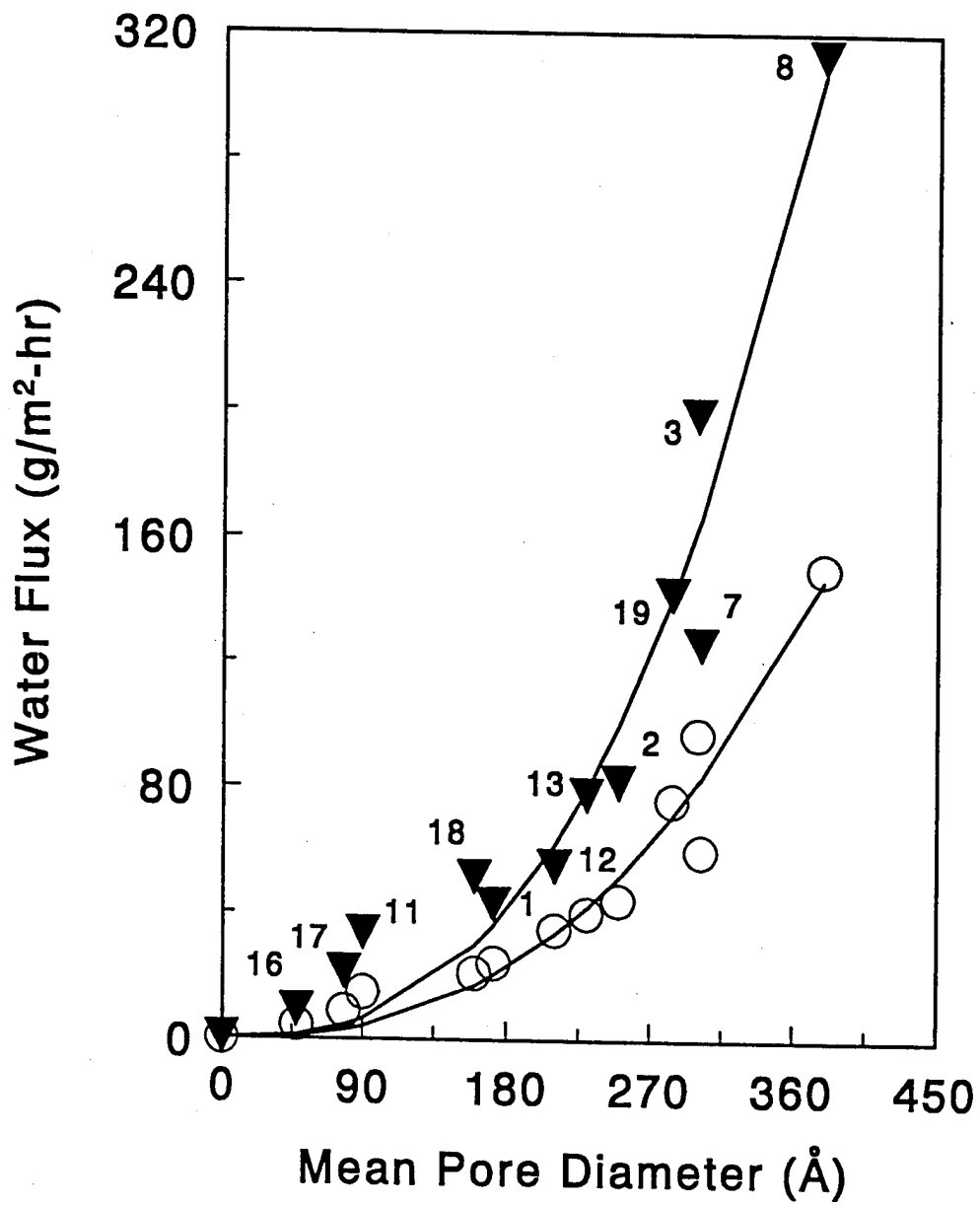
Jian and Pintaur
Figure 11



Jian and Pintauro
Figure 12



Jian and Pintauro
Figure 13



Jian and Pintauro
Figure 14