# Selective Permeation through Hydrophobic–Hydrophilic Membranes

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## Synopsis

Hydrophobic–hydrophilic composite membranes, containing polystyrene as the dispersed phase and polyacrylamide as the continuous phase, have been prepared by the concentrated emulsion polymerization method. They are highly absorptive for methyl chloride, benzene, and toluene, but poorly absorptive for cyclohexane. The absorption from toluene–cyclohexane mixtures was found to increase with increasing temperature and toluene concentration and to decrease with increasing fraction of polyacrylamide in the composite. The absorption is controlled by diffusion. The permeation rate through the membrane, which was determined by the pervaporation method, exhibits similar trends with respect to temperature, concentration, and fraction of polyacrylamide as absorption does. Higher permeation was obtained by increasing the temperature and by increasing the toluene concentration or by decreasing the fraction of polyacrylamide. The selectivity which was in the range of 4–8 varies inversely with the permeation rate through the membrane which was in the range of $2 \times 10^3$–$1.0 \times 10^4$ g/m$^2$ h.

## INTRODUCTION

Selective permeation through polymeric membranes has been used for the separation of azeotropic mixtures, of aromatic and aliphatic hydrocarbons and of close boiling liquids.[1-5] The permeation process consists of selective dissolution (sorption) of the components of the liquid into membrane, their transport by molecular diffusion through it, and evaporation at the membrane surface.[3,6] Of course, the rate of permeation depends on the concentration of the permeant, as well as on the structure and composition of the membrane.[7,8]

A highly soluble polymer can be prevented from being dissolved by its entanglement in a composite (or a blend) with another polymer.[9,10] This allows for a significant swelling of the composite. Membranes prepared from such materials can be employed for selective permeation.

A hydrophobic–hydrophilic composite of polystyrene and polyacrylamide was recently synthesized[11] by the concentrated emulsion polymerization method.[12,13] In this composite, polyacrylamide is in the form of a network of thin films which separate polyhedral cells of polystyrene. Such membranes are expected to be highly permeable to aromatic hydrocarbons and impermeable to aliphatic, since polystyrene is soluble in the former compounds and insoluble in the latter. The separation capabilities of this new type of membranes are investigated in the present paper.

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## EXPERIMENTAL

The materials used as well as the preparation of the concentrated emulsion (gel) were described in a previous paper.[11] Since some of the conditions have been slightly modified, we provide details regarding the preparation of the gel.

### Preparation of the Concentrated Emulsion

A small amount of aqueous solution of acrylamide containing sodium dodecylsulfate (SDS) was placed in a three-neck flash (250 mL capacity) equipped with a mechanical stirrer and an addition funnel. Styrene containing AlBN was placed in the addition funnel. A potassium persulfate solution in water was added to the aqueous solution of acrylamide present in the flask. The preparation of the concentrated emulsion was carried out by dropwise addition of styrene containing AlBN to the stirred aqueous solution containing acrylamide, surfactant, and potassium persulfate. Two sets of amounts of the components involved are listed in Table I.

### Preparation of the Membrane

Two glass plates (10 × 15 cm) were cleaned with detergent and dried at 140°C for 4 h. A small amount of glycerol was placed on the surfaces of the glass plates as lubricant. The concentrated emulsion was set between the two glass plates and squeezed slowly to avoid trapping of air bubbles in the membrane. For polymerization to occur, the glass plates containing the gel between them were placed in a temperature controlled oven at 50°C for 24 h. The membranes were kept at room temperature for 3 days for drying purposes.

TABLE I
Amounts of Components Used in the Preparation of the Polymer Composite

PC1
    The dispersed phase
      Styrene 27 g
      Initiator (AIBN) $2.0 \times 10^{-4}$ g/g styrene
    The continuous phase
      Acrylamide 0.5 g
      Water 4 mL
      Initiator (sodium persulfate) $1.7 \times 10^{-4}$ g/g acrylamide
      Surfactant (SDS) 0.3 g
PC2
    The dispersed phase
      Styrene 27 g
      Initiator (AlBN) $2.0 \times 10^{-4}$ g/g styrene
    The continuous phase
      Acrylamide 0.75 g
      Water 4 mL
      Initiator (sodium persulfate) $2.0 \times 10^{-4}$ g/g acrylamide
      Surfactant (SDS) 0.3 g

## Swelling Experiments

Membrane strips ($\sim$ 600 $\mu$m thick and $\sim$ 1.0 g in weight), which were dried at room temperature for 3 days, were immersed in various liquids for various lengths of time and their weight was measured with a Mettler balance. The weights of the membranes remained constant after 4 days. The latter values represent, therefore, the maximum solubilities.

## Absorption Experiments

In order to understand the kinetics of absorption, membrane strips ($\sim$ 600 $\mu$m thick and $\sim$ 0.2 g in weight), which were dried in air for 3 days, were immersed in various liquids at various temperatures. After various relatively short times, the increase in weight due to absorption was determined with a Mettler balance.

## Pervaporation Experiments

After the membranes have been soaked for 30 min in various liquids or their mixtures, they were inserted into the pervaporation cell sketched in Figure 1, where they are supported on a sintered-glass disk. About 300 mL of solution were placed in the upstream compartment, and the downstream compartment was evacuated to 3 $\pm$ 0.5 torr. A band heater and a mechanical stirrer were used to control the temperature of the liquid in the upstream compartment. The permeate was collected in cold traps which were immersed in a cold bath (below $-40°C$).

## Analysis of the Permeate

The permeate which was trapped in the cold traps was analyzed by HPLC. A $\mu$ Bondapak $C_{18}$ column was used for this purpose and a methanol/water (50/50 vol %) mixture was employed as the mobile phase. Benzene was used as the internal standard for the determination of the absolute amounts of permeated toluene and cyclohexane. The wavelength of the detector was 270
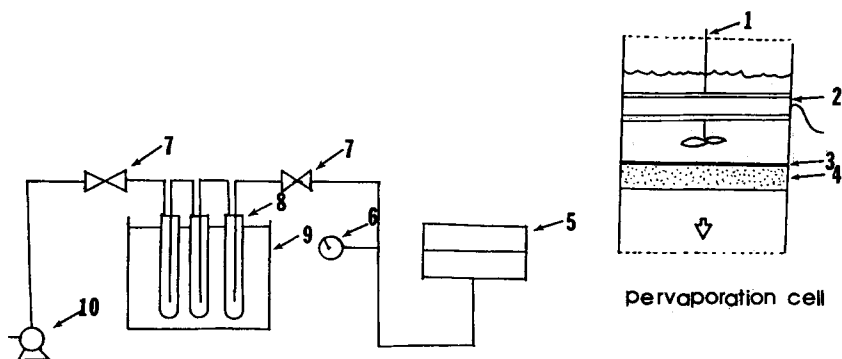


Fig. 1. Sketch of the pervaporation apparatus: (1) mechanical stirrer; (2) band heater; (3) membrane; (4) porous glass supporter; (5) pervaporation cell; (6) pressure gauge; (7) stopcock; (8) cold trap; (9) cooling bath; (10) vacuum pump.

nm. The selectivity $\alpha_{T,C}$ is defined by

$$\alpha_{T,C} = \frac{X_T^P X_C^F}{X_T^F X_C^P}$$

where $X_T^F$, $X_T^P$, $X_C^F$, and $X_C^P$ denote the weight fractions of the components T and C in the feed and permeate, respectively.

## RESULTS AND DISCUSSION

### Absorption Experiments

Methylene chloride, benzene, toluene, and cyclohexane were used as test liquids. The hydrophobic–hydrophilic composites used to prepare the membranes are listed in Table I. As shown in Figure 2, the absorption of methylene chloride in the composites was the highest. While benzene and toluene also exhibited high absorption, the absorption of cyclohexane was relatively low.

The equilibrium absorption of toluene and cyclohexane obtained from the solubility experiment were 14.86 and 1.03 g liquid/g polymer at 30°C, respectively, in composite PC1.

Concerning the behavior of the binary mixture of toluene–cyclohexane, the absorption was larger for higher concentrations of toluene and decreased with increasing fraction of polyacrylamide in the composite. The experimental results are plotted in Figure 3.
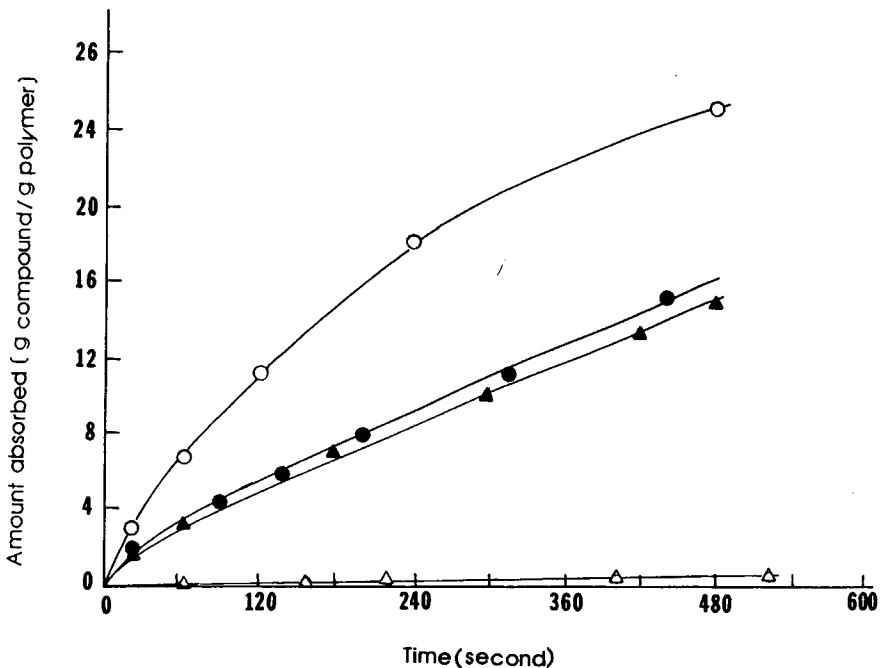


Fig. 2.  Weight absorbed per gram of polymer composite PC1 (see Table I) from liquids as a function of time at 30°C: (O, ●, ▲, △) absorption of methylene chloride, toluene, benzene, and cyclohexane, respectively.
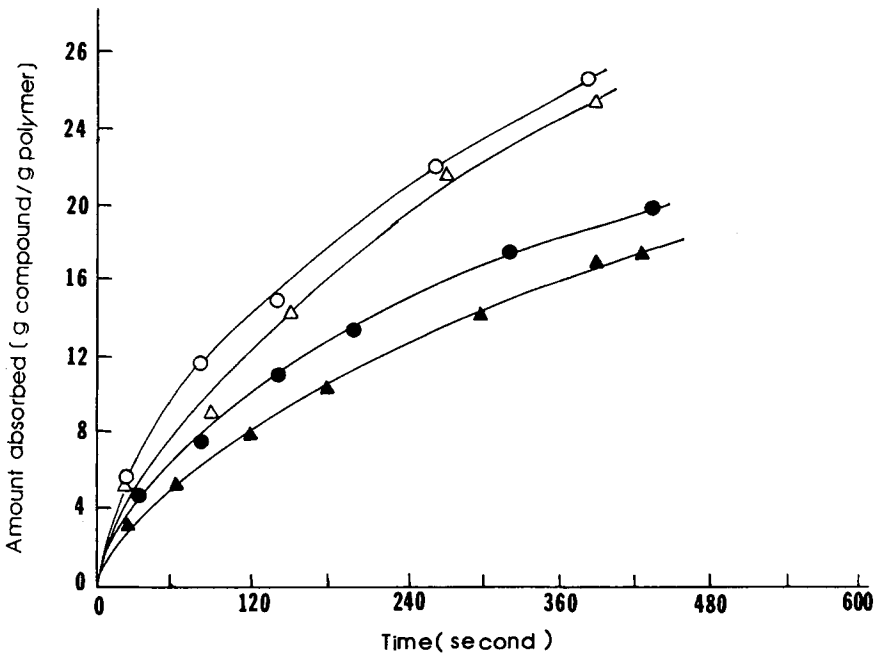
Fig. 3.   Weight absorbed per gram of polymer composite from toluene and toluene-cyclohexane mixtures (1 : 1 by weight) as a function of time at 50°C: (O, △) absorption from toluene in the polymer composite PC1 and the polymer composite PC2, respectively; (●, ▲) absorption from toluene–cyclohexane mixtures in the polymer composite PC1 and polymer composite PC2, respectively.
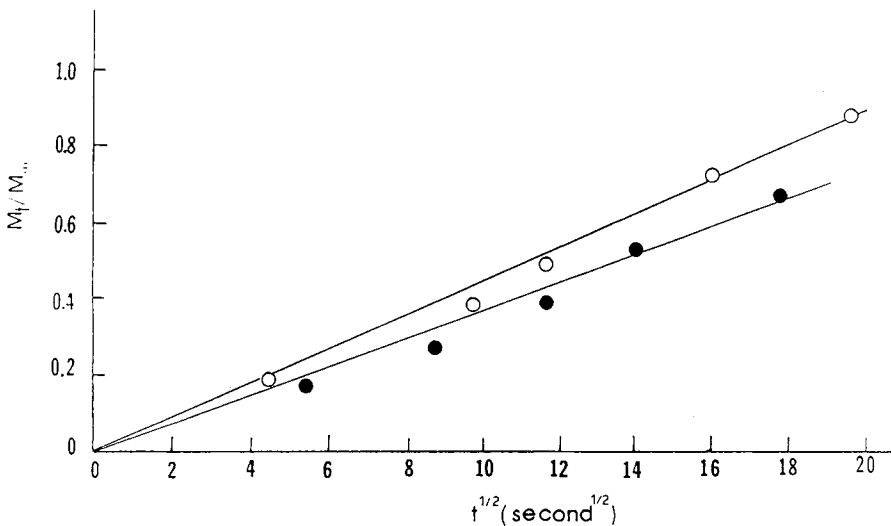


Fig. 4.   $M_t/M_\infty$ versus $t^{1/2}$ for polymer composite PC2 at 50°C: (O) absorption from toluene; (●) absorption from toluene–cyclohexane mixtures (1:1 by weight).
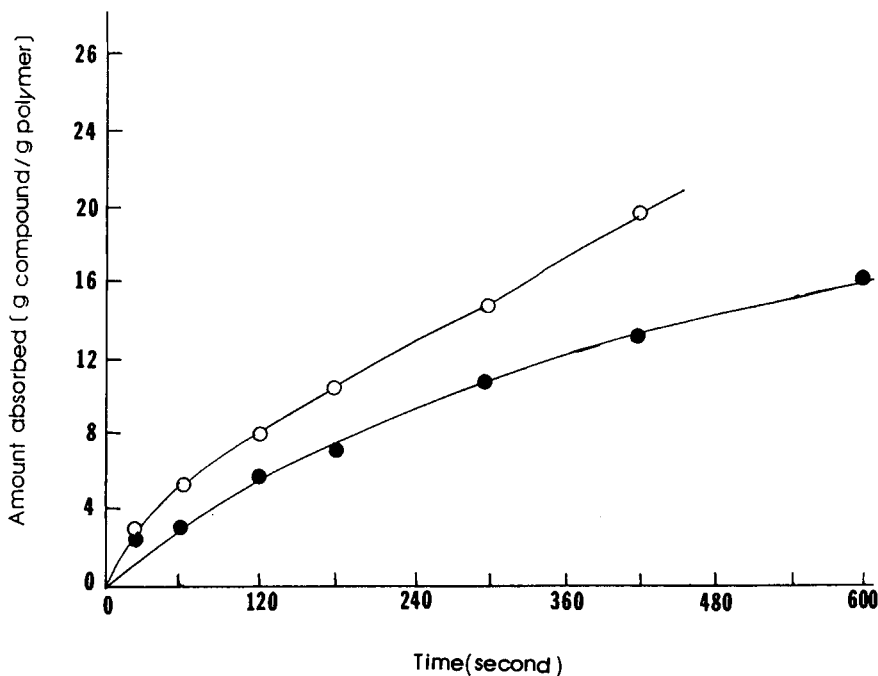
Fig. 5. Weight absorbed per gram of polymer composite PC2 from toluene–cyclohexane mixtures (1:1 by weight) as a function of time: (O) absorption at 50°C; (●) absorption at 30°C.

As shown in Figure 4, a plot of $M_t/M_\infty$ versus $t^{1/2}$ yields a straight line. $M_t$ and $M_\infty$ are the weight of penetrant at time $t$ and at equilibrium, respectively. It is, therefore, clear that the rate of absorption is controlled by the diffusion in the composite. Figure 5 shows that the amount absorbed increases with temperature.

## Permeation Experiments

The permeation of a toluene–cyclohexane mixture through hydrophobic–hydrophilic polymer composites was investigated in the temperature range of 30–70°C. In agreement with the absorption experiments, it was found that the permeation rate increases with temperature and decreases with increasing polyacrylamide fraction in the composite. An Arrhenius type temperature dependence of the permeation rate is evidenced in Figure 6.

The effect of composition of the toluene–cyclohexane mixture on the permeation rate of the liquid at 70°C is examined in Figure 7. The permeation rate increases with the toluene concentration in the feed. The permeation rate of the mixture varied from $2.0 \times 10^3$ to $1.3 \times 10^4$ g/m² h depending upon the concentration of toluene in the feed. The permeation of the pure cyclohexane was 140 g/m² h.

The selectivity $\alpha_{T,C}$ of the membrane depends on the concentration and temperature of the feed solution as well as on the fraction of polyacrylamide in the membrane. The selectivities achieved in these experiments were in the range of 4.75–8.10 (Fig. 8). The selectivity of the membrane decreases with
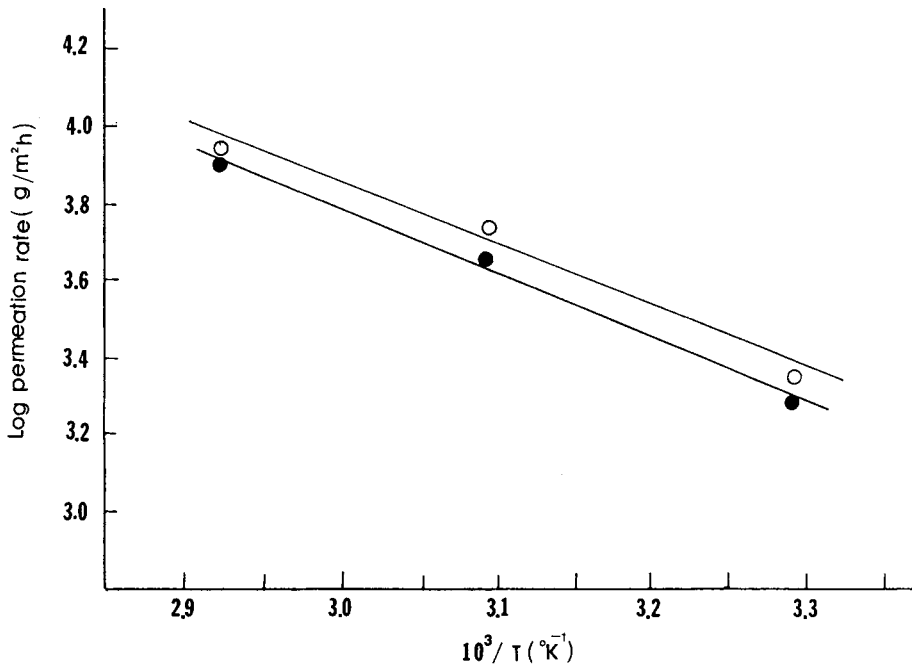
Fig. 6. Log (permeation rate) as a function of $10^3/T$: (O, ●) permeation of toluene–cyclohexane mixture (75:25 by weight) by the pervaporation method through PC1 and PC2, respectively.
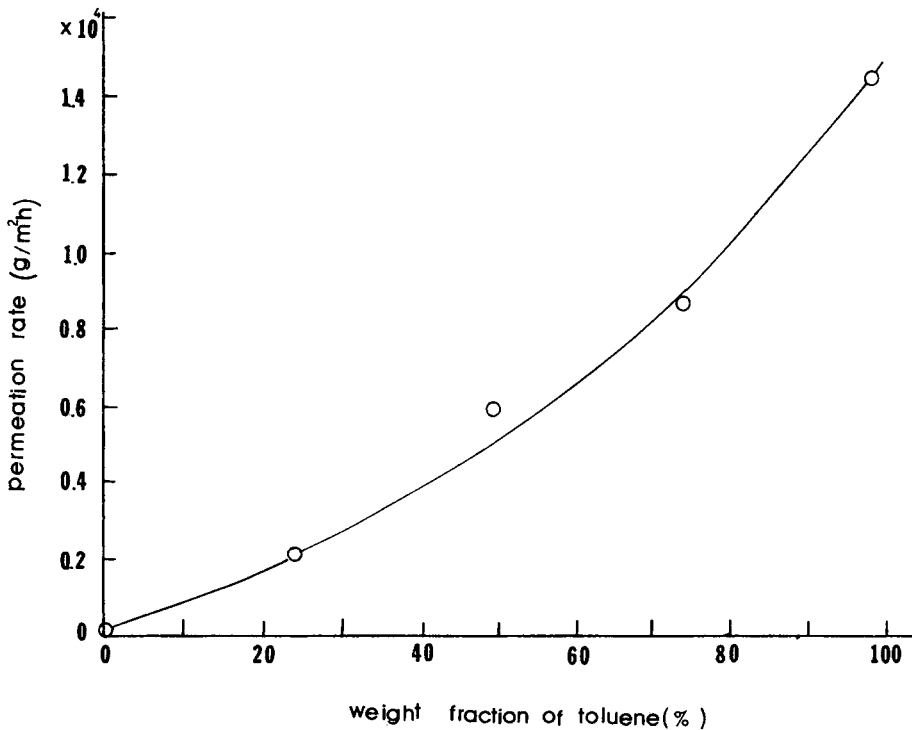


Fig. 7. Permeation rate through PC1 as a function of concentration of toluene.
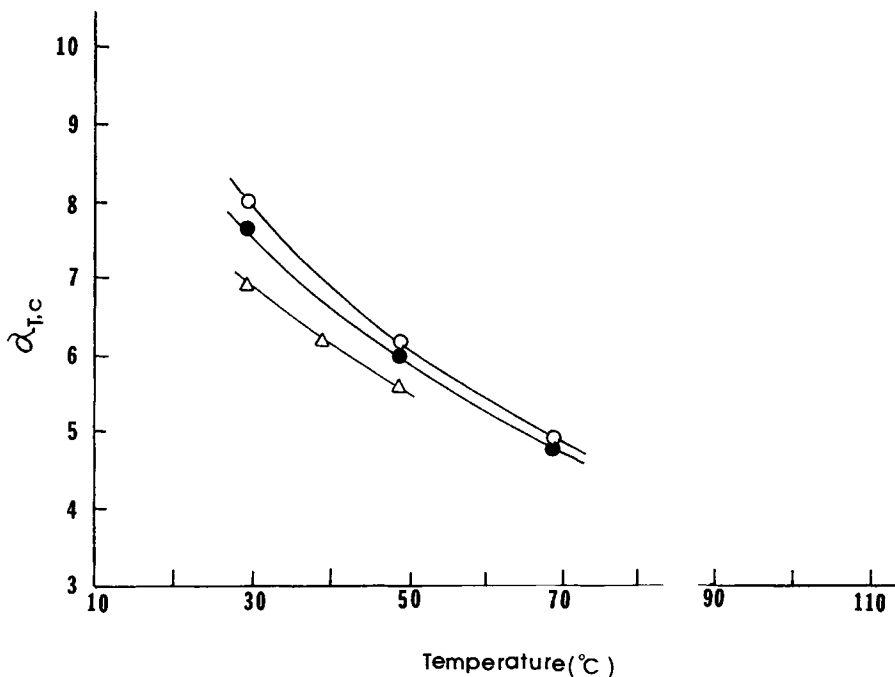
Fig. 8. Selectivity for toluene from toluene–cyclohexane mixtures as a function of tempera-ture: (O, ●) selectivities obtained from toluene–cyclohexane mixture (75 : 25 by weight) through PC1 and PC2, respectively; (△) selectivity obtained for toluene–cyclohexane mixture (1 : 1 by weight) through PC2.

temperature, and increases with decreasing fraction of polyacrylamide in the membrane. Higher selectivities occur for higher concentrations of toluene in the feed solution.

Huang and Lin[3] reported selectivities and permeation rates through polyethylene membranes of the order of 2, while Cabasso et al.[5] reported selectivities and permeation rates through a polymer blend of polyphospho-nates and acetyl cellulose of the order of 12 and 125 $g/m^2$ h, respectively. A comparison of the present results with those previously reported shows that the selectivity is somewhat lower and the permeation rate much higher, by about 2 orders of magnitude, than those reported by Cabasso et al.[5]

## CONCLUSION

The concentrated emulsion polymerization method[11–13] was employed to prepare thin membranes (about 600 $\mu$m thick) which show selectivity in the absorption and permeation of a mixture of toluene and cyclohexane. Sorption experiments as well as permeation experiments by the pervaporation method have been carried out. Higher selectivity was achieved by lowering the temperature and by increasing the fraction of polyacrylamide in the mem-brane. This was, however, associated with a decrease in the permeation rate.

The relatively high selectivities and particularly the high permeation rates of the hydrophobic–hydrophilic composite membrane compared to other

types of membranes may lead to useful applications in the separation of azeotropic and closely boiling liquids.

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