

# Effects of Polymer Solvents on the Performance of Cellulose Acetate Membranes in Methanol/Methyl Tertiary Butyl Ether Separation

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**ABSTRACT:** The performances of cellulose acetate membranes prepared with casting solutions, with acetone, dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP) as solvents, were studied in a series of methanol/methyl tertiary butyl ether separation experiments. The flux and selectivity of the membrane samples were affected by the type of solvent used to prepare the casting solution. The sample with DMF consistently gave the highest selectivity and lowest flux, followed by the samples with NMP and acetone. The differences in the performances were attributed to the effects of the volatility and evaporation rates of the solvents. Scanning electron microscopy and atomic force microscopy techniques were used for comparing the morphologies of the membranes. In addition, we used Raman spectroscopy as a novel technique to study the sorption selectivities of the membrane samples prepared with the three different solvents. In a parallel study, the relation between the polymer concentration in the casting solution and the morphology and performance of the membrane samples was studied. Under similar preparation conditions, the morphology of the membrane changed from being porous to being dense when the membrane was prepared with casting solutions with increasing polymer concentration. Also, the selectivity increased and the permeability decreased with increasing polymer concentration in the casting solution. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2882–2895, 2001

**Key words:** methanol/methyl tertiary butyl ether (MTBE); cellulose acetate membranes; pervaporation; organic/organic separation; Raman spectroscopy; atomic force microscopy (AFM)

## INTRODUCTION

Methyl tertiary butyl ether (MTBE) is an octane enhancer used as a replacement for lead and lead compounds in car fuel. It has been shown that an addition of 10–15% MTBE to gasoline increases the motor octane number by 2–5.<sup>1</sup> Also, because

the presence of MTBE facilitates a more complete combustion, a reduction in air pollution results.

MTBE is produced by a catalytic reaction of methanol (MeOH) and isobutene (iC<sub>4</sub>) at moderate temperatures and pressures. The high selectivity of the catalyst allows a nearly complete conversion of iC<sub>4</sub>. The stoichiometric ratio of MeOH to iC<sub>4</sub> varies from below unity to above unity for different conversion rates and MTBE purities.<sup>1</sup> The chemical reaction leading to the formation of MTBE is as follows:



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**Table I Physical Properties of MeOH and MTBE**

Property	MeOH	MTBE
Chemical formula	CH <sub>3</sub> OH	(CH <sub>3</sub> ) <sub>3</sub> COCH <sub>3</sub>
Molecular weight	32.04	88.15
Boiling point (°C)	65.5	55–56
Freezing point (°C)	–98	–109
Density at 20°C (g/cm <sup>3</sup> )	0.791	0.740

The reaction product contains a mixture of MTBE, MeOH, unreacted C<sub>4</sub>'s, and small amounts of byproducts, including tertiary butyl alcohol and iC<sub>4</sub> diamer. The presence of MeOH and C<sub>4</sub>'s reduces the octane number expected from MTBE. Therefore, the removal of these compounds is essential for MTBE. However, the byproducts do not need to be removed because of their small concentrations and favorite octane number. The physical properties of MeOH and MTBE are shown in Table I.<sup>2,3</sup>

The separation problem arises because MeOH forms azeotropic mixtures with both MTBE and iC<sub>4</sub>. Therefore, conventional processes such as distillation become costly and cumbersome. However, pervaporation (PV) offers a cost-effective alternative to the traditional MTBE separation techniques. In a PV process, the MeOH/MTBE mixture is passed over an MeOH selective membrane module. MeOH preferably permeates through the membrane and is collected downstream. The retentate is then concentrated in MTBE.

A PV process can be used for MeOH/MTBE separation by itself or in combination with conventional techniques. In the latter scheme, an azeotropic mixture from a distillation column is fed into the PV system. The bulk of MeOH is removed and recycled to the reactor, and the MeOH lean stream is returned to the distillation tower for further MTBE recovery. This arrangement reduces the overall size of the separation stage by eliminating the secondary processes required to treat the azeotrope, thereby saving capital and operating costs of the process.

The number of membranes suitable for MeOH/MTBE separation is limited by their chemical resistance to the feed components. Some membranes have been successfully tested for the aforementioned separation, and a few of them are commercially available.

Farnand and Noh<sup>4</sup> screened a series of membranes for the removal of MeOH from MTBE and

tertiary amyl methyl ether. According to their investigations, Nafion and a cellulose-based membrane showed promising results with selectivities of up to 35 and 63 and maximum fluxes of 490 and 102 mL/m<sup>2</sup>h for Nafion and the cellulosic membrane, respectively. Farnand and Noh also concluded that flux increased and selectivity decreased as the MeOH content of the feed increased.

Park and coworkers<sup>5,6</sup> tested blends of poly(acrylic acid) and poly(vinyl alcohol) for the separation of MeOH and ethanol from toluene and MTBE. Selectivities of up to 300 and fluxes of up to 0.700 kg/m<sup>2</sup>h were obtained in their experiments.

Chen et al.<sup>7</sup> (Air Products) reported results from modified Separex cellulose acetate (CA) membranes with the patented TRIM process. They observed selectivities between 6 and 25 for MeOH/MTBE separation.

Because of its availability, favorable characteristics, and ease of manufacturing, CA membrane could be a favored candidate for this separation. However, the commercialization of CA membranes for the PV of MeOH/MTBE is facing major challenges, such as chemical resistance and morphological deterioration. In this study, the effects of two parameters were investigated on the morphology and performance of CA membranes. One was the boiling point of the casting solvents, and the other was the concentration of the polymer in the casting solution. It was speculated that the rate of evaporation of the casting solvent, as a function of the boiling point, governed the morphology and performance of the membrane. In addition, the dependence of the membrane morphology and performance on the concentration of the polymer in the casting solutions was investigated.

## EXPERIMENTAL

We used three solvents in this study to prepare the casting solutions: acetone, dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP). The physical properties of these solvents are listed in Table II. Acetone has the lowest boiling point at 56.5°C, followed by DMF and NMP with boiling points of 153 and 202°C, respectively. The CA membrane samples prepared with these solvents are abbreviated as CA-acetone, CA-DMF, and CA-NMP. The solvents and polymer were purchased from Aldrich Canada (Oakville, Ontar-

**Table II Physical Properties of Acetone, DMF, and NMP Solvents**

Properties	Acetone	DMF	NMP
Chemical formula	$(\text{CH}_3)_2\text{CO}$	$\text{HCON}(\text{CH}_3)_2$	$\text{C}_4\text{H}_8\text{—N—CH}_3$
Molecular weight	58.08	73.10	85.15
Boiling point (°C)	56	153	80–81
Freezing point (°C)	−94	−61	−61
Density at 20°C (g/cm <sup>3</sup> )	0.791	0.944	0.819

io). The CA polymer had a molecular weight of 37,000 with a 39.8% degree of acetylation.

We prepared the casting solutions by dissolving CA polymer in the solvents. To study the effect of the solvents, we prepared 3.3 wt % polymer mixtures. The membrane samples were prepared by 7 g of the solution being poured over a mirror-polished glass plate with a circular edge. The solution was dried in three steps. First, the bulk of the solvent was removed by slow evaporation inside a fume hood at an average humidity of 30% until the membrane solidified. The evaporation temperature was 23°C for acetone and 60°C for DMF and NMP. The membrane was then transferred to an oven set at 70°C and was kept there for 8 h or more. Finally, the trace of the solvent was removed by the membrane being kept overnight in a vacuum oven set at 70°C.

The casting solutions for studying the effects of polymer concentration on the membrane morphology and performance were prepared in a similar manner. In this case, acetone was used as the solvent. Polymer solutions at 1, 3, 6, 10, 15, and 20 wt % were prepared by the dissolution of CA in acetone.

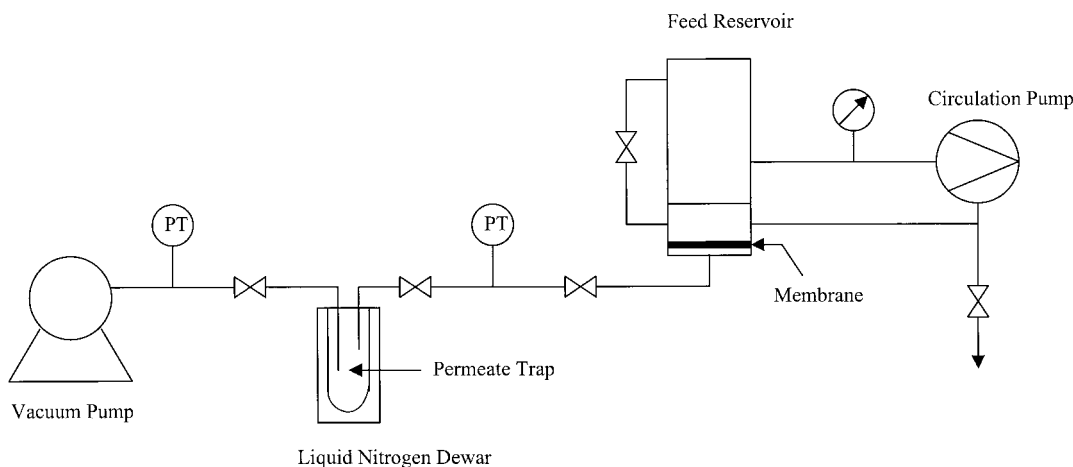
The PV system, shown schematically in Figure 1, was a CM-CELFA unit (model P-28). It con-

sisted of a separation cell, a circulation pump, a permeate trap, and a vacuum pump. The effective membrane surface area was 28 cm<sup>2</sup>. The feed was circulated over the membrane sample through meander-type channels. The permeate was collected in a trap placed in liquid nitrogen. We used a vacuum pump to evacuate the downstream to less than 1 Torr. The feed pressure was kept at 0.5 bar. To compare the performance of the laboratory-made membranes with that of a commercial membrane, we also performed a set of experiments with Nafion-117.

After the completion of each experiment, the permeate collected inside the cold trap was warmed up to room temperature. The permeate was then weighed, and its composition was determined with a Varian 3600 gas chromatograph (Toronto, Ontario, Canada). The total selectivity was calculated with the following equation:

$$\alpha = \frac{\frac{y}{1-y}}{\frac{x}{1-x}}$$

where  $x$  is the concentration of the desired component (MeOH in this study) in the feed and  $y$  is

**Figure 1** Schematic diagram of the PV setup.

**Table III Performance Comparison of CA Membranes Prepared with Acetone, DMF, and NMP as Solvents in MeOH/MTBE Separation Experiments**

Solvent	MeOH Feed wt %	MeOH Permeate wt %	Flux [kg/m <sup>2</sup> h (10 μm)]	Selectivity
Acetone	0.0	0.0	0.014	
	4.6	88.0	0.040	152
	6.0	89.5	0.040	134
	20.0	92.0	0.194	46
	50.1	94.2	0.657	16.2
	65.2	95.2	0.866	10.6
	100.0	100.0	1.491	
DMF	0.0	0.0	0.016	
	3.2	92.1	0.072	353
	4.0	93.0	0.074	319
	20.0	98.4	0.150	246
	45.5	99.1	0.237	132
	70.0	99.5	0.377	85
	100.0	100.0	0.816	
NMP	0.0	0.0	0.012	
	5.0	90.0	0.171	171
	20.3	95.0	0.341	75
	50.0	98.6	0.476	70
	70.0	99.0	0.975	42
	100.0	100.0	1.533	

the concentration of the desired component in the product.

We used scanning electron microscopy (SEM) to observe the cross sections of the new and used membrane samples. Also, atomic force microscopy (AFM) photographs were taken from the surfaces of the membranes before and after use. In addition, the actual sorption selectivity of each membrane sample was estimated with Raman spectroscopy. For this purpose, the membrane samples were swollen in 20% MeOH solution in MTBE for 1 week. Then, the samples were removed from the solution, their surfaces were wiped off, and they were immediately mounted in the spectroscopy. We calculated the relative concentration of components inside the membrane by taking the ratio of the area underneath the corresponding peaks. The actual sorption selectivity was then calculated with the equation for selectivity, as described previously.

## RESULTS AND DISCUSSIONS

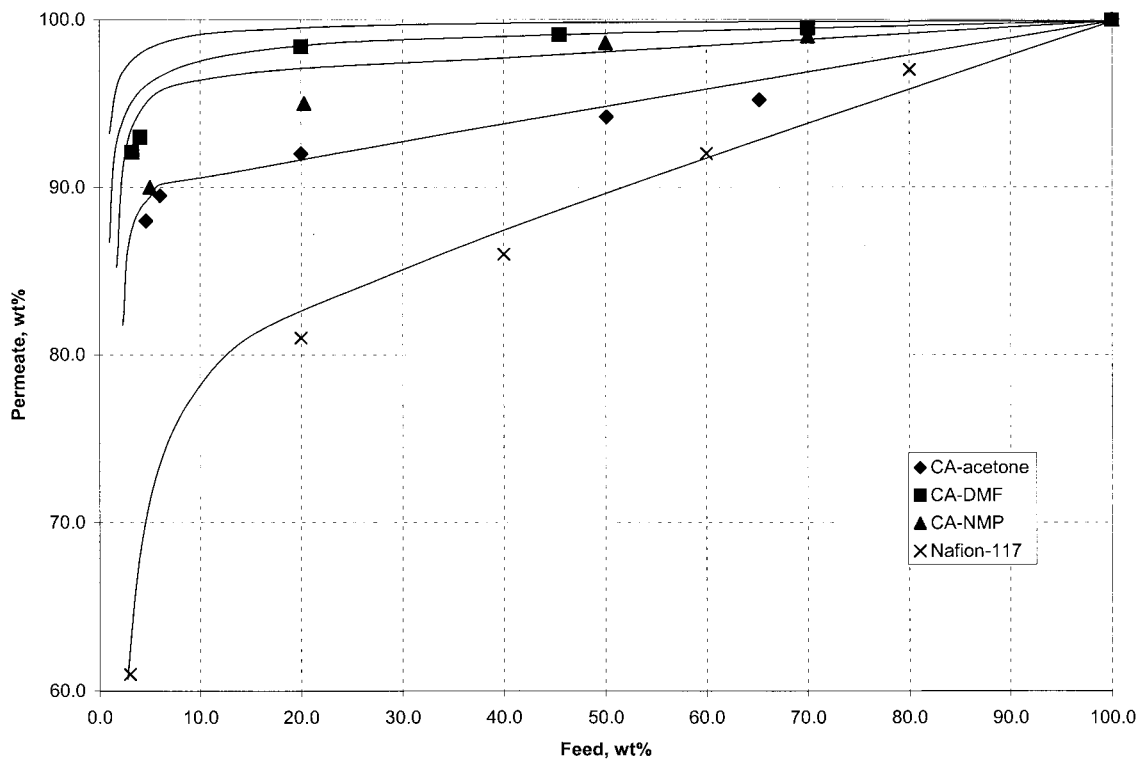
### Solvent Effect

The experimental results are shown in Table III and Figures 2–4. Figure 2 shows the concentration of MeOH in the permeate versus that in the feed for the three CA membrane samples and a

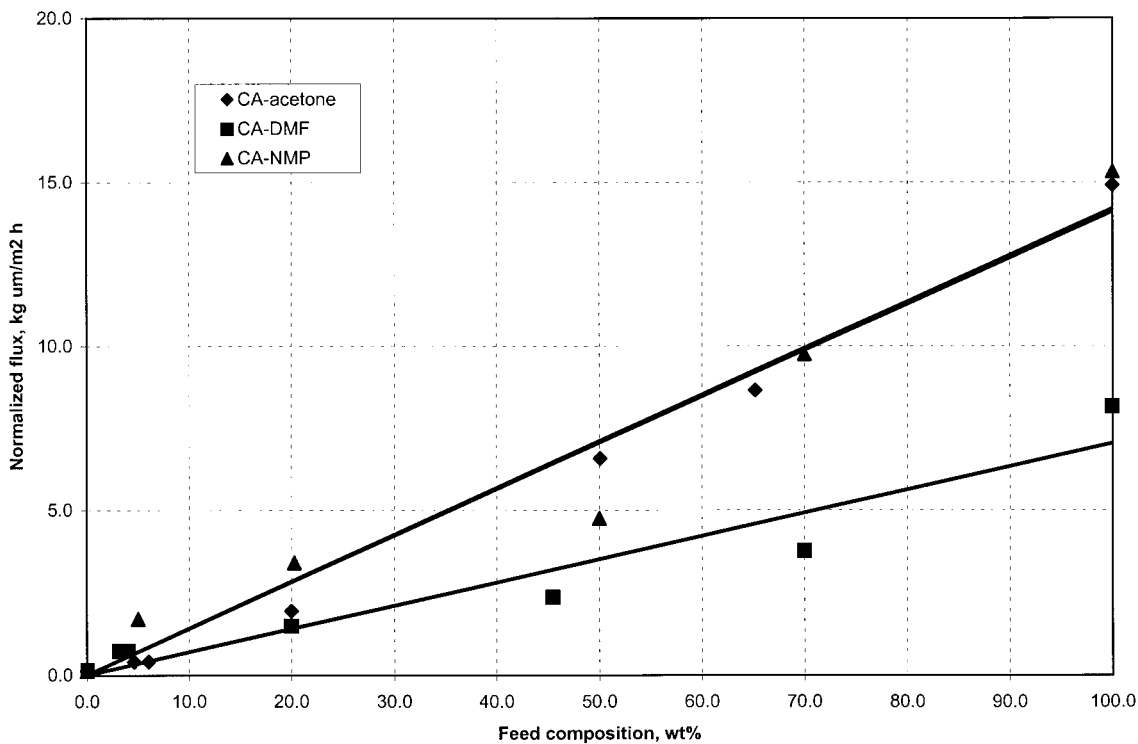
Nafion-117 membrane. All three CA samples showed high affinity toward MeOH. A comparison of the three CA samples indicated that the CA-DMF sample consistently showed a higher permeate concentration. At a low feed concentration of 3.2%, MeOH was enhanced to 92.1% through this sample. At higher feed concentrations, only small MTBE impurities were detected in the permeate. The CA-acetone and CA-NMP samples performed very similarly and followed the sample of CA-DMF.

To compare the separation characteristics of the CA membranes with a commercial membrane, we also show the performance of a Nafion-117 membrane in Figure 2. Nafion-117 has favorable characteristics toward MeOH/MTBE separation. This membrane was tested under experimental conditions similar to those used for the CA membranes. As shown in this figure, all CA membranes performed better than Nafion-117. The results shown in this figure indicate that CA is a favorable candidate for MeOH/MTBE separation from the viewpoint of selectivity.

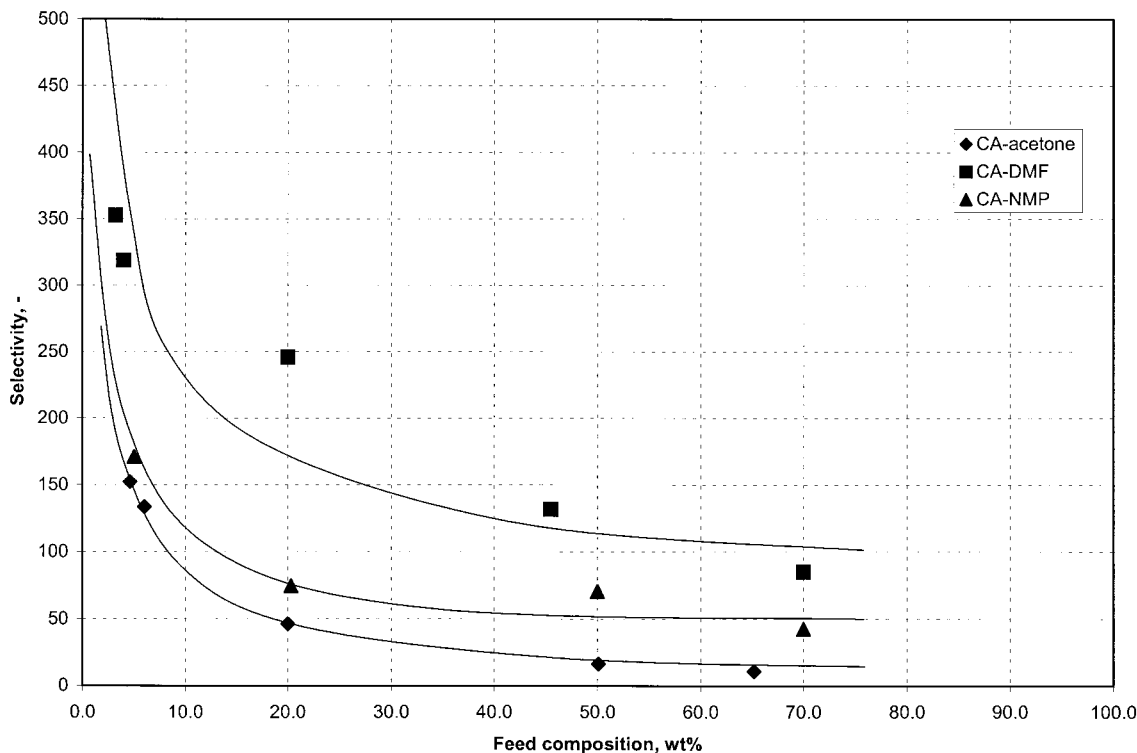
Figure 3 shows the normalized flux values. The CA-DMF sample showed the lowest flux, followed by similar fluxes of the CA-acetone and CA-NMP samples. All fluxes increased with increasing MeOH concentration in the feed. The increase was close to linearity in all three cases. Also, all



**Figure 2** Permeate composition versus feed composition: MeOH/MTBE separation with CA and Nafion-117 membranes.



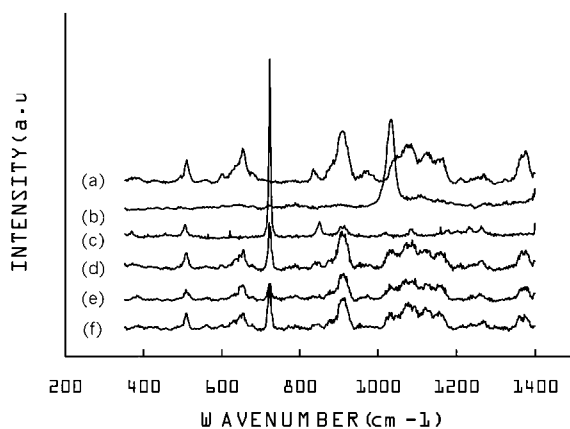
**Figure 3** Flux versus feed composition: MeOH/MTBE separation with CA membranes.



**Figure 4** Selectivity of CA membranes versus feed composition for MeOH/MTBE separation.

three samples showed a jump in the flux at 100% MeOH, which can be attributed to the severe swelling of the membrane by the feed.

The differences in the performances of the membranes are also shown in terms of selectivity



**Figure 5** Raman spectra of (a) a CA membrane, (b) pure MeOH, (c) pure MTBE, (d) a CA membrane prepared from an acetone solution swollen in 20% MeOH/MTBE, (e) a CA membrane prepared from a DMF solution swollen in 20% MeOH/MTBE, and (f) a CA membrane prepared from an NMP solution swollen in 20% MeOH/MTBE.

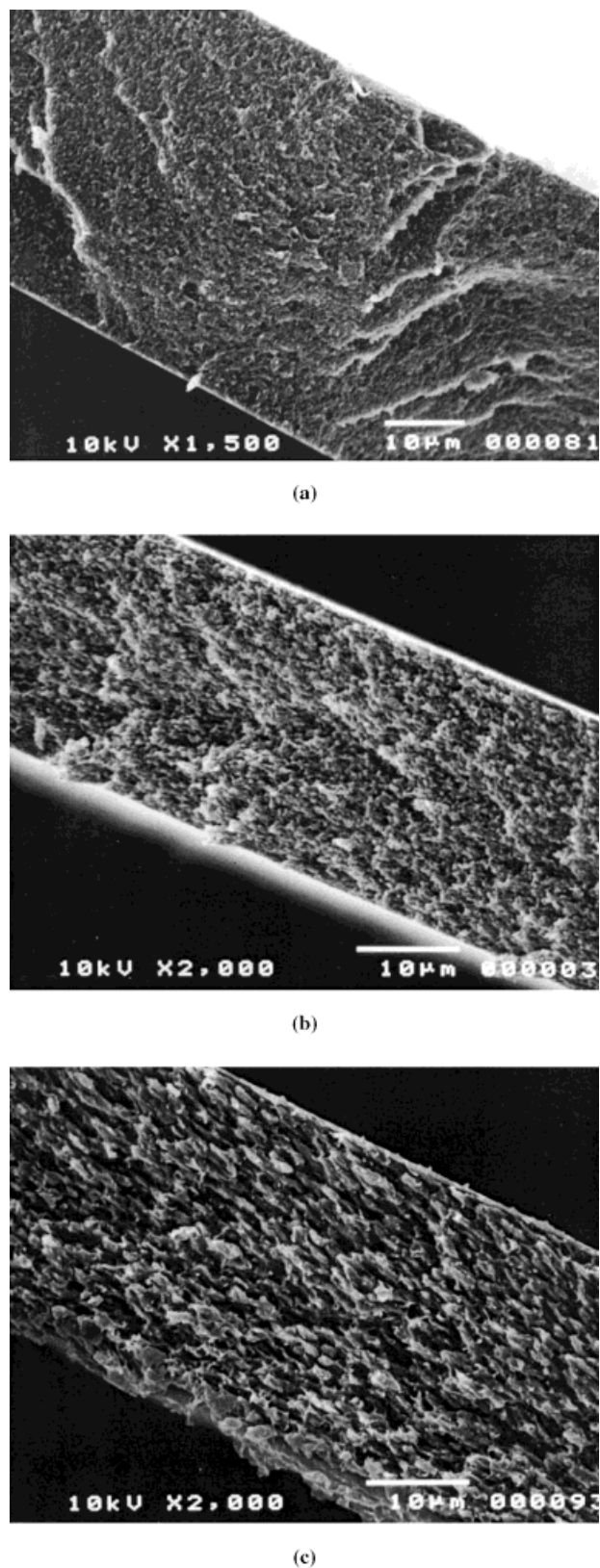
in Figure 4. All three samples showed similar trends in selectivity by having an initial sharp decline followed by passage through a plateau-type region. The CA-DMF sample was consistently more selective than the other two. The selectivity of the CA-DMF sample was 353 at a 3.2% feed concentration, and it declined and stabilized around 100. Although CA-NMP consistently showed slightly higher selectivity than acetone, the difference was not significant. The selectivities of the CA-NMP and CA-acetone samples were 171 and 152 at around a 5% feed

**Table IV** Results of Sorption Selectivity of CA Membrane Obtained with Raman Spectroscopy and the Corresponding Calculated Diffusion Selectivity

	Acetone	DMF	NMP
MeOH (%)	0.41	0.61	0.37
Total selectivity	46	246	75
Sorption selectivity	2.8	6.3	2.3
Diffusion selectivity	16.5	39.3	32.3

Data reported represent a feed mixture containing 20% MeOH in MTBE.

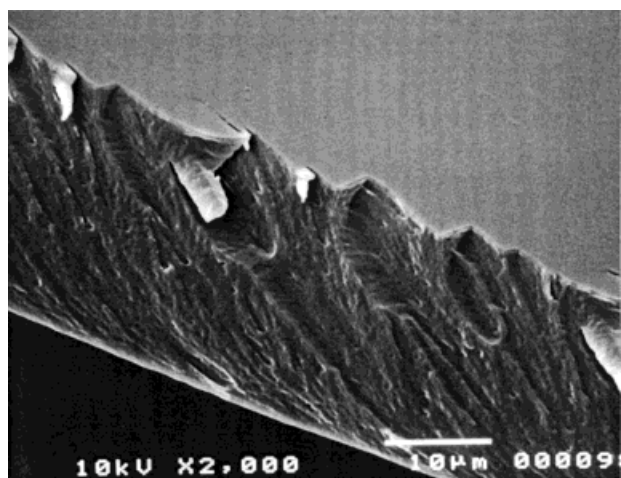




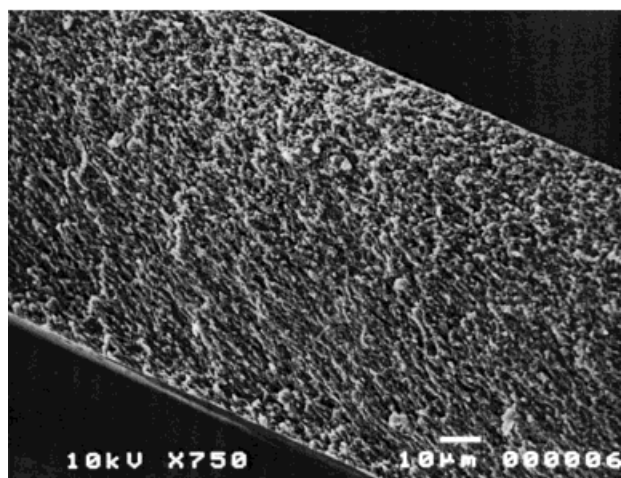
**Figure 6** SEM images of CA membranes prepared with different solvents: (a) CA-acetone, (b) CA-DMF, and (c) CA-NMP.

**Table V** Summary of the Observations from SEM and AFM: Comparison of the Morphologies of CA Membranes Prepared with Acetone, DMF, and NMP as Solvents

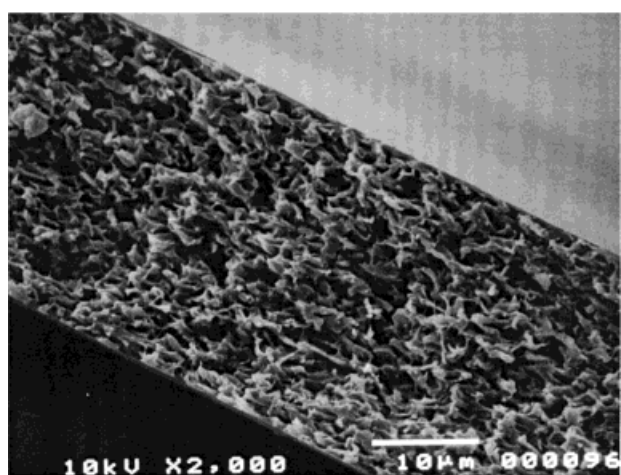
Solvent	Thickness ( $\mu\text{m}$ )		Nodule Size and Shape		Void Size and Shape		Surface Appearance	
	New	Used	New	Used	New	Used	New	Used
Acetone	65	40	0.5–2 $\mu\text{m}$ , sphere	Dense	0.2–0.4 $\mu\text{m}$ , sphere	0.1–0.2 $\mu\text{m}$ , sphere	Smooth, no nodules, no pinholes or valleys	Very rough, nodules, cracks, pinholes
DMF	25	23	1 $\mu\text{m}$ , irregular	1 $\mu\text{m}$ , irregular	1–2 $\mu\text{m}$ , irregular	1.5 $\mu\text{m}$ , irregular	Smooth, no nodules, no pinholes or valleys	Slightly rough, no nodules, no pinholes or valleys
NMP	32	28	1 $\times$ 2–4 $\mu\text{m}$ , fish	1 $\times$ 1–2 $\mu\text{m}$ , fish	1 $\times$ 2–3 $\mu\text{m}$ , fish	1 $\times$ 1–2 $\mu\text{m}$ , fish	Rough, very thin, some pinholes and valleys	Smooth, no nodules, some pinholes and valleys



(a)



(b)



(c)

**Figure 7** SEM images of CA membranes, after use, prepared with different solvents: (a) CA-acetone, (b) CA-DMF, and (c) CA-NMP.

concentration and stabilized at around 50 and 20 at a 70% feed concentration, respectively.

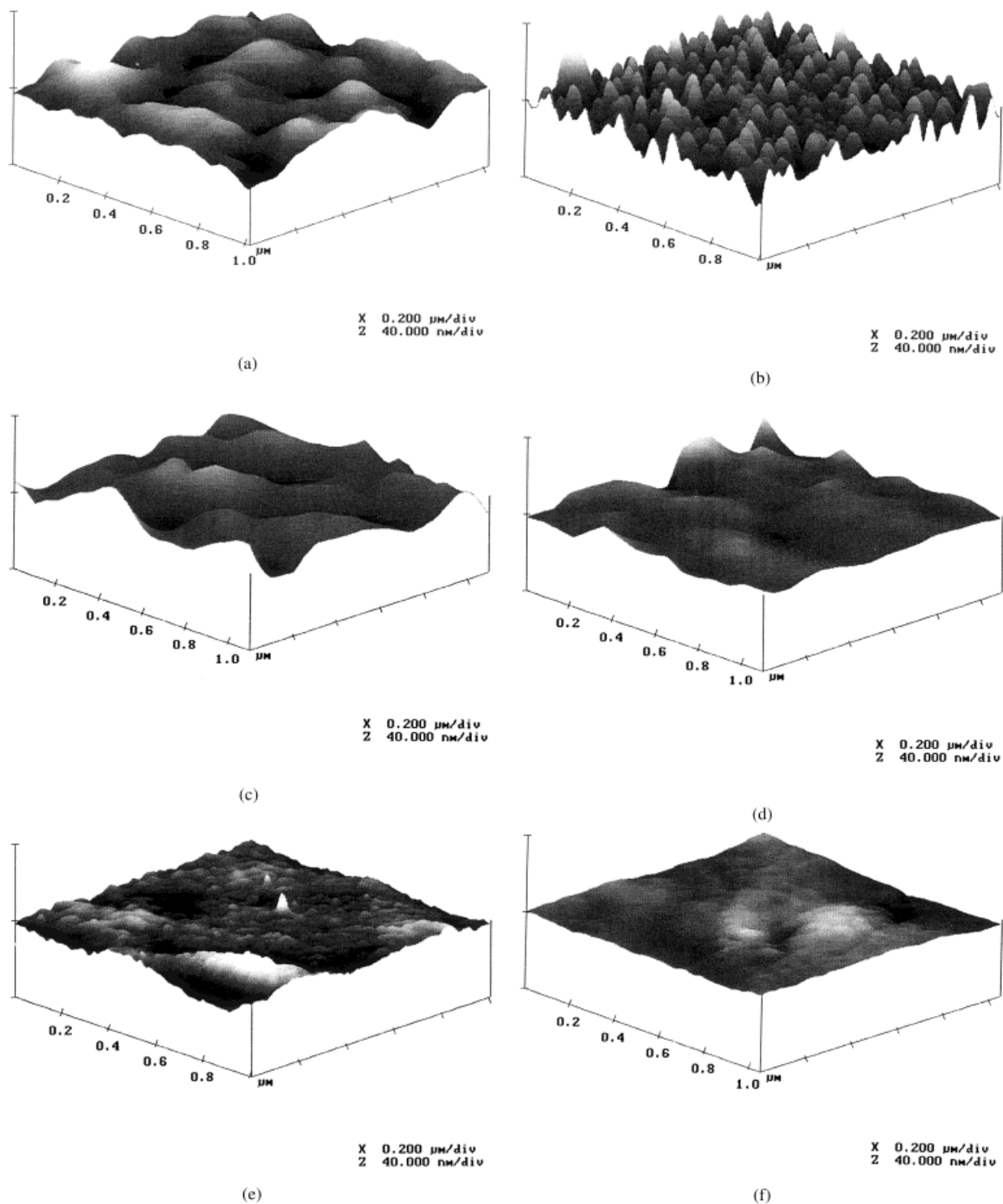
As shown in Figures 2–4, although the performances of all three CA membranes were very similar in terms of selectivity and permeability, some consistent and obvious differences could be observed among them. To investigate and explain these differences, we employed Raman spectroscopy, SEM, and AFM techniques.

We used Raman spectroscopy to quantify the actual sorption selectivities of the three membrane samples toward MeOH and MTBE. The use of Raman spectroscopy for this purpose is a novel technique. The common practice for calculating sorption selectivity is to swell a membrane in pure liquid components and use the ratio of the degree of swelling in each component as the ideal sorption selectivity of that membrane. This procedure leads to inaccurate values because the interaction between the components of the feed and between the feed and membrane are not considered. This novel technique, however, is based on the direct measurement of the concentration of each component inside a membrane after the membrane is swollen in a mixture of the components.

In this study, the Raman spectra of membrane samples swollen in 20% MeOH in an MTBE mixture were compared with those of pure components. Figure 5 shows the spectra obtained from the two feed components and the three membrane samples. The two bottom spectra reflect the peaks obtained from pure MeOH and pure MTBE. The MeOH peak appeared around  $1050\text{ cm}^{-1}$ , and that of MTBE appeared around  $760\text{ cm}^{-1}$ . The top three spectra belong to the three CA membrane samples swollen in the MeOH/MTBE mixture.

In a comparison of these spectra, the presence of MeOH and MTBE in the membrane is obvious. As seen in Figure 5, the MeOH and CA peaks overlapped. To calculate an accurate area of MeOH, we deducted the corresponding CA peak from the total peak area, and the remainder was normalized. The results, shown in Table IV, indicate that all three membranes showed higher affinity toward MeOH than MTBE. The MeOH concentration inside CA-DMF membrane was enhanced to 61%, which is considerably higher than the concentrations of the CA-acetone and CA-NMP. However, CA-acetone and CA-NMP showed similar sorption properties by enhancing the MeOH concentration from 20 to around 40%. The Raman results complemented and confirmed the experimental separation results, which indicated a higher selectivity for CA-DMF than for the other





**Figure 8** AFM images of the surfaces of CA membranes before and after use: (a) CA-acetone, new (43  $\mu\text{m}$  thick); (b) CA-acetone, used; (c) CA-DMF, new; (d) CA-DMF, used; (e) CA-NMP, new; and (f) CA-NMP, used.

two samples. Accordingly, the sorption selectivities of the membrane samples were calculated to be 2.8, 2.3, and 6.3 for CA-acetone, CA-NMP, and

CA-DMF, respectively. The sorption selectivity and total selectivity calculations are described in the Experimental section.

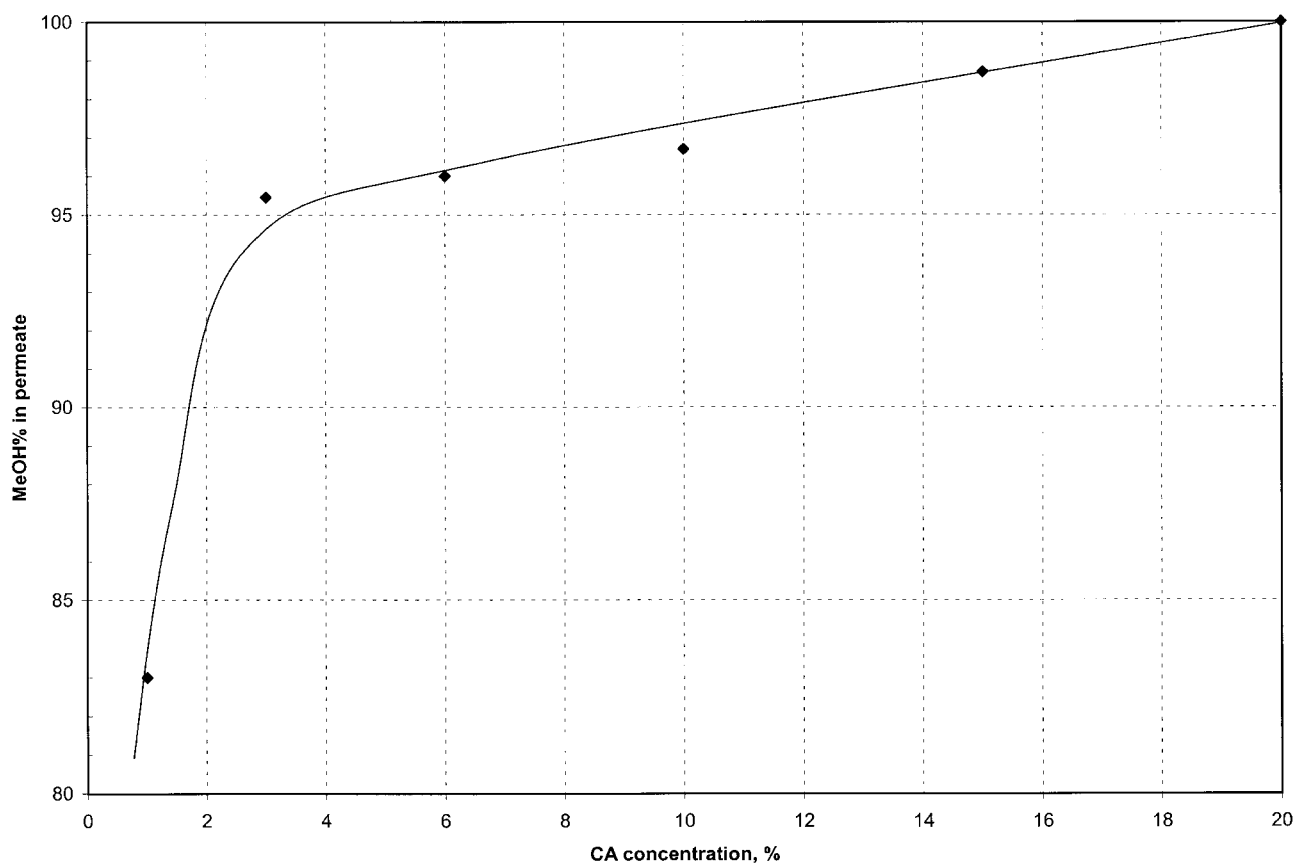
**Table VI** Experimental Data from Pervaporation Experiments with Different Concentrations of CA in Acetone as the Casting Solution

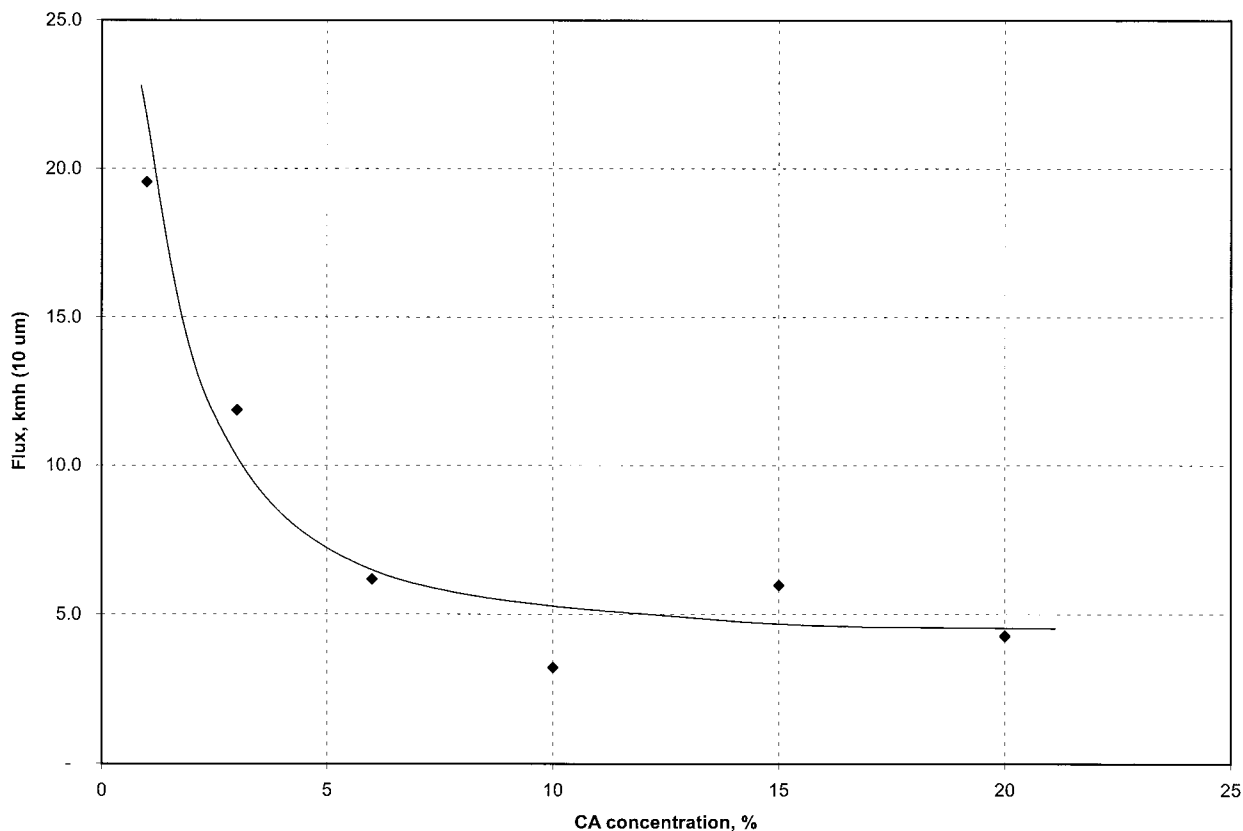
CA wt % in Acetone	Membrane Thickness ( $\mu\text{m}$ )	Flux [ $\text{kg}/\text{m}^2\text{h}$ ( $10 \mu\text{m}$ )]	MeOH wt % in Permeate	Selectivity
1	40.9	1.93	3.0	20
3	59.7	1.18	95.5	84
6	110.4	0.62	99.2	530
10	86.3	0.32	96.7	117
15	134	0.60	98.7	304
20	223	0.43	100	$\infty$

We calculated the diffusion selectivities of the CA membranes by dividing the overall selectivity by the sorption selectivity. These values are shown in the same table. The diffusion selectivities of all three membranes were significantly larger than their sorption selectivities, indicating that the latter governed the separation mechanisms of the two components. CA-acetone had the lowest diffusion selectivity, whereas CA-DMF showed the highest. The magnitude of the diffu-

sion selectivities suggested that the morphology of the membrane samples, rather than their intrinsic properties, affected the separation.

SEM photographs further explain the differences in the performance of the membrane samples. Figure 6 shows SEM pictures of the cross sections of the three membrane samples before use. Observations from these pictures are given in Table V. Although the membranes were prepared with the same amount of polymer solution, the

**Figure 9** MeOH concentration in the permeate versus CA concentration in the casting solution.



**Figure 10** Flux versus CA concentration in the casting solution.

SEM pictures show that the CA-acetone sample was notably thicker than the other two. The cross sections of the membrane samples consisted of defective top and bottom layers and a porous structure between them. The sizes and shapes of the void spaces were different and specific to each sample, as explained in Table V. The void spaces in all three samples were the close-cave type. The CA-acetone sample had a thickness of about 65  $\mu\text{m}$  with spherical voids approximately 0.2–0.5  $\mu\text{m}$  in diameter. The thickness of the CA-NMP sample was 32  $\mu\text{m}$ , with fish-shaped voids 2–4  $\mu\text{m}$  long. Also, the top and bottom layers of the CA-NMP sample were very thin and most defective compared with the other two samples. Finally, CA-DMF was the thinnest of the three samples, with a thickness of about 25  $\mu\text{m}$  and irregular voids about 1  $\mu\text{m}$  in diameter.

Figure 7 compares the morphology of the membrane samples after the completion of the separation experiments. The structure of the CA-acetone sample is notable. The sample significantly shrank, and visible voids disappeared. The CA-NMP sample also shrank but to a smaller extent. The thicknesses of the CA-acetone and CA-NMP samples were 40 and 28  $\mu\text{m}$  after use, which

corresponded to decreases of 40 and 12%, respectively. The CA-DMF sample did not show a notable change in the thickness, with a 4% decrease to 23  $\mu\text{m}$ , which can be attributed to the fluctuations in the thickness at different spots. The nodule and void sizes and shapes of the CA-NMP and CA-DMF samples did not change after use. The results are summarized in Table V.

Further investigations were made with AFM photographs of the surfaces of the samples before and after use, as shown in Figure 8. The results are also summarized in Table V. The CA-acetone sample showed the most severe morphological change after being used. The unused CA-acetone sample had a relatively smooth surface with shallow valleys, short peaks, and no nodules, whereas the surface of the used membrane was very rough, with sharp peaks and valleys. The CA-NMP and CA-DMF samples did not show significant variation in their surface morphology.

The difference in the performances of the membrane samples can be explained in terms of the mechanism of membrane formation in different solvents. Acetone, with the lowest boiling point and highest volatility, evaporates much faster from the casting solution than DMF and NMP.

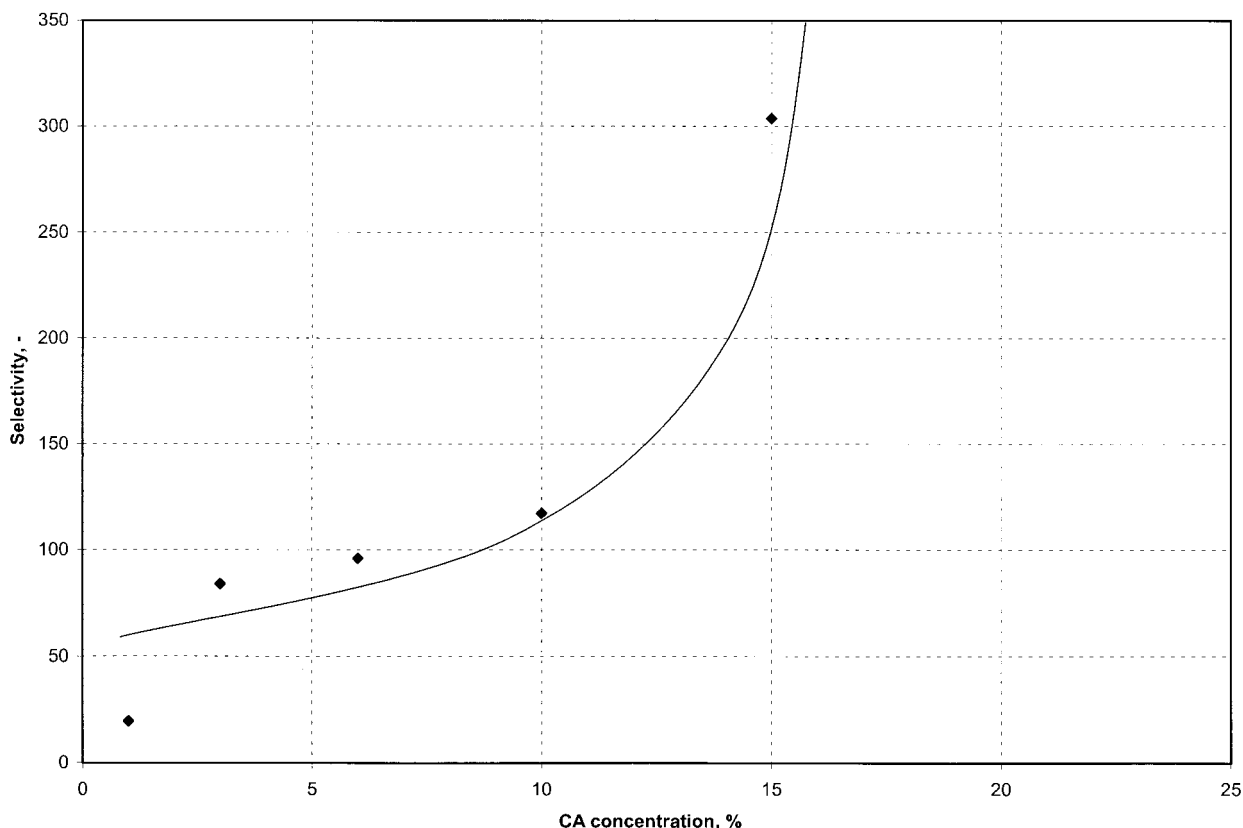


Figure 11 Selectivity versus CA concentration in the casting solution.

Therefore, not having sufficient time to relax, the polymer molecules form a thermodynamically unstable configuration through a freeze-drying-type process. Under such a condition, the polymer-rich phase in the solution freezes with not enough time for the formation of stable nodules and voids. Consequently, a thick and unstable membrane morphology is formed with high porosity and small voids.

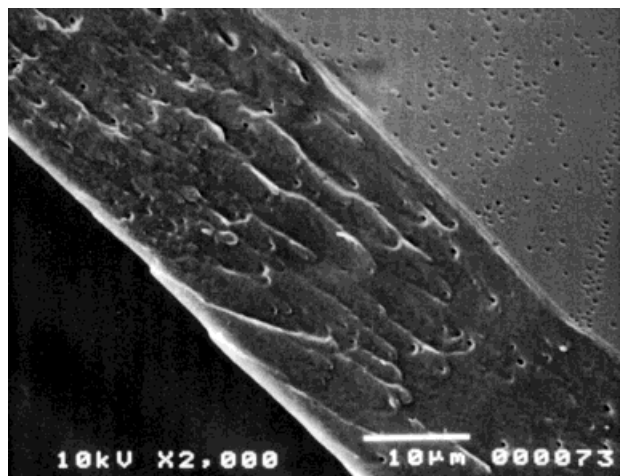
However, because of its low volatility, DMF evaporates from the polymer solution slowly, allowing the polymer chains to go through a long-time relaxation process, resulting in a stable structure and well-packed configuration. The membrane prepared in this manner would have a denser structure. In contact with the feed mixture, the CA-acetone membrane absorbs more of the solution because of its higher porosity. Thus, it forms a thicker swollen phase on the feed side (upstream) and a thinner dry phase on the vacuum side (downstream). As reported by Mulder et al.,<sup>8</sup> the sorption selectivity depends on the degree of swelling of the swollen phase. The sorption selectivity decreases with an increase in the swelling. In contact with MeOH, the unstable morphology of CA-acetone might collapse to a

more stable structure because of a slight flexibility resulting from swelling by MeOH, as can be concluded from a comparison of Figures 6 and 8. Also, the diffusion selectivity is thought to be mainly determined by the density and thickness of the dry phase during the separation process. As a result, compared with the CA-DMF membrane, CA-acetone is more swollen on the feed side and has a thinner dry phase on the vacuum side. Thus, both sorption and diffusion selectivities are low.

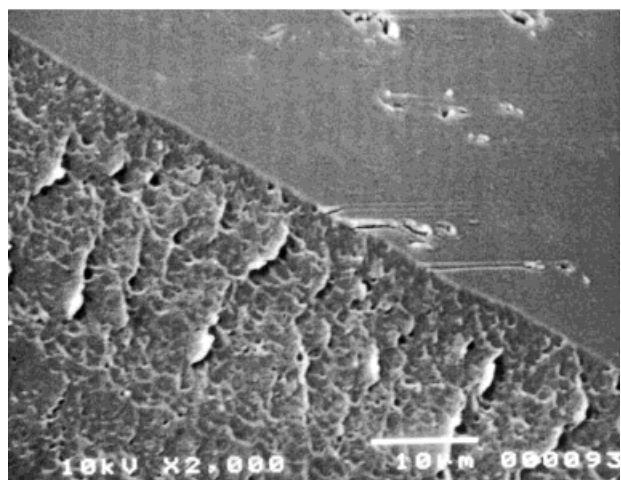
As the boiling point increases and volatility decreases in NMP, it becomes more difficult to remove the solvent completely. Therefore, although the low volatility of the solvent helps the relaxation of the polymer chains, the remaining trace of solvent plasticizes the membrane and reduces its selectivity.

According to the previous observations and discussions, an optimum boiling point exists at which the solvent leaves the solution slowly and completely. At boiling points lower than the optimum value, freezing occurs, whereas at higher boiling points, plasticization happens. Either case results in a reduction in the selectivity and morphological deterioration of the membrane.

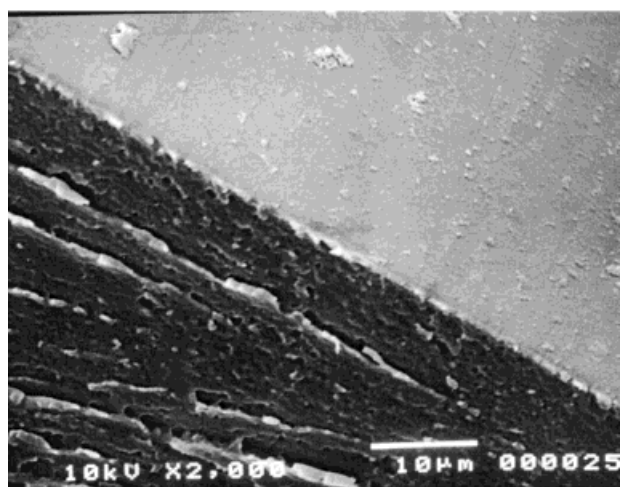




(a)



(b)



(c)

**Figure 12** SEM images of CA membranes with different polymer concentrations in the casting solution: (a) CA-acetone, 1%; (b) CA-acetone, 6%; and (c) CA-acetone, 10%.

An analysis of the experimental results and SEM observations reveals that despite the presence of pinholes, cracks, and voids in the structures of the membranes, they showed favorable separation properties. The high selectivity of the membranes support our close-cave structural model. Therefore, separation occurs at the wall of each cave. MeOH is enhanced while traveling from one cave to the next by penetrating the walls. Because the pinholes and cracks on the surface of the membrane are not connected to the caves underneath, they do not reduce the selectivity of the membranes.

### Effect of the Polymer Solution Concentration

To understand the dependence of membrane performance on the concentration of the casting solution, we prepared a series of membranes from casting solutions with 1–20 wt % CA in acetone. PV experiments were performed with 20% MeOH in an MTBE solution as the feed. The results are summarized in Table VI and Figures 9–12.

Figure 9 shows the concentration of MeOH in the permeate versus the concentration of CA in the casting solution. As shown in this figure and in Table VI, an increasing trend was obvious in the MeOH concentration in the permeate with an increasing casting solution concentration. The lowest MeOH concentration in the permeate was 83% with the 1% CA-acetone membrane. This value jumped to about 95.5% with the 3% membrane and stabilized at concentrations greater than 6%. Finally, a complete separation occurred when a 20% CA-acetone membrane was used. At the latter concentration, no trace of MTBE was detected in the permeate.

The normalized flux data are shown in Figure 10. The flux decreased with increasing polymer concentration. A stable region in the flux was observed at polymer concentrations above 6%, which was consistent with the plateau observed in Figure 9. The decrease in the flux indicated that the membranes became denser as the casting solution became concentrated.

Figure 11 shows the variation of selectivity with CA concentration. As shown in this figure, the selectivity increases sharply at higher concentrations and approaches infinity at 20 wt % CA. This trend indicated that the starting casting solution concentration had a strong influence on the selectivity of the membrane. Also, the enhanced selectivity of the membranes indicated that the microvoids disappear at higher polymer concentrations.

The SEM pictures shown in Figure 12 explain the experimental results shown in Figures 9–11 and Table VI. The cross section of the membranes at 1, 6, and 20% are shown in this figure. The 1% CA-acetone membrane is porous, with lots of visible voids and pinholes both at the surface and in the cross section. The pinholes gradually disappeared and the number of cross-sectional voids was reduced as the concentration of the polymer in the casting solution increased. The 20% CA-acetone membrane was quite dense, with no visible voids or pinholes. A comparison of these figures indicates that there exists an optimum polymer concentration at which the interchain distances are small enough to form a stable and dense structure even at a high evaporation rate of the solvent.

In summary, this study showed that the volatility of the solvent used in the casting solution has a crucial role in the morphological formation of a CA membrane. Two parallel effects govern this process. One is the rate of evaporation of the solvent from the solution, and the other is the complete removal of the solvent from the solution. In fact, an optimum boiling point exists at which the evaporation rate is slow enough to cause the formation of a stable and dense membrane and, at the same time, low enough to help the solvent to leave the solution completely.

It was also observed that the final morphology and the performance of the CA membrane de-

pended on the concentration of the polymer in the casting solution. As this concentration increased, the membrane became denser, its selectivity increased, and its permeability decreased. Also, the positive effects of a high polymer concentration may compensate for the negative effect of the low boiling point of the solvent.

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