

Influence of Quench Medium on the Structure and Gas Permeation Properties of Cellulose Acetate Membranes

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ABSTRACT: Integrally skinned asymmetric cellulose acetate membranes made by the wet phase inversion for removal of CO₂ from natural gas were investigated. The membrane was cast with the membrane-forming systems of cellulose acetate–acetone and quench media, such as methanol, ethanol and isopropanol, respectively, without heat-treating and multistage exchange process. By means of evaluation on separating characteristics of the membrane for CO₂/CH₄, observation of morphologies by scanning electron photomicrographs and analysis of the phase diagrams on the membrane-forming systems, it has shown that the membrane-forming system of cellulose acetate–acetone–methanol is quite suitable to prepare integrally skinned asymmetric cellulose acetate membranes for gas separation with good selectivity CO₂/CH₄ = 30 and flux coefficient = 2.4×10^{-5} cm³/cm² – s – cm Hg. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1269–1276, 1998

Key words: cellulose acetate; membrane; gas; separation

INTRODUCTION

The separation of CO₂/CH₄ is a very important problem in many fields such as CO₂ removal from natural gas streams, production of high purity CO₂ for enhanced oil recovery, and recovery of methane from landfill gas.¹ One of the promising techniques for the separation of CO₂/CH₄ is the membrane process, which offers many advantages, such as efficient energy, ease of scale-up due to modular design, good space and weight efficiency, environmental safety, and great flexibility for handling variations in flow rate, pressure, and composition of feed gas streams.² The processing ease and availability of cellulose acetate have continually made it one of a few polymers currently being used in commercial gas separa-

tions, especially in the separation of CO₂/CH₄.^{2,3} The conventional cellulose acetate membranes for gas separation were shrunk at different temperatures to obtain porous structure on the membrane surface and subsequently dried by a multiple stage solvent exchange technique to use for gas separation experiment. In the drying technique, water in the membranes was replaced by a first solvent in four stages, that is, the first water in the pores was replaced by an aqueous solution containing 25 vol % of the first solvent, which was then replaced by another aqueous solution containing 50 vol % of the first solvent. In the third stage, the aqueous solution was replaced by another aqueous solution containing 75 vol % of the first solvent, which in the fourth stage is replaced by the pure first solvent. Then, the first solvent is replaced by a second solvent, which is nonpolar, volatile, and miscible in the first solvent. The second solvent is air evaporated to obtain the dry membranes.^{4,5} This method based on the concept of the pore on the surface layer of the membrane is very complicated.

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Recently, there are a few successful reports that integrally skinned asymmetric membranes for gas separation are prepared by use of organic medium as coagulants. Pinnau et al.⁶ first made the integrally skinned poly(ether sulfone) asymmetric membranes by dry-wet phase inversion without any needing additional coating. They chose alcohol, such as methanol, ethanol, isopropanol as coagulants and thought that the choice of the quench medium is of utmost importance for the formation of gas separation membranes having high selectivities combined with high gas fluxes. Further, Pinnau and Koros⁷ made use of the same idea to invent the integrally skinned polysulfone membranes.

In this article, we try to use methanol, ethanol, or isopropanol as a coagulant to prepare the integrally skinned asymmetric cellulose acetate membrane for separation of CO₂/CH₄ without heat-treating and multistage solvent exchange processes and to establish relationships between different quench media and the resulting skin layer morphologies of membranes made by wet phase inversion.

METHODS AND EXPERIMENTS

Membrane Preparation

Cellulose acetate was dissolved into acetone. Then additive, such as methanol, ethanol, or isopropanol, was added into the cast solution. All membranes were cast on glass plates of equal nominal thickness at 25°C atmospheric temperature and 55% atmospheric relative humidity and were gelled in a methanol, ethanol, or isopropanol bath after some evaporation time in air.

Gas Permeation Experiment

Pure gas pressure-normalized fluxes reported in this study were obtained at 25°C for membrane samples of 19.6 cm² surface area at a pressure difference of 0.5 MPa. Volumetric gas permeation rates were determined with soap bubble flow meters. The downstream side was always purged with the test gas prior to the permeation measurement.

The feed and permeate compositions of the mixture gas were measured by gas chromatography using GOW-MAC400.

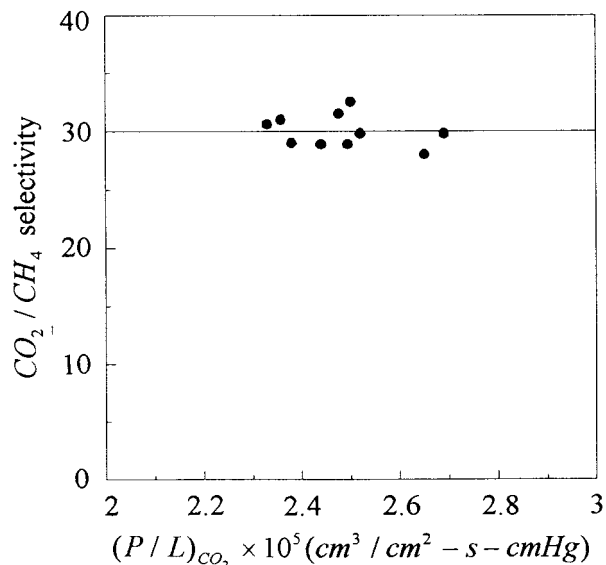


Figure 1 CO₂/CH₄ selectivities and pressure-normalized CO₂ fluxes of methanol-quenched cellulose acetate membranes made by wet phase inversion at the casting condition: CA concentration, 17 wt%; evaporation time, 40 s.

Scanning Electron Microscopy

For structure investigations, the membranes were prepared by cryogenic breaking in liquid nitrogen, followed by sputtering of a thin layer of gold, and examined with a X-650 scanning electron microscope.

RESULTS AND DISCUSSIONS

Methanol-Quenched Membranes

The pure gas permeation properties of integrally skinned asymmetric cellulose acetate membranes made by the wet phase inversion technique shown in Figure 1. The average CO₂/CH₄ selectivity of 10 randomly selected membrane sample was 30. The CO₂/CH₄ selectivity of a solution-cast, dense cellulose acetate film of known thickness was determined to be 32 at 25°C.³ Hence, the average CO₂/CH₄ selectivity of the asymmetric membrane samples was over 85% of the CO₂/CH₄ selectivity of solution-cast cellulose acetate films. These results indicate that the transport properties of the asymmetric membranes were predominantly determined by a solution-diffusion mechanism. Therefore, the skin layers can be considered to be essentially defect-free.

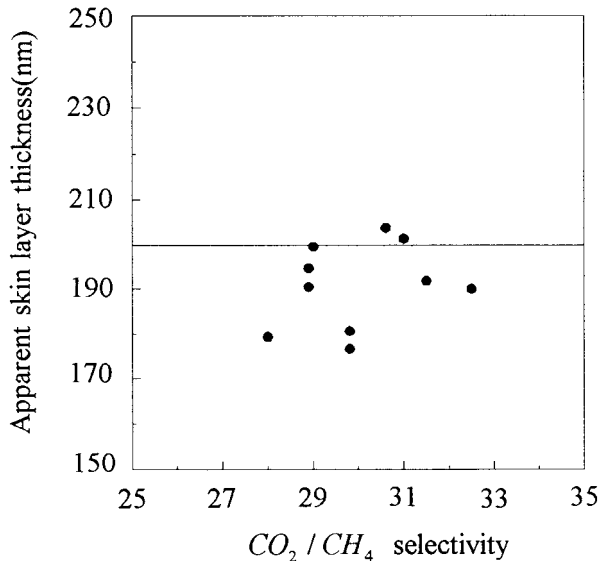


Figure 2 CO_2/CH_4 versus apparent skin layer thickness of methanol-quenched cellulose acetate membranes made by wet phase inversion at the same conditions as in Figure 1.

If the selectivity of an asymmetric membrane is essentially equal to that of the membrane materials, measured at the same temperature and pressure difference, an apparent skin layer thickness can be estimated using eq. (1), as follows:

$$L = P_i / (P/L)_i \quad (1)$$

where P_i is the permeability coefficient of gas i ($cm^3 - cm/cm^2 - s - cm Hg$), determined on isotropic films of known thickness and, $(P/L)_i$ is the pressure-normalized gas flux of an asymmetric membrane ($cm^3/cm^2 - s - cm Hg$). The preceding analysis based on eq. (1) assumes that the resistance to gas transport of the porous substructure can be neglected.⁶ The apparent skin layer thickness was determined based on the cellulose acetate CO_2 permeability coefficient of $4.75 \times 10^{-10} cm^3 - cm/cm^2 - s - cm Hg$.³ The average apparent skin layer thickness of all integrally skinned asymmetric membrane samples tested was 200 nm, as shown in Figure 2. The apparent skin layer of the CA membrane with heat-treating and multistage solvent exchange processes^{4,5} is about 700 nm if with the same calculating method, so the CA membranes for CO_2/CH_4 in this article have been modified greatly and the casting membrane process has been simplified.

Figure 3 shows the effect of the feed composition on the total permeation rate through the integrally skinned asymmetric membrane and separation factors. The permeation rate increased slowly with an increase of CO_2 concentration in the feed, which is expected since CO_2 is the faster permeating gas, unlike the heat-treating CA membrane.⁵ There is very little change in the separation factor.

The structural features of the integrally skinned asymmetric membrane quenched by methanol, in Figures 4 and 5, have been elucidated from scanning electron microscopy (SEM). The top surface of methanol-quenched membrane without evaporation has shown the spinodal decomposition with nodular structures in Figure 4(a). The cross section of the asymmetric cellulose acetate membrane in Figure 4(b) and (c) consists of a loose honeycomb-like structure without any macrovoids. After the evaporation time of 40s on the casting membrane, the skin layer of the membrane was essentially defect-free. But the cross-section of the asymmetric membrane is similar to that without evaporation.

The overall thickness of the top layer is about 200 nm. Because a porous transition layer does not exist clearly, the top layer is an ultrathin, dense skin layer. These structures have met the requirements of ideal asymmetric membranes for gas separation.⁶ But the structures of the integrally skinned CA membrane are obviously different from the other integrally skinned membrane, such as Pinnau and Koros's^{7,8} polysulfone membranes fabricated by a dry-wet phase inversion process using forced convective evaporation or van't Hof et al.'s⁹ polyethersulfone hollow fibers spun by a dual-bath coagulation method. Hence, their forming mechanisms are totally different.¹⁰

Ethanol-Quenched Membranes

The average CO_2/CH_4 selectivity of ethanol-quenched cellulose acetate membranes made by wet phase inversion was 13.35 combined with a pressure-normalized CO_2 flux of $5.575 \times 10^{-7} cm^3/cm^2 - s - cm Hg$. The gas permeation properties of the individual membrane samples are shown in Figure 6. The average CO_2/CH_4 selectivity was less than 85% of that determined for a solution-case, dense cellulose acetate film. Therefore, it seems that the asymmetric membranes may be porous or defective. But at the same

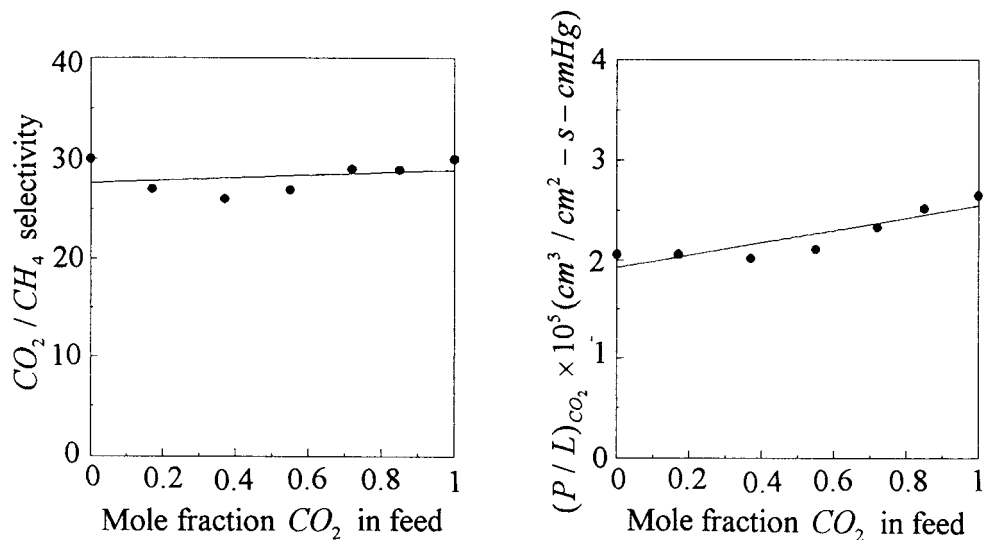


Figure 3 Effect of CO_2 mole fraction in the feed gas mixture on the selectivity and permeation rate.

time, the CO_2 flux (10^{-7}) is far inferior to that of the methanol-quenched cellulose acetate membranes (10^{-5}).

The cross-section of an ethanol-quenched cellulose acetate membrane is shown in Figure 7. The structure appears to be similar to that of the methanol-quenched membranes [Fig. 4(a)]. The top skin layer shown in Figure 7(c) is essentially defect-free, but a compact porous transition layer in the outermost region of the top structure exists,

which leads to a substantial substructure resistance to the gas permeation.¹¹ The selectivities of asymmetric membrane substructures are essentially equal to those predicted by Knudsen flow. However, pressure-normalized gas fluxes of substructures can vary by several orders of magnitude. Therefore, the substructure can exhibit substantial resistance to gas transport through asymmetric membranes. The net result of substantial substructure resistance is a decrease in pressure-

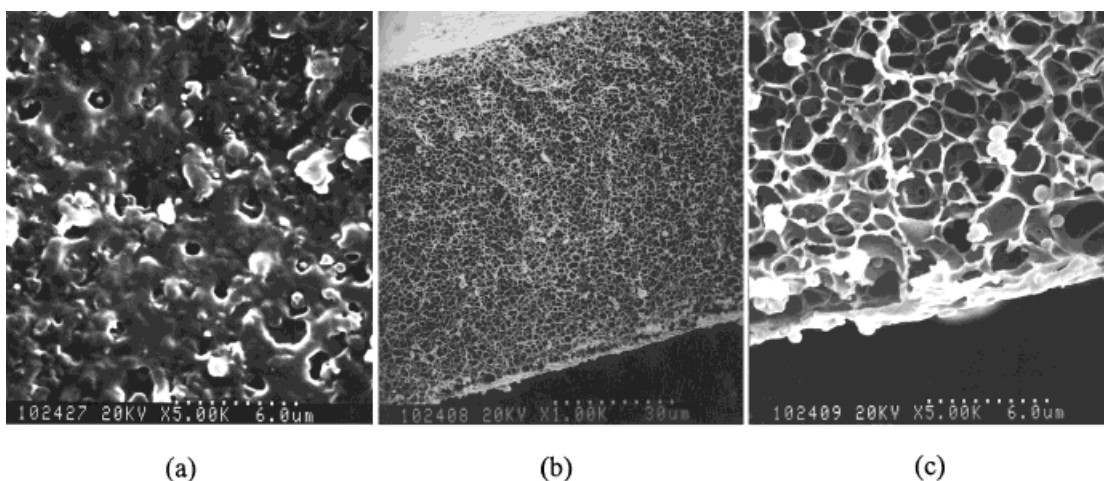


Figure 4 Structure of a methanol-quenched cellulose acetate membrane made by wet phase inversion without evaporation: (a) top skin layer $\times 5000$; (b) cross section $\times 1000$; (c) top structure $\times 5000$.

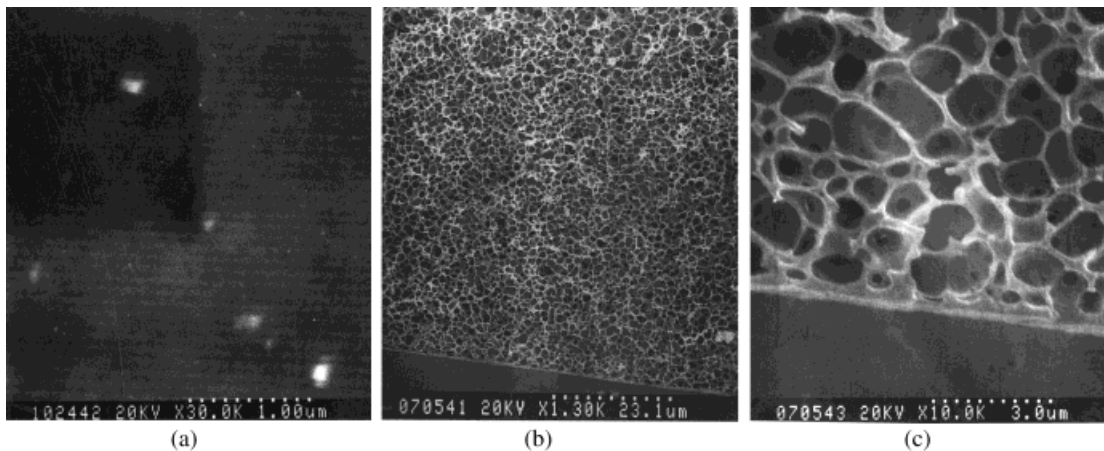


Figure 5 Structure of a methanol-quenched cellulose acetate membrane made by wet phase inversion with an evaporation time 40s: (a) top skin layer $\times 30,000$; (b) cross-section $\times 1300$; (c) top structure $\times 10,000$.

normalized fluxes of fast permeating components that can lead to a decrease in selectivity of defect-free asymmetric membranes. In addition, the top skin of the ethanol-quenched membrane is thicker, which is unacceptable.

Isopropanol-Quenched Membranes

Isopropanol-quenched cellulose acetate membranes made by wet-phase inversion exhibited an

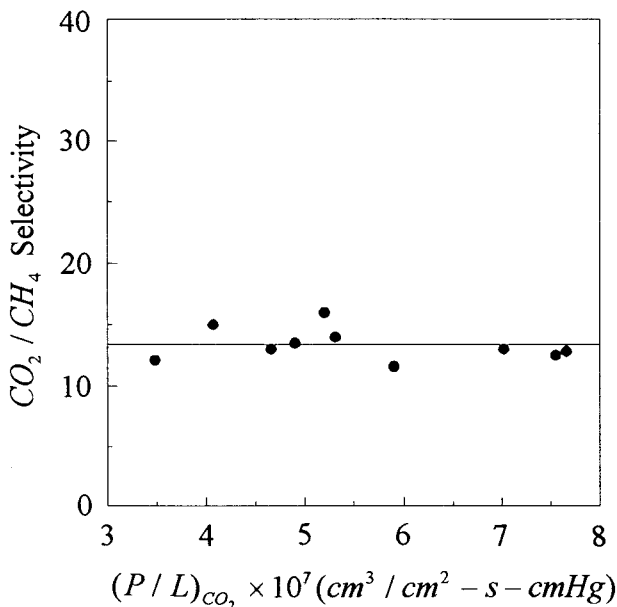


Figure 6 CO_2/CH_4 selectivities and pressure-normalized CO_2 fluxes of ethanol-quenched cellulose acetate membranes made by wet phase inversion without evaporation.

average CO_2/CH_4 selectivity of 10.5 combined with an average pressure-normalized CO_2 flux of $6.9 \times 10^{-7} \text{ cm}^3/\text{cm}^2 - \text{s} - \text{cm Hg}$. The permeation properties of the individual membrane sample are shown in Figure 8. The average CO_2/CH_4 selectivity of isopropanol-quenched membranes was only 32% of that determined for a dense cellulose acetate film. And the CO_2 flux is much low, as in the case of ethanol-quenched membranes.

The morphology of a isopropanol-quenched membrane made by wet phase inversion is shown in Figure 9. The top skin layer in Figure 9(a) is also dense and defect-free. The cross-section structural feature of isopropanol-quenched membranes is similar to that of the ethanol-quenched membranes in Figure 7(a). The estimated skin layer is thick, and the transition layer is denser and thicker than that of ethanol-quenched membranes. This result provides further evidence that the lower selectivities and CO_2 fluxes of the isopropanol-quenched membranes were due to substructure resistance to gas transport.

Thermodynamic Analysis of the Membrane-Forming Systems

For comparison, the phase diagram of water as coagulant were shown in Figure 10. The phase diagrams of nonsolvent-acetone-cellulose acetate systems were calculated according to a new form of Flory-Huggins equation.^{10,12,13} Generally, the single phase region between the binodal and CA-acetone axis increases gradually in the order of water, methanol, ethanol, and isopropanol;

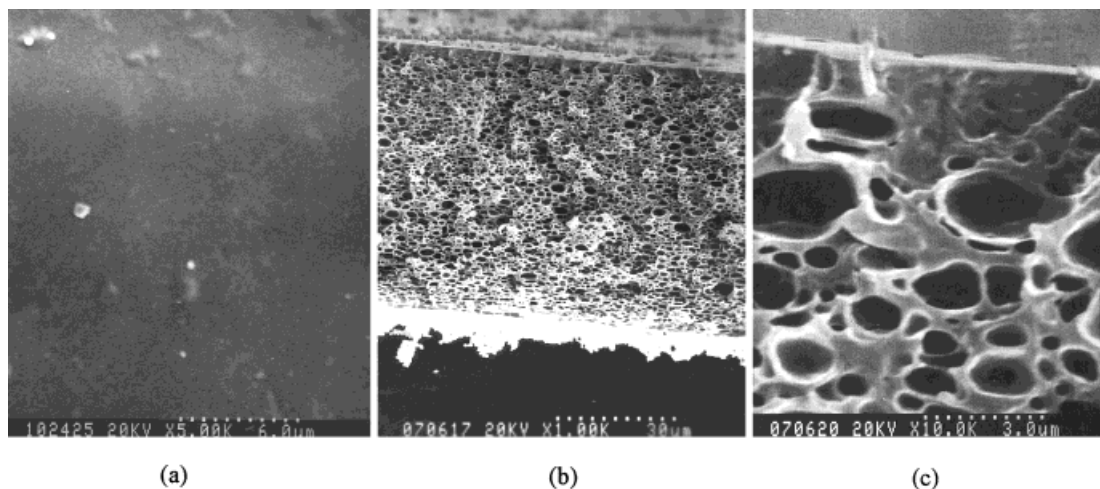


Figure 7 Structure of a ethanol-quenched cellulose acetate membrane made by wet phase inversion without evaporation: (a) top skin layer $\times 5000$; (b) cross-section $\times 1500$; (c) top structure $\times 10,000$.

namely, the cast solution becomes more stable. A microphase separation process may occur more difficult. According to work by Reuvers and Smolders¹⁴ the casting membrane of CA–acetone solution into water during membrane formation may reach the phase separation after a certain time interval. It is deduced that the similar phase separation may happen to other coagulants, methanol,

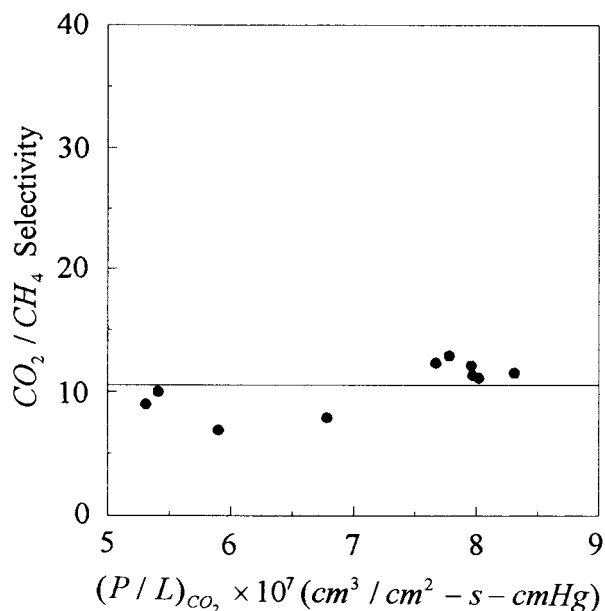


Figure 8 CO_2/CH_4 selectivities and pressure-normalized CO_2 fluxes of isopropanol-quenched cellulose acetate membranes made by wet phase inversion without evaporation.

ethanol, and isopropanol; in that order, the delay time prolongs gradually. The thickness of the concentrated layer in the top section increase with the square root of the delay time. As shown in Figures 4(c), 5(c), 7(c), and 9(c), the skin thickness and transition region become thicker in the order of methanol, ethanol, and isopropanol-quenched membrane. During the delay time, the top surface of the ethanol, isopropanol-quenched membrane have concentrated enough to control formation of the defect-free skin layer on the set of phase separation. As shown in Figure 10, when the cast CA concentration is low between 10–20 vol. %, the binodal of methanol coagulant is nearest to the CA–acetone axis, so the methanol-quenched membrane without evaporation may undergo a spinodal decomposition with nodular structures, as shown in Figure 4(a). With the increase of CA concentration, the metastable regions between the binodal and spinodal boundaries reduce. The phase separation change smoothly from spinodal deposition to nucleation and growth process until gelation transition. At that time, the binodal of methanol coagulant deviates from that of water coagulant and approaches that of the ethanol by degrees. Therefore, the phase separation feature of the methanol-quenched membrane at the high CA concentration is more similar to that of ethanol-quenched membrane. This is why top skin layer of methanol-quenched membrane with a 40-s evaporation time is defect-free, but methanol must penetrate into the dense skin. We hope to report on these data and analyses in future publications.

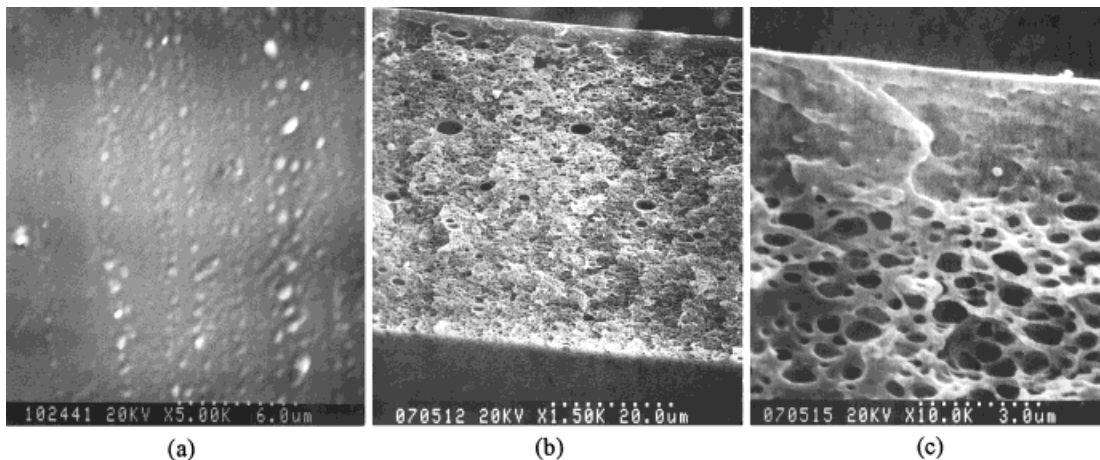


Figure 9 Structure of an isopropanol-quenched cellulose acetate membrane made by wet phase inversion without evaporation: (a) top skin layer $\times 5000$; (b) cross-section $\times 1500$; (c) top structure $\times 10,000$.

CONCLUSION

Essentially defect-free integrally skinned asymmetric cellulose acetate membranes can be fabricated by a wet-phase inversion process with evaporation from the membrane-forming system of CA–acetone–methanol. Optimum membranes consist of an ultrathin skin layer, a thin transition layer, and an open-cell, honeycomb-like substructure.

The choice of the quench medium is of utmost importance for the formation of gas separation membranes having high selectivities combined with high gas fluxes. The selectivities of ethanol- or isopropanol-quenched membranes were lower

compared to those of methanol-quenched membrane, possibly due to substructure resistance to gas transport. Furthermore, the average pressure-normalized CO_2 fluxes were unacceptable.

Their separation performances and structure can be partly explained by their thermodynamic phase diagrams. At a lower CA concentration, ethanol or isopropanol as a coagulant leads to the delayed phase separation. The ethanol- or isopropanol-quenched membranes have displayed a dense and rather thick skin layer supported by a closed cell sponge-like substructure. The methanol-quenched membranes without evaporation have shown the spinodal decomposition.

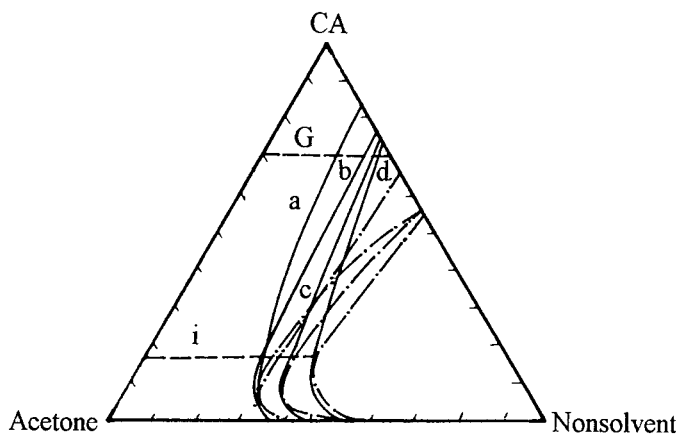


Figure 10 Phase diagrams of nonsolvent–acetone–cellulose acetate system. Coagulants are as follows: (a) water; (b) methanol; (c) ethanol; (d) isopropanol; (—) binodal; (---) spinodal curves; (---) *i* line, cellulose acetate concentration of initial casting solution; (---) *G* line, glass transition.

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