

Influence of the Dilute-Solution Properties of Cellulose Acetate in Solvent Mixtures on the Morphology and Pervaporation Performance of Their Membranes

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ABSTRACT: The pervaporation performance of cellulose acetate (CA) membranes prepared from acetone (AC), acetone/tetrahydrofuran (AC/THF), acetone/chloroform (AC/CF), and acetone/cyclohexane (AC/CYH) was studied for separating MeOH/MTBE (methyl *tert*-butyl ether) mixture with 5 (wt) % MeOH. The dilute-solution properties and Huggins constant (K_H) of CA dissolved in AC and AC/solvent mixtures with 15 vol % of the second solvent (tetrahydrofuran, chloroform, or cyclohexane) were examined. J and α of the CA membranes were affected by the types of solvent mixtures used to prepare the casting solutions. Under the same conditions, the membrane with AC/CYH had the highest J value and the lowest α value, and it was followed by the membranes with AC/CF, AC/THF,

and AC. The increasing value of J and decreasing value of α for the CA membranes from different solvent mixtures were in good agreement with the increasing value of K_H of CA in corresponding solvent mixtures. Furthermore, differences in the morphology from scanning electron microscopy images of the cross sections or from atomic force microscopy photographs of the surfaces of the membranes existed, and they provided proof of the different pervaporation performances of the CA membranes prepared from AC and AC/solvent mixtures. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1891–1898, 2005

Key words: association; membranes; solution properties

INTRODUCTION

A solvent is one of the most important factors when altering the dilute-solution behaviors (association, complex, micelle, and core-shell structure of polymer chains in solution) of a polymer. The measurement of viscosity is the simplest way of assessing the solution properties.^{1–13} The intrinsic viscosity ($[\eta]$), viscosity slope coefficient (b), and Huggins constant (K_H) for the viscosity behavior are common parameters for characterizing the dilute-solution properties of a polymer, especially K_H , which is the theoretical representation of the thermodynamic property and hydrodynamic property¹⁴ of a polymer solution. Therefore, K_H could reflect the nature of the solvent thermodynamically, the interaction between the polymer chain and solvent, and the rheological behavior of the solution.

Extensive studies have been conducted on the effect of casting solvents on the morphology and performance of the resultant membranes prepared via the

wet-phase inversion method, such as ultrafiltration membranes,¹⁵ reverse-osmosis membranes,¹⁶ gas-separation membranes,¹⁷ and pervaporation (PV) membranes.¹⁸ The addition of a second solvent to the casting solution is often used for increasing the permeation flux (J) of a membrane, and the second solvent is mostly a nonsolvent.¹⁹ Some studies^{20–22} have pointed out that the structures, boiling point, and content of the second solvent are factors affecting the performance of membranes. Other studies have shown that the performance of membranes is dependent on $[\eta]$ or the surface tension of the casting solution.^{16,23,24} Therefore, Joly et al.¹ and Khulbe et al.²⁵ pointed out that polymer solution properties should be paid considered for the preparation of membranes.

Usually, a PV membrane is made with a single solvent. Only a small study reported solvent mixture being used to prepare PV membranes by a dry-cast process.²⁶ In addition, cellulose acetate (CA) is a common material for making membranes, but CA membranes give low flux in separating MeOH/methyl *tert*-butyl ether (MTBE) mixtures with a low content of MeOH in the feed.^{26–28}

In this study, CA membranes were fabricated from various solvent mixtures to improve the fluxes. In particular, we explored the effect of K_H of CA in dilute solutions on the morphology and PV performance of the resultant membranes and sought to elucidate the

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TABLE I
Properties of the Solvents Used for the Preparation of the Dilute and Casting Solutions

Solvent	V (cm^3/mol)	T_b ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ρ (g/cm^3 ; 20°C)	η (mPa s ; 25°C)	δ (J/cm^3) $^{1/2}$	δ_d (J/cm^3) $^{1/2}$	δ_p (J/cm^3) $^{1/2}$	δ_h (J/cm^3) $^{1/2}$
AC	73.3	57	-95	0.792	0.32	20.2	15.5	10.4	7.0
THF	81.2	65	-65	0.888	0.36	19.5	17.85	5.7	8.0
CF	79.7	60	-64	1.499	0.54	19	17.9	3.1	5.7
CYH	108	81	7	0.779	0.90	16.7	15.6	0	0

V = molar volume; T_b = boiling temperature; T_m = melting temperature; ρ = surface tension; η = viscosity.

relationship between the flux and K_H in view of chain association and chain aggregation in polymer solutions and membranes.

EXPERIMENTAL

Materials

CA with an acetyl concentration of 39.6 wt % and an $[\eta]$ value of 171.9 mL/g in acetone (AC) at 30° was purchased from Shanghai Chemical Station (Shanghai, China). Acetone (AC), THF, chloroform (CF), and cyclohexane (CYH) solvents for studying the solution properties of CA were analytical reagents, and MeOH and MTBE for PV were industrial reagents.

PV membrane preparation

A casting solution with concentration of 8 g/100 mL was prepared by the dissolution of CA in a solvent mixture at 45°C for 3 days. The membrane was prepared by a dry-cast process; that is, we scratched its solution on the plate surface of a polyacrylonitrile (PAN) ultrafiltration membrane as a support layer and evaporated the solution in an oven without air flow at

about 25°C for 2 days. The dried membrane detached from the glass plate by itself, and the average membrane thickness was $30 \pm 1 \mu\text{m}$.

PV experiments

The PV experiments were conducted with the same equipment reported previously.²⁸ The vacuum system of the downstream side was maintained at about 180 Pa. The experiments were carried out in a continuous steady state at a constant temperature with an MeOH/MTBE mixture with 5 wt % MeOH. The permeation was condensed by liquid nitrogen. J and the separation factor (α) for all membranes were calculated as follows:

$$J = \frac{\Delta g}{S \times \Delta t} \quad (1)$$

$$\alpha = \frac{y_1/y_2}{x_1/x_2} \quad (2)$$

where Δg is the permeation weight collected in cold traps during the operation time Δt ; S is the membrane

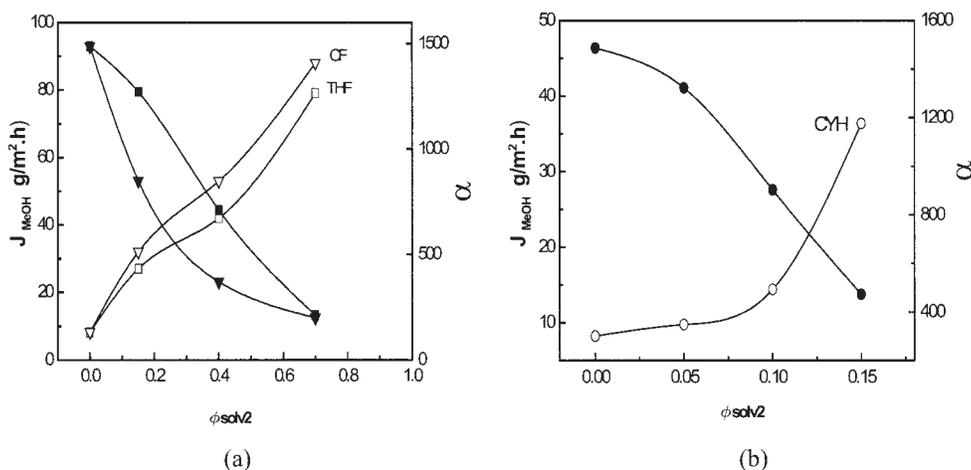


Figure 1 $\phi_{\text{solvent}2}$ dependence of ($\square, \triangle, \circ$) J and ($\blacksquare, \blacktriangle, \bullet$) α values of CA membranes from three kinds of AC/solvent mixtures at a feed temperature of 30°C . The second solvent was (\blacksquare, \square) THF, ($\blacktriangle, \triangle$) CF, or (\bullet, \circ) CYH.

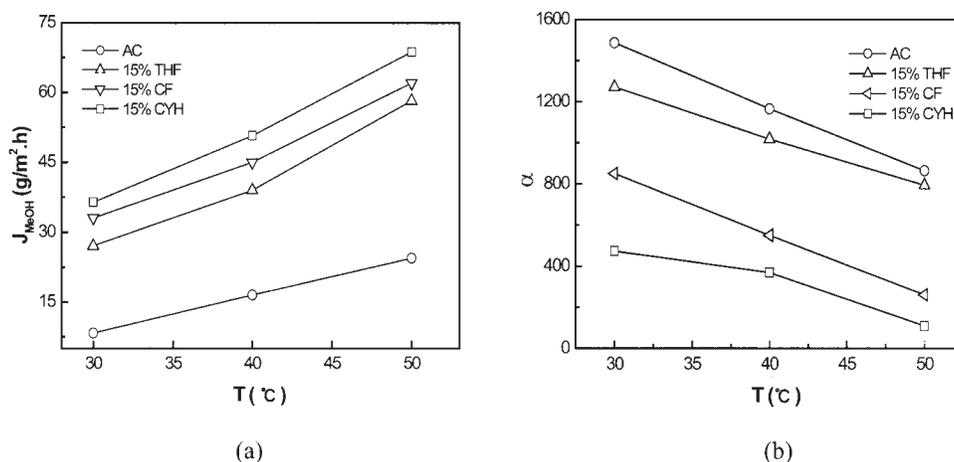


Figure 2 (a) Temperature dependence of J values of CA membranes from the AC and AC/solvent mixtures with 15 vol % of the second solvent and (b) temperature dependence of α values of CA membranes from the AC and AC/solvent mixtures with 15 vol % of the second solvent.

area (15.9 cm²); x and y represent the weight fractions of the corresponding solute in the feed and permeate, respectively; and subscripts 1 and 2 refer to the more permeable component (MeOH) and less permeable one (MTBE).

The physical properties²⁹ of all the solvents are listed in Table I.

Viscosity measurements

CA solutions with AC or different solvent mixtures were prepared at 45°C for 24 h and then filtered through G2 sintered glass filters. Viscosity measurements were performed with an Ubbelohde dilution viscometer at a designated temperature. The flux time was recorded with an accuracy of ± 0.05 s. The extrapolation procedure was used to evaluate K_H , b , and $[\eta]$.

Scanning electron microscopy (SEM) experiments

The membranes were fractured in liquid nitrogen and coated with gold by sputtering. Images were obtained with a JEOL/EO scanning electron microscope (Tokyo, Japan).

Atomic force microscopy (AFM) experiment

A casting solution with a concentration of 2 g/100 mL was prepared by the dissolution of CA in a solvent mixture at 45°C for 3 days. Membranes were cast onto glass plates, and membrane formation was completed in air at $25 \pm 0.2^\circ\text{C}$. The images of the membrane surfaces were obtained on a Seiko SPI3800N machine (Tokyo, Japan) in the tapping mode. All the AFM images were taken at 25°C. The surfaces of the membranes were compared in terms of the mean diameter of the nodules (R_z) and the roughness parameter (R_a). The diameter of the nodules is the average of at least 50 measurements. The mean roughness is the mean value of the surface with respect to the center plane (the plane for which the volumes enclosed by the image above and below the plane are equal) and is calculated as follows:

$$R_a = \frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} |f(x,y)| dx dy \quad (3)$$

TABLE II
Effect of the AC and AC Solvent Mixtures on the Dilute-Solution Properties of CA

	$[\eta]$ (mL/g)	$b \times 10^{-3}$	K_H	$K_m = K_H[\eta]/b$	$\Delta\delta_{p/s}$
AC	171.9	10.94	0.370	10.602	10.90
AC/THF	169.2	10.84	0.379	10.688	10.70
AC/CF	158.4	10.60	0.422	11.141	11.17
AC/CYH	156.2	10.73	0.439	11.429	12.35

Solubility parameters of CA: $\delta = 25.88$ (J/cm³)^{1/2}; $\delta_a = 15.55$ (J/cm³)^{1/2}; $\delta_p = 16.13$ (J/cm³)^{1/2}; $\delta_n = 12.95$ (J/cm³)^{1/2}.²⁰

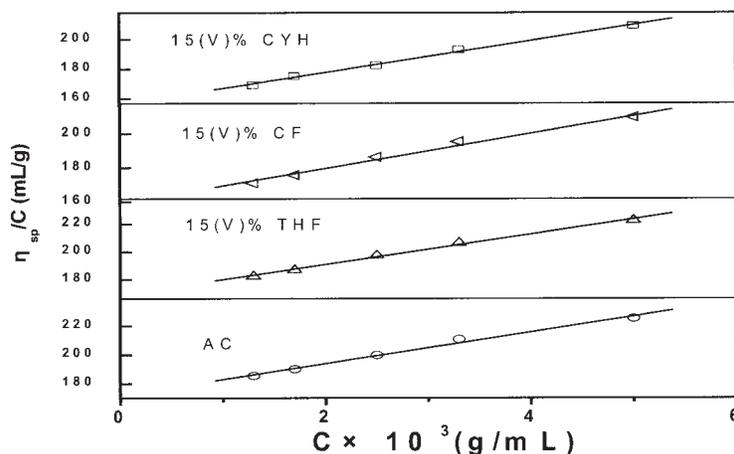


Figure 3 Plots of η_{sp}/C versus C for CA in AC and in AC/THF, AC/CF, and AC/CYH solvent mixtures.

where $f(x,y)$ is the surface with respect to the center line and L_x and L_y are the dimensions of the surface in the x and y directions, respectively.²⁰

RESULTS AND DISCUSSION

PV performance of the CA membranes

Effect of the solvent mixture composition

Figure 1(a,b) presents the variation of J and α values of CA membranes from AC/solvent mixtures with different volume fractions of the second solvents (ϕ_{solvent2}) THF, CF, and CYH at a feed temperature of 30°C. Figure 1 shows that all J values of the CA membranes from the three kinds of AC/solvent mixtures are larger than that from the pure solvent AC and increase with increasing content of the second solvent; this opposite is true for α .

Effect of the feed temperature

Figure 2(a,b) shows the effect of the feed temperature on the J and α values of CA membranes from the AC

and AC/solvent mixtures with 15 vol % of the second solvents. Figure 2 shows that the variation of the J and α values with the feed temperature for CA membranes from three kinds of AC/solvent mixtures with 15 vol % of the second solvents THF, CF, and CYH is similar to that of the CA membrane from the pure solvent AC; that is, J increases and α decreases with increasing feed temperature.

Obviously, the J (or α) values at a given temperature increase (or decrease) with second solvents THF, CF, and CYH in that order and are higher than those of the membrane from the pure solvent AC. Khulbe et al.²² reported the effect of the boiling point of the casting solvent on the membrane performance. They pointed out that the permeability increased and the selectivity decreased for separating O_2/N_2 and CO_2/CH_4 with a dense poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) membrane with an increase in the boiling point. Ru-aan et al.²³ and Tan et al.²⁴ suggested that the morphology or performance of a polymer membrane was affected by the surface tension of the casting solution. Lai et al.³⁰ found that the solubility parameter difference between the polymer and solvent ($\Delta\delta_{p/s}$) was

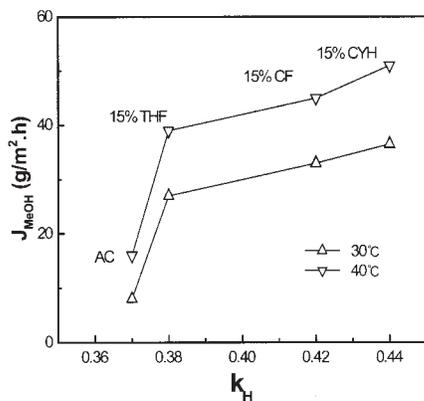


Figure 4 Relation between J and K_H .

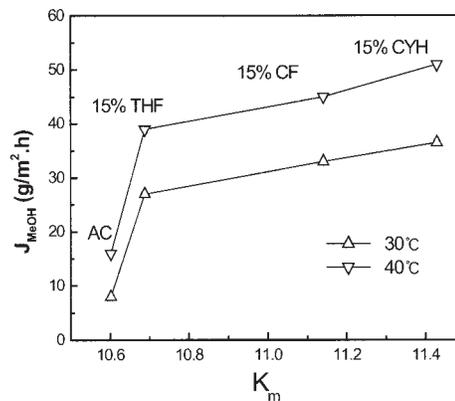


Figure 5 Relation between J and K_m .

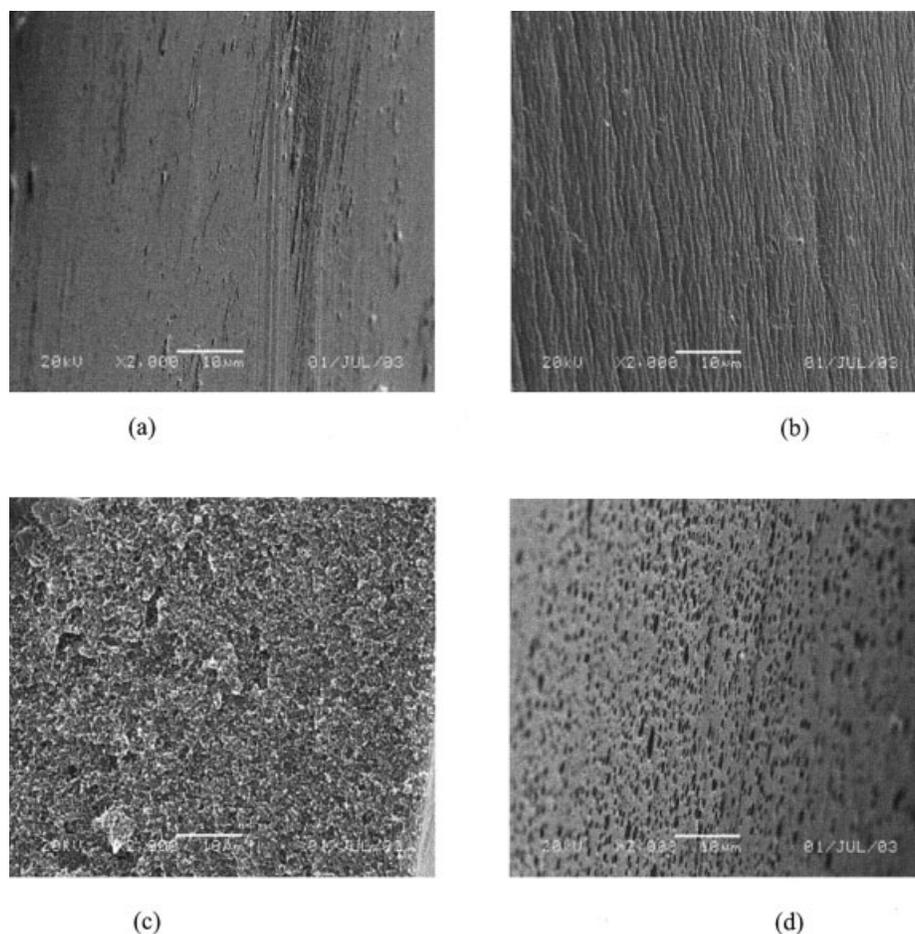


Figure 6 SEM images of CA membranes prepared with different solvent mixtures: (a) AC, (b) AC/THF, (c) AC/CF, and (d) AC/CYH.

proportional to the porosity of asymmetric poly(4-methyl-1-pentene) membranes.

Unfortunately, the flux and separation factor of the CA membranes presented in this study could not be correlated to the boiling point and surface tension of the solvents (see the values of the boiling point and surface tension in Table I), and they are not in agreement with $\Delta\delta_{p/s}$ (see the values of $\Delta\delta_{p/s}$ in Table II). $\Delta\delta_{p/s}$ can be calculated with the following formula:

$$\Delta\delta_{p/s} = [(\Delta\delta_{d,s} - \Delta\delta_{d,p})^2 + (\Delta\delta_{p,s} - \Delta\delta_{p,p})^2 + (\Delta\delta_{h,s} - \Delta\delta_{h,p})^2]^{1/2}$$

where subscripts p and s represent the CA polymer and solvent (solvent mixture), respectively; d , p , and h stand for the dispersion-interaction, polar-bonding, and hydrogen-bonding components, respectively; and δ_s of the solvent mixture (AC and a second solvent) is assumed to be the volume fraction average of the δ values of the pure components (i.e., $\delta_{i,s} = \phi_1\delta_{i,1} + \phi_2\delta_{i,2}$, where ϕ_1 and ϕ_2 represent the solvent AC

and the second solvent THF, CF, or CYH and the subscript i represents d , p , or h , respectively).

Dilute-solution properties of the CA polymer

Solubility tests of CA were conducted in the single solvents AC, THF, CF, and CYH at room temperature. The results demonstrated that CA was soluble in AC and THF, swollen in CF, and insoluble in CYH. They indicated that the thermodynamic properties of the solvents were worse in the order of AC, THF, CF, and CYH. This is in agreement with the trend of their solubility parameters (in Table I).

Figure 3 shows plots of the reduced specific viscosity (η_{sp}/C) versus the concentration (C) for CA in AC and in acetone/tetrahydrofuran (AC/THF), acetone/chloroform (AC/CF), and acetone/cyclohexane (AC/CYH) solvent mixtures at 30°C.

All the curves of η_{sp}/C versus C of CA in the single solvent AC or in the AC/solvent mixtures with 15 vol % of the second solvent remain straight and linear and obey the following Huggins equation:³¹

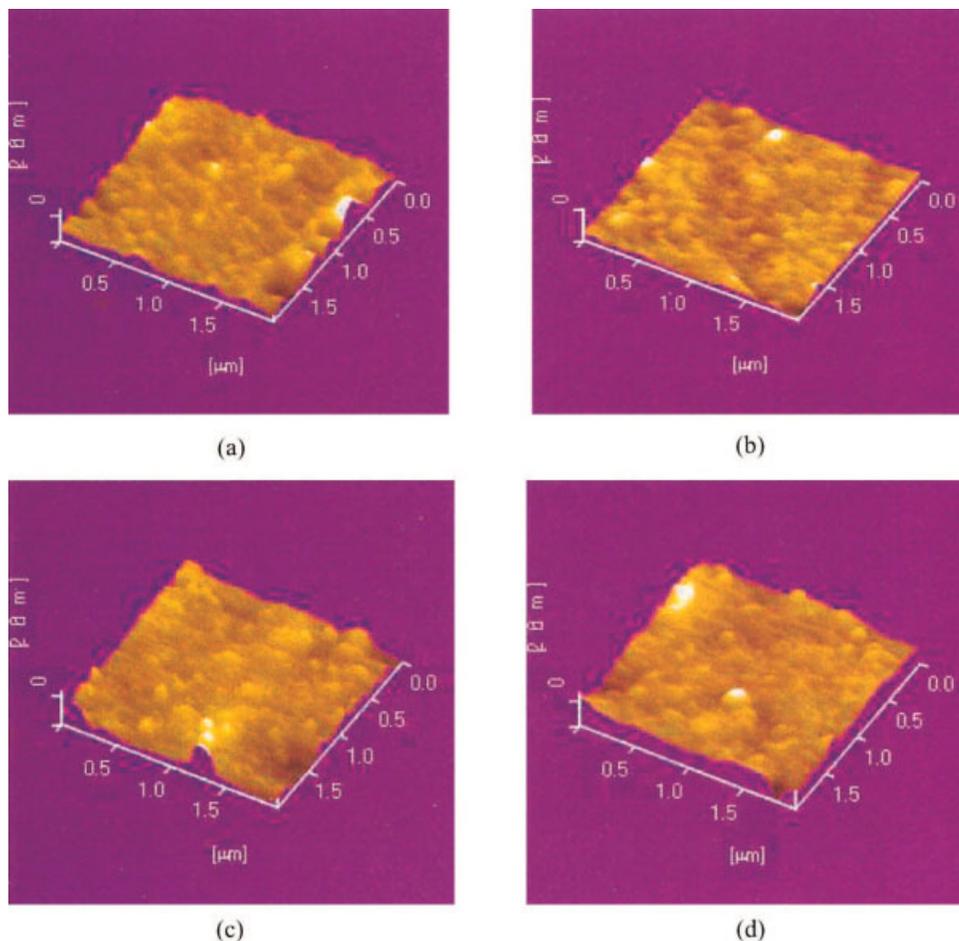


Figure 7 SEM images of CA membranes prepared with different solvent mixtures: (a) AC, (b) AC/THF, (c) AC/CF, and (d) AC/CYH.

$$\eta_{sp}/C = [\eta] + bC = [\eta] + K_H[\eta]^2C \quad (4)$$

where $[\eta]$ is the intrinsic viscosity representing the effective hydrodynamic volume of an isolated macromolecule in solution and b is the viscosity slope coefficient or interaction coefficient characterizing the interaction between polymer species.³² From Figure 3, the values of $[\eta]$, b , and K_H for each polymer–solvent system with or without the second solvent were obtained by the linear regression of each line, and they are listed in Table II.

Relation between the PV performance and the dilute-solution properties

The results from Hamza et al.¹⁶ indicated that $[\eta]$ of a polymer in a casting solution could affect the coil shape in solution and the surface structure of reverse-osmosis membranes. The PV membrane performance from a single solvent was related to the b value, that is, $J \propto b^{-1}$, in our previous study.³³ According to the results of J and K_H in Table II, however, the PV mem-

brane performance from solvent mixtures was better related to the K_H value, and this is shown in Figure 4.

As mentioned previously, K_H reflects the interaction between a polymer and a solvent and also represents the chain shape and molecular dimension. Therefore, K_H is high when the polymer is branched or the polymer is dissolved in a poor solvent.³⁴ Obviously, the increase of K_H here can be attributed to the second solvent getting worse in the order of THF, CF, and CYH. Recently, Cheng et al.^{35,36} proposed a cluster model to describe the concentration dependence on the viscosity of polymers in dilute solutions. According to his model, K_H is equal to $6K_m/[\eta]$, where K_m is the association constant of a polymer in a solution. Figure 5 shows the K_m dependence of J . Therefore, it is believed that the chain association of a polymer in a solution could affect the performance of its membrane. Clearly, the chain association of a polymer in a solution must result in the inhomogeneity of the coil density in the solution, which could affect the morphology and performance of the membrane in bulk. It leads us to consider that K_H or K_m is proved to be a good

TABLE III
Mean Size of Nodules and Surface Roughness Parameter (R_a and R_z) of Membranes Prepared from AC and AC with Different Second Solvents

Cast solvent	Mean size of nodules (nm)	R_a (nm)	R_z (nm)
AC	120.8	0.902	9.92
	116.3	1.17	10.4
AC/THF	119.0	0.76	6.26
	120.1	0.732	5.30
AC/CF	134.8	1.519	12.07
	138.0	1.405	12.50
AC/CYH	181.1	1.86	15.05
	178.1	1.774	15.88

criterion for choosing a suitable casting solvent and predicting membrane performance.

Morphology of the CA membrane from SEM and AFM

Some studies have reported that the chain shape of a polymer in a solution could affect the morphology of the polymer in bulk.^{37–40} SEM images of CA membranes prepared with different solvent mixtures are shown in Figure 6. The CA–AC membrane morphology is dense, smooth, and homogeneous, and the morphologies of the other three kinds of membranes from CA–AC/THF, CA–AC/CF, and CA–AC/CYH seem to be loose and irregular and cellular, leafy, and porelike, respectively. This changing trend of the morphology is probably due to the increase in the chain aggregation inhomogeneity in the membranes with the decrease of the second solvent solvation.

Figure 7 shows AFM photographs for CA membranes prepared by AC and different AC/solvent mixtures. Each micrograph shows that the membrane surface is not smooth and consists of many nodules. These nodules are considered to be aggregates of polymer chains. Some difference can be observed in the nodule size, nodule boundaries, and roughness on each membrane surface. Table III gives the average size of the nodule and roughness calculated via eq. (3).

Obviously, the average size increases as the second solvent solvation decreases in the order of THF, CF, and CYH. In comparison with the nodule model proposed by Kesting,⁴¹ the nodule here is not the nodule aggregate or supernodular aggregate but is just the nodule. However, it can be believed that the chain association in the solution must be one of the factors affecting the nodule morphology of the membrane surface.

CONCLUSIONS

From this study, the following conclusions can be drawn:

1. All CA membranes were prepared by a dry-cast process in three type of casting solvent mixtures (AC/THF, AC/CF, and AC/CYH) and the pure solvent AC. J of the CA membranes from the solvent mixture was always higher than J of the CA membranes from the pure solvent AC for separating MeOH/MTBE mixtures with 5 wt % MeOH, and the flux increased (α decreased) with an increasing second solvent volume fraction. The trend of the flux was $J_{CYH} > J_{CF} > J_{THF}$ at the same second solvent volume fraction in the casting solvent mixture.
2. The types of second solvents significantly influenced the membrane morphology. The SEM images showed that the morphology inside the membranes changed in the order of smooth, cellular, leafy, and porelike, and this was attributed to a solvent effect caused by the different solvents: AC, AC/THF, AC/CF, and AC/CYH, respectively. The average size of the nodule from AFM photography increased with the second solvent in the order of THF, CF, and CYH.
3. The results from the dilute-solution study for the CA polymer showed that K_H of the CA solutions increased with the solvents in the order of AC, AC/THF, AC/CF, and AC/CYH. From a comparison of the solution properties of CA and its membrane performance, $J \propto K_H$ was obtained. This indicates that the K_H value of a polymer solution is an important variable governing the morphology and performance of PV membranes. The reason could be that the chain association in a polymer solution results in macromolecular aggregates in the membranes and brings about different PV performances of the membranes ultimately.

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