Dehydration of an azeotrope of ethanol/water by sodium carboxymethylcellulose membranes cross-linked with organic or inorganic cross-linker

T. Uragami*, D. Wakita, T. Miyata

Department of Chemistry and Materials Engineering, High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan

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Abstract. To control the swelling of sodium carboxymethylcellulose (CMCNa) membranes, mixtures of CMCNa and glutaraldehyde (GA) and mixtures of CMCNa as an organic component and tetraethoxysilane (TEOS) as an inorganic component were prepared, and CMCNa/GA cross-linked membranes and CMCNa/TEOS hybrid membranes were formed. In the separation of an ethanol/water azeotrope by pervaporation (PV), the effects of the GA or TEOS content on the water/ethanol selectivity and permeability of these CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were investigated. Cross-linked and hybrid membranes containing up to 10 wt% GA or 10 wt% TEOS exhibited higher water/ethanol selectivity than CMCNa membrane without any cross-linker. This resulted from both increased density and depressed swelling of the membranes by the formation of a cross-linked structure. The relationship between the structure of the CMCNa/GA cross-linked membranes and CMCNa/TEOS hybrid membranes and their permeation and separation characteristics for an ethanol/water azeotrope during PV is discussed in detail.

Keywords: biopolymers, biocomposite, polymer membranes, bio-ethanol, dehydration

1. Introduction

An aqueous bio-ethanol solution can be produced by fermentation of biomass resources such as dregs of sugar corn, stems of corn and so on, separation and concentration of an aqueous ethanol solution are actively noticed from the viewpoint of a new energy source instead of limited petroleum resource. In general, aqueous alcohol solutions are concentrated by distillation, but an azeotrope (96.5 wt% ethanol) cannot be further separated by distillation. In particular, pervaporation (PV) is a promising technique for separation of azeotropes [1, 2] such as an aqueous solution of 96.5 wt% ethanol, and close boiling point mixtures [3, 4] through polymer membranes. In PV separation, membrane performance is highly dependent upon the physical and

chemical structures of the membrane. Therefore, carefully designing the membrane structure is required to develop membranes with high selectivity and permeability. We have studied several kinds of cross-linked polymer membranes and organic-inorganic hybrid membranes to separate aqueous ethanol solutions during PV. For example, chitosan membranes cross-linked with glutaraldehyde [5], quaternized chitosan membranes cross-linked with glutaraldehyde [6], ethylenglycoldiglycidylether [7] and poly(ethylene oxydiglycolic acid) [8], poly(vinyl alcohol) and tetraethoxysilane (TEOS) [9], poly(vinyl alcohol-co-acrylic acid) and TEOS [10], and quaternized chitosan and TEOS [11] hybrid membranes prepared by sol-gel reaction all showed high water/ethanol selectivity for an

*Corresponding author, e-mail: uragami@kansai-u.ac.jp

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azeotrope of ethanol/water because their membrane swelling could be effectively controlled by cross-linking or hybridization.

In this study, sodium carboxymethylcellulose (CMCNa) was selected as a membrane material because CMCNa can be easily formed into fine membrane. In general, CMCNa has been applied as sizing in paper fabrication, as emulsion stabilizer, in water-borne paints and so on. We prepared sodium carboxymethylcellulose (CMCNa) membranes cross-linked with glutaraldehyde (GA) and novel organic-inorganic hybrid membranes by the sol-gel reaction between CMCNa as an organic component and tetraethoxysilane (TEOS) as an inorganic component in order to reduce the swelling of the CMCNa membranes. Furthermore, the permeation and separation characteristics of an azeotrope of ethanol/water through the CMCNa/GA cross-linked membranes and the CMCNa/TEOS hybrid membranes during PV are discussed as a function of the GA or TEOS content. Recently, organic-inorganic hybrid materials are recognized as significant composite materials with both the functionality of an organic compound and with the strength of an inorganic compound. Therefore, in this study we call CMCNa/TEOS cross-linked membranes as CMCNa/TEOS hybrid membranes.

2. Materials and methods

2.1. Materials

Sodium carboxymethylcellulose (CMCNa), whose degree of sodium carboxymethylation is 0.91 purchased from Tokyo Kasei Industry Co. Ltd., Japan. GA and trifluoroacetic acid anhydride were supplied by Wako Chemical Industry Co. Ltd., Japan. TEOS was supplied by Shinetsu Chemical Industry Co. Ltd., Japan. All other reagents and solvents used in this study were supplied by commercial sources.

2.2. Preparation of CMCNa membrane, CMCNa/GA cross-linked membranes and CMCNa/TEOS hybrid membranes

The CMCNa membranes were prepared by pouring 3 wt% CMCNa in 0.01 M HCl onto a glass plate treated with silicon, allowing water to evaporate at 50°C for 10 h in an oven, and then drying under

reduced pressure. The CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were prepared by pouring 3 wt% CMCNa in 0.01 M HCl with a desired amount of GA as an organic cross-linker or a desired amount of TEOS as an inorganic cross-linker onto a glass plate treated with silicon, allowing water to evaporate at 50°C for 10 h in an oven, and then drying under reduced pressure. The resulting CMCNa membranes, CMCNa/GA cross-linked membranes and CMCNa/TEOS hybrid membranes were kept in a desiccator at room temperature *in vacuo*.

2.3. PV apparatus and measurements

The PV cell and PV apparatus have been described in a previous paper [12]. The effective membrane area was about 13.8 cm². The PV experiments were carried out under the following conditions: permeation temperature, 40°C; and pressure of the permeate side, 1.33 Pa. The feed solution, an aqueous solution of 96.5 wt% ethanol, was circulated between the PV cell and the feed tank to maintain a constant concentration of feed solution in the PV cell. The permeation rate [kg/m²·h] for an azeotrope of ethanol/water during PV was determined from the weight [kg] of permeate collected in a cold trap, the permeation time [h] and the effective membrane area [m²]. The results of the permeation for an azeotrope of ethanol/water by PV were reproducible, and the errors inherent in these permeation measurements ranged within a few percent of the permeation rates through the membranes. The permeation results in this study were determined after steady-state flux.

The ethanol concentration in the feed and permeate was determined by means of a gas chromatograph (Shimadzu GC-14A, Japan) using a flame ionization detector (FID) and a capillary column (Shimadzu Co. Ltd: PorapacQ, Japan) heated to 180°C. The separation factor, $\alpha_{\text{sep.H}_2\text{O/EtOH}}$, was calculated from Equation (1):

$$\alpha_{\text{sep.H}_2\text{O/EtOH}} = \frac{P_{\text{H}_2\text{O}} / P_{\text{EtOH}}}{F_{\text{H}_2\text{O}} / F_{\text{EtOH}}} \quad (1)$$

where F_{EtOH} and $F_{\text{H}_2\text{O}}$ are the weight fractions of ethanol and water in the feed solution, and P_{EtOH} and $P_{\text{H}_2\text{O}}$ are those in the permeate, respectively.

2.4. Composition of solution absorbed into CMCNa/GA cross-linked membranes and CMCNa/TEOS hybrid membranes

The CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were dried completely under reduced pressure at room temperature and weighed. The dried membranes were immersed into an azeotropic mixture of ethanol/water in a sealed vessel at 40°C until equilibrium was reached. A large amount of the swollen CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes was placed in a container as reported in a previous paper [13]. The system was evacuated, and the container with the swollen membranes was then heated. The solution sorbed into the swollen membranes was completely desorbed under reduced pressure, and was collected in a U-tube cooled with liquid nitrogen. The composition of the solutions sorbed into the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes was then determined by measuring the ethanol concentration in the collected solution by gas chromatography (Shimadzu GC-14A). The ethanol/water composition in the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes versus that in the feed solution yielded the sorption selectivity, $\alpha_{\text{sorp.H}_2\text{O/EtOH}}$, as expressed in Equation (2):

$$\alpha_{\text{sorp.H}_2\text{O/EtOH}} = \frac{M_{\text{H}_2\text{O}} / M_{\text{EtOH}}}{F_{\text{H}_2\text{O}} / F_{\text{EtOH}}} \quad (2)$$

where $F_{\text{H}_2\text{O}}$ and F_{EtOH} are the weight fractions of water and ethanol in the feed solution, and $M_{\text{H}_2\text{O}}$ and M_{EtOH} are those sorbed into the membrane, respectively.

2.5. Degree of swelling

The CMCNa and CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were completely dried under reduced pressure at 40°C and weighed. These dried membranes were immersed in an ethanol/water azeotrope (96.5 wt% ethanol) in a sealed vessel at 40°C until equilibrium was reached. The membranes were removed from the vessel, wiped quickly with filter paper, and weighed. The degree of swelling of the membrane (DS) was determined from Equation (3):

$$DS = \frac{W_s}{W_d} \quad (3)$$

where W_d and W_s are the weights of the dried membrane and swollen membrane in the feed, respectively.

2.6. Measurement of the contact angle

The contact angle for methylene iodide on the surface of the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes was measured by a contact angle meter (Dropmaster Kyouwa Sci. Co. Ltd.) at 25°C. The contact angle, θ , was calculated from Equation (4) [14]:

$$\theta = \cos^{-1} \left(\frac{\cos \theta_a + \cos \theta_r}{2} \right) \quad (4)$$

where θ_a and θ_r are the advancing contact angle and the receding contact angle, respectively.

2.7. X-ray photoelectron spectroscopy (XPS) measurements

To characterize the surfaces of the CMCNa membrane, the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes, the hydroxyl groups of their surfaces were fluorinated by trifluoroacetic acid anhydride as shown by Equation (5):

The fluorination was carried out as follows. Specimens of these membranes (5 mm×5 mm) were immersed in a mixture of benzene (20 ml), pyridine (4 ml) and trifluoroacetic acid anhydride (4 ml) for 1.5 h at room temperature, and the immersed specimens were washed with benzene repeatedly. Next, they were placed in a Soxhlet extractor with diethylether for 12 h to completely remove the trifluoroacetic acid anhydride and trifluoroacetic acid, and then dried in a desiccator under reduced pressure at room temperature.

The fluorinated surfaces of these membranes were characterized with an X-ray photoelectron spectroscopy (XPS) (Shimadzu, ESCA-3400, Japan). The typical operating conditions were as follows: $\text{CuK}\alpha$ radiation of 15 kV and 10 mA. The pressure in the instrument chamber was less than $1.0 \cdot 10^{-6}$ Pa. No radiation damage was observed during the data collection time.

The atomic compositions on the surface of the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were determined by Equations (6) and (7):

$$\text{CMCNa} / (\text{CMCNa} + \text{TEOS}) = \text{F} / (\text{F} + \text{Si}) \quad (6)$$

$$\text{CMCNa} / (\text{CMCNa} + \text{GA}) = \text{F} / (\text{F} + \text{O}) \quad (7)$$

where F, Si and O are the fractions of each element on the surface of the CMCNa/GA membranes and CMCNa/TEOS membranes.

2.8. Transmission electron micrographs (TEM)

The CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were embedded in epoxy resin and sliced into thin films (thickness ≈ 50 nm) with a microtome (Leica; Reichert Ultracut E). The structure of the membranes was observed by a transmission electron microscope (TEM) (JEOL JEM-120L, Japan) at an accelerating voltage of 80 kV.

3. Results and discussion

3.1. Effect of the cross-linker content on the permeation and separation characteristics

Figure 1 shows the effects of the cross-linker content on the permeation rate and separation factor for an azeotrope of ethanol/water through the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes during PV. As can be seen from Figure 1, the separation factors of all CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were higher than those of the neat CMCNa membrane. These results support the contention that all membranes had water/ethanol selectivity. The separation factors of the CMCNa/TEOS hybrid membranes were higher than those of CMCNa/GA cross-linked membranes. Furthermore, in both CMCNa/GA cross-linked and CMCNa/TEOS

Figure 1. Effects of the GA or TEOS content on the permeation rate and separation factor for an azeotrope of ethanol/water through CMCNa/GA cross-linked membranes (●) or CMCNa/TEOS hybrid membranes (○) during PV at 40°C

hybrid membranes, the membranes cross-linked with 10 wt% of cross-linker showed the highest separation factors. On the other hand, one can understand that the permeation rates of both CMCNa/TEOS hybrid and CMCNa/GA cross-linked membranes decreased until 10 wt% of cross-linker content, but above this content, the dependency of permeation rate on the cross-linker content significantly differ. Thus, the permeation rate in the CMCNa/TEOS membrane increased but that in the CMCNa/GA membrane decreased slightly.

3.2. Chemical structure of CMCNa/GA cross-linked membranes and CMCNa/TEOS hybrid membranes

In general, the permeation and separation characteristics of these membranes are significantly governed by the chemical and physical structure of the membrane. Thus, it is known that the chemical

structure influences the solubility of the permeants into the membrane and the physical structure affects the diffusivity of the permeants through the membrane. Therefore, we analyzed the chemical structure of the membranes by the measuring the composition of solution in the membrane, the contact angle of the membrane surface and XPS, and the physical structure by the measuring the membrane density, and the degree of swelling of the membranes, and by TEM observation to elucidate their permeation and separation characteristics, as shown in Figure 1.

Figure 2. Effect of the cross-linker content on the ethanol concentration in the CMCNa/GA cross-linked membranes (●) and CMCNa/TEOS hybrid membranes (○) immersed in an aqueous solution of 96.5 wt% ethanol at 40°C

Figure 3. Contact angle for methylene iodide on the surface of CMCNa/GA cross-linked membranes (●) and CMCNa/TEOS hybrid membranes (○) as a function of the cross-linker content

In Figures 2 and 3, the ethanol concentration sorbed into the membrane immersed in an azeotrope of ethanol/water and the contact angle of the membrane surface for methylene iodide as a function of the cross-linker content are shown. As can be seen from Figure 2, the ethanol concentration sorbed into the membrane for both the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes decreased slightly with increasing content up to 10 wt% of GA or TEOS, whereas the ethanol concentration in the CMCNa/TEOS membrane increased faintly, and the ethanol concentration in the CMCNa/GA membrane increased more than 10 wt% of cross-linker content.

On the other hand, the sorbed ethanol concentration for the CMCNa/TEOS hybrid membranes was lower than that of the CMCNa/GA cross-linked membranes over the whole range cross-linker contents. The higher separation factors for the CMCNa/TEOS hybrid membranes in Figure 1 are dependent on this result.

In Figure 3, the increase or decrease in the contact angle for methylene iodide, which is a hydrophobic solvent, suggests that the membrane surface became more hydrophilic or hydrophobic with an increase in the cross-linker content, respectively. The contact angles of the CMCNa/TEOS hybrid membranes were higher than those of the CMCNa/GA cross-linked membranes. This result suggests that the former membranes are more hydrophilic than the latter. In the CMCNa/TEOS hybrid membranes, the contact angle at 10 wt% of TEOS showed a maximum, and all contact angles were higher than that of the CMCNa membrane. These results suggest that the CMCNa/TEOS hybrid membranes are more hydrophilic than CMCNa membranes without TEOS. The contact angles of the CMCNa/GA cross-linked membranes decreased with an increasing GA content, and were lower than that of the membrane without GA. This suggests that the CMCNa/GA cross-linked membranes are more hydrophobic than membranes without GA. The higher hydrophilicity of the CMCNa/TEOS hybrid membranes could be attributed to the fact that some silanol groups from the four silanol groups formed from TEOS form the hydrogen and covalent bonds by reacting with the hydroxyl groups in CMCNa and remained silanol groups from TEOS can be introduced into the CMCNa/TEOS membrane, and consequently hydrophilic silanol groups in CMCNa/

TEOS membrane increase, and thus the higher hydrophobicity of the CMCNa/GA cross-linked membranes could be due to the fact that the hydroxyl groups in the CMCNa molecule can be consumed by the condensation reaction between the aldehyde group in the GA molecule and the hydroxyl group in the CMCNa molecule.

3.3. XPS measurements of the membranes

To determine the chemical structure of the surface of the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes in more detail, the hydroxyl groups on the surface of cross-linked and hybrid membranes were labeled by trifluoroacetic acid anhydride as per Equation (5).

In Figures 4 and 5, the XPS spectra of the fluorinated surfaces of CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes are shown, respectively. In Figure 4, with increasing GA content, the peak intensity assigned to the F atom at 690 eV decreased, whereas the peak intensity due to the O atom at about 532 eV increased. On the other hand, as can be seen in Figure 5, the peak intensity assigned to the Si atom at 105 eV increased and the F atom at 690 eV decreased slightly upon introducing TEOS into the CMCNa membrane. In

Figure 4. XPS spectra of (a) the CMCNa membrane, (b) a GA content of 5 wt%, (c) a GA content of 10 wt%, (d) a GA content of 20 wt% and (e) a GA content of 30 wt% in the CMCNa/GA cross-linked membranes. The surfaces of these membranes were treated with trifluoroacetic acid anhydride

Figure 5. XPS spectra of (a) the CMCNa membrane, (b) a TEOS content of 5 wt%, (c) a TEOS content of 10 wt%, (d) a TEOS content of 20 wt% and (e) a TEOS content of 30 wt% in the CMCNa/TEOS hybrid membranes. The surfaces of these membranes were treated with trifluoroacetic acid anhydride

the spectrum (c) of the CMCNa/TEOS hybrid membrane with a TEOS content of 10 wt%, however, the peak intensity of the F atom increased but that of the Si atom decreased. Above 10 wt% of TEOS content, the peak intensity at the F atom decreased and that of the Si atom increased. The results from Figures 4 and 5 support the results of the contact angle measurements in Figure 3. Thus, it is found that the networks of CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes and the amount of the hydroxyl and silanol groups on the surface of these membranes were significantly influenced by the GA or TEOS content.

In Figure 6, the effects of the cross-linker content on the atomic compositions on the surface of the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes are shown, respectively. With increasing GA content, the amount of F atoms decreased because of the decrease in the hydroxyl group based on the condensation reaction between the hydroxyl groups in the CMCNa molecule and the aldehyde groups in the GA molecule. In Figure 6, the introduction of a small amount of TEOS into the CMCNa accelerated the reactions between the hydroxyl groups and the silanol groups formed due to the hydrolysis of TEOS and the amount of

Figure 6. Effect of the cross-linker content on the atomic composition on the surface of CMCNa/GA cross-linked membranes (●) and CMCNa/TEOS hybrid membranes (○)

hydroxyl groups in the CMCNa molecule decreased and consequently the amount of F atoms decreased. At 10 wt% of TEOS content, the amount of F atoms increased due to the increase in the silanol group during the sol-gel process. Above 10 wt% of TEOS content, since the number of hydroxyl groups were decreased by excess condensation reactions, the amount of F atom decreased. These findings also support those observed in the contact angle measurements.

3.4. Structure of CMCNa/TEOS hybrid membranes

Based on the above results, the structure of CMCNa/TEOS hybrid membranes is illustrated in Figure 7, showing the process polycondensation reaction of TEOS [15]. In the first step of the process of preparing the CMCNa/TEOS hybrid membranes, the silanol groups were formed by hydrolyzing TEOS in the presence of an acid catalyst (A). The resulting silanol groups yielded siloxane bonds due to the dehydration or dealcoholysis

Figure 7. Hydrolysis and condensation scheme for TEOS

Figure 8. Illustration of the interaction between CMCNa and TEOS

reactions with other silanol groups or ethoxy groups during the membrane drying process (B). These reactions led to cohesive bodies between siloxane groups in the membrane. Since the siloxane groups were dispersed in the membrane, the silanol groups in the siloxane and the hydroxyl groups in CMCNa formed hydrogen and covalent bonds, which are the cross-linking points, as illustrated in Figure 8.

However, the dehydration and dealcoholysis reactions occurred predominantly rather than the formation of hydrogen and covalent bonds. Thus, a rough cohesive structure of TEOS was formed, and hence a membrane with a more open structure was produced, leading to a decrease in the water/ethanol selectivity.

3.5. Physical structure of CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes

In Figure 9, the degree of swelling of the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes is shown as a function of the GA or TEOS content. The degree of swelling of both membranes decreased with an increase in the GA or TEOS content. The swelling of the CMCNa/TEOS hybrid membranes was smaller than that of the CMCNa/GA cross-linked membranes. These results can be supported by the results of the membrane density.

Figure 9. Effect of the cross-linker content on the degree of swelling of CMCNa/GA cross-linked membranes (●) and CMCNa/TEOS hybrid membranes (○)

3.6. Permselectivity mechanism of cross-linked and hybrid membranes

In the solution-diffusion model [16, 17] differences in the solubility of the permeants in the membranes and differences in the diffusivity of the permeants in the polymer membranes are very significantly related to their permselectivity [18]. It is very important to determine the sorption selectivity and diffusion selectivity to elucidate the separation mechanism of an azeotrope of ethanol/water through CMCNa/GA cross-linked and MCNa/TEOS hybrid membranes. Thus, in order to discuss the water/ethanol selectivity of an azeotrope of ethanol/water through CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes from the viewpoint of the solution-diffusion mechanism, both the sorption selectivity and the diffusion selectivity must be determined. The sorption selectivity, $\alpha_{\text{sorp.H}_2\text{O/EtOH}}$, was determined from Equation (2), whereas the diffusion selectivity, $\alpha_{\text{diff.H}_2\text{O/EtOH}}$, could be calculated from Equation (8) using Equations (1) and (2):

$$\alpha_{\text{diff.H}_2\text{O/EtOH}} = \frac{\alpha_{\text{sep.H}_2\text{O/EtOH}}}{\alpha_{\text{sorp.H}_2\text{O/EtOH}}} \quad (8)$$

In Figure 10, the separation factor, the sorption selectivity and the diffusion selectivity for an azeotrope of ethanol/water through CMCNa/GA cross-linked or CMCNa/TEOS hybrid membranes are shown as a function of the GA or TEOS content. The sorption selectivities of all membranes

Figure 10. Effects of the cross-linker content on the separation factor, the sorption selectivity and the diffusion selectivity for an azeotrope of ethanol/water through CMCNa/GA cross-linked membranes (●) and CMCNa/TEOS hybrid membranes (○) during PV at 40°C

with various GA or TEOS contents were greater than their diffusion selectivities. This observation suggests that the dehydration process from an aqueous solution of 96.5 wt% ethanol using CMCNa/GA

cross-linked and CMCNa/TEOS hybrid membranes is mainly governed by the sorption process. The fact that water was preferentially absorbed into these membranes rather than ethanol also supports this conclusion. Furthermore, the sorption selectivities of the CMCNa/TEOS hybrid membranes were higher than those of the CMCNa/GA cross-linked membranes. These results are supported by the composition absorbed into the membrane as shown in Figure 2. On the other hand, the diffusion selectivities of the former membranes were smaller than those of the latter membranes. This is due to the fact that with increasing GA or TEOS content, the degree of swelling of the membrane decreased as shown in Figure 9. The increase in the water permselectivity with increasing GA or TEOS content was mainly due to an increase in the solubility of water in the CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes.

3.7. TEM images of cross-linked and hybrid membranes

Figure 11 shows TEM images of the CMCNa membrane, the CMCNa/GA cross-linked membranes and CMCNa/TEOS hybrid membranes with 10 and 30 wt% of GA or TEOS content. The black portion in these images is dependent on the Si atom in TEOS. As can be seen from these TEM images, the structure of the CMCNa membrane was homogeneous but in the CMCNa/TEOS hybrid membranes, a phase separated structure was observed, especially in the hybrid membrane with 30 wt% of TEOS content which showed a heterogeneously dispersed cohesion of TEOS. On the other hand, in the CMCNa/GA cross-linked membranes such a phase separated structure was not observed. Based on the above results, the hypothetical structure of the CMCNa/TEOS hybrid membranes is shown in Figure 12. In the CMCNa/TEOS hybrid

Figure 11. TEM images of : (a) the CMCNa membrane, (b) with a TEOS content of 10 wt%, (c) with a TEOS content of 30 wt% in CMCNa/TEOS hybrid membranes, (d) with a GA content of 10 wt%, (e) with a GA content of 30 wt% in CMCNa/GA cross-linked membrane

Figure 12. Change in the cross-linked structure of CMCNa/TEOS hybrid membranes

membranes containing 10 wt% TEOS or less, the cross-linked structure was formed by smooth reactions between the CMCNa and TEOS and between the TEOS molecules. Consequently, although the permeation rate decreased with increasing TEOS content, the water/ethanol selectivity was improved remarkably, as shown in Figure 1. However, in the CMCNa/TEOS hybrid membrane containing excess TEOS (>10 wt%) the polycondensation reaction between the TEOS molecules proceeds preferentially. Therefore, the cross-linking reaction between CMCNa and TEOS was less favored. The resulting cohesion in the TEOS domains prevents the hydrogen bonds between the CMCNa molecules. These results influence the diffusion path and consequently the permeation rates and the selectivity. Therefore, an increase in the permeation rate and a decrease in the water/ethanol selectivity were observed.

4. Conclusions

Both CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes showed high water/ethanol selectivity. Consequently, it was found that the introduction of the cross-linking structure into CMCNa molecule was very effective. The water/ethanol selectivity of the CMCNa/TEOS hybrid membranes was higher than that of the CMCNa/GA cross-linked membranes. When a suitable amount of TEOS was added to CMCNa, the TEOS was homogeneously dispersed in the membrane, and the most suitable cross-linked structure was formed. Consequently, the best water/ethanol selectivity was obtained. In comparing of the role of TEOS and GA as cross-linkers, since TEOS gave higher cross-link points than GA, a denser cross-linked structure was formed, the swelling of the membrane was effectively controlled. Consequently, the CMCNa/TEOS hybrid membranes showed higher water/ethanol selectivity. The abrupt changes in some properties of CMC membranes cross-linked with 10 wt% of TEOS can be explained as follows: in the sol-gel process the CMC membranes with 10 wt% of TEOS is homogeneous with a lot of hydroxyl groups and consequently chemical and physical structures of this membrane are very fine. In this study, we demonstrated that membranes with high water/ethanol selectivity can be designed

by the hybridization of CMCNa as an organic component and TEOS as an inorganic component using the sol-gel reaction, and CMCNa offers potential for the selective separation of an azeotrope of ethanol/water.

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