EFFECTS OF GEL COMPOSITION ON SEPARATION PROPERTIES OF ETHANOL/WATER MIXTURES BY ACRYLAMIDE GEL MEMBRANES

Shuji SAKOHARA, Yoshihiro MAEKAWA, Yasushi TATEISHI
AND Masashi ASAEDA

Department of Chemical Engineering, Hiroshima University,
Higashi-Hiroshima 724

Separation performance of acrylamide gel membranes for ethanol/water mixtures is greatly affected by the effective size of the pores in the network and the network's homogeneity. With increasing concentration of crosslinker (N,N'-methylenebisacrylamide), coarse and dense parts of a networks, i.e., the heterogeneous structure, are produced in the gels, though the effective size of the pores in the network must be reduced. Such a heterogeneous structure appears remarkably at low concentration of primary monomer (acrylamide). The coarse part of the network significantly affects the leakage of ethanol molecules through a membrane and the state of water in the gels, which is closely related to the selective permeation of water through the membrane. As a result, optimum gel compositions exist for the permeation of water and for the obstruction of ethanol permeation, respectively.

Introduction

Membrane separation of solvent/water mixtures, most of which have azeotropic points, is well known as a useful separation method from the viewpoint of energy conservation. Various types of membranes through which water permeates selectively have been studied for use in separation of such mixtures.

In work described in previous papers,[6,7,9] the authors prepared hydrogel membranes polymerized in the pores of a thin silica-alumina membrane, and reported that acrylamide gel membrane had large flux of water and a high separation factor for separation of various kinds of solvent/water mixtures. Such a high separation factor is considered due to the fact that permeation of solvent molecules can be blocked by the gel network, which shrinks with increasing solvent concentration upstream of the membrane[7,9]. The separation performance, however, depended on preparation conditions of gels such as the concentrations of primary monomer and crosslinker and gelation temperature.[6,8] To prepare a superior gel membrane, the effects of the gel preparation conditions on the separation performance must be examined systematically.

In general, it is well known that gels become transparent or opaque corresponding to preparation conditions. The network of transparent gels is homogeneous macroscopically, while that of opaque gels is composed of dense and coarse parts, namely, a heterogeneous structure.[10] Homogeneity of a network is considered to be an important factor in the separation of solvent/water mixtures, because if the gel membranes have a heterogeneous network structure the leakage of solvent molecules is promoted through the coarse parts of the network.

Such network structures also affect the state of water in the gel, which is classified into three types corresponding to the extent of water/polymer interactions, i.e., nonfreezing water, bound (or associated) water and free water[11]. The properties of these types of water have been studied with different techniques such as NMR,[4,5] DSC[1,5] and IR[2], and it has been recognized that the presence of free water decreases the selectivity of membranes[3,11].

In the present paper, the effects of acrylamide gel compositions on the homogeneity of the network, the state of water in acrylamide gels and the exclusion properties of ethanol molecules by acrylamide gels are examined. Furthermore, the separation properties of acrylamide gel membranes of various compositions for ethanol/water mixtures are discussed.

1. Experiments

1.1 Evaluation of homogeneity of network

Homogeneity of network can be roughly evaluated from the transparency of gels as mentioned above. From this point of view, the transparency of gels prepared with various concentrations of primary monomer and crosslinker was compared photo-

graphically. Sample gels were synthesized in small test tubes by copolymerizing acrylamide (AAm) of primary monomer and N,N′-methylenebisacrylamide (MbAAm) as crosslinker at 70°C. The synthesis procedures are very similar to those described elsewhere[10]. In polymerizing, ammonium persulfate and N,N,N′,N′-tetramethyl ethylenediamine were used as polymerization initiator and accelerator, respectively.

1.2 Measurement of ethanol concentrations in acrylamide gels immersed in aqueous ethanol solutions

Acrylamide gels of rod-shape (0.006 m in diameter and 0.01 m in length) were synthesized with glass tubes at 70°C. The gels were washed with deionized water, and then dried at about 100°C. Several dried gels previously weighed were immersed in aqueous ethanol solution of known concentration and known weight until they reached equilibrium at 30°C. Then the weight of remaining solution was determined from the weight of swollen gels. At the same time, ethanol concentration in the remaining solution was measured with a gas chromatograph. From the mass balance, ethanol concentration in the gels was estimated. Details are shown in the authors' previous paper.[7]

1.3 Evaluation of state of water in acrylamide gels by DSC measurements

Measurements were performed with a differential scanning calorimeter (Shimadzu, DSC-50). An aluminum cell with a sample gel of about 2 mg, having a given water content, was sealed and cooled to −70°C by liquid nitrogen. Then the cell was heated to 100°C at a constant heating rate of 3°C/min. The thermogram caused by the melting of ice crystals was recorded. Reducing the heating rate from 3 to 1°C/min produced no significant change in the thermograms. The accurate water content of sample gel was measured with a thermogravimetric analyzer (Shimadzu, TGA-50).

1.4 Preparation of membrane and separation experiment

Acrylamide gel membranes were prepared in the pores of a thin silica-alumina membrane as in the previous works[6,7,9].

Preparation of a thin, porous silica-alumina membrane   As a supporting substrate of silica–alumina membrane a coarse, porous cylindrical ceramic (0.01 m in outer diameter, 0.001 m in thickness and 0.12 m in length) with a mean pore diameter of 1 μm was used. Near the outer surface of such porous substrate a thin, porous silica–alumina membrane, the thickness of which was less than 10 μm, was formed by the sol-gel method, which was quite similar to that used in the previous work[7]. A schematic figure of the membrane module is shown in the previous paper[7].

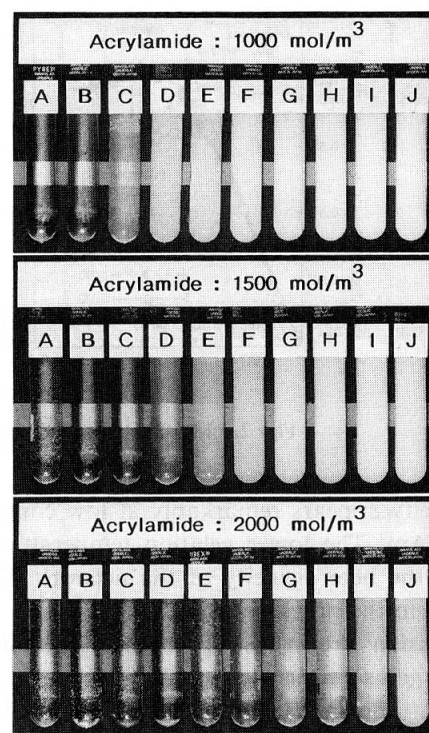Preparation of acrylamide gel membrane   AAm and MbAAm were copolymerized in the pores of

Fig. 1. Photographs of acrylamide gels of various compositions at 70°C. The concentrations of linker (N,N′-methylenebisacrylamide) are shown in Table 1.

Table 1. Concentration of crosslinker (N,N′-methylenebisacrylamide)

Symbol	A	B	C	D	E	F	G	H	I	J
Concentration [mol/m³]	30	40	50	60	70	80	90	100	110	120

silica–alumina membrane at 70°C. The procedures were the same as those proposed in the previous paper[7]. They were repeated in the same manner as in the previous work[7] until no significant change in separation performance was recognized.

Separation experiments   Separation experiments were carried out by the pervaporation method at 50°C with the same apparatus and the same procedures as those in the previous work[7].

2. Results and Discussion

2.1 Effects of acrylamide gel composition on homogeneity of network

Figure 1 shows photographs of acrylamide gels prepared with various concentrations of AAm and MbAAm at relatively high temperature, 70°C. The concentrations of MbAAm are shown in **Table 1**. The gels become milky or opaque with increasing MbAAm concentration, while they become transparent with increasing AAm concentration. These results suggest that the heterogeneity of the network increases with increasing MbAAm concentration, and that the
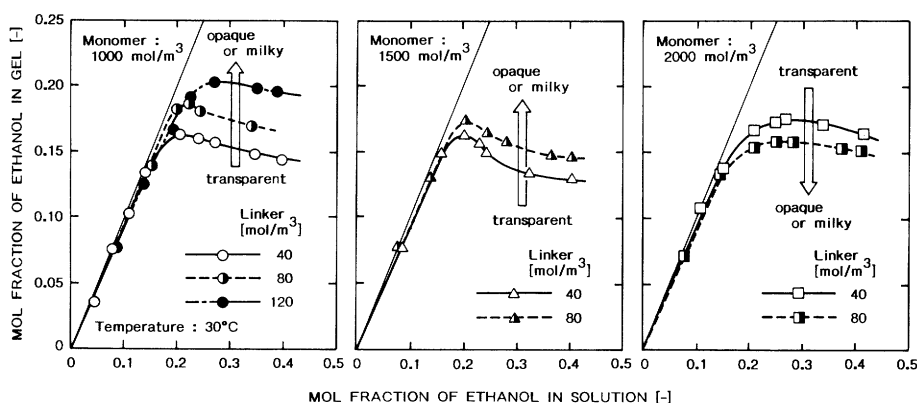
Fig. 2. Mol fraction of ethanol taken into acrylamide gels of various compositions

heterogeneity appears remarkably at low concentration of AAm. The lower gelation temperature also promotes the heterogeneity of the network. Details are shown in the previous paper[8].

2.2 Exclusion properties of ethanol molecules by acylamide gels of various compositions

Figure 2 shows the mol fractions of ethanol taken in acrylamide gels prepared with various concentrations of AAm and MbAAm. For all gels, ethanol concentration in the gel increases with increasing ethanol concentration in the outer solution up to about 20 mol%, and then decreases gradually in the experimental range. This phenomenon is throught to occur because it becomes more difficult for ethanol molecules to enter into the gel according to the shrinking of the network, as discussed in the previous paper[7].

At the compositions of 1000 and 1500 mol-AAm/m^3, ethanol concentrations in the shrunken gels prepared with a low concentration of MbAAm are lower than those prepared with a high concentration of MbAAm. With increasing MbAAm concentration the effective size of the pores in the network—namely, the network size—must be reduced, while the heterogeneity of the network increases as mentioned in the previous section. From these facts it is considered that the heterogeneity of the network rather than network size play a dominant role in the penetration of ethanol molecules into the gel, and that ethanol molecules in the coarse network cause such a higher concentration of ethanol in the opaque gels. Furthermore, it can be said that heterogeneity of the network still remains even in shrunken gels. On the other hand, at a composition of 2000 mol-AAm/m^3, the gel prepared with a concentration of 80 mol-MbAAm/m^3 holds fewer ethanol molecules than that prepared with 40 mol-MbAAm/m^3. In the case of such a high concentration of AAm, the effect of the concentration of MbAAm on the heterogeneity of the network is relatively small, as seen in Fig. 1. These results suggest that an optimum gel composition
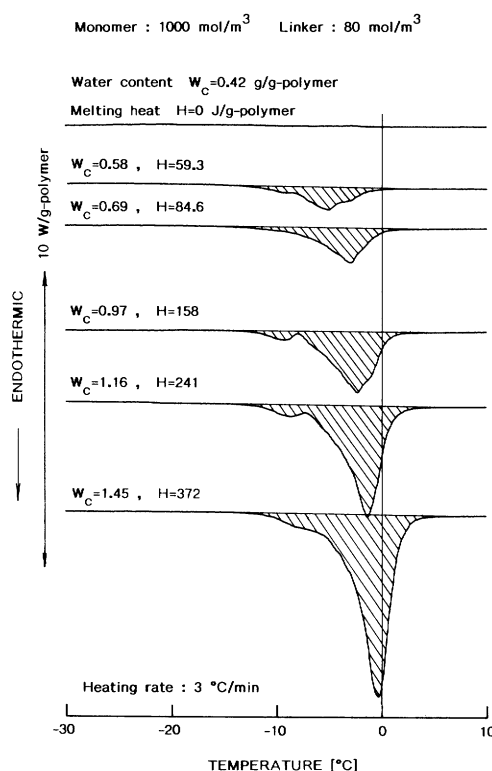

Fig. 3. A typical set of DSC thermograms for acrylamide gels of different water contents

exists for the exclusion of ethanol molecules.

2.3 Water in acrylamide gels of various compositions

DSC thermograms for acrylamide gels   Figure 3 shows a typical set of DSC thermograms for acrylamide gels of various water contents. In the case of extremely low water content, 0.42 g/g-polymer, no peak can be seen in the thermogram. With increasing water content, definite peaks appear in the thermograms, and the peak area, which corresponds to the melting heat of ice crystals, increases. The peak temperature in the thermogram is lower than 0°C, and approaches 0°C with increasing water content. These results suggest that water in acrylamide gels is
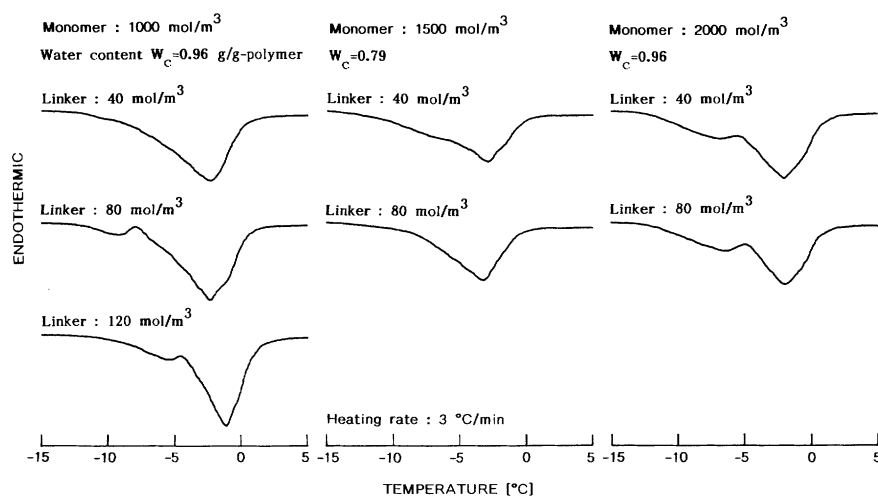
Fig. 4. Comparison of DSC thermograms for acrylamide gels of various compositions. The water contents of each set are almost the same.
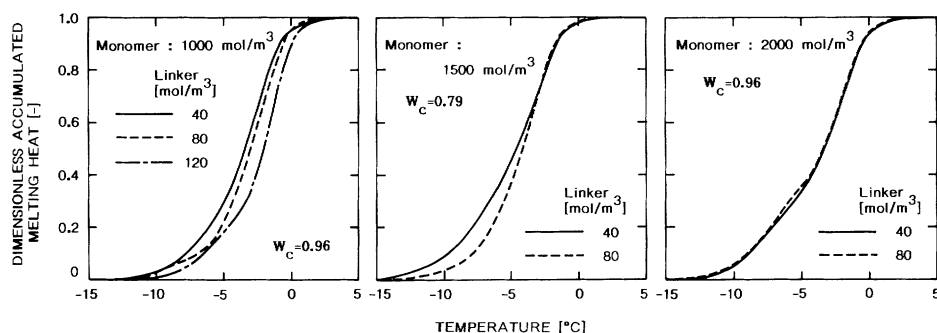

Fig. 5. Dimensionless, accumulated melting heat curves from DSC thermograms shown in Fig. 4

composed of different types, such as nonfreezing water, bound (or associated) water and free (or bulk) water as mentioned above.

Effects of network structure on behavior of water in acrylamide gels The shapes of thermograms depend on gel composition as shown in **Fig. 4**, even if the water contents are almost the same. This means that the state of water in a gel depends on its composition. To clarify this point, the thermograms shown in Fig. 4 were rearranged to **Fig. 5**, in which the accumulated melting heat is normalized by dividing by the total melting heat. At a concentration of $1000\,\text{mol-AAm/m}^3$ the curves shift to higher temperature with increasing MbAAm concentration. The shift indicates that the amount of water which behaves as free water shows a relative increase. With increasing MbAAm concentration, however, the network size must be reduced to decrease the amount of free water. This inconsistency is considered to occur because the heterogeneity of the network increases with increasing MbAAm concentration as mentioned in Sec. 2.1, and that more free water is retained in the coarse network. On the other hand, at a high concentration of AAm, $2000\,\text{mol/m}^3$, two curves with different concentrations of MbAAm are almost the

same. In the case of these compositions, the heterogeneity of the network is relatively small, as seen in Fig. 1. From these results, it can be said that the heterogeneity of a network makes the amount of free water, which decreases the selectivity of gel membrane, show a relative increase.

2.4 Separation results for ethanol/water mixtures by acrylamide gel membranes of various compositions

Permeation properties through a thin, porous silica-alumina membrane **Figure 6** shows the permeation properties of water and ethanol through a thin, porous silica-alumina membrane module. The fluxes of water and ethanol are both quite large, and ethanol concentrations downstream of the membrane are almost the same as those upstream. In this work, several membrane modules were prepared to form gel membranes of different compositions. Each membrane module had almost the same permeation properties as those shown in Fig. 6.

Effects of repetition of gel preparation procedures on separation performance The gel preparation procedures were repeated until no significant change in separation performance was recognized, as mentioned above. By repeating the gel preparation procedures the network entwines, and eventually the
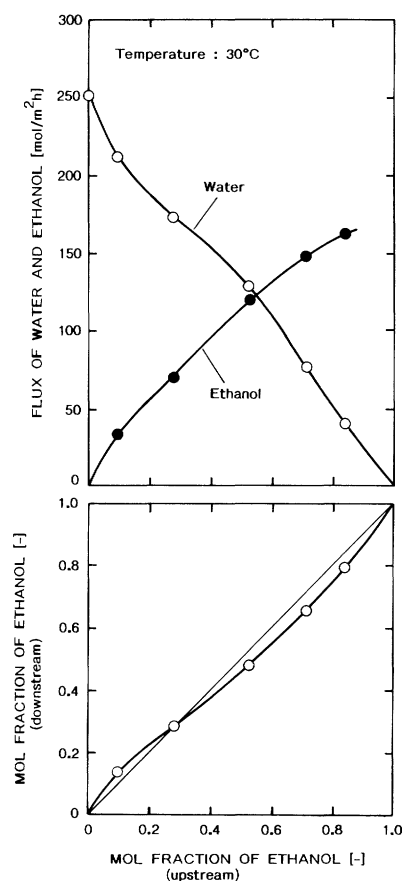
Fig. 6. Permeation properties of water and ethanol through a thin, porous silica-alumina membrane
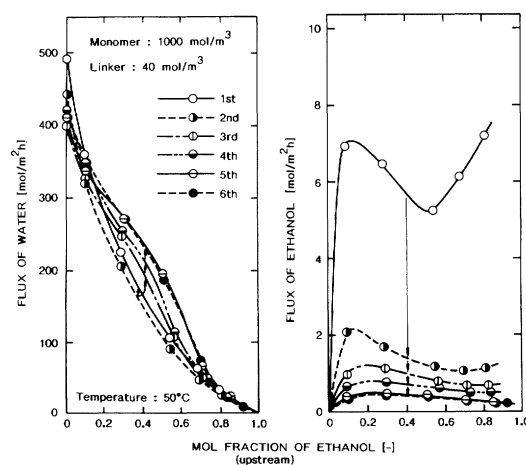

Fig. 7. Changes of flux of water and leakage rate of ethanol due to repeating the gel preparation procedures
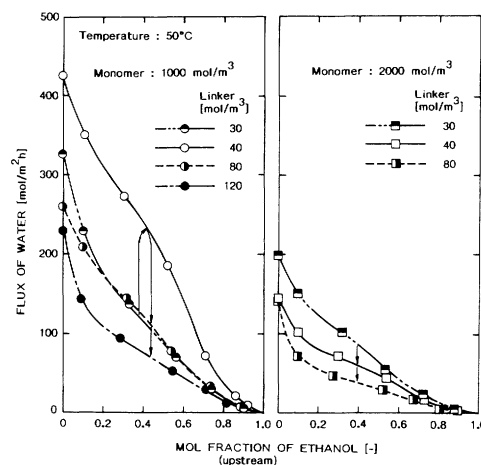

Fig. 8. Fluxes of water through acrylamide gel membranes of various compositions
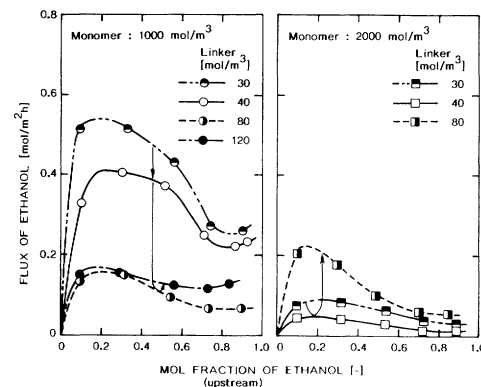

Fig. 9. Leakage rates of ethanol through acrylamide gel membranes of various compositions

network size is reduced.[7] At the same time, the amount of free water decreases by increasing the polymer content. **Figure 7** shows an example of the changes in fluxes of water and ethanol. In this case, the gel preparation procedures were repeated six times. The flux of water decreased at first and then increased with increasing repetitions. Similar phenomena were observed for the membranes prepared with 1000 mol-AAm/m^3. On the other hand, the flux or leakage rate of ethanol decreased monotonously. As a result, high separation performance can be expected. The separation performance, however, depends upon the gel composition being repeated as mentioned in the following section. Therefore, it is essential to retain the homogeneity or heterogeneity of a network even after successive gel preparations. This will be studied further.

Separation results of ethanol/water mixtures by gel membranes of various compositions **Figures 8, 9** and **10** show the separation results. The flux of water increases and then decreases with increasing MbAAm concentration, as seen tipically for the membranes prepared with 1000 mol-AAm/m^3 (see Fig. 8). Therefore, it can be said that an optimum gel composition exists for water permeation. The leakage rate of ethanol decreases and then increases with

increasing MbAAm concentration to yield an optimum composition for the obstruction of ethanol permeation (see Fig. 9). The optimum composition, however, is different from that for water permeation. An extremely high separation factor up to seveal thousand is obtained according to the composition
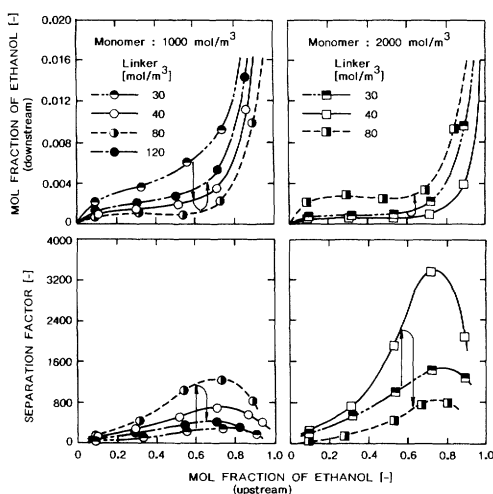
Fig. 10. Ethanol concentrations in the downstream and separation factors. The separation factor is defined as $x/(1-x)\cdot(1-y)/y$, where x and y are the mol fractions of ethanol upstream and downstream respectively.

(see Fig. 10).

In preparing the membrane, a gel of a given composition was prepared repeatedly in the pores of a thin silica-alumina membrane. Therefore, the results obtained in Sec. 2.2 and 2.3 cannot be applied directly to the separation results by the membranes. The separation results, however, also show that separation performance is greatly affected by gel composition, and that an optimum composition for the obstruction of ethanol permeation exists, as foreseen in Sec. 2.2. Furthermore, an optimum composition for water permeation also exists. From these facts, it can be said that the network size and network homogeneity are the key factors in the preparation of a superior gel membrane.

Conclusion

Homogeneity of network of an acrylamide gel is largely affected by the concentrations of primary monomer (AAm) and crosslinker (MbAAm). With increasing MbAAm concentration a fraction of dense and coarse network, i.e., heterogeneous structure, is produced in the gels. Heterogeneity of network appears remarkably at low concentration of AAm. The exclusion properties of ethanol molecules by acrylamide gels and the amount of free water in acrylamide gels, which is closely related to the selectivity of gel membranes, are significantly affected by such a heterogeneous structure. The effective size of the pores in the network and its homogeneity are considered to be the key factors in the preparation of gel membranes. For separation of ethanol/water mixtures, optimum acrylamide gel compositions for both the permeation of water and for the obstruction of ethanol permeation exist. Large flux of water and a high separation factor reaching to several thousand can be obtained by selecting the composition properly.

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