

# SEPARATION OF ALKALINE SOLUTIONS THROUGH ZEOLITIC CERAMIC MEMBRANES

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## ABSTRACT

Membrane separation is one of the efficient separation method. Membrane separation of alkaline solution is very difficult due to low chemical stability of the commercial polymeric membranes. Recently, thermal and chemical stable inorganic membranes have been developed. Zeolites are one of the porous inorganic materials consisted with aluminosilicate crystals. Hydrophilic zeolite membranes such as a MOR zeolite membrane have been developing for a water permselective membrane. However, there were few reports for the separation of alkaline solutions through zeolitic membranes. Dehydration of Ethylenediamine (EDA) solution is one of the important separation application for the alkaline solution. EDA aqueous solution forms an azeotrope mixture, thus distillation separation is not efficient. Thus, membranes that can be employed for separation of the EDA aqueous solution should be developed. In this study, MOR zeolite membranes were used for the separation of the EDA aqueous solution. MOR zeolite membranes were synthesized with MOR seed crystals on porous  $\alpha$ -alumina substrates. Crystallization was carried out based on the recipe described in the former literature [Matsukata et al. 2008]. The composition of the MOR parent gel was kept at  $10\text{Na}_2\text{O}: 15\text{Al}_2\text{O}_3: 36\text{SiO}_2: 960\text{H}_2\text{O}$ . Crystallization procedure was carried out at  $180^\circ\text{C}$  for 6 h in a Teflon autoclave. Concentration of feed EDA aqueous solution was carried out between 10~60 mol% at  $25\sim 90^\circ\text{C}$ . Water permeations were not detected by all the permeation conditions showing that the membrane selectivities were infinity. This selectivity was kept for more than 10 h.

## 1. INTRODUCTION

Hydrophilic zeolite membranes such as a MOR membrane have been developed for water permselective membranes from alcohol aqueous solution [Matsukata et al. 2008]. Separation of the alcohol with a hydrophilic zeolite membrane has been reported [Nomura et al. 1998]. There are few reports for

separation of alkali solutions through zeolitic membranes. Because, Si component in the zeolite structures can be dissolved to alkaline solution [Ogura et al. 2001]. Dehydration demand of alkaline solution is huge. EDA solution is an alkaline solution used as many kinds of chemical products. Distillation of EDA aqueous solution is not efficient, because EDA and water have an azeotropic point. Membrane separation can be the solution to break the azeotropic point. EDA was selectively permeated through the hydrophobic MFI zeolite membranes [Kanemune et al. 2013]. However, the hydrophobic MFI membrane with higher Si content was not stable under alkaline EDA solution. In this study, hydrophobic MOR membranes with lower Si content were applied for EDA separation. Membrane stability and effects of ion exchange of the membranes were discussed.

## 2. EXPERIMENT

### 2.1 Membrane Preparation

MOR zeolite membranes were synthesized with MOR seed crystals on porous  $\alpha$ -alumina substrates ( $\phi$ : 10 mm, 150 nm pore size: Noritake Co.) based on the recipe described in the former literature [Matsukata et al. 2008]. The composition of the MOR parent gel was  $10\text{Na}_2\text{O}: 15\text{Al}_2\text{O}_3: 36\text{SiO}_2: 960\text{H}_2\text{O}$ . Crystallization procedure was carried out at  $180^\circ\text{C}$  for 6 h in a Teflon autoclave.

### 2.2 Pervaporation (PV) Test

A schematic diagram of the experimental apparatus used for the PV tests is shown in Fig.1. Concentration of feed EDA aqueous solution was controlled between 10~60 mol%. The PV tests were carried out at  $25\sim 90^\circ\text{C}$ . and Concentration of feed isopropanol (IPA) aqueous solution was controlled 80 mol%. The PV tests were carried out at  $75^\circ\text{C}$ . The separation factor was defined as follows.

$$\alpha_{\text{water/EDA}} = \frac{Y_{\text{Water}}/Y_{\text{EDA}}}{X_{\text{Water}}/X_{\text{EDA}}}$$

X represents the molar fractions of the feed and Y represents the molar fractions of the permeation.

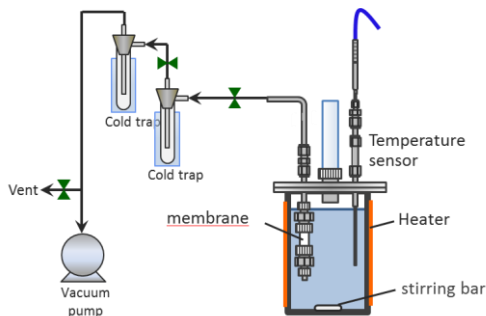


Fig. 1 Schematic diagram of the PV apparatus.

### 3. RESULTS AND DISCUSSION

#### 3.1 EDA PV tests

First, the membrane permeation properties were discussed. Before the PV tests of EDA solution, the obtained MOR membranes were checked by the PV tests of isopropanol (IPA) aqueous solution. All the membranes showed water permselectivity and no isopropanol was found from the permeation. Fig. 2 shows PV test results through the MOR membranes.

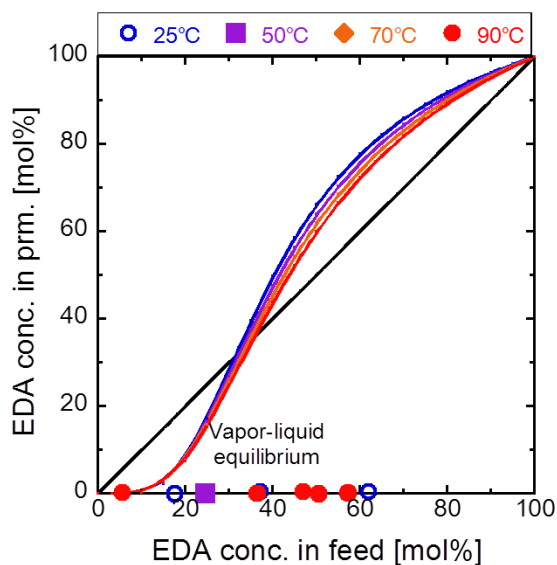


Fig. 2 The PV results through the MOR membranes

The horizontal axis represents the EDA molar concentration of the feed, and the vertical axis represents that of the permeation. EDA was not detected from all the permeation conditions. The permeation through the hydrophilic MFI zeolite membranes, EDA selectivity was found only at the higher permeation conditions [Kanemune et al. 2013]. The MOR membranes showed high water selectivity for all temperatures employed for the PV tests.

#### 3.2 Alkaline resistance of MOR membranes

Fig. 3 shows the PV test results through the MOR membrane.

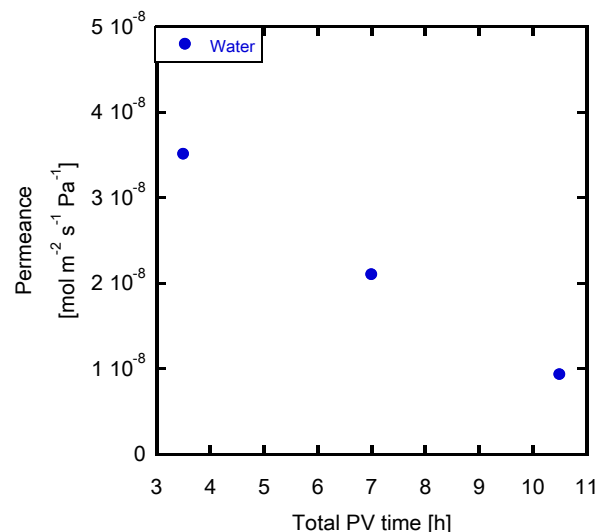


Fig. 3 The PV test results through the MOR membrane

The water permeances through the MOR membrane decreased with increasing the permeation periods. However, EDA was not detected through the MOR membrane showing that the membrane was not broken.

#### 3.3 Effects of ion exchange for the MOR membranes

Fig. 4 shows the effects of EDA permeation on the water permeances.

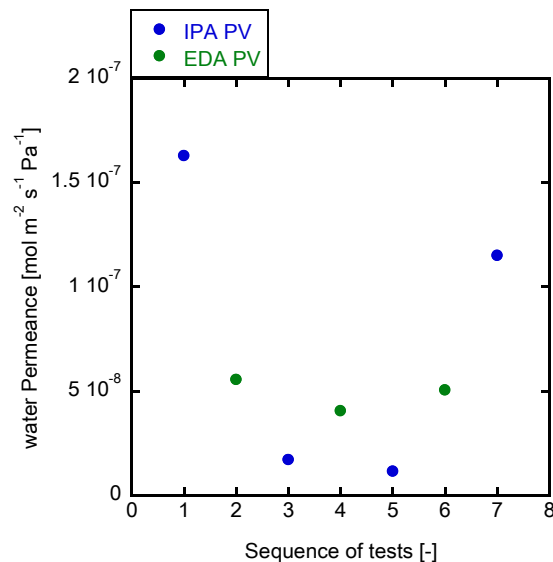


Fig. 4 The effect of ethylene diamine permeation

No. 1 permeation test showed that the PV test of IPA solution. IPA was not detected from the permeation. No.2 permeation test showed that the PV test of EDA

solution. EDA was not detected from the permeation. However, the water permeance decreased with that from the IPA solution. Next, the PV test of IPA solution was repeated. High water selectivity was not changed, while the water permeance decreased to  $1.70 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . These procedures were repeated. The membrane properties were not changed indicating that the membrane was stable under the EAD permeation conditions. Before the No.7 the PV test of IPA solution, ion exchange treatment in the NaCl solution for overnight. Water permeance increased by the treatment indicating that the low water permeance was due to ion exchange of EDA in the MOR pores.

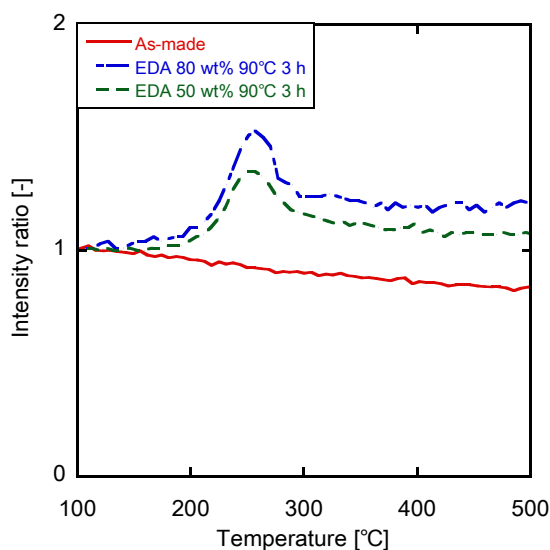


Fig. 5 The result of temperature-programmed desorption of the as-made and EDA ion exchanged MOR powders (mass number, 16)

Fig. 5 shows the result of temperature-programmed desorption of the EDA ion exchanged MOR powder. The vertical axis represents intensity of the detector of the Q-Mass (mass number of 16). The mass number of 16 indicates the amino group. The intensity peak of the as-made sample was not found, while there was desorption peak found at ca. 260 °C from the ion exchanged MOR powders. This temperature is higher than that of the boiling point of EAD. This indicates that the EDA was existed in the pores of the MOR structure.

## CONCLUSION

MOR membranes showed water permselectivities for all the permeation conditions. Water selectivities through the MOR membranes were high that no EAD was detected from the permeation. Water fluxes through the MOR membrane decreased with increasing permeation periods. This decrease can be explained by the ion exchange of EDA to MOR structures.

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