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Membrane reactor for acceleration of esterification using a special ionic liquid with reaction and separation and microwave heating

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ABSTRACT

To improve conversion of *n*-butanol to the corresponding ester using acetic acid, the ionic liquid 1-allyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide ([ABIM]TFSI), which does not dissolve in the water by-product, and poly(vinyl alcohol) (PVA) or PVA–TEOS (tetraethoxysilane) hybrid membranes were employed when using evapomeation (EV), along with microwave heating. The effect on the conversion of *n*-butanol of each individual process variable as well as that of all of the variables used in combination was investigated, and the characteristics of each approach are discussed.

1. Introduction

Esterification reactions of alcohols and carboxylic acids are fundamental reactions in organic synthesis. Ester synthesis is a very important process in manufacturing medicines and solvents. However, the resulting ester is often hydrolyzed by the water that forms as a by-product, and consequently the reaction efficiency is lowered. In industrial processes, special methods such as use of excess alcohol or modification of the carboxylic acid to the acid chloride are adopted to improve the yield. However, these methods create other problems, such as introducing the need for complicated separation processes for obtaining the ester and formation of harmful byproducts.

In previous studies, the pervaporation (PV) membrane separation technique has been applied to accelerate the conversion of esterification reactions. In these applications, liquid by-product water is removed through water-permselective membranes [1–15]. These systems have been considered as potential new membrane reactors.

In this study, we note a novel method that uses both a new membrane separation technique and an ionic liquid as a special solvent and catalyst to continuously remove by-product water from the reaction mixture.

Recently, ionic liquids (ILs) have been investigated in a great number of applications because they have specific properties such as low vapor pressure, involatility, noncombustibility, high ion conductivity and so on, and are regarded as environmentally friendly [16–19]. They are also playing an increasingly important role in the field of separation science as green sustainable compounds for the water treatment [20,21].

Xu et al. have studies esterification of alcohols by acetic acid in a group of Bronsted acidic ionic liquids at the room temperature and obtained good conversion ratio and excellent reaction rate [22]. Esterification catalyzed by ILs also have investigated by Zhang et al. [23] and Yuan et al. [24].

Izak et al. have reported that the esterification conversion in an IL (1-*n*-butyl-3-methyl-imidazolium tetrafluoroborate, [bmim]BF_4) at the room temperature by integrated water removal with PV [14]. An enzymatic esterification associated by IL and PV has been investigated by Belafi-Bako et al. [25] and Gubicza et al. [26,27].

In this study, for the purpose of enhancing the conversion of an esterification reaction, the ionic liquid 1-allyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide ([ABIM]TFSI), which does not dissolve in water but is soluble in a reaction mixture composed of alcohol, carboxylic acid, ester and water, was selected as a reaction solvent and catalyst for the synthesis of butyl acetate. The IL was

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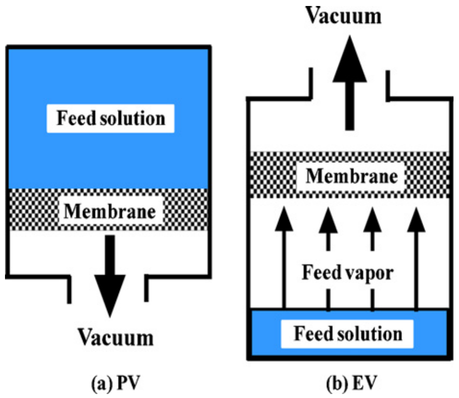


Fig. 1. Principle of PV and EV.

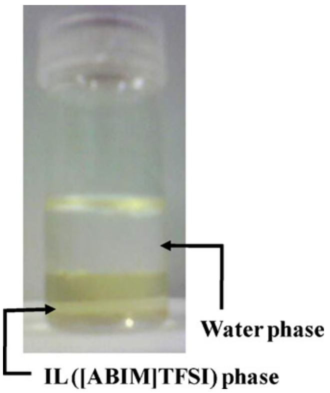


Fig. 2. Phase-separation between the water layer and the ionic liquid layer dissolved in *n*-BuOH, EtCOOH and butyl acetate.

expected to continuously phase separate the water produced as a by-product.

In previous studies [22–24], ILs were employed as only catalysts for the esterification reaction. However, in this study, IL played roles of a catalyst and separation agent for the removal of water as a by-product.

We have also developed evapomeation (EV) as a new membrane separation technique (Fig. 1(b)) that retains the advantages of PV (Fig. 1(a)) while removing the disadvantages and reported EV as a promising method for water-permselective systems [28,29]. In this EV technique, the feed solution is fed to the membrane without directly contacting it. This approach is accomplished by vaporizing the liquid feed. Swelling and shrinking of the polymer membranes due to contact with the feed solutions are therefore minimized. When a water-permselective polymer membrane is used in EV for esterification reactions, the water can be effectively removed from the reaction mixture, and the yield of the esterification reaction is expected to be enhanced.

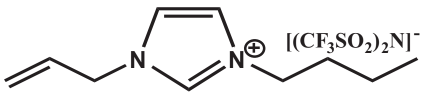
In this study, the effect of an ionic liquid and the membrane separation technique on butanol esterification, and the effect of a system combining the ionic liquid and the EV technique using a water-permselective membrane were investigated.

In addition, a novel esterification process involving the use of microwave heating to accelerated the esterification reaction along with this combined system was studied. The characteristics of the various approaches are discussed in detail below.

2. Experimental

2.1. Materials

The ionic liquid (IL) used in this study was 1-allyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide ([ABIM]TFSI) (**I**), which as supplied by Kanto Chemical Industry Ltd., Japan.



(I)

Perfectly saponified poly(vinyl alcohol) (PVA) was supplied by Wako Chemical Industry Ltd., Japan. Chemical reagents such as *n*-butanol (*n*-BuOH), acetic acid (AcOH), sulfuric acid (H_2SO_4), tetraethoxysilane (TEOS), sodium chloride, phenolphthalein, methylene iodide, and *n*-hexane were supplied by Wako Chemical Industry Ltd., Japan.

2.2. Preparation of PVA and PVA–TEOS membranes

A PVA membrane was made by casting a 2 wt% PVA aqueous solution onto a glass plate with a flame and drying at 50 °C for 24 h. PVA–TEOS hybrid membranes were prepared by the following procedure. PVA was dissolved in DMSO by stirring at 90 °C for 2 h. Prescribed amounts of TEOS per weight of PVA were mixed with the PVA dissolved in the DMSO solution and these mixtures were stirred at 90 °C for 2 h. Then 0.1 M aqueous HCl was added to the PVA–TEOS mixture to catalyze the sol–gel reaction. The amount of HCl added was 0.1 mol% of TEOS. The PVA–TEOS hybrid membranes were prepared by pouring the casting solutions onto glass plate with a flame and completely evaporating the solvents at 80 °C for 50 h.

2.3. Esterification of n-BuOH with EtCOOH using H_2SO_4

A mixture of *n*-BuOH (100 mmol), AcOH (100 mmol) and H_2SO_4 (0.1 ml) as the catalyst was stirred at 100 °C for 2 h in an oil bath.

2.4. Esterification of n-BuOH with AcOH using H_2SO_4 and a membrane in an EV cell

Esterification using H_2SO_4 in an EV permeation cell with a water permselective PVA membrane was carried out. The reaction conditions were as follows: temperature, 100 °C; reaction time, 2 h; pressure on the permeation side, 15 Pa. In this case, water as a by-product in the reaction mixture can be removed.

2.5. Esterification of n-BuOH with AcOH using H_2SO_4 and the IL

The syntheses of butyl acetate was carried out at 100 °C for 2 h in an oil bath by adding prescribed amounts of IL [ABIM]TFSI to a mixture of *n*-BuOH, AcOH and H_2SO_4. In this case, water as a by-product can be phase separated with the IL as shown in Fig. 2.

2.6. Esterification of n-BuOH with AcOH using H_2SO_4, the IL and a membrane in an EV permeation cell

The esterification reaction using a combination of the PVA–TEOS hybrid membrane and the IL was performed in the EV cell. The reaction conditions were the same as those in Section 2.4. In this case, by-product water can be removed from the reaction mixture by both the IL and the water-permselective membrane.

Table 1
List of experiments in this study.

Run	H_2SO_4	IL	EV method	Microwave
1	×	×	×	×
2	○	×	×	×
3	×	○	×	×
4	×	×	PVA	×
5	×	×	×	○
6	○	×	PVA	×
7	○	○	×	×
8	○	○	×	○
9	○	○	PVA	×
10	○	○	PVA–TEOS	×
11	○	○	PVA–TEOS	○

○: done, ×: none, PVA: membrane, PVA–TEOS: membrane.

2.7. *Esterification of n-BuOH with AcOH using H_2SO_4, the IL and a membrane in an EV permeation cell with microwave heating*

The esterification reaction using a combination of the PVA–TEOS hybrid membrane, the IL and microwave heating was performed in an EV cell. The reaction conditions were the same as those in Section 2.4, but the heating method was different from Section 2.6.

2.8. *Determination of the conversion of the esterification*

The conversion of butyl acetate was determined by neutralization titration using 1.0 M NaOH, which was added to the reaction mixture along with a drop of phenolphthalein solution.

2.9. *Degree of swelling of the membrane*

Dried PVA and PVA–TEOS hybrid membranes were weighed and then immersed into an equimolar model mixture of *n*-BuOH, AcOH, butyl acetate and H_2O in a sealed vessel at 40 °C until equilibrium was reached. The membranes were then taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of swelling (*DS*) of the PVA and PVA–TEOS hybrid membranes was then determined from Eq. (1):

$$DS = \frac{W_s}{W_d} \quad (1)$$

where W_s is the weight of the membrane swollen in an equimolar model mixture and W_d is the weight of the dried membrane.

3. Results and discussion

In Table 1, 11 kinds of experiment carried out in this study are listed. The reaction conversion of the synthesis of butyl acetate using only H_2SO_4 was 15.3%.

When the ionic liquid [ABIM]TFSI was added to the mixture containing *n*-BuOH, AcOH, butyl acetate and H_2O, clear phase separation between the water layer and the organic layer containing the ionic liquid layer can be easily observed, as shown in Fig. 2.

3.1. *Effects of reaction time and temperature on conversion in the system with the acid catalyst and the IL*

The effect of the reaction time on conversion in the synthesis of butyl acetate using both H_2SO_4 and [ABIM]TFSI as catalysts can be seen in Fig. 3. Conversion increased during the first 2 h but then remained constant. This result suggests that the esterification reaction reached equilibrium at 2 h. The effect of reaction temperature on conversion for the same system for the first 2 h is shown in Fig. 4. With increasing reaction temperature, the conversion increased, and at 60 °C rose remarkably. This extreme increase can be attributed to the fact that a suitable temperature for [ABIM]TFSI is about 60 °C. Based on these results, further esterification reactions were carried out for 2 h at 100 °C.

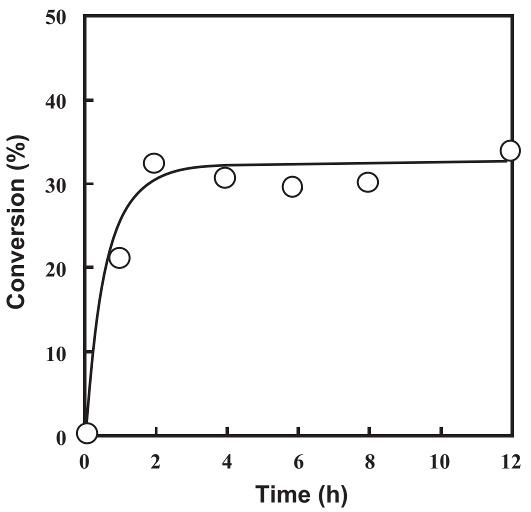


Fig. 3. Effect of reaction time on conversion in the synthesis of butyl acetate using H_2SO_4 and [ABIM]TFSI as the catalyst. Reaction temperature: 100 °C, [ABIM]TFSI: 20 wt%.

3.2. *Effect of IL on conversion*

Conversion to butyl acetate using both 0.1 ml H_2SO_4 and 20 wt% [ABIM]TFSI was enhanced 2 times over that obtained without [ABIM]TFSI. This enhancement in the conversion can be understood as follows. Additional ionic liquid, [ABIM]TFSI, can dissolve *n*-BuOH, AcOH and butyl acetate but not the water formed as a by-product. Therefore, the water is removed from the reaction system, and the reaction equilibrium is moved toward formation of butyl acetate and consequently the conversion is enhanced.

The effect of ionic liquid concentration on conversion to butyl acetate using both H_2SO_4 and [ABIM]TFSI as the catalysts at 100 °C for 2 h is shown as black circles in Fig. 5. The conversion increased with increasing [ABIM]TFSI concentration until the level reached 20 wt%, after which it decreased. The increase in the conversion until 20 wt% [ABIM]TFSI could be due to both the enhancement in the catalytic activity and in the removal performance of water from the reaction mixture. The decrease in the conversion over 20 wt% could be attributed to the fact that the concentration of the reactants decreased with use of greater amounts of [ABIM]TFSI as the reaction solvent.

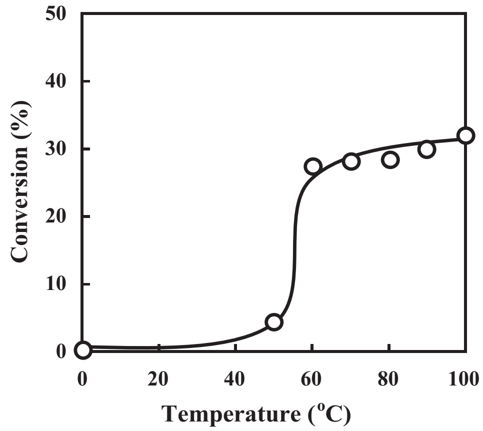


Fig. 4. Effect of reaction temperature on conversion in the synthesis of butyl acetate using H_2SO_4 and [ABIM]TFSI as the catalyst. Reaction time: 2 h, [ABIM]TFSI: 20 wt%.

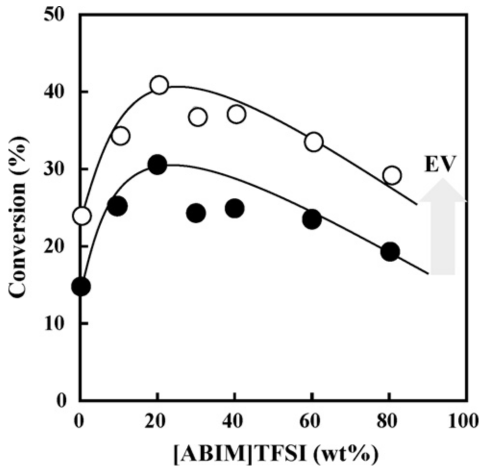


Fig. 5. Effect of [ABIM]TFSI content on conversion in the synthesis of butyl acetate using both H_2SO_4 and [ABIM]TFSI with (○) and without (●) EV. Reaction temperature and time: 100 °C, 2 h.

3.3. *Effect of the EV method on conversion*

The effect of ionic liquid concentration on conversion to butyl acetate using both H_2SO_4 and [ABIM]TFSI as catalysts with and without employing the EV method (PVA membrane) at 100 °C for 2 h can be seen as white circles in Fig. 5. The esterification of (−) berneol with AcOH using the PV method with 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) as the catalyst was investigated by Izak et al. [14]. In their study, [bmim]BF_4 played the role of a catalyst only. As can be easily noted in Fig. 5, the conversion in the combined system using the ionic liquid and the EV method with the water-permselective PVA membrane was significantly enhanced. This enhancement can be attributed to both the liberation of water molecules by [ABIM]TFSI from the reaction mixture and the removal of water molecules through a water-permselective PVA membrane during EV, as is illustrated in Fig. 6.

3.4. *Effect of reaction time on conversion when using the EV method*

Conversion to butyl acetate with and without using the EV method with H_2SO_4 and [ABIM]TFSI as catalyst and separating agent for water at 100 °C as a function of reaction time is displayed in Fig. 7. An equilibrium at 2 h was observed for the reaction run without the EV method as shown in Fig. 3. However, when using the EV method, the equilibrium conversion was not observed at 2 h and the conversion increased with increasing reaction time. The increase in the conversion with reaction time when using the EV method could be due to the fact that by-product water molecules are continuously removed from the reaction mixture. As a result, the conversion when using the EV method is remarkably higher than that obtained without employing the EV method.

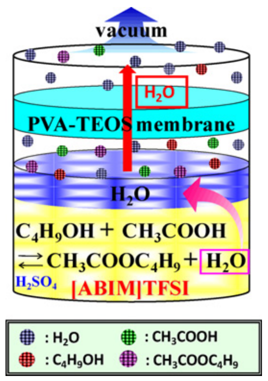


Fig. 6. Illustration of the removal of water as a byproduct in the esterification reaction using both [ABIM]TFSI and the PVA membrane in EV.

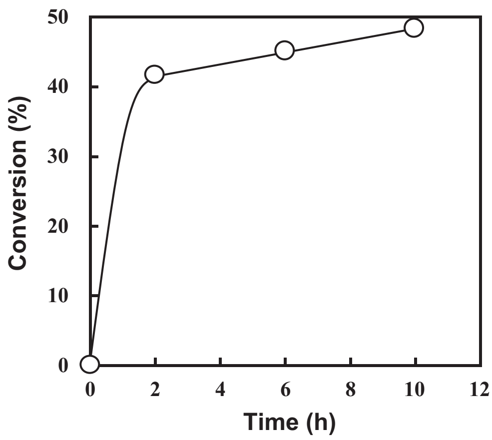


Fig. 7. Conversion as a function of reaction time in the synthesis of butyl acetate using [ABIM]TFSI and the PVA membrane in EV. Reaction temperature: 100 °C, [ABIM]TFSI: 20 wt%.

In previous studies [14,25–27], IL catalyzed the esterification reaction and PV removed one of the reaction products (water) to displace the reaction equilibrium. In this study, [ABIM]TFSI played a role as both catalyst for the esterfication and separating agent for the removal of water as by-product from the reaction mixture, and furthermore the EV with hydrophilic PVA membrane effectively removed water isolated from the reaction mixture using [ABIM]TFSI. Consequently, the esterification conversion was improved significantly.

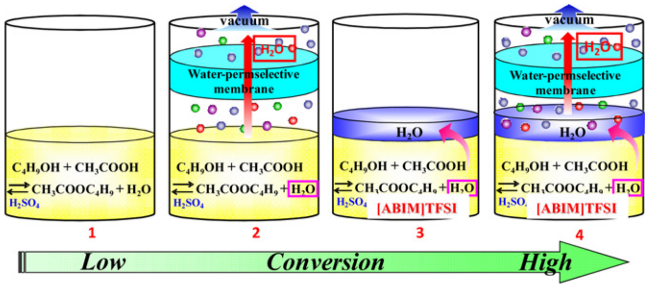
A summary of the conversion values for the esterification of *n*-BuOH to butyl acetate under various conditions is presented in Table 2. From the illustration for each system shown below the table, it can be easily seen that application of both the IL and EV method provides the best results.

3.5. *Effect of TEOS on conversion*

To further improve the conversion in the esterification reaction, higher functioning organic-inorganic hybrid water-permselective membranes were prepared from PVA and TEOS. The effects of TEOS content in the PVA–TEOS hybrid membrane on the conversion and

Table 2
Conversion in the synthesis of butyl acetate under various reaction conditions.

Run	H_2SO_4 (ml)	[ABIM]TFSI (wt%)	EV method	Conversion (%)
1	0.1	None	None	15.3
2	0.1	None	PVA	24.5
3	0.1	20	None	32.2
4	0.1	20	PVA	41.7



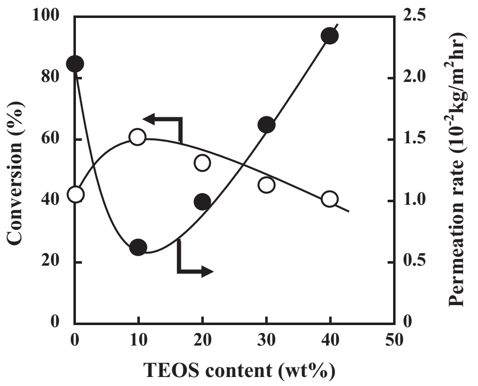


Fig. 8. Effect of TEOS content on the conversion of the esterification reaction (○) and the permeation rate of the reaction mixture (●) in the synthesis of butyl acetate using H_2SO_4, [ABIM]TFSI and the PVA–TEOS hybrid membrane in EV. Reaction temperature and time: 100 °C, 2 h.

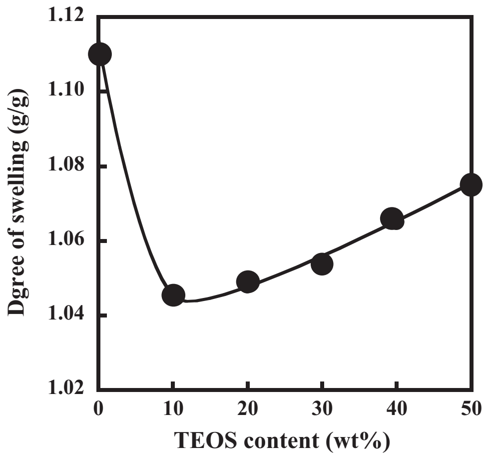


Fig. 9. Degree of swelling of the PVA–TEOS hybrid membrane as a function of TEOS content.

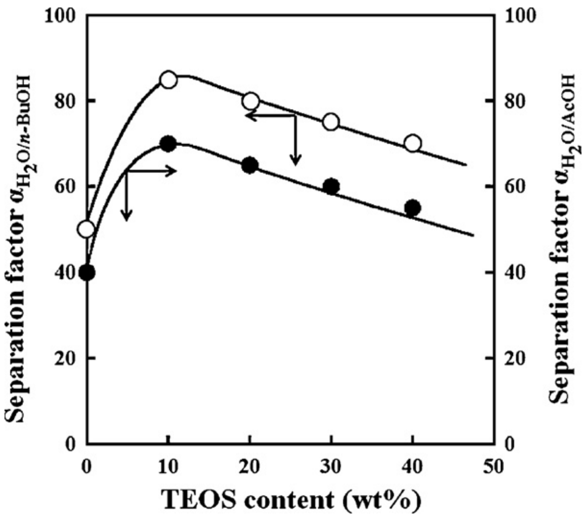


Fig. 10. Relationship between the TEOS content and separation factor for water/n-BuOH (○) and water/AcOH (●) mixture through the PVA–TEOS hybrid membranes during EV at 100 °C.

permeation rate of the reaction in the synthesis of butyl acetate are shown in Fig. 8. In the figure, the open circles represent the conversion values and the closed circles the permeation rates for all permeants. Conversion values were higher for the PVA–TEOS hybridized membranes than for the PVA membrane. The conversion and permeation rate at 10 wt% TEOS were a maximum and minimum, respectively. To gain insight into the reasons for the enhancement of conversion with the hybridized membrane and the behavior of the conversion and permeation characteristics at 10 wt% TEOS, the degree of swelling of the membrane was measured. The effect of TEOS content on the degree of swelling of the membrane is shown in Fig. 9. At 10 wt% TEOS, the degree of swelling of the membrane showed a minimum, and the degree of swelling of the PVA–TEOS hybrid membranes was lower than that of the PVA membrane. The reduced swelling in the hybrid membrane compared to the PVA membrane explains the increased conversion, while the fact that the membrane reached its minimum swelling at 10 wt% explains the reduced permeation rate.

On the other hand, to explain a maximum conversion in Fig. 8, the selectivity for water/n-BuOH and water/AcOH mixtures through the PVA–TEOS hybrid membranes during EV was investigated. In Fig. 10, the effect of TEOS content of the PVA–TEOS hybrid membranes on the separation factor for the water/n-BuOH and water/AcOH mixtures is shown. A maximum conversion could be explained by their maximum separation factors. Namely, the increase in the conversion could be attributed to the fact that the water as a by-product could be easily removed from the reaction mixture by a higher water-permselective PVA–TEOS hybrid membrane.

3.6. Structure of the PVA–TEOS hybrid membrane

The formation of the PVA–TEOS hybrid membrane is shown in Figs. 11 and 12. Fig. 11 depicts the polycondensation reaction for preparation of TEOS [30–33]. In the first step of the process for preparing the PVA/TEOS hybrid membranes, TEOS was hydrolyzed in the presence of an acid catalyst (A), and silanol groups were formed. These resulting silanol groups yielded siloxane bonds due to dehydration or dealcoholysis reactions (B) during membrane drying. These reactions led to formation of cohesive siloxane oligomers in the membrane. Since these oligomers of siloxane were dispersed in the membrane, the silanol groups in the siloxane and the hydroxyl groups in the PVA formed hydrogen, and ultimately

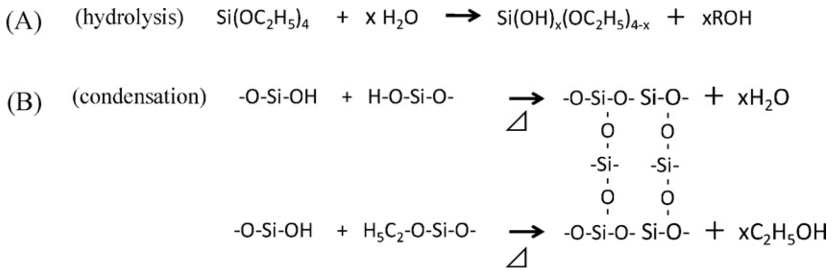


Fig. 11. Hydrolysis and condensation reactions of TEOS.

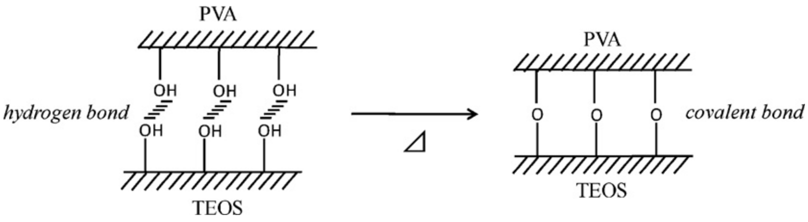


Fig. 12. Tentative illustration for the interaction between PVA and TEOS.

upon heating, covalent bonds that serve as cross-linking points, as illustrated in Fig. 12.

3.7. SEM images of PVA–TEOS hybrid membranes

SEM images of PVA–TEOS hybrid membranes are shown in Fig. 13. In these images, the white part is the TEOS. In the PVA–TEOS membrane at 10 wt% TEOS, a cohesive structure for TEOS was not observed; it was seen, however, in membranes with over 20 wt%. In Fig. 8, the fact that the permeation rate through the PVA–TEOS membranes with over 10 wt% TEOS increased is due to the formation of a cohesive TEOS structure. Namely, the permeants other than by-product water easily passed through the PVA–TEOS hybrid membrane.

On the basis of these results, the water-permselectivity can be explained by the illustrations shown in Fig. 14. At up to 10 wt% TEOS, a cross-linked structure in which TEOS is homogeneously dispersed in the membrane is formed, and the swelling of the membrane is effectively depressed. As a consequence, water with its smaller molecular size was selectively permeated compared to the larger organic compounds *n*-BuOH, AcOH and butyl acetate. However, when TEOS was added in excess to PVA, reactions occurred not only between PVA and TEOS but also between TEOS and TEOS, and the membrane became a heterogeneously opened structure. Because the larger organic compounds were easily permeated through these membranes, the water-permselectivity was lowered. It is therefore presumed that the PVA–TEOS hybrid membrane with 10 wt% TEOS has a suitable structure for water-permselectivity.

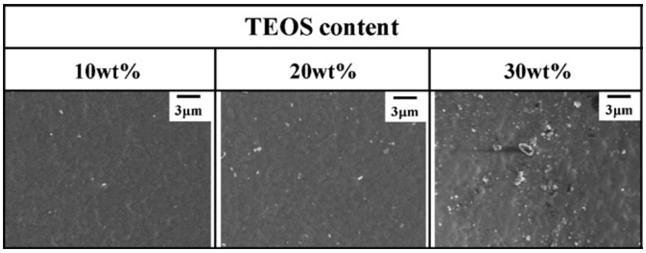


Fig. 13. Scanning electron microscope image of the surface of PVA–TEOS hybrid membranes with varying TEOS content.

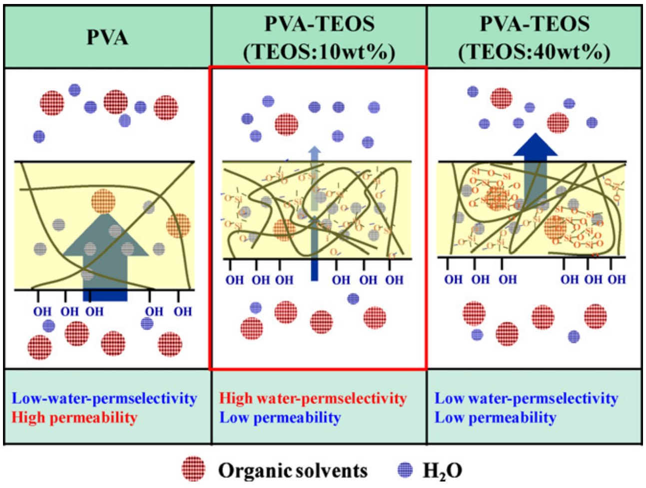


Fig. 14. Illustration of permeability and water-permselectivity as a function of TEOS content in the PVA–TEOS hybrid membrane.

3.8. Effect of microwave heating on conversion with IL

Major et al. [34] have employed a microwave to assist enzymatic esterfication of lactic acid and ethanol in phosphonium type ionic liquid as co-solvents and achieved a higher ester conversion in the esterification reaction.

Once again, to further enhance the conversion to butyl acetate, heating with microwaves was employed instead of heating with an oil bath. The effect of the microwaves on conversion to butyl acetate can be seen in Fig. 15. In this figure, the black circle represents the conversion value at 100 °C for 2 h using the oil bath. The open circles show the conversion at 100 °C using the microwaves. As can be seen, the equilibrium of the esterification reaction heated by the microwaves was reached after only about 10 min and thus the reaction time for formation of the ester was extremely reduced compared to that for the oil bath system. In addition, the conversion when using microwave heating was higher than that when heating with the oil bath. These results can be attributed to the fact that heating with microwaves is more homogeneous, and consequently the collision probability between the *n*-BuOH and AcCOOH molecules is effectively enhanced.

3.9. Conversion under various conditions

Conversion values for the esterification reaction under various conditions are summarized in Table 3. From the table it can be seen that use of a catalyst, the IL, the EV method and microwave

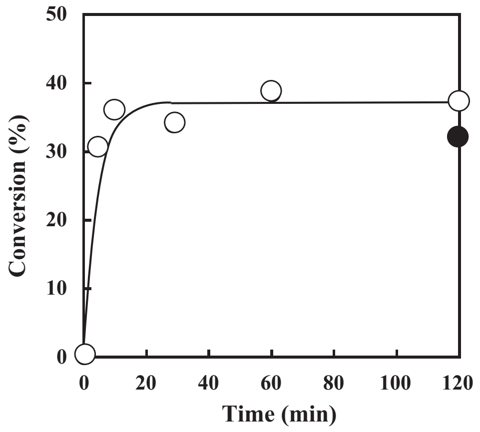


Fig. 15. Conversion in the synthesis of butyl acetate using H_2SO_4, [ABIM]TFSI and microwave as a function of reaction time. Reaction temperature: 100 °C. (●) Without microwave heating.

Table 3
Conversion in the synthesis of butyl acetate under various reaction conditions.

H_2SO_4 (ml)	IL (wt%)	EV method	Microwave	Conversion (%)
None	None	None	None	5.1[a]
0.1	None	None	None	15.3[a]
None	20	None	None	9.2[a]
None	None	PVA	None	9.0[a]
None	None	None	Microwave	6.1[b]
0.1	None	PVA	None	24.5[a]
0.1	20	None	None	32.2[a]
0.1	20	None	Microwave	37.8[b]
0.1	20	PVA	None	41.7[a]
0.1	20	PVA–TEOS (10 wt%)	None	60.2[a]
0.1	20	PVA–TEOS (10 wt%)	Microwave	76.5[b]

[a] 100 °C, 2 h.
[b] 100 °C, 10 min.

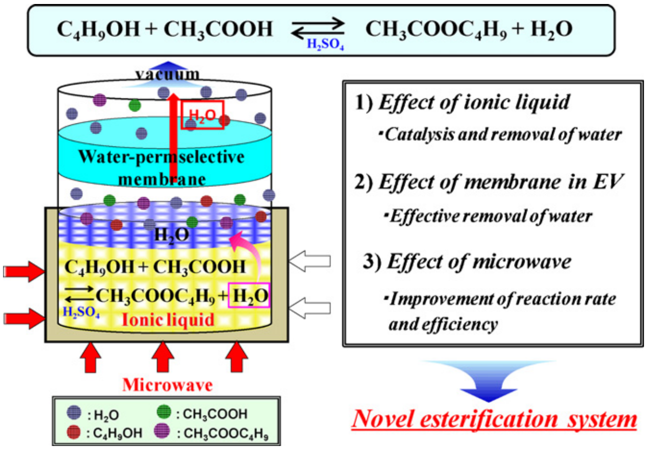


Fig. 16. Illustration of the features of the combined system using the ionic liquid, water-permselective membrane in an EV cell and microwave heating.

heating each effectively contributed to enhancement of the conversion of the esterification reaction. Furthermore, the combined use of each esterification method showed a multiplicative effect and gave a much higher conversion. When the catalyst, IL, EV method and microwave heating were combined and the PVA–TEOS hybrid membrane with 10 wt% TEOS was used, the conversion was 5 times higher that when only the catalyst H_2SO_4 was employed.

4. Conclusions

The results of this study can be explained using the illustration in Fig. 16. For the esterification of *n*-BuOH with AcOH, an ionic liquid acted as a catalyst and separating reagent for by-product water, a water-permselective polymer membrane was effective for continuous removal of by-product water, and microwave heating achieved higher esterification conversion.

References

[1] H. Kita, K. Tanaka, K. Okamoto, M. Yamamoto, Chemistry Letters (1987) 2053.
[2] H. Kita, S. Sasaki, K. Tanaka, K. Okamoto, M. Yamamoto, Chemistry Letters (1988) 2025.
[3] H. Kita, S. Sasaki, K. Tanaka, K. Okamoto, M. Yamamoto, Kagaku Kougaku Ronbunshu 15 (1989) 604.
[4] M.O. David, R. Gref, T.Q. Nguyen, J. Neel, Transactions of Institute of Chemical Engineers 69 (1991) 335.
[5] M.O. David, T.Q. Nguyen, J. Neel, Transactions of Institute of Chemical Engineers 69 (1991) 341.
[6] K. Okamoto, T. Semoto, K. Tanaka, H. Kita, Chemistry Letters (1991) 167.
[7] K. Okamoto, Chemical Engineering 36 (1991) 213.
[8] K. Okamoto, M. Yamamoto, Y. Otoshi, T. Semoto, M. Yano, K. Tanaka, H. Kita, Journal of Chemical Engineering of Japan 26 (1993) 475.
[9] K. Okamoto, M. Yamamoto, S. Noda, T. Semoto, Y. Otoshi, K. Tanaka, H. Kita, Industrial and Engineering Chemistry Research 33 (1994) 849.
[10] M. Yamamoto, N. Munehisa, M. Kaibara, K. Horii, K. Tanaka, H. Kita, K. Okamoto, Maku (Membrane) 20 (1995) 143.
[11] Y. Zhu, H. Chen, Journal of Membrane Science 138 (1998) 123.
[12] R.W. Lipnizki, P.K. Field, Journal of Membrane Science 153 (1999) 183.
[13] Q.L. Liu, H.F. Chen, Journal of Membrane Science 196 (2002) 171.
[14] P. Izak, N.M.M. Mateus, C.A.M. Afonso, J.G. Crespo, Separation and Purification Technology 41 (2005) 141.
[15] A. Hasanoglu, Y. Salt, S. Keleser, S. Ozkan, S. Dincer, Chemical Engineering and Processing 46 (2007) 300.
[16] J.D. Horbrey, K.R. Seddon, Journal of the Chemical Society – Dalton Transactions (1999) 2133.
[17] T. Welton, Chemical Reviews 99 (1999) 2071.
[18] P. Wasserscheid, W. Keim, Angewandte Chemie International Edition 39 (2000) 3772.
[19] J. Duppont, R.F. Souza, P.A.Z. Suarez, Chemical Reviews 102 (2002) 3667.
[20] C.A.M. Afonso, J.G. Crespo (Eds.), Green Separation Processes, Wiley-VCH, Weinheim, 2005.
[21] X. Han, D.W. Armstrong, Academy of Chemical Research 40 (2007) 1079.
[22] F. Xu, H.Y. Chen, H.B. Zhang, G.Z. Cheng, Journal of Molecular Catalysis A – Chemical 307 (2009) 9.
[23] H.B. Zhang, F. Xu, Xh Zhau, G.Y. Zhang, C.X. Wang, Green Chemistry 9 (2007) 1208.
[24] T.Q. Yuan, S.N. Sun, F. Xu, R.C. Sun, Journal of Agricultural and Food Chemistry 58 (2010) 11302.
[25] K. Belafi-Bako, N. Dormo, O. Ulbet, L. Gubicza, Desalination 149 (2002) 267.
[26] L. Gubicza, N. Nemestothy, T. Frater, K. Belafi-Bako, Green Chemistry 5 (2003) 236.
[27] L. Gubicza, K. Belafi-Bako, E. Frater, Green Chemistry 10 (2008) 1284.
[28] T. Uragami, M. Saito, K. Takigawa, Makromolekulare Chemie – Rapid Communication 9 (1988) 361.
[29] T. Uragami, M. Saito, Separation Science and Technology 24 (1989) 541.
[30] S. Sakka, S. Ito, K. Kamiya, Journal of Non-Crystalline Solids 71 (1985) 311.
[31] T. Uragami, K. Okazaki, H. Matsugi, T. Miyata, Macromolecules 35 (2002) 9156.
[32] T. Ohshima, M. Matsumoto, T. Miyata, T. Uragami, Macromolecular Chemistry and Physics 206 (2005) 1638.
[33] T. Uragami, H. Matsugi, T. Miyata, Macromolecules 38 (2005) 8440.
[34] B. Major, I. Kelemen-Horvath, Z. Casanadi, K. Belafi-Bako, L. Gubiczh, Green Chemistry 11 (2009) 614.