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Kinetic study of phenol recovery using phase-transfer catalysis in horizontal membrane reactor

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ABSTRACT

Quaternary ammonium membrane was made from polymerizing chloromethylstyrene crosslinking with divinylbenzene by the paste method, and immobilized with tertiary amine (tri-methylamine, triethylamine, tripropylamine or tri-*n*-butylamine). Phenol was recovered from 2500 ppm to 2 ppm from the simulated waste water in the form of useful product allyl phenyl ether using quaternary ammonium salt as phase-transfer catalyst in a horizontal membrane reactor. The ion-exchange capacity, water content and thickness in the membrane were determined. The turnover numbers of the phenol allylation for different quaternary ammonium membranes were also calculated by means of response surface methodology method.

1. Introduction

Effluent wastewater from most industries (product of synthetic resins, dyes, pharmaceutical, wood products, paint and antiseptics) contains high concentrations of phenol which is one of the pollutants. The phenol concentration in wastes of this kind varies in wide range from several ppm to 2–3% [1]. Hence, the treatment of this wastewater to remove the phenol is one of the problems because it could contaminate ground water. On the other hand, the phenolic compounds are considered to be the valuable chemicals for industrial processes. In general, phenol can be degraded by microorganisms. However, this process taking phenol at high concentration cannot be degraded by microorganisms. Phenol can be also recovered from wastewater using solvent extraction, activated carbon and polymer adsorption, membrane processes, and phase-transfer catalysis. The quaternary ammonium salt as phase-transfer catalyst had been verified to have a catalytic effect in a two-phase reaction system [2–4]. Therefore, the separation and recovery of phenolic compounds is considered from wastewater by phase-transfer catalysis. The ion-exchange membranes are one of the most advanced separation membranes. Many studies have successfully used anion exchange membrane in the seawater desalination, the recovery of metal ions from wastewater and the electrodialysis experiments [5–6]. However, the application of anion-exchange membrane in the reaction system is rare. This study will carry out the allylation of phenol in a horizontal membrane reactor.

Various methods to prepare ion-exchange membranes for various purposes have been proposed and industrially practiced, such as copolymerizing divinylbenzene and other vinyl monomers, e.g. styrene, chloromethystyrene, and vinylpyridine into a membranous copolymer by using the paste method, and then to introduce ion-exchange groups into the copolymer [7–9], cast the polymer solution on a flat plate and remove the solvent [10–11]. Most of the commercial anion-exchange membranes have benzyl trimethylammonium or *N*-alkyl pyridinium groups as anion-exchange groups, and are crosslinked with divinylbenzene. Basically, the backbone polymer of the membranes is hydrophobic, and the active ion-exchange group is hydrophilic. A previous work using commercial membrane as phase-transfer catalyst in the allylation of phenol revealed that the reactivity of commercial membrane was lower than that of general phase-transfer catalyst because the ion-exchange group in the commercial membrane was more hydrophilic [12,13]. Hence, this work aims to prepare a higher reactivity of the anion-exchange membranes from polychloromethylstyrene crosslinking with divinylbenzene, and activating with trimethylamine, triethylamine, tripropylamine or tri-*n*-butylamine. The various types of ion-exchange groups in the membrane were made from hydrophobic type to hydrophilic type to test the reactivity of allylation of phenol. These experimental results were employed to estimate the feasibility of recovering the higher concentration of phenol from simulated wastewater using quaternary ammonium salt in the phase-transfer catalytic system in a horizontal membrane.

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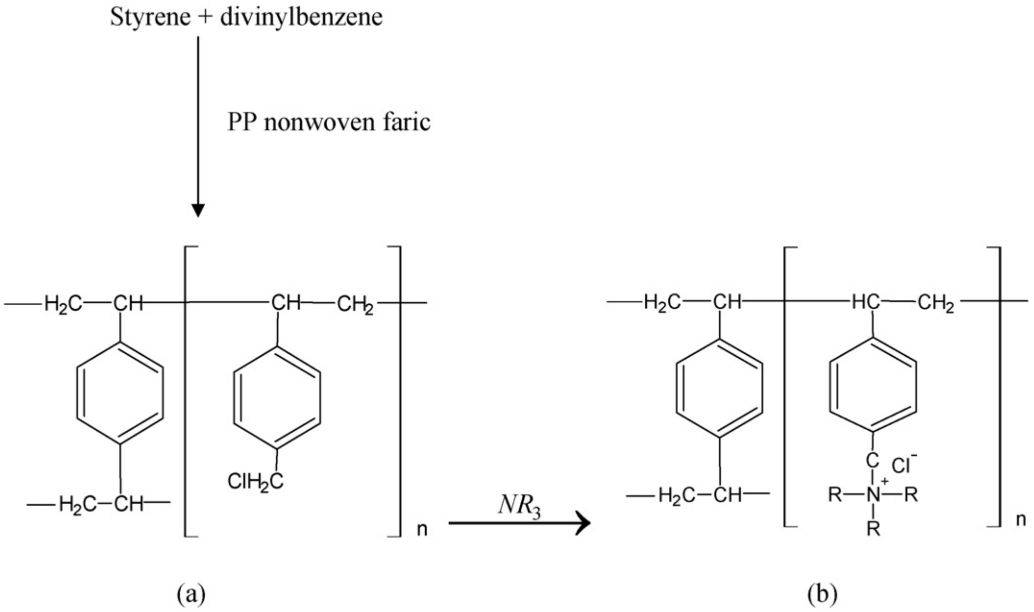


Scheme 1. Structure of (a) base membrane and (b) quaternary ammonium membrane.

2. Experimental

2.1. Materials

Allyl bromide (Fluka, 99.5%), phenol (RDH, 99%), chloromethylstyrene (Aldrich, 97%), divinylbenzene (Aldrich, 80%), polypropylene (PP) non-woven fabric (ITRI, Taiwan), styrene-butadiene rubber (TSRC, Taiwan) and other reagents are all expanded chemicals.

2.2. Preparation of anion exchange membrane

Four kinds of anion exchange membranes with different functional groups of the amines were prepared with the reaction of the membranous copolymer (composed of chloromethylstyrene (CMS type) and divinylbenzene) and various amines (trimethylamine, triethylamine, tri-*n*-propylamine and tri-*n*-butylamine), named as TMA, TEA, TPA and TBA. The structures of base membrane and anion exchange membrane were shown in Scheme 1. The synthesis of base membrane and the procedure of immobilized amine in the base membrane are described in the following.

The base membrane was made from chloromethylstyrene, divinylbenzene and PP (polypropylene) non-woven fabric. The copolymerization of chloromethylstyrene and divinylbenzene was carried out with the paste method. A solution of chloromethylstyrene (0.127 mol) with divinylbenzene (0.0054 mol), and styrene-butadiene rubber (SBR, 2.0 g) dissolved in THF (10 cm^3) was prepared. After benzoyl peroxide (0.0021 mol) was added to the solution, the pasty material was coated on PP non-woven fabric (9 cm × 9 cm). The copolymerization was conducted for 16 h at 80 °C under nitrogen atmosphere in an oven. The degree of crosslinkage in the membrane was 4 mol%. The degree of crosslinkage in the membrane was defined as degree of crosslinkage (%) = divinylbenzene (mol)/(chloromethylstyrene (mol) + divinylbenzene (mol)) × 100.

Four anion exchange membranes of TMA, TEA, TPA and TBA were immobilized with trimethylamine, triethylamine, tri-*n*-propylamine and tri-*n*-butylamine, respectively. The tertiary amine concentration in the methanol solution was 0.1 mol/dm^3. The standard immobilizing conditions for TMA, TEA, TPA and TBA were at 24 h and 30 °C, 48 h and 50 °C, 48 h and 50 °C, as well as 72 h and 50 °C, respectively, and 450 rpm. After reaction, the membranes were thoroughly washed alternately with deionized water, methyl alcohol and hydrochloric acid solution (1.0 mol/dm^3). These membranes were stored in a sodium chloride solution (0.5 mol/dm^3). The ion-exchange capacity (i.e. chloride density) in the membrane was determined by Volhard method.

2.3. Thickness for the membrane

The base membrane or anion-exchange membrane was dried in a vacuum oven at 30 °C for 48 h. The thickness of the membrane was determined by a digital gauge meter (Mitutoyo IDF-112).

2.4. Water content in the membrane

The membrane was washed with deionized water, and then immersed in deionized water for 60 min, alternately two times. The wet membrane was weighed after removing the surface moisture of the membrane. The above procedures were carried out at least three times in order to obtain an accuracy within 5%. The dry membrane was weighed after drying at 60 °C. The water content can be calculated from $W_C(\%) = (W_W - W)/W_W \times 100$ in which W_C, W_W and W denote water content in the membrane, weight of wet membrane after wiping and weight of dry membrane, respectively.

2.5. Kinetics of membrane-based stirred cell

The experimental apparatus of membrane-based stirred reactor is shown in Fig. 1. The membrane reactor was thermostated by an external circulatory bath to maintain an isothermal condition. The two liquid phases were stirred with a flat-bladed Teflon stirrer. An aqueous solution (55 cm^3) of sodium hydroxide (0.00334 mol) and phenol (0.002 mol) was prepared and introduced into the left side of the membrane reactor, which was thermostated at the desired temperature. Known quantities of allyl bromide (0.03 mol), dichloroethane (55 cm^3) and diphenyl ether (internal standard) were prepared and also thermostated at the desired temperature, and then introduced into the right side of the reactor. The interfacial area between two phases was 6.0×10^{-4} m^2.

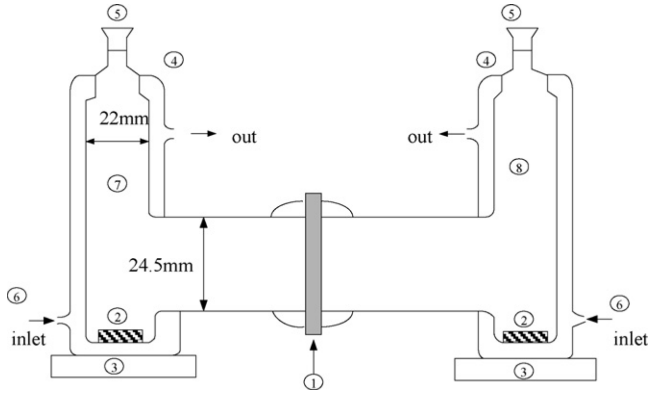


Fig. 1. Experimental diagram of horizontal membrane reactor. 1: membrane, 2: Teflon stir bar, 3: magnetic stirrer, 4: membrane reactor, 5: sampling point, 6: heating circulator bath 7: aqueous phase, 8: organic phase.

The reaction temperature was operated at selected temperature of 45–65 °C.

For a kinetic run, a sample was withdrawn from the reaction solution at selected time intervals. The sample (0.1 cm^3) was immediately added to dichloroethane (0.3 cm^3) to quench the reaction. The organic phase content was then quantitatively analyzed by means of high performance liquid chromatograph (Shimadzu LC-10A) using the method of internal standard. The accuracy of these analytical techniques was within 2–3% and the data was correctly reproduced within 5% of the values reported in this work.

3. Results and discussion

3.1. Characterization of quaternary ammonium membrane

The base membrane and various quaternary ammonium membranes were dried at 30 °C in an oven, and one determined the thickness of membrane. The average thickness of the base membrane was 0.254 ± 0.003 mm. The thicknesses of quaternary ammonius membranes are in the range of 0.4–0.6 mm, as listed in Table 1. This finding reveals that the different immobilized conditions made the different swelling degree of the membrane, and the swelling degree influenced the thickness of membrane. Otherwise, the increment of the temperature increased the swelling rate of membrane. Hence, both kind of amine and the temperature influenced the thickness of quaternary ammonium membrane. If the membrane was thick, the mass-transfer resistance between two phases was increased. If the membrane was thin, the membrane would be broken, and caused interflow between two phases. The swollen ratio, comparing base membrane (9 cm × 9 cm) with quaternary ammonium membrane listed in Table 1. For different immobilized conditions, the swollen percentages of surface area and volume were different, as listed in Table 1. The sequences of degree of swollen and volume for membrane were TMA > TEA > TPA ≒ TBA and TBA > TPA > TMA > TEA, respectively, because the thickness of membrane was increased with increasing the carbon number in the alkane group of the membrane.

According to the experimental result of water content, the water contents were different for various membranes. However, the water content was dependant of the Cl^- density in the membrane. The sequence of water content is TMA > TEA > TPA > TBA. The ion-exchange capacity (IEC) in the membrane determined by Volhard method increased when the carbon number in the alkyl group of the amine decreased. Because the carbon number in the alkyl group of amine increased, the three-dimensional structure of quaternary ammonium group was large and hindered the transfer of the amine reactant in the membrane in the immobilization. That is, the base membrane activating with high carbon number in the alkyl group of amine had to enhance the immobilized reaction condition of reaction time or temperature, as listed in Table 1. The sequence of IEC for membrane was TMA > TEA > TPA > TBA.

The surface images by scanning electron microscope (SEM) of PP non-woven fabric, base membrane and TEA membrane were observed after drying. Fig. 2a shows that the support material non-woven fabric was made up by fibers. There were some pores within the membrane. This support material membrane was a low-density fabric. Fig. 2b shows that the surface of base membrane was not smooth. There were some holes on the membrane surface. The black stripes in the photo are PP non-woven fabric's fibers. Fig. 2c is the SEM image of quaternary ammonium membrane. The surface of the membrane is very smooth. This finding demonstrates that the swollen degree for quaternary ammonium poly(methylstyrene-*co*-styrene) was larger than that of PP non-woven fabric. After immobilization, the poly(methylstyrene-*co*-styrene) chain was immerged into the membrane. According to the cross-section of the membranes, the surface of the membrane forms to be denser than the central of the membrane.

3.2. Rate expression of allylation of phenol

This work is mainly to test the quaternary ammonium anion-exchange membrane by using phenol allylation in the horizontal membrane reactor. Allyl bromide was the organic phase reactant, and sodium phenoxide was the aqueous phase reactant. In this reaction system, the organic solvent and the aqueous solvent were 1,2-dichloroethane and water, respectively. Use the quaternary ammonium membrane as phase-transfer catalyst, which was set at the interface between the organic phase and the aqueous phase in Fig. 1. The reaction of phenol and ally bromide belongs to a nucleophilic substitution reaction (S_N2). This work used the initial reaction rate method to calculate the chemical kinetic parameters. The chemical reaction is expressed as follows:

$$C_6H_5OH_{(a)} + NaOH_{(a)} + C_3H_5Br_{(o)} \xrightarrow{\text{Ion exchange membrane}} C_6H_5OC_3H_5 + NaBr_{(a)} + H_2O \quad (1)$$

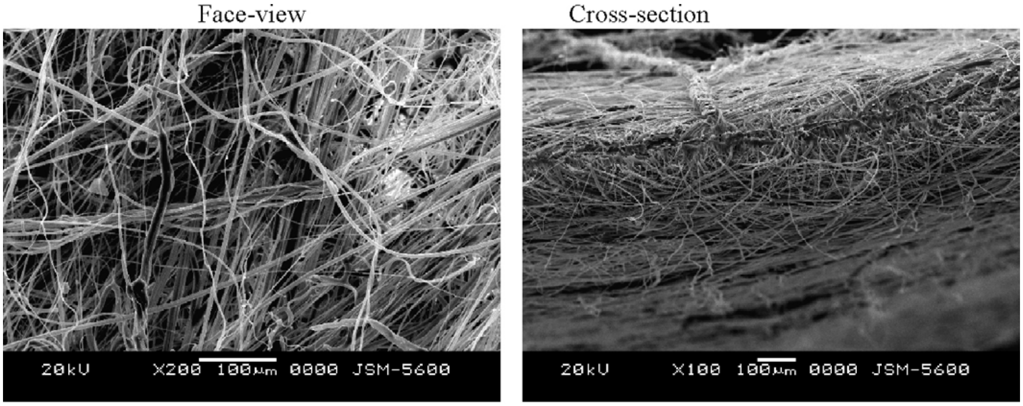
The rate expression give

$$r = -\frac{d[C_6C_5OH]}{dt}. \quad (2)$$

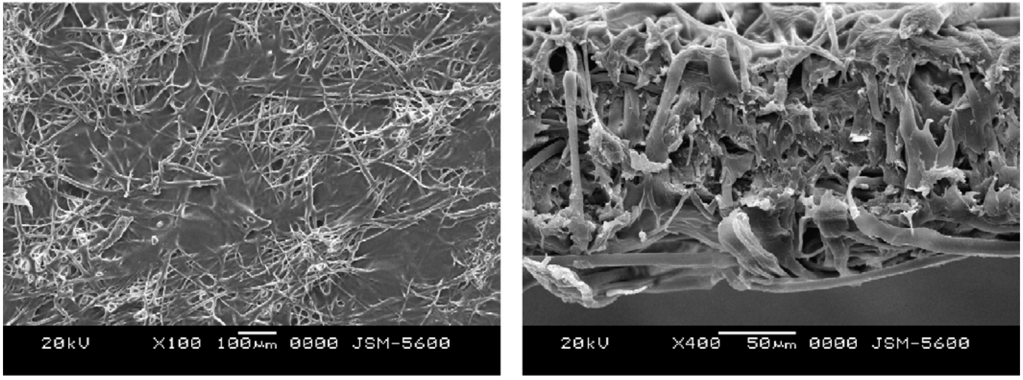
Table 1
Physical property at different membranes

Membrane	Immobilization condition	Thickness (mm)[a]	Area swelling (%)[a]	Volume swelling (%)[a]	Water content (%)[a]	IEC (mmol/g)[a]
TMA	24 h, 30 °C	0.423	63	171	66	2.4
TEA	48 h, 50 °C	0.434	45	147	64	2.2
TPA	48 h, 50 °C	0.588	26	191	56	1.7
TBA	72 h, 50 °C	0.608	25	199	55	1.5

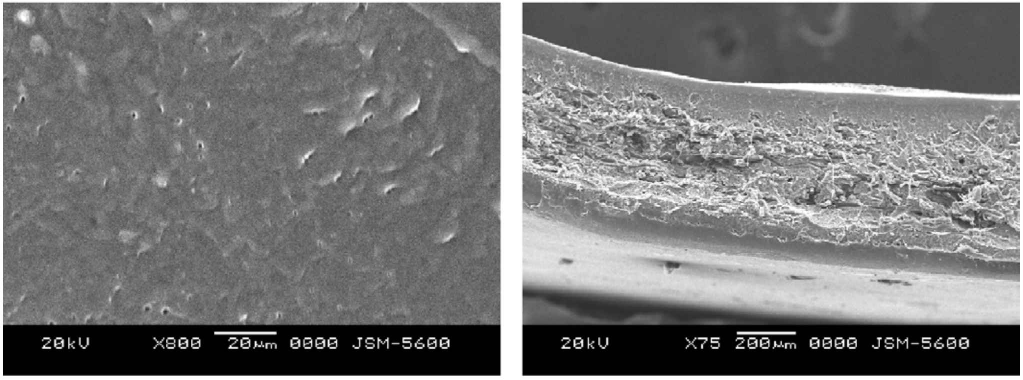
[a] Measured more than three times for different runs.



(a) .P.P. non-woven fabric (support material)



(b) .Base membrane (CL=4mol%)



(c).Quaternary ammonium membrane (triethylamine 48hr 50°C)

Fig. 2. SEM image of plate-section and cross-section for TEA membrane.

Our previous work reported that the organic solution would leak slight into aqueous solution during the course of the reaction because of gravity to reduce the reactivity of active site on the membrane in the vertical membrane reactor [13]. Hence, the vertical membrane reactor was replaced with a horizontal membrane reactor to avoid the gravity problem to test the reactivity of the allylation of phenol. The leaking phenomenon was reduced in the horizontal membrane reactor. According to previous result, the reaction rate in the horizontal membrane reactor was larger than that in the vertical membrane reactor. Therefore, we will discuss the reactivity of membrane in the horizontal reactor and obtain the optimum condition using statistic method of response surface methodology (RSM) method. Furthermore, use this membrane technology to recover phenol from simulated waste water.

3.3. Reactivity of turnover number

The turnover number stands for the number of substrate molecules converted to product by one molecule of catalyst per unit time when the reaction rate is maximal and the substrate is saturated. That is, turnover number (s^{-1}) is defined as the maximum consumed mole of substrate per catalyst per time. The turnover number is defined as

$$\text{Turnover Number} = \frac{r_{\max}}{M_c} \qquad (3)$$

in which $r_{\max}$ denotes the maximum reaction rate (mol/m^2 s) and M_c is the amount of the catalyst per area (mol/m^2). Based on the previous experimental data, one can understand that the yield of allyl phenyl ether increased when the organic concentration in excess increased. The different reaction conditions had different maximum reaction rate or yield of PhOR. Hence, the RSM was conducted to obtain the maximal reaction rate, furthermore, to find turnover number. There are several standard steps for using RSM, for example for TMA membrane:

a. First, choose the suitable factors. The factors have a direct effect on the experiment. Then find a suitable range for every factor; the maximum value is +1 and the minimum is −1.
b. Use a simulated program to get a two level model. By doing some experiment given by the program, it is possible to get the formula of the model.
c. Then the two levels model is converted into a new model with the real values. In order to do this, one use the path method of steepest ascent by closing the value of new range. Then the plot will find a new origin point and new range.
d. Take the new origin point and the new range into the RSM. Some experiments suggested from the program was carried out, and then input the results of experiments in the program. The program will fit a new formula and it is then possible to get the maximum value by using this new formula.

First, in the two-level method, it is important to choose a range for the organic and aqueous phase concentrations. The concentration of phenol in the aqueous phase was in the range of 1500–25000 ppm, and the concentration of allyl bromide in the organic reactant was 25-folds more than that of the aqueous reactant because the organic reactant was in excess. The maximum concentration value would be set at +1 and the minimum concentration would be set at −1. Then, design 8 experiments to establish the model. The equation was given as

$$r = 0.0163 + 0.00777\,\text{phenol} + 0.0166\,\text{allyl bromide} + 0.00571\,\text{phenol} \cdot \text{allyl bromde} \tag{4}$$

The range of concentration from 1500 ppm to 25000 ppm was modified by means of those Eqs. (5) and (6) in the following.

$$M_{a_2} = \frac{A_1}{\sqrt{{A_1}^2 + {B_1}^2}} \times M_{a_1} \tag{5}$$

$$M_{b_2} = \frac{B_1}{\sqrt{{A_1}^2 + {B_1}^2}} \times M_{b_1} \tag{6}$$

in which A_1 and B_1 are coefficients of allyl bromide and phenol, respectively, estimated from two level model, M_a is the concentration range of aqueous reactant, and M_b is the concentration range of organic reactant. The values of A_1 and B_1 for TMA membrane are 0.00777 and 0.0116, respectively.

After modifying the range of concentration, use the new range to find the maximum reaction rate. The new original point was obtained after Path Method of Steepest Ascent method. By using the new formula in a plot program, the curved surface for TMA is shown in Fig. 3. TMA membrane had the maximum rate $r_{\max} = 0.0609\ \text{mol/m}^2\cdot\text{min}$ when aqueous reactant was 0.00804 mol and organic reactant was 0.228 mol. The maximum rate is divided by the amount of the catalyst to obtain turnover number (=$7.71 \times 10^{-4}\ \text{s}^{-1}$). In similar, TEA membrane had the maximum rate $r_{\max} = 0.0312\ \text{mol/m}^2\cdot\text{min}$ when the aqueous reactant was 0.00537 mol and the organic reactant was 0.202 mol. The turnover number calculated was $3.85 \times 10^{-4}\ \text{s}^{-1}$. Next, TPA membrane had the maximum rate $r_{\max} = 0.0229\ \text{mol/m}^2\cdot\text{min}$ when the aqueous reactant was 0.00497 mol and the organic reactant was 0.196 mol. The turnover number calculated was $2.78 \times 10^{-4}\ \text{s}^{-1}$. Final, TBA membrane had the maximum rate $r_{\max} = 0.0162\ \text{mol/m}^2\cdot\text{min}$ as aqueous reactant 0.00504 mol and organic reactant 0.193 mol. The turnover number calculated was $2.23 \times 10^{-4}\ \text{s}^{-1}$. These turnover numbers at 45 °C are larger than that ($7.05 \times 10^{-5}\ \text{s}^{-1}$ at 45 °C) with TBA reported by Wu and Wu with [13] and lower than that ($1.53 \times 10^{-3}\ \text{s}^{-1}$ at 65 °C) with a pyridinium group reported by Wu and Lo [14]. According to the result of turn over number, the reactivity of substrate molecules converted to product by one molecule of catalyst per unit time was decreased with increasing the carbon number in the alkane group of the membrane. The trend is similar to that of IEC in the membrane because of steric hindrance.

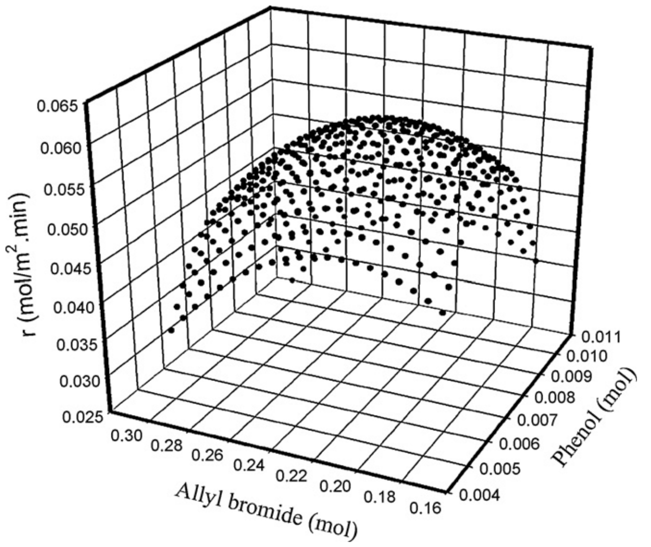


Fig. 3. RSM curve for TMA membrane. 45 °C, 400 rpm, aqueous phase 35 cm^3; 0.002 mol of phenol, 0.0033 mol of NaOH, organic phase 35 cm^3.

3.4. Recovery of phenol using quaternary ammonium membranes

This work used the various lab-produced quaternary ammonium membranes (TMA, TEA, TPA, and TBA) was conducted in the allylation of phenol. The concentration of organic reactant exceeded more than that of aqueous reactant for 1, 5 or 10-fold when the concentration of the aqueous reactant kept constant (0.002 mol). Fig. 4 shows that TMA membrane had the best yield of allyl phenyl ether (PhOR) in the allylation of phenol among four membranes. The yield of PhOR was increased with increasing initial ratio of organic reactant to aqueous reactant. When the concentration ratio of organic reactant to aqueous reactant was 10, the yield was 85% after reaction time of 210 min for TMA. The sequence of yield of PhOR for membrane was TMA > TEA > TPA > TBA. This result corresponds to the sequence of IEC, which were 2.4, 2.2, 1.7 and 1.5 mmol/g in Table 1. When IEC value was larger, the allylation rate was higher.

The initial concentration of phenol in the aqueous solution was set at 2500 ppm, and the final concentration of phenol at 210 min in this phase-transfer catalytic reaction was measured by means of HLPC. Both organic and aqueous agitation rates were fixed at 400 rpm. The molar ratio of allyl bromide to phenol was conducted at selected ratio intervals when the concentrations of phenol were kept constant of 2500 ppm. Table 2 lists the residual concentration of phenol in the aqueous solution. The reaction rate of allylation of phenol was increased with increasing temperature or ratio of allyl bromide to phenol. These results demonstrate that the phase-transfer catalytic reaction using membrane as the catalyst prefers to deal with the organic reactant

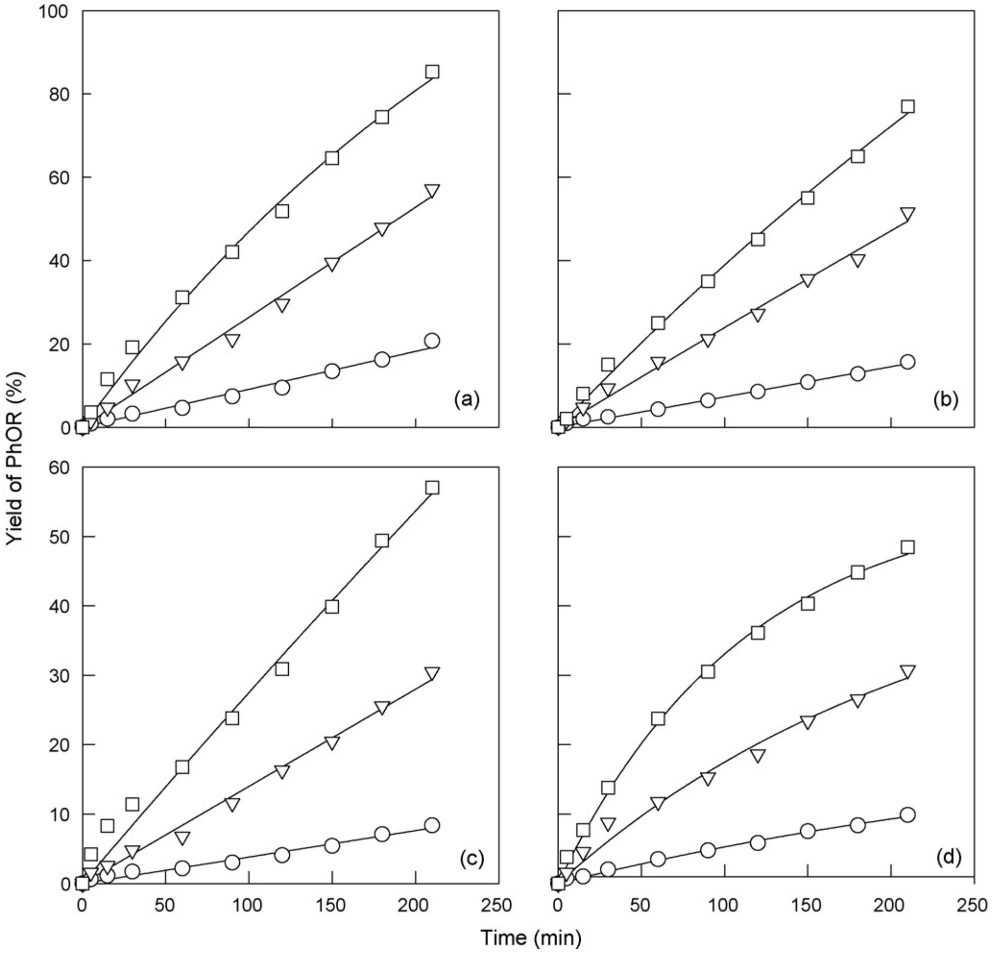


Fig. 4. Yield of PhOR in organic excess with various membrane. 45 °C,400 rpm, aqueous phase 35 cm^3; 0.002 mol of phenol, 0.0033 mol of NaOH, organic phase 35 cm^3, phenol:allyl bromide = (O)1:1, (▽)1:5, (□)1:10.

Table 2
Residual concentration of phenol in the aqueous solution[a]

Organic to aqueous concentration ratio	45 °C		65 °C	
	Yield of allyl phenyl ether (%)	Residual[b] Phenol (ppm)	Yield of allyl phenyl ether (%)	Residual[b] Phenol (ppm)
1:5	57	2121	87	792
1:10	85	769	99	47
1:15	94	389	~100	2.4
1:20	98	84	~100	1.8

[a] Reaction conditions: TMA membrane, 400 rpm, aqueous phase = 35 cm^3; initial phenol = 2500 ppm, NaOH = 3.3 × 10^{-3} mol, organic phase (1,2-$C_2H_4Cl_2$) = 35 cm^3.

[b] The residual phenol was determined at the reaction time of 210 min.

in an excess reaction system. The residual phenol concentrations obtained at temperatures of 65 °C from wastewater by quaternary ammonium membrane in a batch reactor were low. The residual phenol concentration could be reduced below 2 ppm, and on the other hand, that for 45 °C was reduced to 84 ppm. The recovery rate of phenol is around 11.9 ppm/min (=(2500–2)ppm/210 min) at 65 °C.

4. Conclusions

The allylation of phenol was carried out by using quaternary ammonium membrane as phase-transfer catalyst in a 1,2-dichloroethane and aqueous solution. Four quaternary ammonium membranes were prepared to test the phase-transfer catalytic reaction. And obtain good performance in this reaction. The sequence of the reaction kinetics for membrane was TMA > TEA > TPA > TBA. The turnover numbers were easily calculated by response surface methodology. The phenol could be recovered to get a useful product from 2500 ppm to 2 ppm in the aqueous solution. Therefore, using phase-transfer catalysis in the membrane system can apply in the phenol recovery system in the future.

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