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Effect of third-phase properties on benzyl-*n*-butyl ether synthesis in phase transfer catalytic system

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Abstract

The production of benzyl-*n*-butyl ether from benzyl chloride and *n*-butanol is studied in phase transfer catalytic system. A third phase is formed when polyethylene glycol (PEG) and dodecane are used as the phase transfer catalyst (PTC) and an organic solvent, respectively. The production rate at the three-phase system is higher by seven times than that at the two-phase system. The ether production rate and its selectivity are dependent on the initial concentration of *n*-butanol. These are affected by the properties of the third phase, especially the concentrations of *n*-butanol and water in the third phase.

n-Butanol reacts with benzyl chloride and potassium hydroxide simultaneously. The reaction between *n*-butanol and potassium hydroxide occurs in the aqueous phase. Then, the selectivity of ether on a basis of initial *n*-butanol is below 0.6 in a stirred tank batch reactor. The selectivity is much improved at 0.9 by using a static triphase batch reactor in which the organic and aqueous phases are separated by the third phase. The interphase mass transfer can be accelerated by ultrasonic device.

Keywords: Chemical reaction; Phase transfer catalyst; Catalytic activity; Third phase; Ether synthesis

1. Introduction

The synthesis process between reagents in two immiscible phases can be simplified by using phase transfer catalyst (abbreviated as PTC) [1].

For example, the following two-step process is required for the traditional Williamson ether synthesis.

Step 1. Potassium alkoxide synthesis from alcohol and potassium:

$$2ROH + 2K \rightarrow 2ROK + H_2 \tag{1}$$

Step 2. Ether synthesis from potassium alkoxide and alkyl halide:

$$ROK + R'X \rightarrow ROR' + KX \tag{2}$$

In this process, metal potassium is consumed and potassium halide becomes waste.

On the other hand, if PTC is used, the process can be simplified as one-step process, i.e., alcohol and alkyl halide can react directly to produce an ether [2]

$$\underset{(org)}{ROH} + \underset{(org)}{R'X} + \underset{(aq)}{KOH} \xrightarrow{PTC} \underset{(org)}{ROR'} + \underset{(aq)}{H_2O} + \underset{(aq)}{KX} \tag{3}$$

Some works have been done on ether synthesis. Neumann and Sasson [3] reported synthesis of alkyl

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Nomenclature

$C_{A,0}$	feed concentration of benzyl chloride in organic phase (mol/m^3-org)
$C_{A,org}$	concentration of benzyl chloride in organic phase (mol/m^3-org)
$C_{A,third}$	concentration of benzyl chloride in third phase (mol/m^3-third)
$C_{B,0}$	feed concentration of *n*-butanol in organic phase (mol/m^3-org)
$C_{B,org}$	concentration of *n*-butanol in organic phase (mol/m^3-org)
$C_{B,third}$	concentration of *n*-butanol in third phase (mol/m^3-third)
C_{H_2O}	concentration of water in third phase (mol/m^3-third)
$k_{R,obs}$	ether production rate constant (s^{-1})
$m_{i,0}$	feed mole of benzyl chloride or *n*-butanol (mol)
$m_{i,org}$	mole of benzyl chloride, *n*-butanol or ether in organic phase (mol)
$m_{i,third}$	mole of benzyl chloride, *n*-butanol or ether in organic phase (mol)
$m_{alkoxide,aq}$	the moles of alcohol alkoxide produced in the aqueous phase (mol)
$S_{R,i}$	selectivity of ether based on initial reactant i
t	reaction time (s)
V_{org}	volume of organic phase (m^3)
V_{third}	volume of third phase (m^3)
$y_{A,org}$	dimensionless concentration of benzyl chloride in organic phase, $C_{A,org}/C_{A,0}$ $(-)$
$y_{B,org}$	dimensionless concentration of *n*-butanol in organic phase, $C_{B,org}/C_{B,0}$ $(-)$
ω	concentration of PEG based on the volume of organic phase, m_P/V_{org} (mol/m^3-org)
ξ_{KOH}	dimensionless concentration of potassium hydroxide in the aqueous phase $(-)$

Subscripts

A	benzyl chloride
B	*n*-butanol
R	benzyl-*n*-butyl ether
i	A or B
aq	aqueous phase
cat	catalyst ((Hex)$_4$NBr or PEG3000)
org	organic phase
third	third phase

aryl ethers from alkoxylation of halobenzens by using different molecular weights of polyethylene glycol (PEG) in two-phase systems. The greater molecular weights were found to be more effective catalytic activities.

Wang and Chang [4] studied the ether synthesis from sodium phenolate and allyl chloride with PEG in two-phase system. The reaction rates in both the organic and aqueous phases were increased by PEG.

Wang and Weng [5] reported the ether synthesis from sodium phenolate and *n*-butyl bromide with tetrabutylammonium bromide in three-phase system. The formation of third phase and the reaction rates were significantly dependent on the solvents and salts.

However, the main disadvantage of PTC, especially in commercial applications, is the difficulty of separation from the products in the organic phase. To solve this disadvantage, PTC system with a catalyst-rich third phase has been proposed. A third phase may be formed when PTC cannot be dissolved in either organic or aqueous phase, and once a third phase is formed, the reaction rate increases sharply and the catalyst can be reused easily [6]. In our previous paper [7], the relationship between the properties and catalytic activity of the third phase was investigated by carrying out the dehydrohalogenation of 2-bromooctane on quaternary ammonium salts catalysts. Furthermore, a synergetic effect of PTC was observed for the combination of tetrahexyl ammonium bromide ((Hex)$_4$NBr), and polyethylene glycol (PEG) in a third phase. The observed reaction rate constant could be related to the water concentration in the third phase drastically [8].

In general, PEG and their many derivatives have been extensively investigated as phase transfer catalysts and are used in many commercial processes [9]. These materials are inexpensive, thermally stable in the presence of strong bases, nontoxic, easily biodegradable.

Dehydrohalogenation of 2-bromooctane was investigated by using PEG as a catalyst and toluene as an organic solvent in the saturation of potassium hydroxide in an aqueous solution [10]. When adequate amounts of methanol were added in this system, the third phase appeared [11]. When the concentration of PEG in the organic phase became zero by the addition of methanol, the condition was optimum for repeated use [12].

Another advantage to use the third-phase system is that the organic phase does not contact with the aqueous phase if the catalyst-rich third phase presents between organic and aqueous phases in the reactor without stirring. This reactor may be named as a static triphase batch reactor. In our previous paper [13], this reactor was used for the halogen substitution reaction from benzyl chloride to benzyl bromide and the reaction was promoted by ultrasonic waves.

Stanley and John [14] implemented a porous solid membrane reactor to avoid direct contact between organic and aqueous phases. This membrane reactor was continuously operated for the displacement reaction from bromooctane to iodooctane.

As far as our knowledge is concerned, no studies have been done on one step Williamson ether synthesis from alcohol and allyl halogen in base-catalyzed reaction with a third-phase transfer catalytic system.

This paper attempts to investigate this possibility. The reaction is as follows:

$$\underset{(A)}{C_6H_5CH_2Cl} + \underset{(B)}{C_4H_9OH} \underset{\text{PTC with OH}^-}{\rightarrow} \underset{(R)}{C_6H_5CH_2\text{–O–}C_4H_9} + HCl \qquad (4)$$

The reaction mechanism of this three phase shows as below.

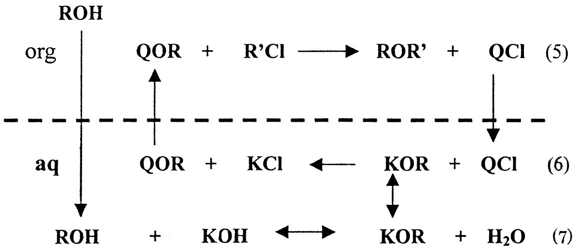
Dodecane and toluene are used as a nonpolar and a weakly polar organic solvent, respectively. Tetrahexyl ammonium bromide ($(Hex)_4NBr$) and PEG (with molecular weight of 3000) are used as PTC. At first, the conditions to form the third phase were determined by changing the concentration of potassium hydroxide (KOH) in the aqueous phase. Then, the effects of initial concentrations of benzyl chloride (A) and *n*-butanol (B) on the reaction rate and the selectivity of benzyl-*n*-butanol ether (R) were investigated in a stirred tank batch reactor. In this reactor, the undesired side reaction, Eq. (7) may take place because the organic and aqueous phases can contact each other.

Finally, a static triphase batch reactor with ultrasonic device was used to improve the ether selectivity by avoiding the direct contact between the organic and aqueous phases.

2. Three types of reaction mechanism

2.1. Reaction mechanism in two-phase system

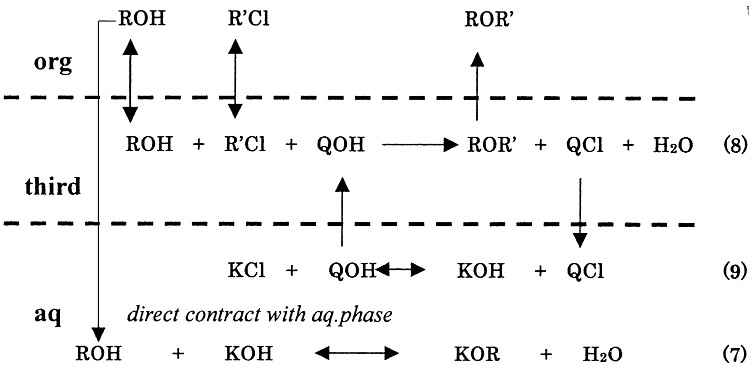
The mechanism of Eq. (3) was proposed by several authors [15]. In this case, PTC is usually ammonium salt.



Alkoxide is formed by Eq. (7) in the aqueous phase. The alkoxide combines with catalyst to form ion-pair Q^+OR^- by Eq. (6). Ion-pair Q^+OR^- is extracted from the aqueous phase into the bulk of organic phase. Q^+OR^- reacts with $R'X$ to form an ether and to release the catalyst into the aqueous phase for another catalytic cycle (Eq. (5)).

2.2. Reaction mechanism in third-phase system with stirring

The mechanism of Eq. (3) in third phase would be as follows [6]:

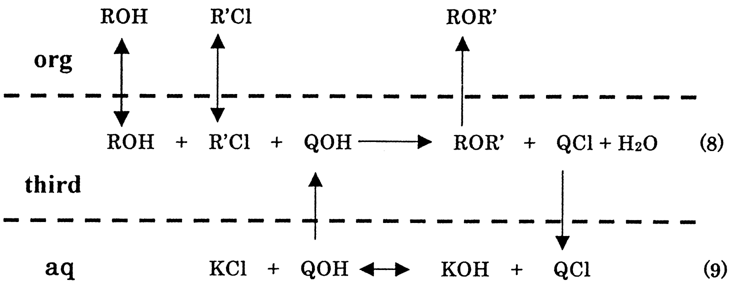


Both reactants, ROH and R′Cl, are dissolved into the third phase which has a form of QOH with a high base strength [7]. The ether ROR′ can be synthesized by Eq. (8).

In this case, however, if both the organic and aqueous phases are directly contacted with each other by stirring, the formation of alkoxide, KOR, may proceed simultaneously by the side reaction, Eq. (7), which is not desirable.

2.3. Reaction mechanism in third-phase system without stirring

If both organic and aqueous phases are completely separated from each other without stirring, the reaction given by Eq. (7) does not take place.



3. Experimental

3.1. Catalysts and reagents

Tetrahexyl ammonium bromide ($(\mathrm{Hex})_4\mathrm{NBr}$) and polyethylene glycol with the molecular weight of 3000 (abbreviated as PEG3000) were used as phase transfer catalysts. All chemicals with GR grade were commercially available (tetrahexyl ammonium bromide from Aldrich Chemical and other reagents from Wako Pure Chemical Industries) and used without any purifications.

3.2. Determination of third-phase composition

These experiments were done as the same way in the previous paper [7]. The water contents in the third phase were determined using a gas chromatograph with TCD. The contents of *n*-butanol were also determined using a gas chromatograph with FID.

3.3. Kinetic measurements

3.3.1. Stirred tank batch reactor

The same stirred tank batch reactor at constant temperature of 323 K was used in the previous paper [7] except for adding *n*-decane as an internal standard. The initial volumes of both organic and aqueous phases were always equal to 50 cm^3.

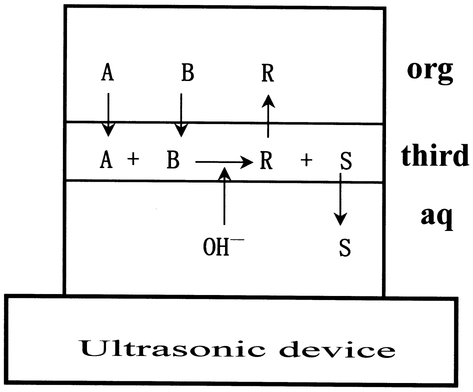


Fig. 1. Schematic diagram of static triphase batch reactor.

3.3.2. Static triphase batch reactor

Fig. 1 shows a schematic diagram of static triphase batch reactor. The direct contact between organic and aqueous phases can be avoided by the third phase. The ultrasonic device (Yamato Sci., 3QT/H with 50 W of supersonic power and 47 kHz of frequency) under the reactor was used to promote the interphase mass transfer rates.

The static triphase batch reactor was placed in a constant temperature (323 K) water bath with known amount of H_2O, catalyst, KOH and organic solvent (one-third of all). Then, known quantity of *n*-decane (as internal standard), benzyl chloride and *n*-butanol dissolved in organic solvent, respectively, were finally added and a kinetic run was started. The initial volumes of both organic and aqueous phases were always equal to 10 cm^3. At given intervals, samples of 0.2 cm^3 were taken from the organic phase. The contents of benzyl chloride, *n*-butanol as well as the product (benzyl-*n*-butanol ether) in the organic phase were analyzed by a gas chromatograph (Yanaco G1800) with FID. The column was the same as that in our previous paper [7].

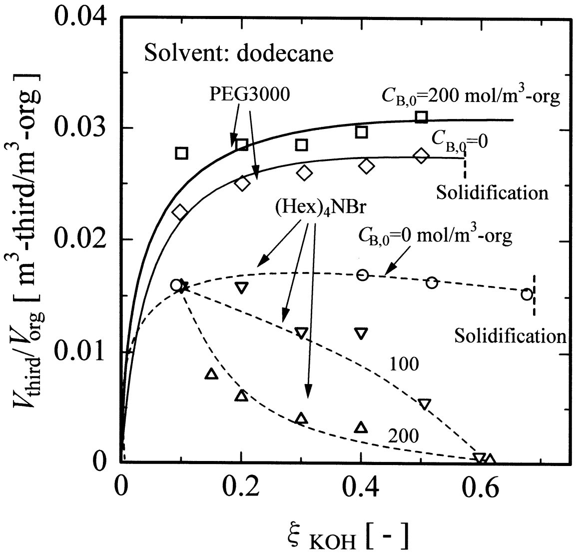


Fig. 2. Effect of catalyst and KOH concentration in the aqueous phase on the formation of third phase (ω = 10 mol/m^3-org at PEG3000, ω = 25 mol/m^3-org at (Hex)$_4$NBr).

4. Experimental results and discussion

4.1. The formation and volume of third phase

4.1.1. Condition of forming a third phase

Preliminary experiments were carried out in order to determine the conditions of formation of the third phase by varying the concentrations of potassium hydroxide (KOH) in the aqueous phase as well as the initial concentration of *n*-butanol in the organic phase. No formation of third phase was found in any conditions in the case of toluene (weakly polar organic solvent).

In the case of dodecane (nonpolar organic solvent), the third phase was formed as shown in Fig. 2. The value of ξ_{KOH} represents the dimensionless concentration of KOH in the aqueous phase. When the aqueous phase is saturated with KOH (1.76×10^4 mol-KOH/m^3-aq), ξ_{KOH} equals unity.

In the case of (Hex)$_4$NBr, the third phase is formed without *n*-butanol as shown in our previous paper [7]. As the concentration of *n*-butanol increases, the volume is decreased at higher values of ξ_{KOH}. Especially, the volume of the third phase is disappeared at $\xi_{KOH} > 0.7$. The disappearance of the third phase may be explained by the similar mechanism in Eqs. (6) and (7), that is, the ammonium salt (Q^+X^-) in the third phase may be extracted to the organic phase.

However, in the case of PEG3000, the volume of third phase increases with the addition of *n*-butanol and KOH because the reaction given by Eq. (6) does not occur with only polyethylene glycol (PEG). PEG3000 as phase transfer catalyst has rings such as crown ether [16] while the ammonium salt (Q^+X^-) does not have them.

At higher ξ_{KOH} without *n*-butanol, the third liquid phase disappeared and in turn, the solidification occurred. This solidification phenomenon was also observed by Masson et al. [17] and Jin et al. [7]. They explained the phenomena by dehydration of catalyst phase (third phase), causing its precipitation of catalyst.

The solidification was not observed by adding *n*-butanol to moderate the dehydration of catalyst phase.

4.1.2. Effect of n-butanol concentration on third-phase volume

Fig. 3 shows the effect of *n*-butanol concentration on the volume of the third phase at $\xi_{KOH} = 0.5$ and 1.0 in the case of PEG3000. As the concentration of *n*-butanol, $C_{B,org}$ is increased, the volume of third phase increases independently of the concentration of KOH in the aqueous phase except for lower concentrations of *n*-butanol where the solidification occurs at $\xi_{KOH} = 1.0$. These results suggest that substantial quantity of *n*-butanol may be dissolved into the third phase during reaction.

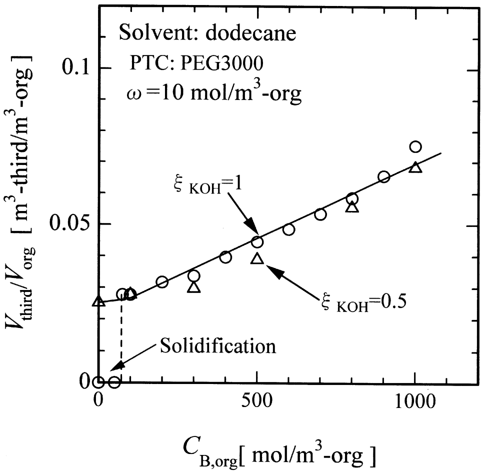


Fig. 3. Effect of *n*-butanol concentration on volume of third phase.

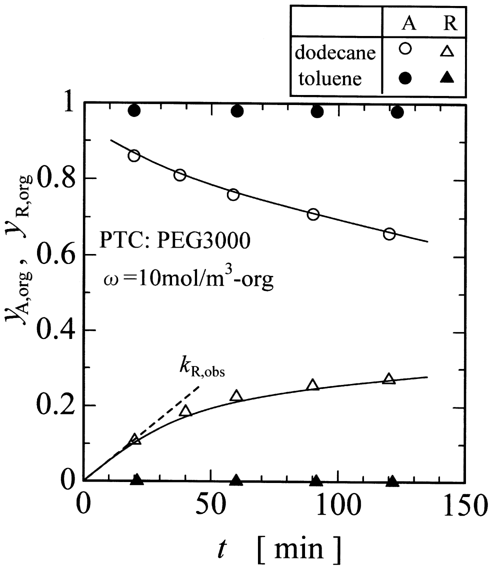


Fig. 4. Time course of reactant and product in toluene and dodecane ($\xi_{KOH} = 0.5$, $C_{A,0} = C_{B,0} = 200\,mol/m^3$-org).

4.2. Reaction rate in the stirred tank batch reactor

4.2.1. Effect of third phase on the reaction

Fig. 4 shows concentration profiles of the reactant (A) and the product (R) with time in both cases of toluene and dodecane as organic solvent, respectively.

In the case of toluene where the third phase is not formed, no reactions occur. On the other hand, in the case of dodecane where the third phase is formed, the etherification can take place. It is revealed that the third phase may play a significant role in the reaction [6].

The observed rate constant, $k_{R,obs}$ was determined from the slope of the plots between y_R and t at the initial stage as shown in Fig. 4.

4.2.2. Effect of A and B concentration on the reaction rate

Fig. 5 shows the results of the observed rate constant of ether (R) for various concentrations of benzyl chloride (A) and *n*-butanol (B).

The rate constant is almost independent of the concentration of benzyl chloride (A) at the constant concentration of *n*-butanol (B), 200 mol/m^3-org. However, the rate constant increases dramatically with *n*-butanol (B) concentration at the constant concentration of benzyl chloride (A), 200 mol/m^3-org. These imply that the

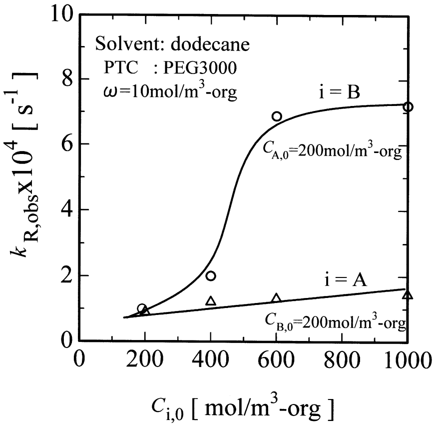


Fig. 5. Effect of *n*-butanol and benzyl-chloride concentrations in the organic phase on production rate of ether ($\xi_{KOH} = 1.0$).

properties of the third phase for the two cases differ from each other and these variations in properties may be due to the composition changes in the third phase. In this regard, further studies are done as follows.

4.2.3. Compositions of the third phase

The reactants and products may be dissolved into PTC to form the third phase. As the initial concentration of *n*-butanol in the organic phase increases, *n*-butanol in the third phase increases while water decreases as shown in Fig. 6. Benzyl chloride was not added to avoid the reaction. The decrease in the water concentration in the third phase in Fig. 6 may cause the increase in the rate constant with the increase in the initial concentration of B in Fig. 5. This is consistent with the results obtained in the previous papers [7,8].

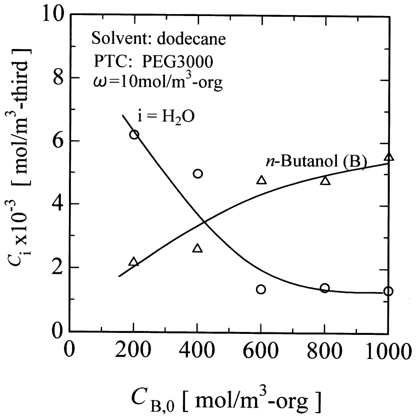


Fig. 6. Effect of initial *n*-butanol concentration in organic phase on the compositions of the third phase ($\xi_{KOH} = 1.0$, $C_{A,0} = 0\,\mathrm{mol/m^3}$-org).

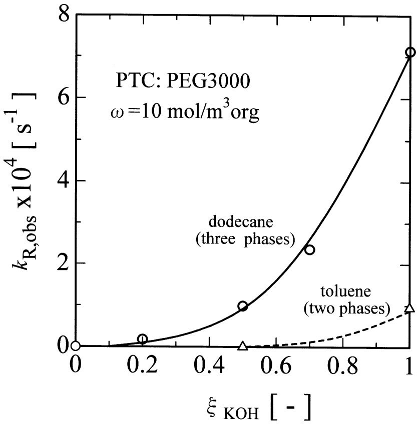


Fig. 7. Dependence of k_{obs} on the KOH concentration in aqueous phase in two or three phase ($C_{A,0} = 200\,\mathrm{mol/m^3}$-org, $C_{B,0} = 1000\,\mathrm{mol/m^3}$-org).

4.2.4. Effect of KOH concentration on the reaction rate

Fig. 7 shows the effect of KOH concentration in the aqueous phase (ξ_{KOH}) on the ether production rate in both cases of toluene and dodecane.

In the case of toluene (two-phase system), the reaction occurs only at higher concentrations of KOH.

In the case of dodecane (three-phase system), the rate constant, $k_{R,obs}$ increases sharply with the increase in ξ_{KOH}.

The reaction rate in the three-phase system can be higher by seven times than that in the two-phase system at $\xi_{KOH} = 1.0$.

4.3. Selectivity

4.3.1. Time course of reactants and product and their selectivities

Equal concentrations of benzyl chloride and *n*-butanol ($C_{A,0} = C_{B,0} = 200\,\mathrm{mol/m^3}$-org) were added to the batch reactor and the concentrations of benzyl chloride (A), *n*-butanol (B) and the ether (R) were determined with time. The results are shown in Fig. 8.

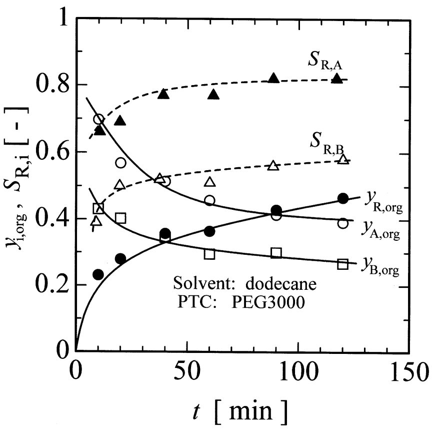


Fig. 8. Time course of reactants, product and selectivity in a stirred tank batch reactor ($\xi_{KOH} = 1.0$, $C_{A,0} = C_{B,0} = 200\,mol/m^3$-org).

Even if the reactants are stoichiometrically the same, the decrease in *n*-butanol (B) is greater than that in benzyl chloride (A). This may be due to the side reaction, Eq. (7).

The ether selectivity based on benzyl chloride (A) or *n*-butanol (B) are defined as follows:

$$S_{R,i} = \frac{m_{R,org}}{m_{i,0} - m_{i,org}}, \quad i = A \text{ or } B \tag{10}$$

In the case of benzyl chloride (A), 1 mol of A is consumed to produce 1 mol of R by Eq. (4). Both A and R may exist in organic or third phases because they are not dissolved in the aqueous phase.

$$m_{A,0} = m_{A,org} + m_{R,org} + m_{A,third} + m_{R,third} \tag{11}$$

Therefore, Eq. (10) can reduce to the following equation:

$$S_{R,A} = \frac{m_{R,org}}{m_{R,org} + m_{A,third} + m_{R,third}} \tag{12}$$

The fact that $S_{R,A}$ is around 0.8 in Fig. 8 may be explained by Eq. (12) which indicates that the components dissolved in the third phase ($m_{A,third} + m_{R,third}$) cannot be neglected.

On the other hand, the selectivity of $S_{R,B}$ is around 0.5. This may be explained by the additional consumption of *n*-butanol (B) due to the side reaction, Eq. (7), that is,

$$S_{R,B} = \frac{m_{R,org}}{m_{R,org} + m_{B,third} + m_{R,third} + m_{alkoxide,aq}} \tag{13}$$

where $m_{alkoxide,aq}$ are the moles of alcohol alkoxide produced in the aqueous phase by consuming *n*-butanol (B).

4.3.2. Behavior of *n*-butanol in the organic phase

n-Butanol concentration in the organic phase was measured with time for three cases as follows:

(a) Without PEG3000 ($\omega = 0\,mol/m^3$) without benzyl chloride ($C_{A,0} = 0\,mol/m^3$-org).
(b) With PEG3000 ($\omega = 10\,mol/m^3$) without benzyl chloride ($C_{A,0} = 0\,mol/m^3$-org).
(c) With PEG3000 ($\omega = 10\,mol/m^3$) with benzyl chloride ($C_{A,0} = 200\,mol/m^3$-org).

The initial concentration of *n*-butanol in the organic phase was fixed at $C_{B,0} = 1000\,mol/m^3$-org in any case.

The results are shown in Fig. 9. Even when the third phase cannot be formed in Case (a) without PEG3000, *n*-butanol is consumed by the reaction of Eq. (7). The addition of PEG3000 in Case (b) does not affect the consumption rate of B as shown in the dotted line in Fig. 9 although the third phase is formed in Case (b).

In both Cases (a) and (b), *n*-butanol concentration in the organic phase attains steady state after 300 min. This means that the equilibrium holds at the reaction, Eq. (7). However, in Case (c) where both reactants, A and B are present with PEG3000, *n*-butanol (B) is consumed faster than other two Cases (a) and (b) because two reactions, Eqs. (7) and (8) occur simultaneously.

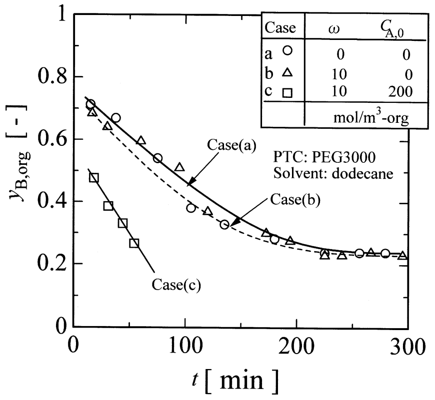


Fig. 9. Time course of *n*-butanol in organic phase for three cases ($\xi_{KOH} = 1.0$, $C_{B,0} = 1000\,mol/m^3$-org).

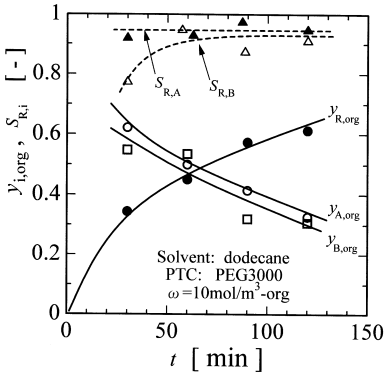


Fig. 10. Time course of reactants, product and selectivity in a static triphase batch reactor ($\xi_{KOH} = 1.0$, $C_{A,0} = C_{B,0} = 200$ mol/m^3-org).

4.4. *Selectivity in the static triphase batch reactor*

The static triphase batch reactor was used to improve the selectivity of ether (R) by suppressing the reaction, Eq. (7).

Fig. 10 shows the selectivities, $S_{R,A}$ and $S_{R,B}$ together with the dimensionless concentrations, $y_{A,org}$, $y_{B,org}$ and $y_{R,org}$. Both lines of $y_{A,org}$ and $y_{B,org}$ are close to each other. It indicates that the reaction, Eq. (7) is not significant. Therefore, the selectivities, $S_{R,A}$ and $S_{R,B}$ are as high as 0.9.

It is seen from Fig. 10 that the side reaction, Eq. (7) can be suppressed by separating the organic and aqueous phases in the static triphase batch reactor.

Furthermore, the production rate of ether is higher than that of Fig. 8 in the stirred tank reactor. This result suggests that the water concentration in the third phase decreases in the static reactor as shown in Section 2.2.

5. Conclusion

The reaction of benzyl-*n*-butyl ether from benzyl chloride and *n*-butanol was investigated in details and the following conclusions could be deduced:

1. A third phase was formed when PEG3000 was used as phase transfer catalyst with dodecane as the organic solvent.
2. The ether production rate in the three-phase system was seven times greater than that of the two-phase system.
3. In a stirred tank batch reactor, *n*-butanol reacts with benzyl chloride and potassium hydroxide simultaneously. The selectivity of ether on a basis of initial *n*-butanol is below 0.6.
4. In a static triphase batch reactor, the undesirable side reaction is suppressed. The selectivity is much improved as high as 0.9.

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