



Phase-transfer catalyzed benzylation of sodium benzoate using aliquat 336 as catalyst in liquid–liquid system

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Abstract

Kinetics of the reaction between benzyl bromide (RBr) and sodium benzoate (C_6H_5COONa , $PhCOONa$) in liquid–liquid system catalyzed by aliquat 336 (QCl) was investigated in the present study. The yield of product benzyl benzoate ($PhCOOR$) was obtained above 98% at 70 °C within 3 h of reaction using chlorobenzene as the solvent. During the progress of reaction, about 80% of the catalyst was present as the catalytic intermediate in the organic phase, which is generated from the reaction of aqueous sodium benzoate with aliquat 336 at the aqueous–organic interface. When a great excess amount of aqueous reactant was employed, the concentration of catalytic intermediate was kept at near constant after the induction period. A conspicuous reduction of 40% of interfacial tension by forming catalytic intermediate methyltrioctylammonium benzoate ($PhCOOQ$) was applied to describe the interfacial phenomenon. A kinetic model describing the behavior of interfacial catalysis was proposed, and the experimental data were interpreted as a pseudo-first-order reaction, although the catalytic intermediate was produced in the interfacial region. The effects of temperature, organic solvent and amounts of catalyst were investigated and the apparent activation energy was estimated at 63.96 kJ/mol in chlorobenzene. The present benzylation reaction catalyzed by aliquat 336 shows characteristics of the intermediate in phase-transfer catalysis (PTC).

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1. Introduction

Phase-transfer catalysis (PTC) benefits various types of reactions in organic synthesis very efficiently, especially for the reactants each residing in immiscible phases, and is now widely applied in the processes for manufacturing specialty chemicals [1,2]. The first reaction scheme addressed by Starks in 1971 was for the reaction of aqueous sodium cyanide and organic 1-chlorooctane. This cyanide displacement reaction takes place rapidly by adding 1% of the qua-

ternary ammonium salt ($C_6H_{13})_4N^+Cl^-$ to achieve near 100% of product yield in 2–3 h, and that is in contrast with the result of no reaction observed after 24 h in the absence of any catalyst [1]. Nowadays, synthetic methods including alkylation, oxidation, reduction, addition, hydrolysis, etherification, esterification, carbene reaction, chiral reaction, polymerization, and biochemical reactions, are confirmed to have promising results by applying phase-transfer catalysis techniques [2,3].

The feature of a PTC reaction is that it is carried out in at least two immiscible phases by employing the phase-transfer catalyst, which can transport back and forth from one of the phases to the others. The nature of the interface and the properties

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of the reacting compounds at the interface become very important to conduct the desired reaction with a satisfactory reaction rate. In an agitated liquid–liquid system, one phase will be dispersed into the other phase as droplets, whereby a larger interfacial area between the two phases is generated. Several efforts have been made in developing the theory of chemical reactions in liquid–liquid phases. Sada et al. [4] developed the diffusion equation with chemical reaction in two-liquid phase by applying film theory. They assumed the chemical reaction occurred in the film in which the concentration profiles of reactants on either side were obtained for flat interface. It is noted that the nature of the interface affects the reaction rate and is determined from the surface tension of solvents, the presence or absence of surfactants, and the degree of agitation rate. These factors result in the sharpness of the interface and the thickness of interfacial film, the droplet sizes, and the interfacial area available to the transportation of the reacting anion.

Inoue and Nakashio [5] investigated the mass transfer accompanied by chemical reaction at the surface of a single droplet for both neglecting and accounting the mass transfer resistances in the continuous phase. Wang and Yang [6] investigated the dynamic behavior of phase-transfer catalyzed reactions and determined the parameters accounting for mass transfer and kinetics in a two-phase system by applying film theory to the catalyst and active intermediate. Asai et al. [7] reported the alkaline hydrolysis of *n*-butyl acetate and oxidation of benzyl alcohol in an agitated vessel, where the overall reaction rate of phase-transfer catalysis with mass transfer at a flat interface was concluded to be proportional to the interfacial concentration of the actual reactant. Generally speaking, interfacial phenomena of reacting anions include surface equilibrium distributions of the active intermediate and the catalyst, the penetration depth from the interface into the other phase, and the mass transfer rate across the interfacial region. Yang [8,9] developed mathematical models to describe the dynamics of phase-transfer catalyzed reaction in a dispersed system of liquid–liquid phases and compared the importance of reversible aqueous reaction to the behavior of active intermediate. However, the analysis of interfacial catalyzed reaction to generate the active intermediate in the interfacial region is still lacking.

The properties of the interfacial region can be altered by many methods, one of which is by adding extra salts that alters the original reaction zone. Regarding the catalytic efficiency in PTC, the behavior of the catalyst and its active intermediate in the interface would play important roles on the overall reaction rate. In the present study, the esterification of sodium benzoate (C_6H_5COONa , $PhCOONa$) and benzyl bromide (RBr) to produce benzyl benzoate ($PhCOOR$) catalyzed by aliquat 336 (QCI) catalyst in a liquid–liquid system was investigated. The phase-transfer catalyst aliquat 336, which is a highly lipophilic compound, was employed to explore the variation of the interfacial behavior of the active intermediate. The effects of operating conditions on the characteristics of active intermediate were investigated to clarify the phenomenon of interfacial catalysis for phase-transfer system. An appropriate kinetic expression was also proposed for the present esterification reaction system.

2. Experimental

Reagent sodium benzoate from Merck is used as the aqueous reactant without further treatment. Aliquat 336, benzyl bromide, benzyl benzoate (used as the standard in the analysis) and other reagents are all reagent-grade chemicals from Fluka, Lancaster and Aldrich.

2.1. Formation of the catalytic intermediate

The catalytic intermediate was prepared from the interfacial reaction of sodium benzoate in the aqueous phase and aliquat 336 (methyltriethylammonium chloride) in dichloromethane solvent. Definite amounts of aliquat 336 and sodium benzoate were introduced into a three-necked flask in which water and dichloromethane and the mixture was agitated isothermally. Without the addition of organic solvent, the liquid aliquat 336 would form a thin layer over the aqueous solution due to its extremely low solubility in water. The catalytic intermediate methyltriethylammonium benzoate ($PhCOOQ$) was produced and subsequently extracted into the organic solution, which was then separated and concentrated after the completeness of reaction. The catalytic intermediate

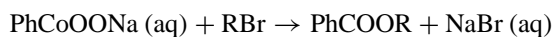
was obtained by removing the solvent, and purified to get the desired compound for identification.

2.2. Kinetic reactions in aqueous–organic phases

Known quantities of phase-transfer catalyst and benzyl bromide together with a definite quantity of diphenylmethane (the internal standard) were added into a 250 cm³ three-necked flask which was immersed in a constant-temperature water bath. For a batch run, a known quantity of sodium benzoate pre-dissolved in water was put into the reactor to start the phase-transfer reaction. The agitation speed and the reaction temperature were controlled at the desired values. During the reaction, 0.2 cm³ of the organic sample was withdrawn at the chosen time and diluted into 4 cm³ of acetonitrile. The concentrations of RBr, PhCOOQ and PhCOOR were measured by the internal standard method. The sample was analyzed with HPLC and a variable-wavelength UV detector at 254 nm. The eluent condition was set at a volumetric ratio of acetonitrile/water to be 70/30. The flow rate was 1.0 cm³/min. The column was C-18 (5-μm) type.

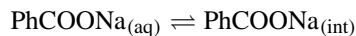
3. Kinetic model

In the liquid–liquid phase-transfer catalyzed system, the anion of catalyst aliquat 336 will change into QBr, and since the solubility of QCl or QBr in the aqueous phase is very low, the catalytic intermediate PhCOOQ will be formed at the interface from the reaction of aqueous sodium benzoate with organic aliquat 336, then transferring into the organic phase to conduct the intrinsic organic reaction. The overall reaction and the reaction scheme are:



The steps involved in the overall reaction are:

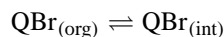
1. Transport of sodium benzoate from the aqueous phase to the liquid–liquid interface to be adsorbed on the interface with adsorption equilibrium constant K_{a1} :



$$K_{a1} = \frac{C_{\text{PhCOONa}}^{\text{int}}}{C_{\text{PhCOONa}}^{\text{aq}}} \quad (1)$$

where $C_{\text{PhCOONa}}^{\text{int}}$ is the surface concentration of PhCOONa in the interface (mol/dm³).

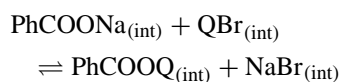
2. Transport of catalyst QBr from the organic phase to the liquid–liquid interface to be adsorbed on the interface with adsorption equilibrium constant K_{a2} :



$$K_{a2} = \frac{C_{\text{QBr}}^{\text{int}}}{C_{\text{QBr}}^{\text{org}}} \quad (2)$$

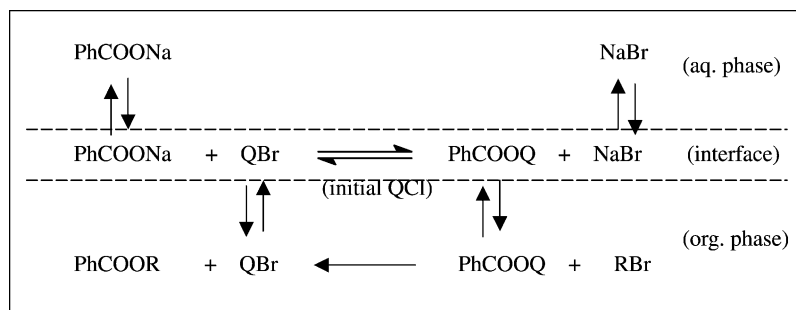
where $C_{\text{QBr}}^{\text{int}}$ is the surface concentration of QBr in the interface (mol/dm³).

3. Interfacial reaction of PhCOONa and QBr at the interface with the reaction rate r_1 , forward rate constant k_1 , and the equilibrium constant K_1 :

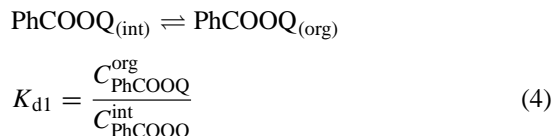


$$r_1 = k_1 (C_{\text{PhCOONa}}^{\text{int}} C_{\text{QBr}}^{\text{int}} - \frac{1}{K_1} C_{\text{PhCOOQ}}^{\text{int}} C_{\text{NaBr}}^{\text{int}}) \quad (3)$$

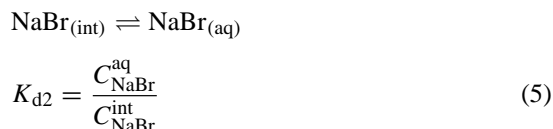
where $C_{\text{PhCOOQ}}^{\text{int}}$ is the surface concentration of PhCOOQ in the interface (mol/dm³).



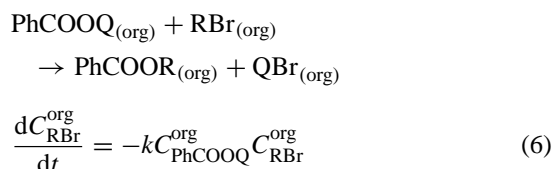
4. Desorption of PhCOOQ and transport from the interface to the organic phase with desorption equilibrium constant K_{d1} :



5. Desorption and mass transfer of NaBr from the interface to the aqueous phase with desorption equilibrium constant K_{d2} :



6. Intrinsic reaction of PhCOOQ with RBr in the organic phase with the rate constant k :



Taking mass balance for Q of catalyst yields:

$$V^{\text{org}}C_{\text{QCl},0} = V^{\text{org}}(C_{\text{QBr}}^{\text{org}} + C_{\text{PhCOOQ}}^{\text{org}}) + V^{\text{int}}(C_{\text{QBr}}^{\text{int}} + C_{\text{PhCOOQ}}^{\text{int}}) \quad (7)$$

Substituting Eqs. (2) and (4) into (7), we have:

$$C_{\text{QCl},0} = (C_{\text{QBr}}^{\text{org}} + C_{\text{PhCOOQ}}^{\text{org}}) + \frac{V^{\text{int}}}{V^{\text{org}}} \left(\frac{K_{a2}C_{\text{QBr}}^{\text{org}} + C_{\text{PhCOOQ}}^{\text{org}}}{K_{d1}} \right) \quad (8)$$

and the concentration of PhCOOQ is expressed as

$$C_{\text{PhCOOQ}}^{\text{org}} = \frac{C_{\text{QCl},0} - (1 + (V^{\text{int}}K_{a2}/V^{\text{org}}))C_{\text{QBr}}^{\text{org}}}{1 + (V^{\text{int}}/V^{\text{org}}K_{d1})} \quad (9)$$

Since the term $V^{\text{int}}/V^{\text{org}}$ is negligibly very small, it leads to $1 + (V^{\text{int}}/V^{\text{org}}K_{d1}) \approx 1$. Hence, Eq. (9) can be reduced as

$$C_{\text{PhCOOQ}}^{\text{org}} = C_{\text{QCl},0} \left[1 - \left(1 + \frac{V^{\text{int}}K_{a2}}{V^{\text{org}}} \right) \frac{C_{\text{QBr}}^{\text{org}}}{C_{\text{QCl},0}} \right] \quad (10)$$

In Eq. (10), the term within the bracket of the right-hand side denotes the fraction of QCl in the form of PhCOOQ, and has a value about 80% after the induction period from the observation of the experimental runs. Defining the product yield $Y = C_{\text{PhCOOR}}^{\text{org}}/C_{\text{RBr},0}$, and from the material balance of RBr, we have:

$$C_{\text{RBr},0} = C_{\text{PhCOOR}}^{\text{org}} + C_{\text{RBr}}^{\text{org}} \quad \text{and}$$

$$C_{\text{RBr}}^{\text{org}} = C_{\text{RBr},0}(1 - Y) \quad (11)$$

Substitution of Eq. (11) into (6) yields:

$$\frac{dY}{dt} = -kC_{\text{PhCOOQ}}^{\text{org}}(1 - Y) \quad (12)$$

From the experimental data, the kinetic behavior of pseudo-first-order reaction was observed, and the concentration of PhCOOQ in the organic phase after the induction period would be maintained at an almost constant value. The apparent reaction rate constant k_{app} can be used to interpret the experimental results by integrating Eq. (12) as follows:

$$-\ln(1 - Y) = k_{\text{app}}t \quad (13)$$

where

$$k_{\text{app}} = kC_{\text{QCl},0} \left[1 - \left(1 + \frac{V^{\text{int}}K_{a2}}{V^{\text{org}}} \right) \frac{C_{\text{QBr}}^{\text{org}}}{C_{\text{QCl},0}} \right] \quad (14)$$

Applying the Arrhenius' equation, $k_{\text{app}} = A \exp(-E_{\text{app}}/RT)$, the apparent activation energy E_{app} can be estimated.

4. Results and discussion

4.1. Interfacial tension of aqueous–organic phases

The properties of the interfacial region can be altered by many methods, and one of which is adding extra salts. This alters the original reaction zone because the properties of the interface have been changed. In the present esterification reaction, adding aliquat 336 promotes the formation of the catalytic intermediate. The solubility of aliquat 336 in water is very small due to the long alkyl chain of aliquat 336. Measurements of interfacial tension for investigating the effect of methyltrioctylammonium benzoate or aliquat 336

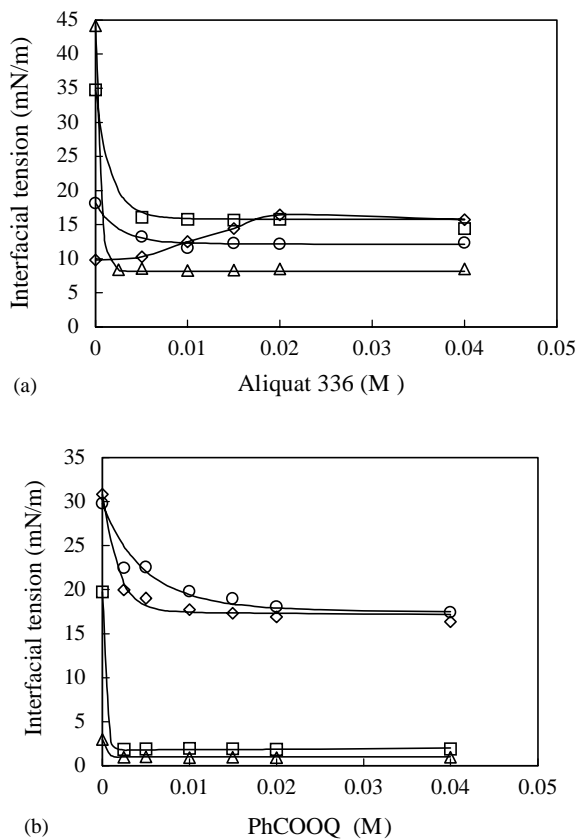


Fig. 1. (a) Effect of aliquat 336 and 0.4 M of sodium benzoate on interfacial tension, (b) effect of methyltriethylammonium benzoate on interfacial tension. Organic solvent 16 cm³, aqueous solution 16 cm³, temperature 26 °C. Organic solvents: (◇) C₆H₅Cl, (□) C₆H₅CH₃, (△) *n*-C₇H₁₆, (○) CH₂Cl₂.

in organic phase with definite amounts of sodium benzoate in the aqueous phase were performed using the circular-ring method.

Fig. 1(a) shows the interfacial tension for aliquat 336 accompanied with 0.4 M aqueous sodium benzoate in chlorobenzene, toluene, *n*-heptane, and dichloromethane solvent individually. It is seen that, in toluene, *n*-heptane and dichloromethane as solvent, the interfacial tension decreases drastically with the increase in the amount of aliquat 336 up to 0.005 M, and then reaches a constant value regardless of more aliquat 336 added. For chlorobenzene, the interfacial tension without aliquat 336 was the smallest among the solvents tested; however, adding aliquat 336 would slightly increase the interfacial

tension up to 0.02 M. This phenomenon reveals that under non-agitated conditions the reaction of aliquat 336 with sodium benzoate would proceed but cannot produce enough catalytic intermediate, and that the behavior can be confirmed by directly adding methyltriethylammonium benzoate in the solution as shown in Fig. 1(b). The introduction of methyltriethylammonium benzoate indeed greatly reduces the interfacial tension between water and organic solvent. The interfacial tension reduces from 30.8 to 16.4 mN/m for the chlorobenzene/water system, and from 19.7 to 1.88 mN/m for the toluene/water system. This indicates that methyltriethylammonium benzoate has the great potential for enhancing the two-phase reaction.

4.2. Esterification catalyzed by aliquat 336

Fig. 2(a) shows that the overall reaction was conducted in a very low rate with less than 10% of product yield for 3 h of reaction without catalyst; however, the reaction rates were greatly enhanced by adding little amounts of aliquat 336 as the catalyst. From the plot, the reaction rates at different amounts of aliquat 336 can be well described by the pseudo-first-order kinetics. With 0.001 mol of aliquat 336, 0.02 mol of sodium benzoate and 0.005 mol of benzyl bromide, the product yield was 98.3% for 3 h of reaction, and the pseudo-first-order reaction rate constant was 0.0255 min⁻¹. The apparent rate constant increased with increasing amounts of aliquat 336.

The concentrations of the catalytic intermediate PhCOOQ in the organic phase for different amounts of aliquat 336 are shown in Fig. 2(b). The amount of PhCOOQ increased quickly within the induction period up to a certain value, and then was maintained approximately at this value till the completion of reaction. It should be noted that the moles of sodium benzoate used was four times those of benzyl bromide. Thus, after the complete consumption of RBr, there would still be enough PhCOONa to react with the catalyst to produce catalytic intermediate in the organic phase. The expression of PhCOOQ in Eq. (12) is consistent with the experimental results provided that the overall equilibrium constant K_{ov} is large; moreover, about 80% of the aliquat 336 added would be present in the form of PhCOOQ as estimated from the plot in Fig. 2(b). In addition, the linear dependence of apparent reaction rate constant on the initial concentration

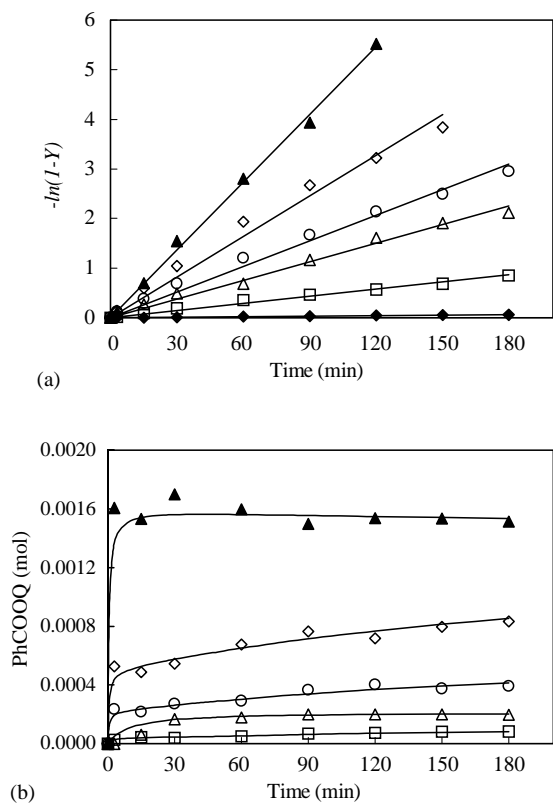


Fig. 2. (a) Plot of $-\ln(1-Y)$ vs. time for different amounts of aliquat 336, (b) variation of PhCOOQ at various amounts of aliquat 336. Sodium benzoate 0.02 mol, benzyl bromide 0.005 mol, chlorobenzene 50 cm^3 , water 50 cm^3 , temperature 70°C , 400 rpm. Aliquat 336: (\blacklozenge) 0 mol, (\square) 0.0001 mol, (\triangle) 0.0002 mol, (\circ) 0.0004 mol, (\diamond) 0.001 mol, (\blacktriangle) 0.002 mol.

of aliquat 336 was also observed, as shown in Fig. 3. The slope of the plot as the product of intrinsic rate constant and the fraction of initial QCl in the form of PhCOOQ was estimated as 1.617, and the intrinsic rate constant in chlorobenzene at 70°C proved to be approximately as $2.02 \text{ (dm}^3/(\text{mol min}))$. This value shows the high reactivity of catalytic intermediate with benzyl bromide using aliquat 336 as the catalyst.

4.3. Effect of agitation on the variation of catalytic intermediate

Agitation enhances the transport of compounds between immiscible phases. Fig. 4 shows the product yields for different agitation speeds. Without agit-

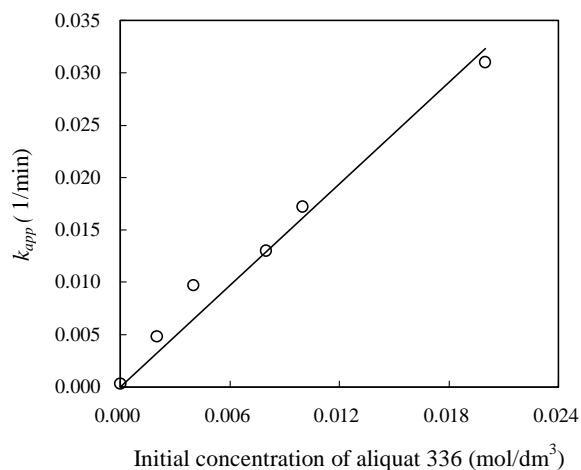


Fig. 3. Apparent rate constants at various amounts of aliquat 336: sodium benzoate 0.02 mol, benzyl bromide 0.005 mol, chlorobenzene 50 cm^3 , water 50 cm^3 , temperature 70°C , 400 rpm.

ing the two-liquid system, the interfacial reaction of PhCOONa with QBr to form PhCOOQ still occurred at a flat interface and the amount of PhCOOQ in the organic phase is large enough to conduct the intrinsic organic reaction. The product yield was above 80% without stirring as shown in Fig. 4. It is seen that the overall reaction rate is not influenced by the stirring speed that exceeds 100 rpm. This low limiting

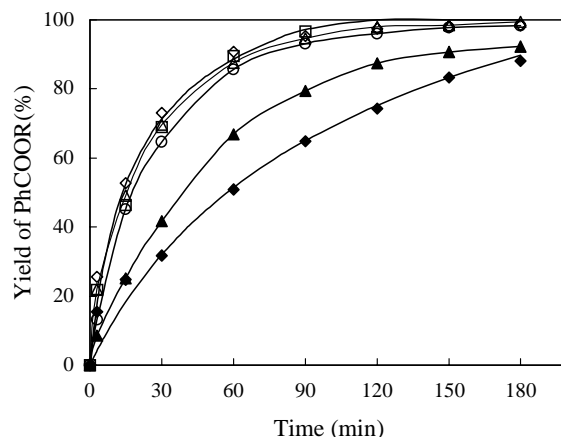


Fig. 4. Effect of agitation on product yield: 0.001 mol of aliquat 336, sodium benzoate 0.02 mol, benzyl bromide 0.005 mol, chlorobenzene 50 cm^3 , water 50 cm^3 , temperature 70°C . Agitation speed: (\blacklozenge) 0 rpm, (\blacktriangle) 50 rpm, (\square) 100 rpm, (\triangle) 200 rpm, (\diamond) 300 rpm, (\circ) 400 rpm.

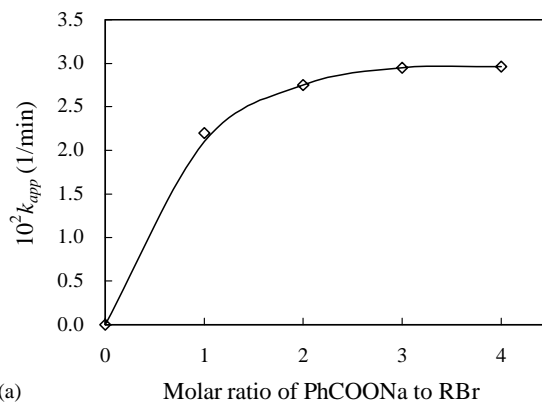
agitation speed implies that the interfacial concentration of aqueous sodium benzoate is not affected by the mass transfer rate between the aqueous phase and aqueous–organic interface when PhCOOQ is generated at an agitation speed greater than 100 rpm. The observed pseudo-first-order behavior also indicates that although the formation of catalytic intermediate occurred in the interface, the interfacial reaction is still not the rate-controlling step.

4.4. Effects of relative amounts of reactants

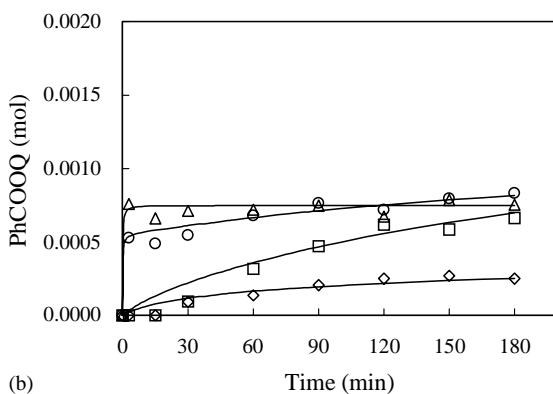
The relative usage of aqueous and organic reactants may affect the overall reaction especially on the concentration of catalytic intermediate due to the nature of phase-transfer catalyzed reaction. Fig. 5(a) shows the plot of apparent rate constant versus molar ratio of the sodium benzoate to benzyl bromide (r -value). The effect of relative usage of reactants is insignificant when r is greater than 4. This phenomenon may be due to the adsorption of sodium benzoate occupying a monolayer on the interface when r is less than 4. Thus, to generate maximum PhCOOQ at the interface, the usage of sodium benzoate must be set at least 4 to fully occupy the vacant site of aqueous-interface side. The variation of PhCOOQ for different amounts of sodium benzoate used is shown in Fig. 5(b). When r equals 3 to 4, the amount of PhCOOQ in the organic phase would quickly reach about 80% of the initial amount within a very short induction period. With a smaller ratio of PhCOONa to RBr ($r = 1$ –2) the concentration of PhCOOQ would gradually cumulate up to 80% of catalyst usage within 3 h of operation and with a longer induction period.

4.5. Effects of solvent and temperature on the catalytic efficiency

The physical properties of organic solvent play an important role on the phase-transfer catalyzed reaction, not only influencing the intrinsic organic reaction but also determining the interfacial behavior. From the previous discussion, the reduction of interfacial tension due to the existence of methyltrioctylammonium benzoate produces great differences in different solvents. This will affect the catalytic efficiency of phase-transfer catalyst. Table 1 shows the results of using different organic solvents at various temperatures.



(a)



(b)

Fig. 5. (a) k_{app} vs. different molar ratio of PhCOONa to RBr (r -value), (b) effect of r -value on PhCOOQ. 0.001 mol of aliquat 336, benzyl bromide 0.005 mol, chlorobenzene 50 cm³, water 50 cm³, temperature 70 °C. Molar ratio (r -value): (◇) 1, (□) 2, (△) 3, (○) 4.

At the temperature of 30 °C, the order of reactivity was dichloromethane > chlorobenzene > *n*-heptane, which is consistent with the order of solvent polarity. Hence, the parameters influencing the catalytic reactivity of aliquat 336 on the present esterification reaction are not just the reduction of liquid–liquid interfacial tension but including the effect of environment provided by solvents. Results at different reaction temperatures also show that the order of reactivity in various solvents is dichloromethane > chlorobenzene > toluene > *n*-heptane. The apparent activation energies were estimated at 25.21 kJ/mol for dichloromethane, 63.96 kJ/mol for chlorobenzene, 68.47 kJ/mol for toluene, and 54.08 kJ/mol for *n*-heptane.

Table 1
Effect of solvent on reactivity of aliquat 336

Solvent	Temperature (°C)	k_{app} ($\times 10^2$, min^{-1})	Yield of PhCOOQ, Y (% , 3 h)
CH ₂ Cl ₂	20	0.22	25.0
	25	0.24	27.0
	30	0.28	39.8
	35	0.36	47.8
C ₆ H ₅ Cl	30	0.12	19.2
	40	0.33	43.7
	50	0.70	71.3
	60	1.43	91.3
	70	2.55	98.3
C ₆ H ₅ CH ₃	40	0.11	17.9
	50	0.27	38.3
	60	0.63	66.3
	70	1.16	85.5
C ₇ H ₁₆	30	0.06	8.1
	40	0.09	15.1
	50	0.22	31.5
	60	0.41	50.8

Reaction conditions: solvent 50 cm³, water 50 cm³, sodium benzoate 0.02 mol, benzyl bromide 0.005 mol, 0.001 mol of aliquat 336, agitation 400 rpm.

Although the apparent activation energy and reactivity for *n*-heptane are smaller than for chlorobenzene and toluene, the amount of catalytic intermediate in *n*-heptane proved to be no less than in other solvents, as shown in Fig. 6 for chlorobenzene and Fig. 7 for *n*-heptane. Figs. 6 and 7 show that the variation of amounts of PhCOOQ at different temperatures are insignificant either in chlorobenzene or in *n*-heptane, and that the utilization of catalyst (that is the ratio of PhCOOQ to initial QCl used) is slightly greater in chlorobenzene than in *n*-heptane. In the present reaction system, the polarity of solvent is much more important than other factors.

4.6. Reaction catalyzed by other phase-transfer catalysts

The structure of the catalytic intermediate is an important factor in catalyzing the benzylation of sodium benzoate. The cation type of the phase-transfer catalyst will influence the ease of formation of the catalytic intermediate and its inherent solubility in the selected organic phase, that in turn affecting the reac-

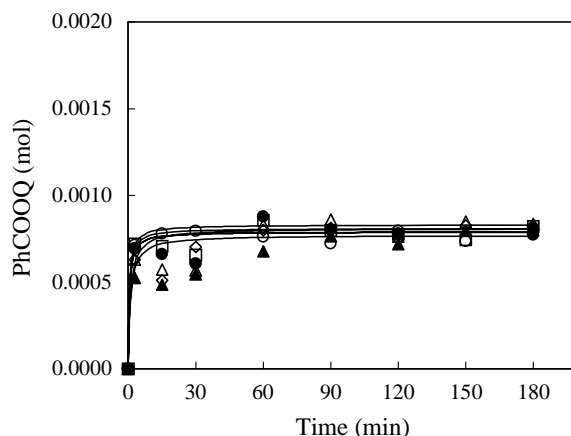


Fig. 6. Temperature effect on PhCOOQ in chlorobenzene; 0.001 mol of aliquat 336, sodium benzoate 0.02 mol, benzyl bromide 0.005 mol, chlorobenzene 50 cm³, water 50 cm³, 400 rpm. Temperature: (◇) 30 °C, (□) 40 °C, (△) 50 °C, (○) 60 °C, (▲) 70 °C, (●) 80 °C.

tivity of the catalytic intermediate with the reactant in the organic phase. In the present reaction system, the ion pair formed from benzoate anion in the aqueous phase with tetrabutylammonium cation is of loose bonding, and is difficult to transport into the organic solvent in a satisfactory amount. Hence, the intrinsic reaction of tetrabutylammonium benzoate with benzyl bromide would proceed mainly at the interfacial region of the aqueous and the organic phases, which

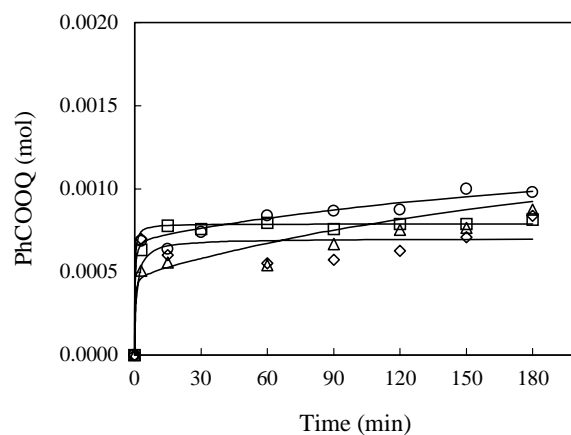
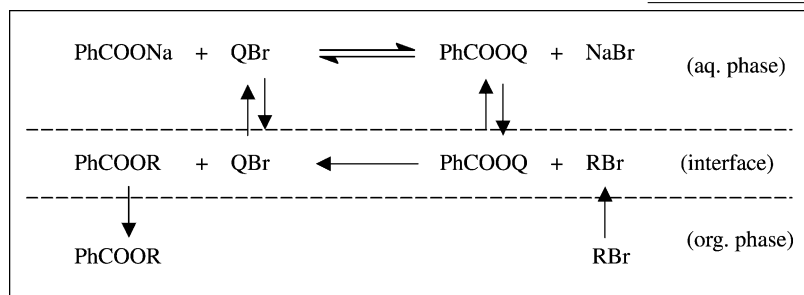


Fig. 7. Temperature effect on PhCOOQ in *n*-heptane: 0.001 mol of aliquat 336, sodium benzoate 0.02 mol, benzyl bromide 0.005 mol, *n*-heptane 50 cm³, water 50 cm³, 400 rpm. Temperature: (◇) 30 °C, (□) 40 °C, (△) 50 °C, (○) 60 °C.

shows different mechanisms from those for aliquat 336 as the catalyst. The reaction scheme using tetrabutylammonium halide is proposed as the follows.



When aliquat 336 is used as the catalyst, the formation of the catalytic intermediate occurs in the interfacial region due to its extremely low solubility in the aqueous phase, and the intrinsic reaction of the catalytic intermediate will thus be conducted mainly in the bulk organic phase. Table 2 shows

Table 2
Comparison of different phase-transfer catalysts on the esterification of sodium benzoate

PTC	Temperature (°C)	k_{app} ($\times 10^2$, min^{-1})	Yield of PhCOOR, Y (% , 3 h)
TBAB	50	0.06	10.2
	60	0.16	25.0
	70	0.48	57.4
	80	0.96	80.8
TBPB	50	0.02	30.7
	60	0.77	74.6
	70	1.43	92.6
	80	2.30	93.9
TBAHS	50	0.11	17.4
	60	0.26	36.8
	70	0.57	64.4
	80	0.99	81.1
TBAI	50	0.09	15.4
	60	0.25	36.8
	70	0.61	67.0
	80	0.98	84.6
Aliquat 336	30	0.12	19.2
	40	0.33	43.7
	50	0.70	71.3
	60	1.43	91.3
	70	2.55	98.3

Reaction conditions: chlorobenzene 50 cm³, water 50 cm³, sodium benzoate 0.02 mol, benzyl bromide 0.005 mol, 0.001 mol of phase-transfer catalyst, agitation 400 rpm.

the performance of different phase-transfer catalysts on the reaction. Although the ion-exchange reaction of tetrabutylammonium cation with the benzoate

anion mainly proceed in the bulk aqueous phase, and which phenomenon is absolutely different from aliquat 336; however, the pseudo-first-order kinetics for overall reaction rates are still observed. The order of reactivity in chlorobenzene solvent was found aliquat 336 > tetrabutylphosphonium bromide (TBPB) > tetrabutylammonium iodide (TBAI) > tetrabutylammonium hydrogen sulfate (TBAHS) > tetrabutylammonium bromide (TBAB). This shows that the larger alkyl group will benefit the formation of PhCOOQ. The apparent activation energy estimated from Arrhenius' plot are 64 kJ/mol for aliquat 336, 71 kJ/mol for TBPB, 77 kJ/mol for TBAI, 70 kJ/mol for TBAHS, and 142 kJ/mol for TBAB. TBAB shows the highest apparent activation energy and the lowest reactivity for the present reaction system, among the tested PT catalysts. This might be due to the fact that the catalytic intermediate is not easily generated by competitive reaction of benzoate anion with bromide ion in the aqueous phase. As the catalytic intermediate is generated, it is somewhat difficult to transport into the organic phase to conduct the intrinsic reaction, leading the lower reaction rate observed.

5. Conclusion

In present liquid–liquid phase-transfer catalyzed esterification, the aqueous-phase reactant sodium benzoate can be transported from the aqueous phase to the organic one by the reaction with aliquat 336 in the interfacial region. The catalytic behavior and the generation of PhCOOQ in the interface were explored. Using aliquat 336 as the catalyst, higher than 98% yield of benzyl benzoate can be easily

achieved within 3 h at 70 °C in chlorobenzene. The pseudo-first-order reaction can be applied to describe the overall reaction rate successfully. The concentration of the catalytic intermediate was kept at an almost constant value after the induction period, and about 80% of the catalyst was present in the form of PhCOOQ during the progress of reaction. The mass transfer resistance at the liquid–liquid interface can be ignored when the agitation speed exceeds 100 rpm. Different phase-transfer catalysts were employed to compare their catalytic efficiency, and the reactivity order was found aliquat 336 > TBPB > TBAI > TBAHS > TBAB. The interfacial catalytic behavior of phase-transfer catalysis using aliquat 336 was thoroughly analyzed in the present study.

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