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Kinetics for synthesizing benzyl salicylate by third-liquid phase-transfer catalysis

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Abstract

The kinetics of esterification of sodium salicylate with benzyl bromide to produce benzyl salicylate was investigated via third-liquid phase-transfer catalysis. The formation of the third-liquid phase from the interaction of aqueous reactant, inorganic salts, organic solvent, and catalyst was investigated to find the characteristics of catalytic intermediate in the tri-liquid system. The minimum quantity of tetra-*n*-butylphosphonium bromide (TBPB) required to form the third-liquid phase was affected by the addition of NaBr, but the variation was insignificant with greater amount of TBPB. The volume of third-liquid increased with increasing amount of TBPB, and using 20–70 cm^3 of water for 30 cm^3 of *n*-heptane solvent favors the formation of the third-liquid phase. The interfacial tension between the aqueous and the third-liquid phases was 1–3 mN/m, much less than 9–12 mN/m for the third-liquid/heptane interface, indicating that the mass transfer resistance dominates in the heptane side. The product can be present in both organic and third-liquid phases, and above 85% of the product yield in the organic phase can be obtained using 0.006 mol of TBPB to form the third-liquid phase. The distribution of the catalytic intermediate between the aqueous and the third-liquid phases was measured, and above 86% of catalyst in the third-liquid phase is in the form of catalytic intermediate. The reaction mechanism and kinetic model were proposed and the pseudo-first-order kinetics was successfully applied, the apparent activation energy in heptane being 73.94 kJ/mol when TBPB was used as the catalyst.

Keywords: Third-liquid phase; Phase-transfer catalysis; Interfacial tension; Esterification reaction

1. Introduction

Phase-transfer catalysis (PTC) is an important tool in organic synthesis and is widely applied in pharmaceuticals, flavors, dyes, perfumes, etc. The multiphase system of phase-transfer catalysis can be divided into liquid-liquid, solid-liquid, gas-liquid, solid-liquid-liquid, and liquid-liquid-liquid phases, among which the reuse of catalyst in tri-liquid phase-transfer catalysis can overcome drawbacks of other systems. The process using tri-liquid phase-transfer catalysis would be more efficient by considering the catalyst reuse, catalyst separation, and higher reaction rates, etc. In 1984, Neumann and Sasson investigated the isomerization of allylanisole using polyethylene glycol as the catalyst in a toluene and aqueous KOH solution and observed a third-liquid phase formed between the aqueous and the organic phases [1].

Wang and Weng performed the reaction of benzyl chloride and sodium bromide using tetra-*n*-butylammonium bromide as the phase-transfer catalyst in liquid-liquid phases, and found that the overall reaction rate rapidly increased when the amount of catalyst exceeded a critical value, above which a viscous liquid phase concentrated with the catalyst was insoluble in both aqueous and organic phases [2]. This viscous phase called the third-liquid phase enhances the reaction rate even several fold compared to liquid-liquid PTC conditions. Wang and Weng explored the effects of solvents and salts on the formation of a third-liquid phase for the reaction of *n*-butyl bromide and sodium phenolate [3]. They concluded that the solvent of different polarities and the amount of NaOH were two important factors in forming a third-liquid phase full of catalyst and enhancing the reaction rate. The aqueous reactant NaOPh is also important in some certain conditions. Ido et al. reported that a halogen substitution between benzyl chloride in the organic phase and KBr in the aqueous phase was efficiently catalyzed by the third-liquid phase which was formed by changing the concentration of KBr, types of PTC, and organic solvents [4].

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Besides the investigations of necessary factors in the formation of the third-liquid phase, Yang developed a theoretical model for the reaction mechanism of tri-liquid phase-transfer catalysis by concerning the mass-transfer and reaction of the key reacting components within the third-liquid phase [5]. Jin et al. performed the dehydrohalogenation of 2-bromooctane using dodecane as the solvent and with aqueous KOH solution to investigate the synergetic effect of tetrahexylammonium bromide and polyethylene glycol under the tri-liquid system, and concluded that the catalytic activity of tetrahexylammonium bromide was reduced as the amount of PEG increased [6]. Yadav and Reddy investigated the *n*-butoxylation of *p*-chloronitrobenzene (PCNB) using NaOH under tri-liquid phases conditions; a distribution of catalyst between the organic and third-liquid phases indicated about 89% of total catalyst residing in the third-liquid phase [7]. Ohtani et al. investigated the phase behavior of tetrabutylammonium salts under the situation of interface-mediated catalysis and found that the phase behavior and component composition of coexisting phases in the tetrabutylammonium bromide/benzene/water/NaBr four-component system were strongly influenced by the temperature, catalyst content and NaBr concentration. Their results suggested that the catalysis was attributable to the interfacial reaction of tetrabutylammonium salts with the organic substrate [8].

In the past, the phenomena of catalytic intermediate in the third-liquid phase-transfer catalyzed system were seldom studied. Recently, Lin and Yang investigated the kinetics of etherification of sodium *o*-nitrophenoxide via third-liquid phase-transfer catalysis and found that the consumption rate of the catalytic intermediate in the third-liquid phase increased with the increase in reaction rates for a large excess of organic reactant used, and the measurements of interfacial tension between phases revealed that the interfacial tension for the organic/third-liquid interface was less than that for the aqueous/third-liquid interface, which contributed to the faster reaction of organic substrate with the catalytic intermediate in the third-liquid phase [9]. Huang and Yang reported that the reaction rate of the benzoylation of sodium 4-acetylphenoxide in a third-liquid phase-transfer catalyzed system was faster than that conducted in a liquid-liquid PTC system by 25–28 times and the concentration of catalytic intermediate in the third-liquid phase slightly decreased with increasing reaction time [10]. However, the investigation of catalytic intermediate, which generally shows hydrophobic property in PTC systems, is important in developing an effective PTC process. The aims of the present study are to further investigate the behavior of catalytic intermediate in the third-liquid phase-transfer catalysis for the esterification of sodium salicylate with benzyl bromide and to propose a kinetic model for properly describing the present third-liquid phase-transfer catalyzed system.

2. Experimental

2.1. Materials

Reagent sodium salicylate ($C_6H_4(OH)COONa$, denoted as ArCOONa) from Merck is used as the aqueous reactant without further treatment. Tetra-*n*-butylphosphonium bromide (Bu_4PBr, TBPB or QBr in general), benzyl bromide ($C_6H_5CH_2Br$, RBr), the desired product benzyl salicylate ($C_6H_4(OH)COOCH_2C_6H_5$, denoted as ArCOOR, used as the standard in the analysis) and other reagents are all reagent-grade chemicals from Fluka, Lancaster and Aldrich.

2.2. Formation of third-liquid phase and synthesis of ArCOOQ

A definite amount of sodium salicylate (ArCOONa) was introduced into 20 cm^3 of deionized water and 30 cm^3 of *n*-heptane with phase-transfer catalyst (QBr) tetrabutylphosphonium bromide, TBPB (or benzyltributylammonium bromide, BTBAB) to form the third-liquid phase and to produce the catalytic intermediate, tetrabutylphosphonium salicylate ArCOOQ (or benzyltributylammonium salicylate). After 1 h of shaking at 60 °C, the third-liquid phase was separated and then mixed with 10 cm^3 of deionized water. The catalytic intermediate was extracted with 10 cm^3 of chloroform three times and purified to give the gel form of ArCOOQ, which was then identified.

2.3. Analysis of ArCOOQ in the third-liquid phase

The concentration of benzyltributylammonium cation or tetra-*n*-butylphosphonium cation (denoted as Q^+) was determined by the titration method in the water-chloroform system using sodium tetraphenyl borate (Na^+TBP^-) as the titrant and bromophenol blue (0.2% in ethanol) as the indicator [11]. For the determination, 20 cm^3 of chloroform, 20 cm^3 of water and several drops of bromophenol blue were added to the sample in a flask and then the mixture was titrated with 0.05 N Na^+TBP^- solution. When the end point is reached, the color of the chloroform layer changes from blue to colorless.

For determining the amount of ArCOOQ in the third-liquid phase, the third-liquid phase was separated and poured into 20 cm^3 of deionized water to remove a trace amount of aqueous reactant ArCOONa, and the catalytic intermediate ArCOOQ was then extracted from this aqueous solution several times with chlorobenzene as the solvent. With the chlorobenzene-solution containing the catalytic intermediate, an excess amount of benzyl bromide (RBr) together with diphenylmethane (the internal standard) was introduced to start the reaction of ArCOOQ and RBr. During the reaction, 0.2 cm^3 of the sample was withdrawn at the chosen time and diluted with 4 cm^3 of acetonitrile to analyze the amount of the product ArCOOR by the internal standard method using HPLC. After no significant variation in the amount of ArCOOR was detected at the chosen time, the solution was checked for the inexistence of Q and the amount of ArCOOQ was then determined. The reaction of ArCOOQ and excess RBr in chlorobenzene can be completed within less than one hour.

2.4. Analysis of interfacial tensions

For measuring the interfacial tension between aqueous and third-liquid phases or between organic and third-liquid phases, definite amounts of sodium salicylate, phase-transfer catalyst, and inorganic salt were added into the deionized water and *n*-heptane solvent. The mixtures were agitated for 10 min to promote the formation of the third-liquid phase. Small amounts of the aqueous and third-liquid phases or the organic and third-liquid phases were withdrawn to measure their interfacial tensions for at least three times by using a DoNoUy surface tension analyzer which used a ring method for determining the force to detach a ring or loop of wire from the interface of liquids. The measured values of interfacial tension were then averaged.

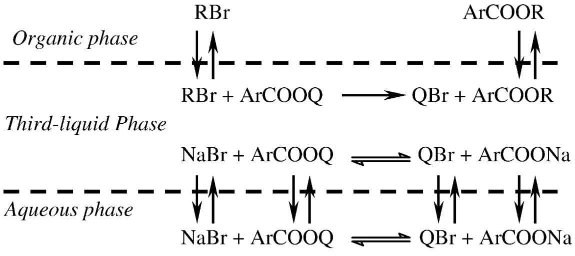
2.5. Kinetic measurements of third-liquid phase catalytic esterification

For the kinetic analysis, the third-liquid phase was first prepared and separated to measure the volume and then analyzed. The third-liquid phase, benzyl bromide (RBr) together with a definite quantity of diphenylmethane (the internal standard) were added and agitated in a 250 cm^3 three-necked batch reactor, which was immersed in a constant-temperature water bath. For a batch run, a known quantity of sodium salicylate was added 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 cm^3 of the organic sample or the third-liquid phase was withdrawn at the chosen time.

To determine the volume of each phase at different reaction times, the reaction should be terminated at each chosen time for separating the aqueous, the organic and the third-liquid phases to measure their volumes individually. Thus, a separate kinetic run was needed for each chosen reaction time at the same operating conditions. The amount of total catalyst Q$^+$ in the third-liquid phase was determined by the Volhard's method, and the organic sample as well as the third-liquid sample was diluted into 4 cm^3 of acetonitrile to determine the product with an internal method using HPLC with a C-18 (5-μm) type column and a variable-wavelength UV detector at 254 nm. The flow rate of the eluent with a volumetric acetonitrile/water ratio of 70/30 was 1.0 cm^3 min^{-1}.

3. Kinetic model

In the present phase-transfer catalyzed esterification via third-liquid phase-transfer catalyst, the key reaction step is the formation of the catalytic intermediate, which is formed from the ionic-exchange reaction of sodium salicylate (ArCOONa) with catalyst QBr in the aqueous phase. The reaction scheme is as follows:



The reaction and mass-transfer steps involved in the above overall reaction are:

(1) catalyst QBr reacted with ArCOONa in the aqueous phase to form ArCOOQ and transferred into the third-liquid phase,

$$\mathrm{ArCOONa\,(aq) + QBr\,(aq) \rightleftharpoons ArCOOQ\,(aq) + NaBr\,(aq)},$$

with the reaction rate,

$$r_1 = k_1\left(C^{\mathrm{aq}}_{\mathrm{QBr}}C^{\mathrm{aq}}_{\mathrm{ArCOONa}} - \frac{C^{\mathrm{aq}}_{\mathrm{ArCOOQ}}C^{\mathrm{aq}}_{\mathrm{NaBr}}}{K_1}\right), \tag{1}$$

and with the distribution relation between aqueous and third-liquid phases

$$K_{\mathrm{ArCOOQ}} = \frac{C^{\mathrm{third}}_{\mathrm{ArCOOQ}}}{C^{\mathrm{aq}}_{\mathrm{ArCOOQ}}}, \tag{2}$$

(2) transfer of RBr into the third-liquid phase from the organic phase with the distribution relation

$$K_{\mathrm{RBr}} = \frac{C^{\mathrm{third}}_{\mathrm{RBr}}}{C^{\mathrm{org}}_{\mathrm{RBr}}}, \tag{3}$$

(3) intrinsic reaction of ArCOOQ and RBr in the third-liquid phase,

$$\mathrm{ArCOOQ\,(third) + RBr\,(third)} \\ \rightarrow \mathrm{ArCOOR\,(third) + QBr\,(third)},$$

with the reaction rate of RBr

$$\frac{\mathrm{d}C^{\mathrm{third}}_{\mathrm{RBr}}}{\mathrm{d}t} = -kC^{\mathrm{third}}_{\mathrm{ArCOOQ}}C^{\mathrm{third}}_{\mathrm{RBr}}, \tag{4}$$

(4) transfer of regenerated QBr into the aqueous phase from the third-liquid phase with the distribution relation

$$K_{\mathrm{QBr}} = \frac{C^{\mathrm{aq}}_{\mathrm{QBr}}}{C^{\mathrm{third}}_{\mathrm{QBr}}}, \tag{5}$$

(5) transfer of product ArCOOR from the third-liquid phase into the organic phase with the distribution relation,

$$K_{\mathrm{ArCOOR}} = \frac{C^{\mathrm{third}}_{\mathrm{ArCOOR}}}{C^{\mathrm{org}}_{\mathrm{ArCOOR}}}. \tag{6}$$

Taking mass balance for RBr gives

$$V^{\mathrm{org}}C_{\mathrm{RBr,o}} = V^{\mathrm{org}}(C^{\mathrm{org}}_{\mathrm{RBr}} + C^{\mathrm{org}}_{\mathrm{ArCOOR}}) \\ + V^{\mathrm{third}}(C^{\mathrm{third}}_{\mathrm{RBr}} + C^{\mathrm{third}}_{\mathrm{ArCOOR}}). \tag{7}$$

Defining the product yield (Y_{app}) based on the limiting reactant in the organic phase as $Y_{\mathrm{app}} = (C^{\mathrm{org}}_{\mathrm{ArCOOR}}/C_{\mathrm{RBr,o}})$ and substituting it and Eq. (6) into (7), we have

$$\frac{C^{\mathrm{org}}_{\mathrm{RBr}}}{C_{\mathrm{RBr,0}}} = \frac{1 - MY_{\mathrm{app}}}{1 + V^{\mathrm{third}}K_{\mathrm{RBr}}/V^{\mathrm{org}}}, \tag{8}$$

where $M = 1 + V^{\mathrm{third}}K_{\mathrm{ArCOOR}}/V^{\mathrm{org}}$.

Substituting Eqs. (4) and (8) for (2), the intrinsic reaction rate becomes

$$M\frac{\mathrm{d}Y_{\mathrm{app}}}{\mathrm{d}t}=kC_{\mathrm{ArCOOQ}}^{\mathrm{third}}(1-MY_{\mathrm{app}}).$$

From the experimental observations, the amount of ArCOOQ in the third-liquid phase can be maintained at near constant and the above equation is integrated to give a pseudo-first-order relation

$$-\ln(1-MY_{\mathrm{app}})=k_{\mathrm{app}}t,$$

where

$$k_{\mathrm{app}}=kC_{\mathrm{ArCOOQ}}^{\mathrm{third}}.$$

The apparent activation energy can be estimated from the Arrhenius' equation:

$$k_{\mathrm{app}}=A\exp\left(-\frac{E_{\mathrm{app}}}{RT}\right).$$

For correlating the kinetic data, the value of M should be obtained first. For determining the M value, the values of K_{ArCOOR}, V_{third} and V_{org} should be measured for each reaction time, as described in the experimental Section 2.5. The values of M at different reaction times were then estimated and averaged as 1.11, 1.11, 1.12, and 1.10 for 20, 30, 40, and 50 cm^3 of water, 1.11, 1.11, and 1.09 for 0.01, 0.02, and 0.03 mol of ArCOONa, 1.07, 1.11, and 1.14 for 0.003, 0.006, and 0.009 mol of TBPB, respectively. It revealed that the variation of M value for different conditions is substantially small. Thus, a value of M can be conservatively averaged as 1.10 for simplicity and applied in the kinetic equation to describe the present system successfully.

4. Results and discussion

4.1. Formation of third-liquid phase

The volumes of the third-liquid phase formed by introducing phase-transfer catalyst TBPB, sodium salicylate, and different amounts of NaBr exceeding the critical amounts are shown in Fig. 1. It shows that the volume of the third-liquid phase increases with increasing amount of TBPB employed, and a greater usage for TBPB is required to form the third-liquid phase with a lesser amount of NaBr. When 0.175 mol of NaBr was used, only 0.002 mol of TBPB is needed to show the third-liquid phase. This fact indicates that the total concentration of various salts or ionic strength in the aqueous phase affects the formation of the third-liquid phase significantly. In addition, the solubility of inorganic salt in the aqueous phase also strongly influences the formation of the third-liquid phase. Under the conditions of 0.02 mol of sodium salicylate, 0.006 mol of TBPB, 30 cm^3 of water and 30 cm^3 of n-heptane at 60 °C, the volumes of third-liquid phase with 0.125 mol of NaOH, KOH, NaBr, KBr, NaI, and KI, respectively, were 3.6 cm^3 for NaBr, 3.5 cm^3 for KBr, 2.1 cm^3 for NaI and 2.0 cm^3 for KI, and no third-liquid phase was formed for NaOH and KOH. This shows that the type of anion strongly affects the salting-out effect of the third-liquid phase from the aqueous solution. The inorganic salt with greater solubility in water leads to the retardation of formation of the third-liquid phase.

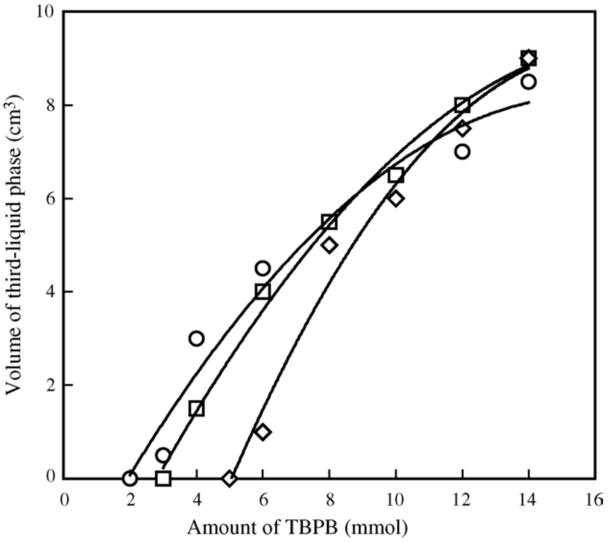


Fig. 1. Effect of catalyst TBPB on the volume of the third-liquid. Water 30 mL, sodium salicylate 0.02 mol, n-heptane 30 cm^3, temperature 60 °C; NaBr (mol): (◊) 0.1; (□) 0.15; (○) 0.175.

Fig. 2 shows the volume of the third-liquid phase for varying amount of water or n-heptane with the amount of the other phase kept. It is seen that the amount of water strongly affects the formation of the third-liquid phase; the volume of the third-liquid phase decreases with increasing water amount. This is expected due to the significant effect of hydrogen bonding between tetrabutylphosphonium salicylate ion-pair with water. With the aqueous reactant having –OH group, the third-liquid phase would be much more hardly formed due to a higher solubility of the produced catalytic intermediate in water. Moreover, the polarity of organic solvent also influences the quantity of the third-liquid phase formed. Table 1 shows the effect of different solvents on the formation of the third-liquid phase. Chlorobenzene with

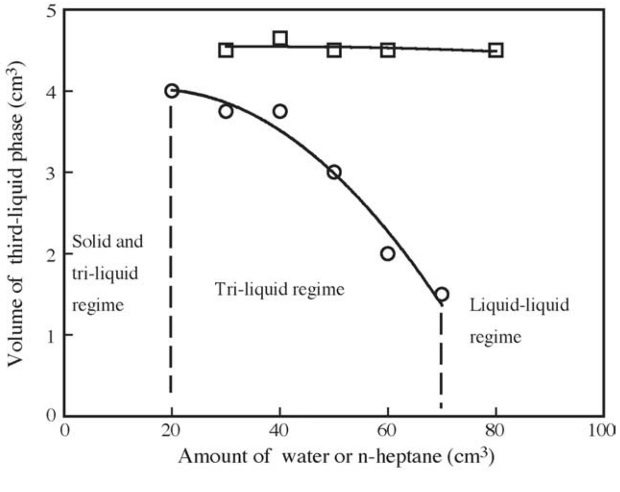


Fig. 2. Effect of amounts of water or n-heptane on the volume of third-liquid phase. TBPB 0.006 mol, NaBr 0.125 mol, temperature 60 °C; (○) n-heptane 30 cm^3, sodium salicylate 0.02 mol; (□) water 30 cm^3, sodium salicylate 0.03 mol.

Table 1
Interfacial tension of third-liquid phase and organic phase for different solvents[a]

Solvent	Polarity	Volume of third-liquid phase (mL)	Interfacial tension of third-liquid phase and organic phase (mN/m)
Chlorobenzene	>0.27	0	–
n-Heptane	0.01	3.6	9.6
n-Hexane	0.01	3.6	8.1
Toluene	0.27	3.5	2.9

[a] Conditions: sodium salicylate 0.02 mol, TBPB 0.006 mol, solvent 30 cm^3, temperature 60 °C.

polarity greater than 0.27 cannot be used to form the third-liquid phase, while *n*-heptane, *n*-hexane, and toluene can be applied to form the third-liquid phase with almost the same volume of 3.6 cm^3. In the present system, the third-liquid phase can be prepared by adding large amounts of extra inorganic salt even with the hydrogen-bonding effect of catalytic intermediate in water.

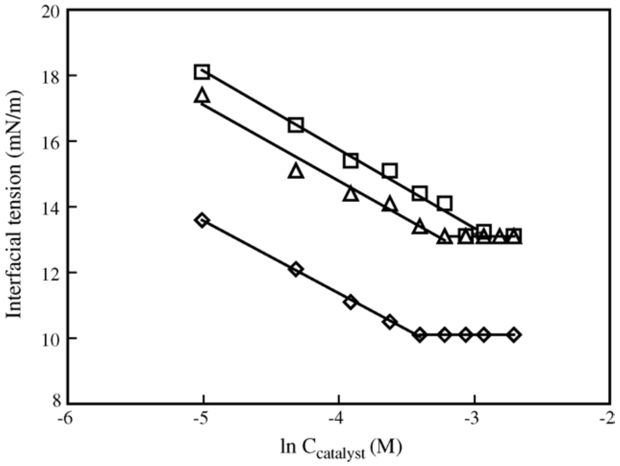


Fig. 3. Plot of interfacial tension vs. ln C for different PTC. Water 30 cm^3, sodium salicylate 0.02 mol, NaBr 0.125 mol, *n*-heptane 30 cm^3, temperature 60 °C; PTC: (□) TBAB; (△) TBAI; (◇) TBPB.

4.2. Characteristics of catalytic intermediate in the tri-liquid system

In a liquid-liquid system, when the amount of PTC exceeds some critical point, the micelles may be formed. This critical point depends on the type of phase-transfer catalyst used. The formation of micelles might be beneficial to the formation of third-liquid phase. When the molecules of PTC and catalytic intermediate form the micelles as a thin adsorption layer in the interface of aqueous and organic phases, the near-hydrophobic effect of catalytic intermediate would make the layer thicker to appear as a separated phase between aqueous and organic phases. Fig. 3 shows the plot of interfacial tension versus logarithm of catalyst concentration for tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI) and tetrabutylphosphonium bromide (TBPB) under the following conditions: 0.02 mol of sodium salicylate, 0.125 mol of NaBr, 30 cm^3 of water, and 30 cm^3 of *n*-heptane at 60 °C. The transition into constant interfacial tension reveals that the micelle can be formed when the quantities of PTC exceed the critical point; furthermore, the interfacial tension for TBPB is smaller than that for TBAI and TBAB, implying that TBPB would be much better to produce the third-liquid phase in the present system.

Since the reaction is mainly conducted in the third-liquid phase, the resistance of transporting organic reactant and the catalytic intermediate into the third-liquid phase may also affect the reaction rate. The interfacial tension between organic and aqueous phases can be reduced through the formation of the third-liquid layer between them. Table 2 shows the variation of interfacial tension for different amounts of sodium salicylate or water. When the third-liquid phase is not formed, the interfacial tension between organic and aqueous phases is about 9–12 mN/m; it is about 1–3 mN/m between the third-liquid and aqueous phases if the third-liquid phase is formed. Hence, the catalytic intermediate transported from the aqueous to organic phase in a liquid-liquid system would only be transported from

Table 2
Interfacial tensions for different amounts of sodium salicylate and water[a]

Sodium salicylate (mol)	Water (cm^3)	Formation of third-liquid phase	Interfacial tension between organic and aqueous phases (mN/m)	Interfacial tension between third-liquid and aqueous phases (mN/m)
0.005	30	Yes	–	1.5
0.01	30	Yes	–	1.6
0.02	30	Yes	–	1.5
0.03	30	Yes	–	1.6
0.04	30	No	11.1	–
0.05	30	No	11.7	–
0.06	30	No	11.1	–
0.02	20	Yes	–	2.6
0.02	40	Yes	–	1.1
0.02	50	Yes	–	1.4
0.02	60	No	9.3	–
0.02	70	No	9.1	–
0.02	80	No	9.1	–

[a] Catalyst TBPB 0.006 mol, NaBr 0.125 mol, solvent *n*-heptane 30 cm^3, temperature 60 °C.

the aqueous to third-liquid phase, resulting in a much faster rate of reaction for the concentrated ArCOOQ and RBr within such a thin layer of third-liquid phase.

For determining the amount of ArCOOQ in the third-liquid phase, the method of accelerating the reaction of ArCOOQ with excess RBr in chlorobenzene solvent was applied, as described in Section 2. The third-liquid phases for different types of PTC were first prepared using 0.006 mol of PTC, and the third-liquid phases were separated. Then the third-liquid phase containing ArCOOQ dissolved in 30 cm^3 of chlorobenzene to react with 0.01 mol of benzyl bromide. The amount of ArCOOQ in the third-liquid phase was equivalent to the amount of ArCOOR produced, and the reaction results for different types of PTC are shown in Fig. 4, in which the product yield is based on the initial amount of benzyl bromide. A larger amount of ArCOOQ existing in the third-liquid phase initially reflects a faster catalytic reaction rate with the organic substrate. Thus, it is necessary to identify the distribution of PTC between phases to search for the catalyst efficient in forming the third-liquid phase for acquiring a higher reaction rate. To obtain the distribution coefficient of PTC between phases, the third-liquid phase was first prepared, followed by separating each phase to measure their volumes individually, and the amounts of QBr and ArCOOQ in each phase were then detected. Table 3 depicts the distribution of QBr and ArCOOQ in the third-liquid phase for different catalysts. Apparently, the amount of QBr in the form of ArCOOQ in the third-liquid phase is the highest for TBPB and the lowest for TBAB, and the order is TBPB > BTBAB > TBAI > TBAB. The distribution of catalyst shows that TBPB and BTBAB are much easier to form the third-liquid phase by producing more hydrophobic ArCOOQ, and that the distribution of TBPB increases with increasing amount of catalyst, as shown in Table 4. Above 86% of catalyst was in the form of ArCOOQ in the third-liquid phase when TBPB was used. This demonstrates that the key component in the third-liquid phase is the catalytic intermediate ArCOOQ, enhancing the rate of substitution reaction with the organic reactant transported from the organic phase.

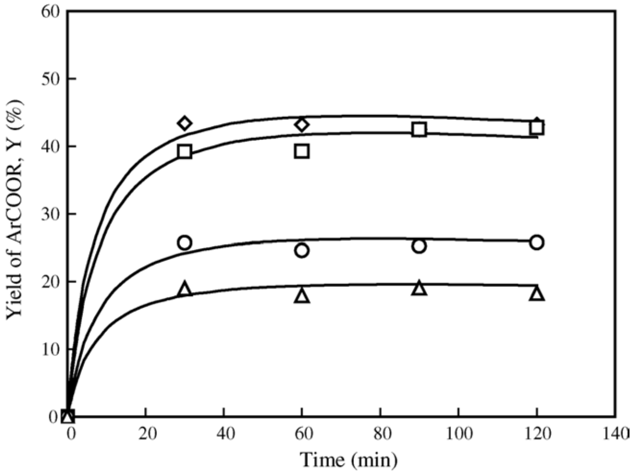


Fig. 4. Determination of ArCOOQ in third-liquid phase. Formation conditions of third-liquid phase: sodium salicylate 0.02 mol, NaBr 0.125 mol, PTC 0.006 mol, water 30 cm^3; reaction condition: benzyl bromide 0.01 mol, chlorobenzene 30 cm^3, temperature 60 °C, agitation speed 350rpm; PTC: (◊) TBPB; (□) BTBAB; (◯) TBAB; (△) TBAI.

Table 3
Distribution and amounts of PTC and catalytic intermediates in third-liquid phase[a]

Type of PTC	QBr_{aq} (mmol)	$\text{QBr}_{\text{third}}$ (mmol)	$\text{ArCOOQ}_{\text{third}}$ (mmol)	$V_{\text{third}}/V_{\text{aq}}$ (cm^3/cm^3)	$\text{ArCOOQ}_{\text{third}}/\text{Q}_{\text{third}}$ (%)[b]	Distribution of QBr $D^{\text{QBr}}_{\text{third-aq}}$ [c]
TBPB	0.58	0.72	4.70	3.7/33	86.7	11.00
BTBAB	0.74	1.13	4.12	3.7/33	78.5	13.41
TBAB	2.46	1.90	1.63	3.75/33	46.2	6.89
TBAI	3.40	1.10	1.50	4.2/33	57.7	2.54

[a] Operating conditions to form the third-liquid phase: 0.02 mol of sodium salicylate, 0.125 mol of NaBr, 0.006 mol of PTC, 30 cm^3 of water, 30 cm^3 of heptane, and temperature 60 °C.

[b] Q is the amounts of QBr and catalytic intermediate ArCOOQ in the third-liquid phase.

[c] $D^{\text{QBr}}_{\text{third-aq}}$ is the concentration ratio of QBr in third-liquid phase to that in the aqueous phase.

Table 4
Distribution and amounts of TBPB and its catalytic intermediate in third-liquid phase[a]

Amounts of TBPB (mol)	QBr_{aq} (mmol)	$\text{QBr}_{\text{third}}$ (mmol)	$\text{ArCOOQ}_{\text{third}}$ (mmol)	$V_{\text{third}}/V_{\text{aq}}$ (cm^3/cm^3)	$\text{ArCOOQ}_{\text{third}}/\text{Q}_{\text{third}}$ (%)[b]	Distribution of QBr $D^{\text{QBr}}_{\text{third-aq}}$ [c]
0.003	1.28	0.18	1.54	1.6/33	89.5	2.87
0.006	0.58	0.72	4.70	3.7/33	86.7	11.00
0.009	0.48	1.07	7.45	5.4/33	87.4	13.53

[a] Operating conditions to form the third-liquid phase: 0.02 mol of sodium salicylate, 0.125 mol of NaBr, 30 cm^3 of water, 30 cm^3 of heptane, and temperature 60 °C.

[b] Q is the amounts of QBr and catalytic intermediate ArCOOQ in the third-liquid phase.

[c] $D^{\text{QBr}}_{\text{third-aq}}$ is the concentration ratio of QBr in third-liquid phase to that in the aqueous phase.

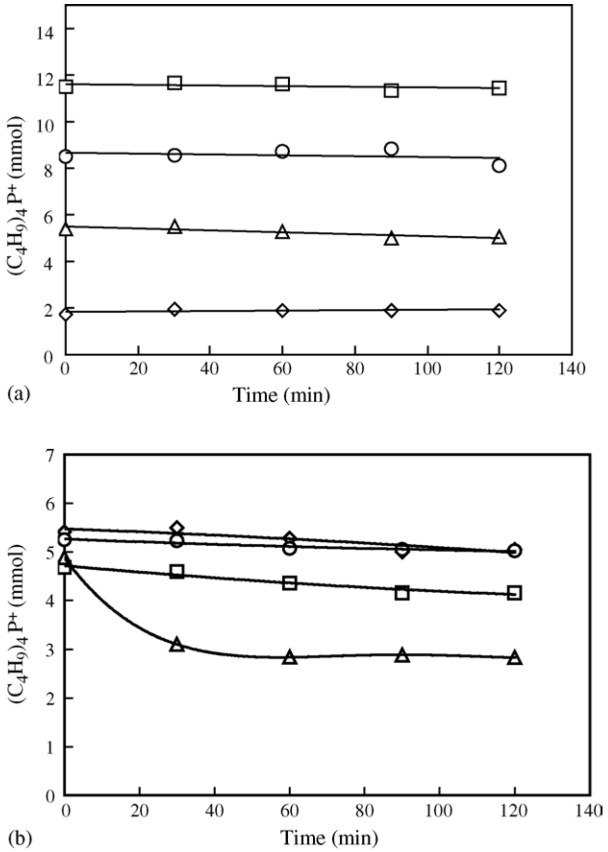


Fig. 5. Dependence of amounts of Q in third-liquid phase on different amounts of: (a) TBPB; and (b) sodium salicylate. Water 30 cm^3, NaBr 0.125 mol, *n*-heptane 30 cm^3, benzyl bromide 0.01 mol, temperature 60 °C, agitation speed 350 rpm; (a) sodium salicylate 0.02 mol, TBPB (mol): (□) 0.012; (○) 0.009; (△) 0.006; (◇) 0.003; (b) TBPB 0.006 mol, sodium salicylate (mol): (□) 0.03; (◇) 0.02; (○) 0.01; (△) 0.005.

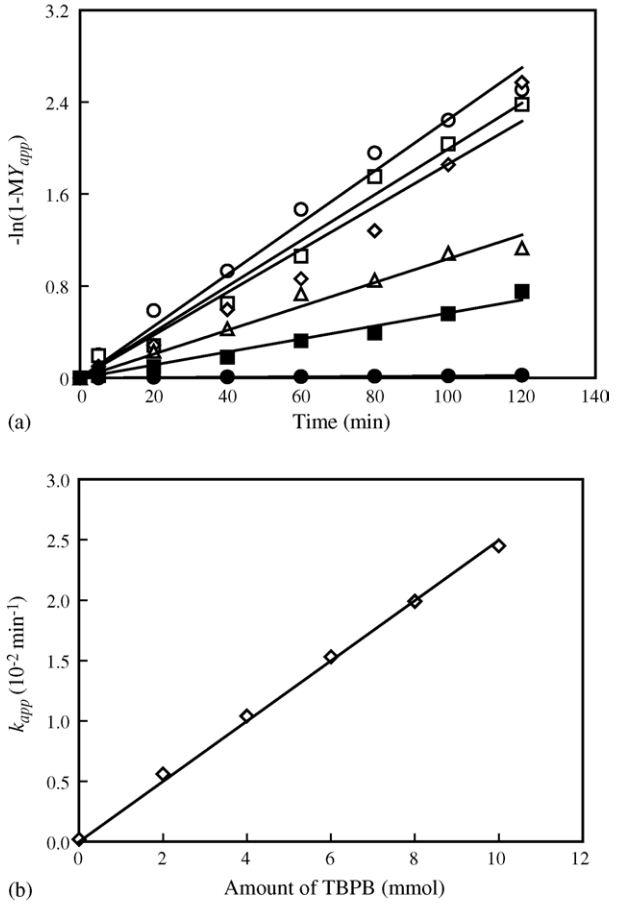


Fig. 6. (a) Plot of $-\ln(1-MY_{\mathrm{app}})$ vs. time for different amounts of TBPB; (b) dependence of apparent rate constant on the amount of TBPB. Sodium salicylate 0.02 mol, NaBr 0.125 mol, water 30 cm^3, *n*-heptane 30 cm^3, benzyl bromide 0.01 mol, temperature 60 °C, agitation 350 rpm; TBPB (mol): (○) 0.01; (□) 0.008; (◇) 0.006; (△) 0.004; (■) 0.002; (●) 0.

4.3. Effects of operating conditions on third-liquid phase catalyzed esterification

The concentration of ArCOOQ in the third-liquid phase strongly affects the overall reaction. An almost constant concentration of ArCOOQ in the third-liquid phase during the reaction would result in a pseudo-first-order kinetic behavior to favorably describe the present third-liquid phase-transfer catalyzed esterification of sodium salicylate. Fig. 5(a and b) shows the total amount of tetrabutylphosphonium ion (Q^+) in the third-liquid phase for different quantities of TBPB and sodium salicylate used. It is seen that the amount of Q^+ in the third-liquid phase was kept nearly constant during the progress of reaction with the fraction of Q^+ in the third-liquid phase increasing with the increase in the TBPB amount. When 0.005 mol of sodium salicylate and 0.006 mol of TBPB were used, the amount of Q^+ in the third-liquid would be quickly reduced to a constant, due to the initial consumption rate of ArCOOQ faster than its production rate in the third-liquid phase. In addition, when 0.03 mol of sodium salicylate and 0.006 mol of TBPB were used, the constant content of Q^+ in the third-liquid phase was less than 0.01 and 0.02 mol of sodium salicylate, resulting from the strong hydrogen bonding of salicylates with water molecules to retard the formation of ArCOOQ in the aqueous phase.

Fig. 6(a) is the plot of $-\ln(1-MY_{\mathrm{app}})$ versus time for different amounts of TBPB. Without using PTC, the product yield is only 2.01%; while it is above 85% in *n*-heptane at 60 °C within 2 h of reaction when 0.006 mol of TBPB was used, and the apparent rate constants are 0.0056 for 0.002 mol, 0.0104 for 0.004 mol, 0.0153 for 0.006 mol, 0.0199 for 0.008 mol, and 0.0245 min^{-1} for 0.01 mol of TBPB. The pseudo-first-order kinetic model can be successfully applied to describe the esterification reaction of sodium salicylate in this tri-liquid system. A linear relationship of apparent rate constant with the amount of TBPB is observed, as shown in Fig. 6(b), indicating that the concentration of ArCOOQ in the third-liquid phase is almost linearly increased with the increase in TBPB. This fact can also be shown in Table 4, from which a linear relationship of ArCOOQ in the third-liquid phase to TBPB employed is also obtained, indicating that ArCOOQ in the third-liquid phase is the key reacting component.

The appearance of third-liquid phase mainly resulted from the formation of hydrophobic ArCOOQ by the reaction of sodium salicylate and PTC; hence, the concentration of sodium salicy-

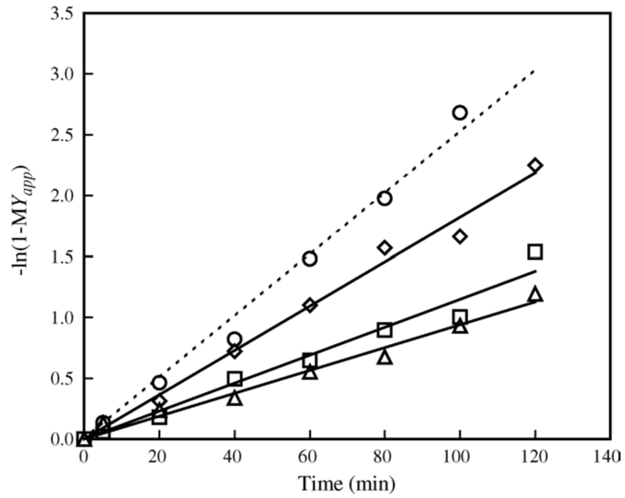


Fig. 7. Plot of $-\ln(1-MY_{\mathrm{app}})$ vs. time for different amounts of sodium salicylate. TBPB 0.006 mol, NaBr 0.125 mol, water 30 cm^3, *n*-heptane 30 cm^3, benzyl bromide 0.01 mol, temperature 60 °C, agitation 350 rpm; sodium salicylate (mol): (◯) 0.01; (◊) 0.02; (□) 0.03; (△) 0.04.

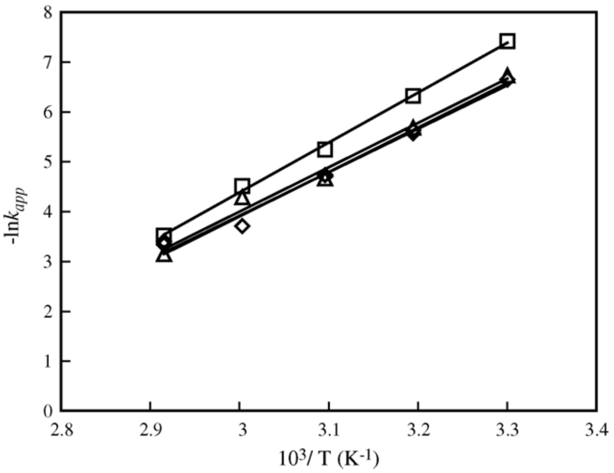


Fig. 8. Arrhenius' plot for different phase-transfer catalysts. Sodium salicylate 0.02 mol, NaBr 0.125 mol, water 30 cm^3, *n*-heptane 30 cm^3, agitation speed 350 rpm, benzyl bromide 0.01 mol: (□) TBPB; (◯) TBAB; (△) TBAI; (◊) BTBAB.

late and its physical property can affect the overall reaction rate. Fig. 7 shows the effect of different amounts of sodium salicylate on the reaction rate and the product yields. Because of the hydrogen bonding of sodium salicylate with water molecules, the formation of ArCOOQ was much suppressed under heavy usage of sodium salicylate, leading to the apparent reaction rate decreasing with increasing sodium salicylate amount in the range of 0.01–0.04 mol. As a conservative estimate for the degree of reduction of k_{app}, a value 0.007 min^{-1} reduced per 0.01 mol of sodium salicylate increased is deduced. Fig. 8 shows the Arrhenius' plot for different phase-transfer catalysts to describe the effect of temperature on the reaction rate. The apparent activation energies in heptane can be estimated at 73.94 kJ/mol for TBPB, 83.06 kJ/mol for TBAB, 73.90 kJ/mol for TBAI, and 72.48 kJ/mol for BTBAB, showing that TBPB has the highest catalytic activity in the present system.

5. Conclusion

The kinetics of esterification of sodium salicylate with benzyl bromide to produce benzyl salicylate was investigated via third-liquid phase-transfer catalysis in the present study. The formation of third-liquid phase from the interaction of aqueous reactant, inorganic salts, organic solvent, and catalyst was carried out to find the characteristics of catalytic intermediate in the tri-liquid system. The volume of third-liquid increased with increasing the amount of TBPB, and using 20–70 cm^3 of water for 30 cm^3 of *n*-heptane solvent favors the formation of the third-liquid phase. The interfacial phenomena between aqueous and third-liquid phases exhibit the mass transfer resistance dominating in the heptane side. The product can be present in both organic and third-liquid phases, and above 85% of the product yield in the organic phase and 93.5% of overall yield can be obtained by using 0.006 mol of TBPB. The measurement of distribution of catalyst shows that above 86% of TBPB in the third-liquid phase is in the form of catalytic intermediate. The reaction mechanism and kinetic model were proposed and the pseudo-first-order kinetics was successfully applied, the apparent activation energy in heptane being 73.94 kJ/mol when TBPB was used as the catalyst.

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