

# Synthesis of novel multi-site phase-transfer catalyst and its application in the reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl with 1-butanol

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## Abstract

This work describes the etherification of 4,4'-bis(chloromethyl)-1,1'-biphenyl and 1-butanol catalyzed by a new multi-site phase-transfer catalyst as carried out in an alkaline solution/organic solvent two-phase medium. The new multi-site phase-transfer catalysts were obtained from the reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl and tertiary amines. During or after completing the reaction, the mono-substituted product (4,4'-(butoxymethyl)-1,1'-biphenyl) and di-substituted product (4,4'-bis(butoxymethyl)-1,1'-biphenyl) are both produced. A rational mechanism of the etherification was proposed based on the experimental observation and a kinetic model was developed. The two apparent rate constants of the organic-phase reactions were obtained via experimental data. The reaction is greatly enhanced by adding a small quantity of the new multi-site phase-transfer catalysts. This new novel phase-transfer catalyst exhibits higher reactivity than the "single-site" quaternary ammonium salts. Preliminary studies on the kinetics and the effect of various parameters such as agitation speed, amount of organic solvent, multi-site catalysts, potassium hydroxide, water, organic solvents, inorganic salt and temperature were investigated in detail. Rational explanations of the results are made.

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## 1. Introduction

The technology of phase-transfer catalysis (PTC) was originally developed in the mid-1960s to enhance chemical reactions catalyzed by quaternary ammonium salts in which the reactants are in two separate phases [1]. By now, the phase-transfer catalyst is now considered to be one of the most effective tools for organic synthesis from two or more immiscible solutions [2–4]. The methodology of phase-transfer catalysis involves a reactant (organic-soluble compound) and an anionic reactant (often an aqueous-soluble nucleophile). The organic-soluble reactant and the water-soluble anion are then brought together by a catalyst, which transports the anion into the organic phase where reaction takes place with

the organic reactant. Quaternary ammonium and phosphonium salts with their unique capability to dissolve in both aqueous and organic liquids are the catalysts of choice for most phase-transfer applications [5]. The benefits of PTC lie in the elimination of organic solvents and dangerous or expensive bases, together with simplicity of the procedure, and its high yields and the purity of the products. This is particularly attractive due to the increasing number of environmental laws since PTC processes always produce much less industrial waste and consume less energy than traditional processes.

In general, ethers are one of the most high added-value chemicals extensively used in various industries as the additives for petroleum chemicals and extractants [6–8]. Therefore, the potential value of the quaternary ammonium catalyst for Williamson synthesis of ethers and its versatility in the synthesis of methyl ethers and other alkyl ethers was soon

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established after the development of PTC [9,10]. The application of phase-transfer catalysis to the Williamson synthesis of ethers has been exploited widely and is far superior to any classical method for the synthesis of aliphatic ethers. Potassium alkoxides tend to produce higher yields of the ethers than do the corresponding sodium derivatives [11]. However, it is frequently found that a relatively large amount of quaternary ammonium or phosphonium salt must be used as a phase-transfer catalyst in the substitution reaction, in order for it to proceed rapidly enough to produce the ether products in an economically feasible time period.

It is of interest, therefore, to develop new phase-transfer catalysts which can be used in smaller proportions. In order to satisfy these needs in a more pronounced manner, novel “multi-site” PTCs are introduced in this work [12]. Several soluble “multi-site” ammonium catalysts have previously been synthesized [13–16]. Catalysts such as these have the advantage over single site catalysts in reactions involving divalent anions that they generally need less of the salt to obtain a catalytic effect. In general, multi-site phase-transfer catalysts have a greater phase-transfer catalytic activity [15,16]. However, the synthesis of “multi-site” PTCs have been less explored than the “single-site” PTC. The present work synthesizes a novel “multi-site” PTC based on quaternary ammonium salt in only one synthetic step. A principle object of this work, therefore, is to provide novel and efficient bis-quaternary ammonium salts and to investigate the kinetics of the reactions. The kinetics of synthesizing 4,4'-bis(butoxymethyl)-1,1'-biphenyl from the reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl and 1-butanol in an alkaline solution/chlorobenzene two-phase medium were investigated in detail.

## 2. Experimental

### 2.1. Materials

All reagents, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 1-butanol, acetonitrile, aliquat 336 (tricaprylmethylammonium chloride), chlorobenzene, cuprous bromide, cuprous chloride, cyclohexane, dichloromethane, diethyl ether, tetrabutylammonium bromide (TBAB), tetraoctylammonium bromide (TOAB), toluene, tributylamine, triethylamine, tripropylamine and tri-sodium phosphate were guaranteed grade (G.R.) chemicals.

### 2.2. Procedures

#### 2.2.1. Synthesis of bis-quaternary ammonium salts 4,4'-bis(triethylmethylammonium)-1,1'-biphenyl dichloride (4,4'-B(TEMA)-1,1'-BP DC)

A mixture of 12.56 g (0.05 mol) of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 10.12 g (0.10 mol) of triethylamine and 70 mL of acetonitrile were placed in a 150-mL three-necked round-bottomed Pyrex flask. The mixture solution was

stirred continuously using a mechanical mixer at 600 rpm. The reaction was carried out at 70 °C for 24 h and was gently refluxed. Then, the crude product was evaporated in a vacuum evaporator to remove the solvent yielding a white solid of 4,4'-bis(triethylmethylammonium)-1,1'-biphenyl dichloride. The product (bis-quaternary ammonium salts) was stored in CaCl<sub>2</sub> desiccator.

Similarly, 4,4'-bis(triisopropylmethylammonium)-1,1'-biphenyl dichloride (4,4'-B(TPMA)-1,1'-BP DC) and 4,4'-bis(tributylmethylammonium)-1,1'-biphenyl dichloride (4,4'-B(TBMA)-1,1'-BP DC) were obtained from the reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl with equi-molar tripropylamine and tributylamine, respectively. The products were identified with an elemental analyzer.

#### 2.2.2. Synthesis of 4,4'-(butoxymethyl chloromethyl)-1,1'-biphenyl and 4,4'-bis(butoxymethyl)-1,1'-biphenyl and their purification

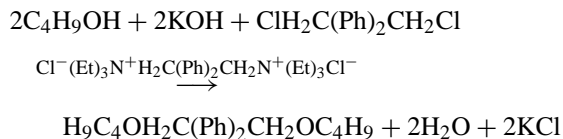
The reactor was exactly the same as that used in Section 2.2.1. Measured quantities of 4,4'-bis(chloromethyl)-1,1'-biphenyl (20 mmol), 1-butanol (150 mmol), potassium hydroxide (20 g) and TBAB (0.5 mmol) were dissolved in a mixture of 50 mL chlorobenzene and 20 mL of water at 45 °C. The mixture was stirred continuously using a mechanical mixer at 800 rpm. After 3 h of reaction, the two-phase solution was separated and the portion of organic solution was washed five times with an alkaline solution to remove the TBAB catalyst. The organic solvent was evaporated in a vacuum evaporator. Then, the mixture was separated by pressurized column chromatography. The mono-substituted product and the di-substituted product were separated using silica gel as adsorbent and dichloromethane as eluent. Finally, the products were identified by mass spectrum for molecular weight and NMR (<sup>1</sup>H NMR and <sup>13</sup>C NMR) for functional groups.

#### 2.2.3. Kinetic study of the experimental runs

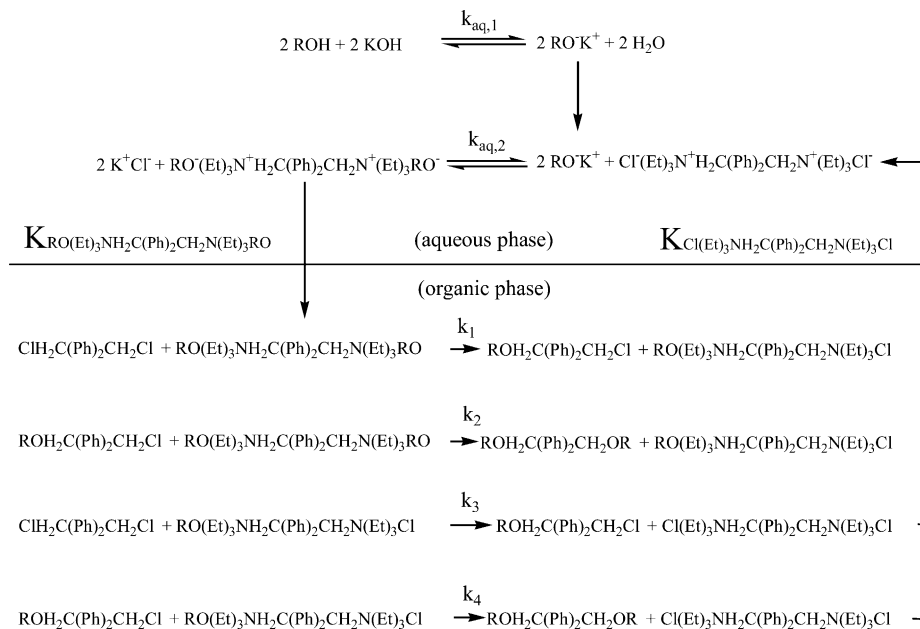
The reactor was a 150-mL three-necked round-bottomed Pyrex flask submerged in a constant-temperature water-bath which was controlled to within ±0.1 °C. To start a kinetic run, known measured quantities of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 1-butanol, water, organic solvent, potassium hydroxide, biphenyl (internal standard) and phase-transfer catalyst were introduced into the reactor. The reactor was set at the desired temperature and the solution was mixed at the desired agitation speed. An aliquot sample was withdrawn from the solution at a chosen time. The sample was immediately added to a cold methanol to retard the reaction and then analyzed quantitatively by the high-performance liquid chromatography (HPLC) using the method of internal standard (biphenyl). An SPD-10AVP model with analyzed software glass vp 5.0 and photodiode array detector (UV wavelength 269 nm) from Shimadzu was used for HPLC analysis. The column used was Lichrosorb RP-18e (5 μm, Applied Merck Co.). The eluent were acetonitrile/deionized water with gradient concentration.

### 3. Reaction mechanism and kinetics

A total reaction for the present system is



For that, a rational reaction mechanism is proposed as follows:



The mechanism was formulated on the basis of Starks' extraction model [2,3]. An organic-soluble active catalyst, ROQ(Ph)<sub>2</sub>QOR (i.e. RO(Et)<sub>3</sub>NH<sub>2</sub>C(Ph)<sub>2</sub>CH<sub>2</sub>N(Et)<sub>3</sub>OR), which is an organic-soluble compound, was produced from the aqueous solution by reacting the catalyst ClQ(Ph)<sub>2</sub>QCl (i.e. Cl<sup>-</sup>(Et)<sub>3</sub>NH<sub>2</sub>C(Ph)<sub>2</sub>CH<sub>2</sub>N(Et)<sub>3</sub>Cl<sup>-</sup>) and potassium alkoxides (RO<sup>-</sup>K<sup>+</sup>). The concentration of ROQ(Ph)<sub>2</sub>QOR in the organic phase is kept at a constant value using a large excess of 1-butanol. Then, ROQ(Ph)<sub>2</sub>QOR, which is transferred from aqueous phase into organic phase, reacts with 4,4'-bis(chloromethyl)-1,1'-biphenyl (ClH<sub>2</sub>C(Ph)<sub>2</sub>CH<sub>2</sub>Cl) undergoing four sequential reactions in the organic phase to produce a mono-ether compound, 4,4'-(butoxymethyl chloromethyl)-1,1'-biphenyl (ROH<sub>2</sub>C(Ph)<sub>2</sub>CH<sub>2</sub>Cl) and di-ether compounds, 4,4'-(bis(butoxymethyl)-1,1'-biphenyl (ROH<sub>2</sub>C(Ph)<sub>2</sub>CH<sub>2</sub>OR), respectively. Based on the experimental data, material balances for the reactant, mono-substituted product and di-substituted product are satisfactorily made. It also indicates that no by-products were produced in the solution. The ion exchange in aqueous phase is all rapid. Therefore, the etherification in organic phase is the rate-determining step for the whole reaction system. Based on the proposed mechanism and two-film theory, material balances for the regenerated catalyst ClQ(Ph)<sub>2</sub>QCl

and the active catalyst (ROQ(Ph)<sub>2</sub>QOR) in the bulk of organic and aqueous phases are:

$$\frac{d[\text{ROQ}(\text{Ph})_2\text{QOR}]_o}{dt}$$

$$= K_{\text{ROQ}(\text{Ph})_2\text{QOR}} A$$

$$\times \left( [\text{RO}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{OR}^-]_a - \frac{[\text{ROQ}(\text{Ph})_2\text{QOR}]_o}{M_{\text{ROQ}(\text{Ph})_2\text{QOR}}} \right)$$

$$- k_1[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o[\text{ROQ}(\text{Ph})_2\text{QOR}]_o$$

$$- k_2[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o[\text{ROQ}(\text{Ph})_2\text{QOR}]_o \quad (1)$$

$$\frac{d[\text{RO}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{OR}^-]_a}{dt}$$

$$= k_{\text{aq},2}[\text{RO}^-\text{K}^+]_a[\text{Cl}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a$$

$$- K_{\text{ROQ}(\text{Ph})_2\text{QOR}} A f$$

$$\times \left( [\text{RO}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{OR}^-]_a - \frac{[\text{ROQ}(\text{Ph})_2\text{QOR}]_o}{M_{\text{ROQ}(\text{Ph})_2\text{QOR}}} \right) \quad (2)$$

$$\frac{d[\text{Cl}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a}{dt}$$

$$= K_{\text{ClQ}(\text{Ph})_2\text{QCl}} A f([\text{ClQ}(\text{Ph})_2\text{QCl}]_o$$

$$- M_{\text{ClQ}(\text{Ph})_2\text{QCl}}[\text{Cl}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a)$$

$$- k_{\text{aq},2}[\text{RO}^-\text{K}^+]_a[\text{Cl}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a \quad (3)$$

$$\frac{d[\text{ClQ}(\text{Ph})_2\text{QCl}]_o}{dt}$$

$$= k_3[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o[\text{ROQ}(\text{Ph})_2\text{QCl}]_o$$

$$+ k_4[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o[\text{ROQ}(\text{Ph})_2\text{QCl}]_o$$

$$- K_{\text{ClQ}(\text{Ph})_2\text{QCl}} A f([\text{ClQ}(\text{Ph})_2\text{QCl}]_o$$

$$- M_{\text{ClQ}(\text{Ph})_2\text{QCl}}[\text{Cl}^-\text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a) \quad (4)$$

The total amount of catalyst  $E_0$  in the solution is:

$$E_0 = V_o([\text{ROQ}(\text{Ph})_2\text{QOR}]_o + [\text{ROQ}(\text{Ph})_2\text{QCl}]_o + [\text{ClQ}(\text{Ph})_2\text{QCl}]_o) + V_a([\text{RO}^- \text{Q}^+(\text{Ph})_2\text{Q}^+\text{OR}^-]_a + [\text{Cl}^- \text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a) \quad (5)$$

where  $f$  is the volume ratio of the organic solution ( $V_o$ ) to the aqueous solution ( $V_a$ );  $Q$  denotes the  $-\text{CH}_2\text{N}(\text{Et})_3$  group; and the subscripts, “o” and “a” denote the characteristics of the

$$\begin{aligned} \frac{d[\text{ROQ}(\text{Ph})_2\text{QOR}]_o}{dt} &= 0, & \frac{d[\text{RO}^- \text{Q}^+(\text{Ph})_2\text{Q}^+\text{OR}^-]_a}{dt} &= 0, \\ \frac{d[\text{ROQ}(\text{Ph})_2\text{QOCl}]_o}{dt} &= 0, & \frac{d[\text{RO}^- \text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a}{dt} &= 0, \\ \frac{d[\text{Cl}^- \text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_a}{dt} &= 0, & \frac{d[\text{ClQ}(\text{Ph})_2\text{QCl}]_o}{dt} &= 0 \end{aligned} \quad (8)$$

Combining Eqs. (1)–(5) and (8), we obtain:

$$\begin{aligned} [\text{ROQ}(\text{Ph})_2\text{QOR}]_o &= \frac{Q_0}{V_o} \left\{ \left( 1 + \frac{1}{fM_{\text{ROQ}(\text{Ph})_2\text{QOR}}} \right) \right. \\ &+ \left( 1 + fM_{\text{ClQ}(\text{Ph})_2\text{QCl}} + \frac{k_{\text{aq},2}[\text{RO}^- \text{K}^+]_a + fM_{\text{ClQ}(\text{Ph})_2\text{QCl}}^2 A - fM_{\text{ROQ}(\text{Ph})_2\text{QOR}}M_{\text{ClQ}(\text{Ph})_2\text{QCl}}A^2}{k_3[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o + k_4[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o} \right) \\ &\times \left( \frac{k_1[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o + k_2[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o}{k_{\text{aq},2}[\text{RO}^- \text{K}^+]_a} \right) + \left( \frac{1}{K_{\text{ClQ}(\text{Ph})_2\text{QCl}}A} + \frac{1}{fK_{\text{ROQ}(\text{Ph})_2\text{QOR}}A} \right) \\ &\left. \times (k_1[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o + k_2[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o) \right\}^{-1} \end{aligned} \quad (9)$$

species in the bulk of organic and aqueous phases, respectively. Furthermore,  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ , are the intrinsic rate constants of the four reactions in the organic phase, while  $k_{\text{aq},1}$  and  $k_{\text{aq},2}$  are the intrinsic rate constants of the two ionic reactions in the aqueous phase.  $A$  is the interfacial area between two phases.  $K_{\text{ROQ}(\text{Ph})_2\text{QOR}}$  and  $K_{\text{ClQ}(\text{Ph})_2\text{QCl}}$  are the mass transfer coefficients of  $\text{ROQ}(\text{Ph})_2\text{QOR}$  and  $\text{ClQ}(\text{Ph})_2\text{QCl}$  between the two phases.  $M_{\text{ROQ}(\text{Ph})_2\text{QOR}}$  and  $M_{\text{ClQ}(\text{Ph})_2\text{QCl}}$  are the distribution coefficients of  $\text{ROQ}(\text{Ph})_2\text{QOR}$  and  $\text{ClQ}(\text{Ph})_2\text{QCl}$  between two phases, respectively, i.e.:

$$M_{\text{ROQ}(\text{Ph})_2\text{QOR}} = \frac{[\text{ROQ}(\text{Ph})_2\text{QOR}]_{o,s}}{[\text{RO}^- \text{Q}^+(\text{Ph})_2\text{Q}^+\text{OR}^-]_{a,s}} \quad (6)$$

$$M_{\text{ClQ}(\text{Ph})_2\text{QCl}} = \frac{[\text{ClQ}(\text{Ph})_2\text{QCl}]_{o,s}}{[\text{Cl}^- \text{Q}^+(\text{Ph})_2\text{Q}^+\text{Cl}^-]_{a,s}} \quad (7)$$

On the basis of the experimental observation, the concentrations of  $\text{ROQ}(\text{Ph})_2\text{QOR}$ ,  $\text{ROQ}(\text{Ph})_2\text{QCl}$  and  $\text{ClQ}(\text{Ph})_2\text{QCl}$  in organic and aqueous phases reaches constant values at the beginning of the reaction [17,18]. Therefore, a pseudo-steady-state hypothesis (PSSH) is applied, i.e.:

The following Damkohler numbers,  $Da_{\text{ClQ}(\text{Ph})_2\text{QCl},1}$ ,  $Da_{\text{ClQ}(\text{Ph})_2\text{QCl},2}$ ,  $Da_{\text{ROQ}(\text{Ph})_2\text{QOR},1}$  and  $Da_{\text{ROQ}(\text{Ph})_2\text{QOR},2}$  are defined as:

$$Da_{\text{ClQ}(\text{Ph})_2\text{QCl},1} = \frac{k_1[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o}{K_{\text{ClQ}(\text{Ph})_2\text{QCl}}A} \quad (10)$$

$$Da_{\text{ClQ}(\text{Ph})_2\text{QCl},2} = \frac{k_2[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o}{K_{\text{ClQ}(\text{Ph})_2\text{QCl}}A} \quad (11)$$

$$Da_{\text{ROQ}(\text{Ph})_2\text{QOR},1} = \frac{k_1[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o}{K_{\text{ROQ}(\text{Ph})_2\text{QOR}}A} \quad (12)$$

$$Da_{\text{ROQ}(\text{Ph})_2\text{QOR},2} = \frac{k_2[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o}{K_{\text{ROQ}(\text{Ph})_2\text{QOR}}A} \quad (13)$$

$R_i$  (i.e.  $R_1$  and  $R_2$ ) are defined as the ratio of the organic-phase reaction rate to the aqueous-phase reaction rate, i.e.:

$$R_1 = \frac{k_1[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o}{k_{\text{aq},2}[\text{RO}^- \text{K}^+]_a} \quad (14)$$

$$R_2 = \frac{k_2[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o}{k_{\text{aq},2}[\text{RO}^- \text{K}^+]_a} \quad (15)$$

Combining Eqs. (10)–(15) and (9), we have:

$$\begin{aligned} [\text{ROQ}(\text{Ph})_2\text{QOR}]_o &= \frac{Q_0}{V_o} \left\{ \left( 1 + \frac{1}{fM_{\text{ROQ}(\text{Ph})_2\text{QOR}}} \right) \right. \\ &+ \left( 1 + fM_{\text{ClQ}(\text{Ph})_2\text{QCl}} + \frac{k_{\text{aq},2}[\text{RO}^- \text{K}^+]_a + fM_{\text{ClQ}(\text{Ph})_2\text{QCl}}^2 A - fM_{\text{ROQ}(\text{Ph})_2\text{QOR}}M_{\text{ClQ}(\text{Ph})_2\text{QCl}}A^2}{k_3[\text{ClH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o + k_4[\text{ROH}_2\text{C}(\text{Ph})_2\text{CH}_2\text{Cl}]_o} \right) \\ &\times (R_1 + R_2) + (Da_{\text{ClQ}(\text{Ph})_2\text{QCl},1} + Da_{\text{ClQ}(\text{Ph})_2\text{QCl},2}) + \left( \frac{Da_{\text{ROQ}(\text{Ph})_2\text{QOR},1} + Da_{\text{ROQ}(\text{Ph})_2\text{QOR},2}}{f} \right) \left. \right\}^{-1} \end{aligned} \quad (16)$$

Several experiments were carried out to measure the concentration of ROQ(Ph)<sub>2</sub>QOR in the aqueous and organic phases. It was found that the concentration of ROQ(Ph)<sub>2</sub>QOR in the organic phase maintained a constant value after 1 min of reaction. This result indicates that the mass transfer rates of ROQ(Ph)<sub>2</sub>QOR and ClQ(Ph)<sub>2</sub>QCl between the two phases are rapid compared to the organic-phase reaction. Furthermore, the rates of aqueous ion-exchange are faster than those of organic phase. Based on the experimental evidence, both the Damkohler numbers as well as  $R_1$  and  $R_2$  are small. Therefore, Eq. (16) can be simplified to:

$$[\text{ROQ(Ph)}_2\text{QOR}]_o = \frac{fM_{\text{ROQ(Ph)}_2\text{QOR}}}{1 + fM_{\text{ROQ(Ph)}_2\text{QOR}}} \frac{Q_0}{V_o} \quad (17)$$

From Eq. (17), it is clear that  $[\text{ROQ(Ph)}_2\text{QOR}]_o$  is a constant value. Moreover, material balances for the reactant and the two products in the reaction solution are:

$$\begin{aligned} \frac{d[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o}{dt} &= k_1[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QOR}]_o \\ &+ k_3[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QCl}]_o \end{aligned} \quad (18)$$

$$\begin{aligned} \frac{d[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o}{dt} &= k_1[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QOR}]_o \\ &+ k_3[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QCl}]_o \\ &- k_2[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QOR}]_o \\ &- k_4[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QCl}]_o \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{d[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{OR}]_o}{dt} &= k_2[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QOR}]_o \\ &+ k_4[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o[\text{ROQ(Ph)}_2\text{QCl}]_o \end{aligned} \quad (20)$$

The amount of ROQ(Ph)<sub>2</sub>QOR in organic phase maintained a constant value, which indicates that  $[\text{ROQ(Ph)}_2\text{QCl}]_o$  also maintained a constant value. Eq. (18) becomes:

$$-\frac{d[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o}{dt} = k_{\text{app},1}[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o \quad (21)$$

where  $k_{\text{app},1} = k_1[\text{ROQ(Ph)}_2\text{QOR}]_o + k_3[\text{ROQ(Ph)}_2\text{QCl}]_o$ .

The data obtained from the kinetic runs were analyzed using the integral method of rate data analysis showing that the reaction followed a pseudo-first-order rate law for all experimental runs. Integrating Eq. (21) yields:

$$-\ln(1 - X) = k_{\text{app},1}t \quad (22)$$

where  $X$  is the conversion of  $\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}$ , i.e.:

$$X = 1 - \frac{[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o}{[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_{o,0}} \quad (23)$$

where  $[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_{o,0}$  denotes the initial concentration of 4,4'-bis(chloromethyl)-1,1'-biphenyl in the organic phase. Thus, the value of  $k_{\text{app},1}$  can be obtained from experimental data in conjunction with Eq. (22). Then, Eq. (19) is rewritten as:

$$\begin{aligned} \frac{d[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o}{dt} &= k_{\text{app},1}[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o \\ &- k_{\text{app},2}[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o \end{aligned} \quad (24)$$

where  $k_{\text{app},2} = k_2[\text{ROQ(Ph)}_2\text{QOR}]_o + k_4[\text{ROQ(Ph)}_2\text{QCl}]_o$ . Substituting Eq. (23) into Eq. (24), we obtain:

$$\begin{aligned} \frac{[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o}{[\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_{o,0}} &= \frac{k_{\text{app},1}}{k_{\text{app},2} - k_{\text{app},1}} [\exp(-k_{\text{app},1}t) - \exp(-k_{\text{app},2}t)] \end{aligned} \quad (25)$$

Based on the experimental data for  $[\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_o$ , the value of  $k_{\text{app},2}$  can be obtained from Eq. (25) with the previous knowledge of  $k_{\text{app},1}$  via the technique of parameter estimation. The kinetic parameters of the equation were obtained using a computer program (software Fortran 90). Combining Eqs. (20) and (25), we obtain:

$$\begin{aligned} [\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{OR}]_o &= [\text{ClH}_2\text{C(Ph)}_2\text{CH}_2\text{Cl}]_{o,0} \\ &\times \left[ 1 + \frac{k_{\text{app},1}}{k_{\text{app},2} - k_{\text{app},1}} \exp(-k_{\text{app},2}t) \right. \\ &\left. - \frac{k_{\text{app},2}}{k_{\text{app},2} - k_{\text{app},1}} \exp(-k_{\text{app},1}t) \right] \end{aligned} \quad (26)$$

The concentration of the di-substituted compound  $\text{ROH}_2\text{C(Ph)}_2\text{CH}_2\text{OR}$  could be estimated from the previous knowledge of  $k_{\text{app},1}$  and  $k_{\text{app},2}$ . The estimated value is consistent with the experimental value which was obtained from the HPLC analysis.

#### 4. Results and discussion

The propose of this work is to study the etherification of 4,4'-bis(chloromethyl)-1,1'-biphenyl in order to synthesize a mono-substituted product (4,4'-(butoxymethyl chloromethyl)-1,1'-biphenyl) and a di-substituted product (4,4'-bis(butoxymethyl)-1,1'-biphenyl) in an alkaline solution/chlorobenzene two-phase medium. The products were successfully separated and purified from the reaction solution by pressurized column chromatography. No by-products were observed during or after reaction. Material balances for the reactant, mono-substituted product and di-substituted product were satisfactorily made. The effects of the operating conditions on the reaction rate are discussed in the following.

#### 4.1. Effect of the agitation speed

In principle, the active catalyst,  $\text{RO}^- \text{Q}^+(\text{Ph})_2 \text{Q}^+ \text{OR}^-$ , is required to be physically transferred from the aqueous phase into the organic phase in a phase-transfer catalyst chemical environment. With agitation, a maximal interfacial area is obtained. In order to ascertain that agitation would lead to an increase in the interfacial area. The surface concentration of the reactive species results in accelerating the mass transfer rate. As the transfer rate of the active catalyst substantially surpasses the intrinsic reaction rate of the organic phase, after which the rate of a phase-transfer catalytic reaction would become independent of agitation speed. As shown in Fig. 1, no improvement in the reaction rate is observed when the agitation rate exceeds 600 rpm. This behavior is in contrast to those reactions taking place at a water–organic phase boundary, where the reaction rate is directly proportional to stirring rate [19]. Below 600 rpm, the reaction rate is highly dependent on the agitation speed because mass transfer plays an important role in affecting the reaction rate. Therefore, the agitation rate was set at 800 rpm for studying the reaction behaviors from which the resistance of mass transfer is kept at a minimum constant value or zero value. Thus, the apparent rate constants reach constant values for the agitation speed 600–800 rpm. The value of the first apparent rate constant  $k_{\text{app},1}$  is larger than that of the second apparent rate constant  $k_{\text{app},2}$ , which indicates that the first substitution reaction is faster than the second one in the organic phase. The organic-phase reactant has two chlorine atoms to be substituted by alkoxides. Therefore, the probability of collision alkoxides with any one of the two chlorine atoms of the organic-phase reactant to produce mono-substituted is greater than that of collision alkoxides with the single chlorine atom of the mono-substituted product to produce di-substituted product.

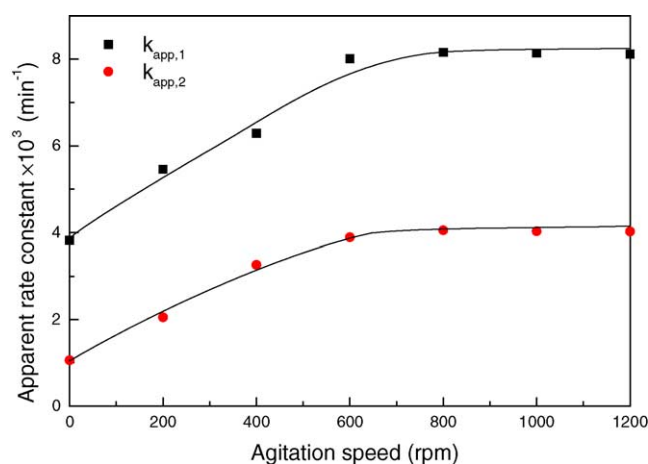


Fig. 1. Effect of the agitation speed on the two apparent rate constants,  $k_{\text{app},1}$  and  $k_{\text{app},2}$ ; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 20 mL of water, 45 °C.

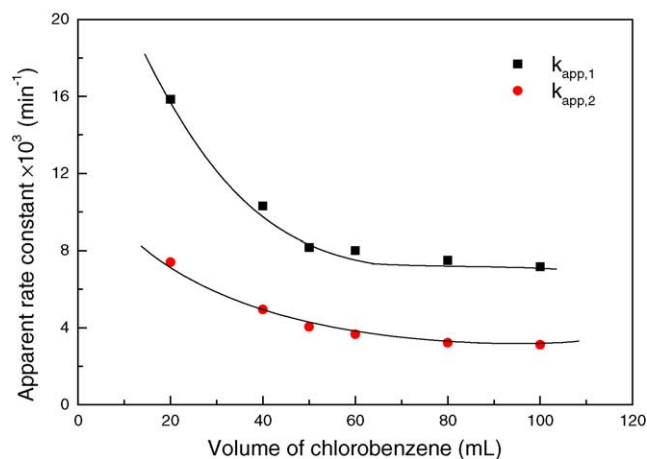


Fig. 2. Effect of the volume of chlorobenzene on the two apparent rate constants,  $k_{\text{app},1}$  and  $k_{\text{app},2}$ ; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 20 mL of water, 800 rpm, 45 °C.

#### 4.2. Effect of the volume of the organic solvent

Some phase-transfer catalytic reactions were conducted under “solvent-free” conditions [20,21]. Nevertheless, phase-transfer catalytic reactions are frequently carried out in the presence of an organic solvent or co-solvent, especially if the organic reagent is in a solid form. In this experiment, the organic-phase reactant, 4,4'-bis(chloromethyl)-1,1'-biphenyl, is in solid form, so it is necessary to add adequate organic solvent to dissolve the organic-phase reactant. In this case, chlorobenzene was chosen as the organic solvent in this etherification reaction, and results are shown in Fig. 2. In general, the concentration of the active catalyst and the interfacial area between the organic phase and aqueous phase are highly affected by the volume of organic solvents. The concentration of the active catalyst is decreased by increasing the volume of the organic solvent, whereas, the interfacial area is increased by increasing the volume of the organic solvent. From the experimental results, it is clear that the dilution effect substantially surpasses the interfacial area effect. In another word, the effect of the concentration of the active catalyst on the reaction rate is still greater than that of the interfacial area on the reaction rate. It is easy to recognize that the experimental condition was set at high agitation speed, so the interfacial area effect would no longer dominate the conversion.

#### 4.3. Effect of the catalysts

For promoting phase-transfer catalytic reaction, the development of a new phase-transfer catalyst often plays the most important role, together with the choice of the most appropriate phase-transfer catalyst. For this, quaternary ammonium salts are frequently used due to their low cost and good availability. In this work, the newly synthesized 4,4'-bis(triethylmethylammonium)-1,1'-biphenyl dichloride (4,4'-

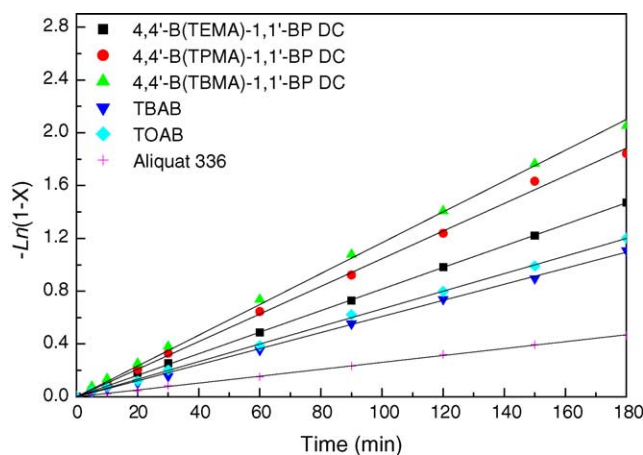


Fig. 3. A plot of  $-\ln(1-X)$  of 4,4'-bis(chloromethyl)-1,1'-biphenyl vs. time with different catalysts; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of catalyst, 20 g of potassium hydroxide, 20 mL of water, 800 rpm, 45 °C.

B(TEMA)-1,1'-BP DC), 4,4'-bis(triethylmethylammonium)-1,1'-biphenyl dichloride (4,4'-B(TPMA)-1,1'-BP DC) and 4,4'-bis(tributylmethylammonium)-1,1'-biphenyl dichloride (4,4'-B(TBMA)-1,1'-BP DC) were employed as the phase-transfer catalysts, and their reactivities were compared with those of the conventional quaternary ammonium salts, such as TBAB, TOAB and Aliquat 336. The results are given in Fig. 3, indicating that the reaction follows a pseudo-first-order rate law. The following order illustrates the relative catalytic activity of different catalysts in the etherification reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl with 1-butanol: Aliquat 336 < TBAB < TOAB < 4,4'-B(TEMA)-1,1'-BP DC < 4,4'-B(TPMA)-1,1'-BP DC < 4,4'-B(TBMA)-1,1'-BP DC. Aliquat 336, which is quite inexpensive, did not give satisfactory results in the case of etherification. The catalytic effect of the symmetric quaternary ammonium salts, TBAB and TOAB, show that they are good catalysts. A higher total carbon number in the alkyl groups gives a higher reaction rate since the lipophilicity and extraction capability of quaternary ammonium salts would be increased with the increase in the number of carbon atoms. The more lipophilic the quaternary ammonium cation, the greater is its effectiveness in transferring nucleophilic anions into the organic phase. The newly synthesized multi-site phase-transfer catalysts had excellent catalytic effect with less expensive raw material, 4,4'-bis(chloromethyl)-1,1'-biphenyl and tertiary amine. It is noteworthy that the multi-site catalyst possesses a higher reactivity than single-site catalyst, although the total carbon number of 4,4'-B(TEMA)-1,1'-BP DC is lower than that of TOAB. The phenomena can be ascribed mainly to the molecular structure. The molecular structure of bis-quaternary ammonium salts are analogic with the organic reactant, 4,4'-bis(chloromethyl)-1,1'-biphenyl, which would make the active catalytic be more compatible with this organic reactant. In applying Eqs. (23) and (26),

Table 1

Effect of the new multi-site catalyst and the conventional quaternary ammonium salts on the two apparent rate constants,  $k_{app,1}$  and  $k_{app,2}$

Phase-transfer catalysts	$k_{app,1}$ ( $\times 10^3 \text{ min}^{-1}$ )	$k_{app,2}$ ( $\times 10^3 \text{ min}^{-1}$ )
4,4'-B(TEMA)-1,1'-BP DC	8.16	4.05
4,4'-B(TPMA)-1,1'-BP DC	10.46	5.23
4,4'-B(TBMA)-1,1'-BP DC	11.67	5.79
TBAB	6.09	2.13
TOAB	6.67	2.35
Aliquat 336	2.61	0.98

Reaction conditions: 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of catalyst, 20 g of potassium hydroxide, 20 mL of water, 800 rpm, 45 °C.

the apparent rate constants,  $k_{app,1}$  and  $k_{app,2}$  for these new multi-site catalysts, quaternary ammonium salts are given in Table 1.

#### 4.4. Effect of the amount of multi-site catalysts

The effect of amount of catalyst, 4,4'-B(TEMA)-1,1'-BP DC, on the conversion was also studied. As shown in Fig. 4, the two apparent rate constants are plotted against different amounts of the catalyst. The consumption of 4,4'-bis(chloromethyl)-1,1'-biphenyl is directly proportional to the concentration of catalyst added. Extrapolating the line of  $k_{app,1}$  intersects the ordinate at a positive value, since the reaction could occur without any catalyst, although it would be extremely slow. In the absence of 4,4'-B(TEMA)-1,1'-BP DC, only 8.6% conversion of 4,4'-bis(chloromethyl)-1,1'-biphenyl is obtained after 180 min. Nevertheless, the conversion is reached 77% after 180 min of reaction when merely 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC catalyst was added. This shows that the catalytic activity of 4,4'-B(TEMA)-1,1'-BP DC is quite sufficient for the etherifica-

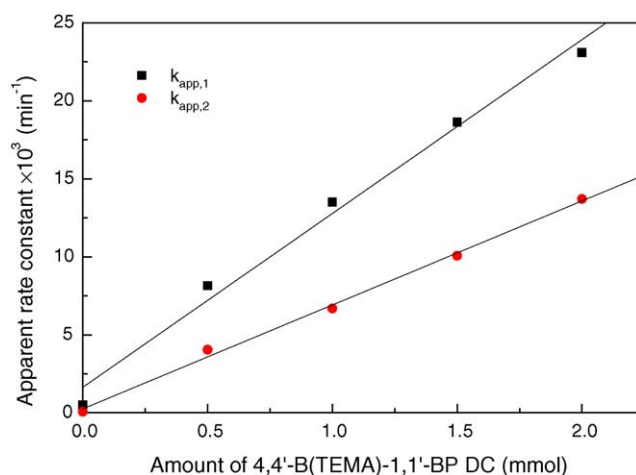


Fig. 4. Effect of the amount of 4,4'-B(TEMA)-1,1'-BP DC catalyst on the two apparent rate constants,  $k_{app,1}$  and  $k_{app,2}$ ; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 20 g of potassium hydroxide, 20 mL of water, 800 rpm, 45 °C.

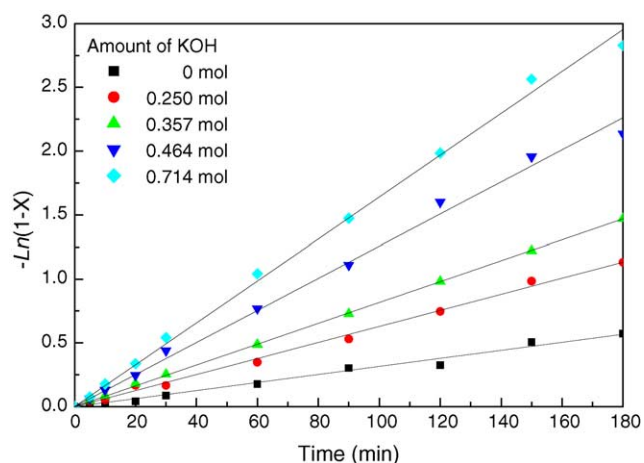


Fig. 5. Effect of the amount of potassium hydroxide on the two apparent rate constants,  $k_{app,1}$  and  $k_{app,2}$ ; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 mL of water, 800 rpm, 45 °C.

tion reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl with 1-butanol.

#### 4.5. Effect of the amount of potassium hydroxide

These procedures were also used to assess the effect of amount of potassium hydroxide on the process of etherification reaction, with results as shown in Fig. 5. These results show that the etherification is highly dependent on the amount of potassium hydroxide, and the reaction also follows a pseudo-first-order rate law. The amount of alkoxides, the distribution of the active catalysts and the hydration number of the active catalysts are all affected by the addition of KOH. These three factors contribute to the enhancement of the etherification reaction rate. First, it is obvious that the amount of alkoxides would be increased when the more amount of potassium hydroxide was added. Second, the concentration of the active catalysts, ROQ(Ph)<sub>2</sub>QOR, in the organic phase is increased by increasing the concentration of potassium hydroxide in the aqueous phase. Third, the hydration shell, specific for the active catalysts, reduces the rate of the chemical reaction in the organic phase. The extent of anion hydration depends mainly on its polarizability and electronegativity, with solvent and cation generally showing a negligible effect. Hard anions such as OH<sup>-</sup> and F<sup>-</sup> have the greatest hydration numbers, whereas the hydration number is low with soft anions such as I<sup>-</sup> [22]. More OH<sup>-</sup> would decrease the hydration of the active catalysts, and thus it would increase the reactivity of the active catalysts.

#### 4.6. Effect of the amount of water

In this work, the effect of the volume of water on the two apparent constants is investigated with results as shown in Fig. 6. It can be seen that the two apparent rate constants

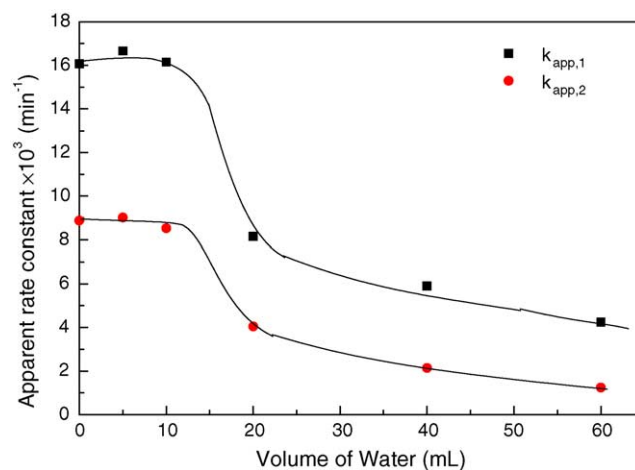


Fig. 6. Effect of the volume of water on the two apparent rate constants,  $k_{app,1}$  and  $k_{app,2}$ ; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 800 rpm, 45 °C.

( $k_{app,1}$  and  $k_{app,2}$ ) would stay at constant at 0–10 mL until the volume of water increased over 10 mL, when the two apparent rate constants decreased with increased volume of water. Two facts should be clarified. First, the quantity of 1-butanol is larger than that of the organic reactant in our experimental conditions. Therefore, the reaction rate is not affected by the change of the concentration of 1-butanol with the increase of the volume of water. Second, the interfacial area is increased with the increase in the volume of water. However, this change in interfacial area would not affect the reaction rate since the experiment was conducted entirely at high agitation speed. In another words, the change of the reaction rate was not due to the increase of the contact of the interfacial area. In the range of 0–10 mL of water, the active catalyst, ROQ(Ph)<sub>2</sub>QOR, in the organic phase would form in a local saturated state. For this reason, the two apparent rate constants were maintained at constant values. Nevertheless, the concentration of the active catalyst is decreased with the increase in the volume of water within the range of 20–60 mL, so the reaction is decreased. Moreover, the concentration of alkali compound in aqueous solution is decreased with the increase in the volume of water. This situation would dramatically reveal the hydration effect of the active catalyst as the volume of water changed from 20 to 60 mL. The concentration of the alkali compound in aqueous solution would also affect the distribution of the active catalysts between two phases. Thus, less active catalyst exists in the organic phase.

#### 4.7. Effect of the organic solvents

In this study, the Starks' extraction mechanism was employed to explain the reaction characteristics. For this, chlorobenzene, cyclohexane, dibutyl ether and toluene were used as the organic solvents to investigate their influences on the reactivity with results as shown in Fig. 7. The phase-



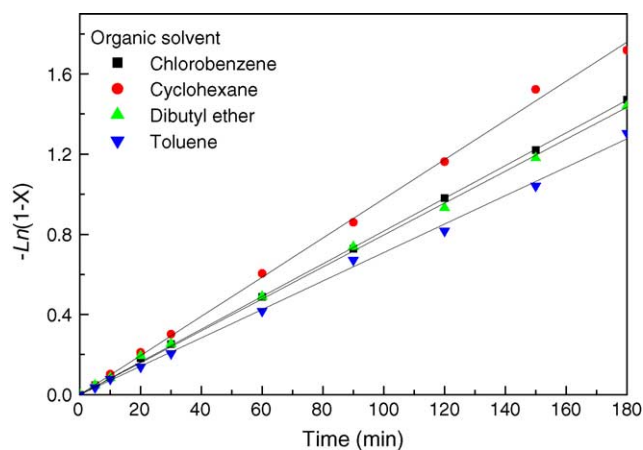


Fig. 7. A plot of  $-\ln(1-X)$  of 4,4'-bis(chloromethyl)-1,1'-biphenyl vs. time with different organic solvents; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of organic solvent, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 20 mL of water, 800 rpm, 45 °C.

transfer catalysts must have the ability to transfer the reactive anion into the organic phase reacting with organic-phase reactant. In the phase-transfer catalytic etherification reaction, the solvent indeed influences the reactive activity. The corresponding pseudo-first-order constants are given in a Table 2. The order of the relative activities of these organic solvents is: cyclohexane > chlorobenzene > dibutyl ether > toluene. In most applications, it appears that the chlorohydrocarbons are more effective than those of the hydrocarbon solvents.

It is clear that a higher conversion is obtained using cyclohexane as the organic solvent. Since the phase-transfer catalytic reaction is the intrinsic reaction rate limited, i.e. the non-polar solvent promotes the rate-determining step in the organic phase by reducing the extent of solvation (including hydration) of reactant anion and by increasing the concentration of quaternary ammonium cation in the organic phase [23]. In other words, more polar organic solvents allow smaller quaternary salts to be successfully partitioned into the organic phase. As shown in Table 2, the activity is not simply proportional to the solvent parameter such as dielectric constant ( $\epsilon$ ) or Reichardt's solvatochromic parameter ( $E_T^N$ ) [24].

Table 2  
Effect of the organic solvents on the two organic phase apparent rate constants

Organic solvent	$\epsilon$	$E_T^N$	$k_{app,1}$ ( $\times 10^3 \text{ min}^{-1}$ )	$k_{app,2}$ ( $\times 10^3 \text{ min}^{-1}$ )
Chlorobenzene	5.6	0.19	8.16	4.05
Cyclohexane	2.0	0.01	9.77	5.19
Dibutyl ether	2.8	0.07	7.97	3.83
Toluene	2.4	0.10	7.09	3.49

Reaction conditions: 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of organic solvent, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 20 mL of water, 800 rpm, 45 °C.

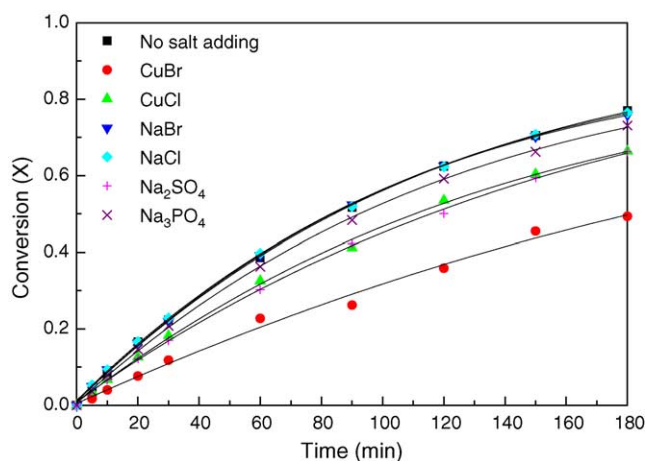


Fig. 8. A plot of  $-\ln(1-X)$  of 4,4'-bis(chloromethyl)-1,1'-biphenyl vs. time with different inorganic salts added; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 20 mL of water, 0.1 mol of inorganic salt, 800 rpm, 45 °C.

#### 4.8. Effect of the inorganic salt

In the etherification reaction, the inorganic salts extra added sometimes influence the conversion. To investigate the effect of the inorganic salts added on the etherification system, cuprous bromide, cuprous chloride, sodium bromide, sodium chloride, sodium sulfate and tri-sodium phosphate were used as inorganic salts in this reaction system. The conversion is plotted against time for different inorganic salts with results as shown in Fig. 8. In general, the hydration levels of all ions present in the system tend to decrease as the salt concentration in the aqueous phase increase, since the added salt ties up water molecular and has a dehydrating effect on the ions present in the system [25]. Nevertheless, the extra addition of inorganic salt did not increase the reaction in this etherification system, indicating that the effect of adding sodium bromide or sodium chloride is not significant. Moreover, the addition of sodium sulfate or tri-sodium phosphate would be clearly decreasing the reaction rate or the conversion. These results indicate that a larger sulfate anion group or phosphate anion group has a greater salting-out effect. However, small anions, such as the bromide ion or the chloride ion, do not have the capability to affect the reaction rate or the conversion. The salting-out effect enables the use of bis-quaternary ammonium salts which usually unfavorably partitions in the organic phase in base-promoted reactions. In addition, it has been reported that cuprous salts as a co-catalyst together with ordinary phase-transfer catalysts can often accelerate two-phase reactions in substitution reaction under solid-liquid PTC conditions [26,27]. However, it is peculiar that the extra cuprous bromide or cuprous chloride added would dramatically decrease the reaction rate in the etherification system. This phenomenon could be ascribed to the fact that the cuprous salts in the concentrated alkali solution produce the insoluble basic cupric salt during the

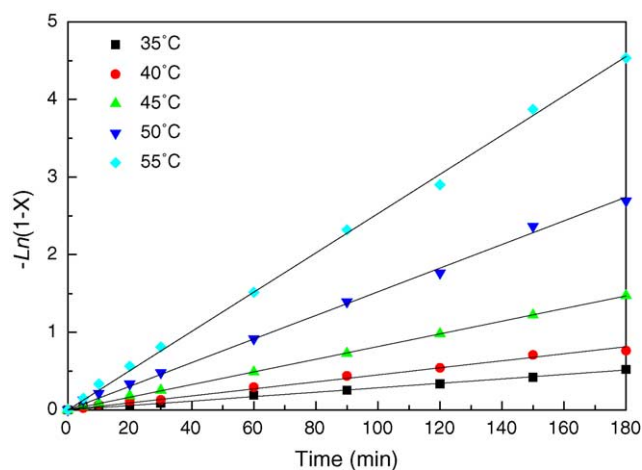


Fig. 9. A plot of  $-\ln(1-X)$  of 4,4'-bis(chloromethyl)-1,1'-biphenyl vs. time with various reaction temperatures; 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 20 mL of water, 800 rpm.

reaction dramatically decreasing the concentration of alkali in aqueous solution. Hence, the reaction rate is dramatically decreased.

#### 4.9. Effect of the temperature

The present work investigates the reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl and 1-butanol catalyzed by a new catalyst 4,4'-B(TEMA)-1,1'-BP DC in the presence of alkaline solution under various reaction temperatures in the range of 35–55 °C. The results are given in Fig. 9. As expected, the rates of most organic reactions increase with the increase in temperature from the transition-state theory. For this reason, it is considered that increasing temperature is likely to promote slow organic phase reactions in a phase-transfer catalyst system. Moreover, the reaction follows a pseudo-first-order rate law. The first apparent rate constant  $k_{app,1}$  and the second apparent rate constant  $k_{app,2}$  are listed in Table 3. The two activation energies ( $E_{a1}$  and  $E_{a2}$ ) obtained were 22.19 and 29.56 kcal/mol, by plotting  $\ln(k_{app})$  versus  $1/T$  from the Arrhenius equation. The activation energy shows that the etherification reaction is under kinetically control.

Table 3  
Effect of temperature on the two organic-phase apparent rate constants

Temperature (°C)	$k_{app,1}$ ( $\times 10^3 \text{ min}^{-1}$ )	$k_{app,2}$ ( $\times 10^3 \text{ min}^{-1}$ )
35	2.86	0.89
40	4.52	1.77
45	8.16	4.05
50	15.22	7.97
55	25.29	17.17

Reaction conditions: 4 mmol of 4,4'-bis(chloromethyl)-1,1'-biphenyl, 150 mmol of 1-butanol, 50 mL of chlorobenzene, 0.5 eq. mmol of 4,4'-B(TEMA)-1,1'-BP DC, 20 g of potassium hydroxide, 20 mL of water, 800 rpm.

## 5. Conclusion

This work describes the catalysis of the etherification of 4,4'-bis(chloromethyl)-1,1'-biphenyl catalyzed by a new synthesizing multi-site phase-transfer catalysts, 4,4'-bis(triethylmethylammonium) dichloride were carried out in an alkaline solution of KOH/organic solvent two-phase medium. The catalytic activity of multi-site phase-transfer catalysts was quite sufficient for the etherification reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl with 1-butanol. The kinetic model was constructed. The mass transfer of species and the phase equilibrium of the catalysts between two phases were also considered by the two-film theory. The multi-site phase-transfer catalysts have a greater phase-transfer catalytic activity than do the conventional quaternary ammonium salts. It is also found that cyclohexane was the best organic solvent to obtain a higher conversion among the several organic solvents for this present system of etherification reaction. The order of the relative activities of these organic solvents is cyclohexane > chlorobenzene > dibutyl ether > toluene. Larger anion groups decrease the reaction rate because of the salting-out effect. In addition, the addition of cuprous salts would dramatically decrease the reaction rate. That was ascribed mainly to the produce of insoluble basic cupric salt during the reaction. The two activation energies  $E_{a1}$  and  $E_{a2}$  were 22.19 and 29.56 kcal/mol, respectively.

## Acknowledgement

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