Phase transfer catalytic reaction of *n*-bromobutane and sodium sulfide in a two-phase solution and its kinetics

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Abstract

The reaction between sodium sulfide (Na_2S) and *n*-bromobutane ($1\text{-}C_4H_9Br$) to synthesize di-*n*-butyl sulfide (RSR; R: C_4H_9) was carried out for in an organic solvent/alkaline solution two-phase medium under phase transfer catalysis (PTC) conditions. A rational reaction mechanism and a kinetic model were satisfactorily developed by considering the reactions from which two sites of nucleophiles on a molecule displaced the organic-phase reactant. The two-film theory, which includes mass transfer and phase equilibrium of the catalysts between two phases, was employed to describe the dynamic behavior of the reaction system. In this system, the two-site active catalyst, QSQ (Q^+: $(C_4H_9)_4N^+$), which was produced from the reaction of sodium sulfide and quaternary ammonium salt, was first synthesized in the aqueous phase, and then transferred to the organic phase in preparation for further reaction. QSR was produced from the first reaction of the organic solution, and RSR was produced from the second reaction of the organic solution. Neither of these two-site active catalysts were isolated from the solution, nor were they detected from the solution during the reaction. Only the first apparent constant of the organic-phase reaction ($k_{app,1}$) was obtained via experimental data. Detailed investigation was made for: effect of agitation, temperature, amount of sodium sulfide, organic solvents, catalysts, amount of TBAB catalyst, amount of sodium hydroxide, volume of sodium sulfide solution, volume of organic solvent, and amount of water on the reaction rate and the conversion. The results were explained satisfactorily by considering the interaction between the reactants and the environmental species.
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1. Introduction

Phase transfer catalysis (PTC) technology has recently been widely applied to synthesize specialty chemicals from organic reactions [1–4]. The primary advantage of this technique is to elevate the reaction rate and increase the selectivity in mild conditions. Since Jarrouse [5] found that quaternary ammonium salt is an effective catalyst for enhancing the two-phase reaction, many chemists have investigated phase transfer catalysis in numerous reactions, such as substitution, displacement, condensation, epoxidation, ylide-mediated reaction, electro-oxidation, electro-reduction, polymerization, modification of polymer, etc. As a result, PTC considered to have great potential for industrial-scale application [6].

The reaction of organic halides (e.g. *n*-butyl bromide) with sulfide ion results in the formation of

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dialkyl sulfides, which is one of the thioethers with many applications as additives in flavors, cross-link agents and inverse phase transfer catalysts (IPTC). Conventional methods to synthesize dialkyl sulfides involve heating an aqueous methanolic solution of sodium sulfide with organic halide under continuous stirring and refluxing temperature [7,8]. However, these methods require a long reaction time to obtain low product selectivity, even under vigorous reaction conditions. Therefore, there are limited industrial applications. Herriott and Picker [9], and Landini and Rolla [10] improved the reaction rate of the two-phase reaction with the use of tributylhexadecyl phosphonium bromide and Aliquat 336 as the phase transfer catalysts. Both of those studies pointed out that the advantages of the phase transfer catalysis in synthesizing dialkyl sulfides include high selectivity, short reaction time, and mild reaction conditions. Nevertheless, the reaction mechanism still requires investigation.

In this current work, the mass transfer through two-phase interface and organic nucleophilic substitution law are applied to study the reaction mechanism. The reaction of sodium sulfide and n-bromobutane to synthesize di-n-butyl sulfides were carried out in an alkaline solution/organic solvent two-phase medium under phase transfer catalysis conditions. Two substitution steps of bromide from bromoalkane were proceeded in an organic solution in which two sites of nucleophiles on the active intermediate displace the bromide of the organic-phase reactant. Two active catalysts, di-tetrabutylammonium sulfide (($C_4H_9)_4N^+$–S^{-2}– $N^+(C_4H_9)_4$, QSQ), produced from aqueous phase; and tetrabutylammonium alkyl sulfide (($C_4H_9)_4N^+$–S^-–C_4H_9, QSR), produced from organic phase; were obtained using tetrabutylammonium bromide (TBAB or QBr) as the regenerated catalyst. Using n-bromobutane as the organic-phase reactant, the condition for a high yield of di-n-butyl sulfide was obtained. Due to its high reactivity, the active catalyst was not detected in the organic phase during or after the reaction. A mechanism for the alkylation via PTC was proposed and the reaction kinetics was obtained. A pseudo steady-state hypothesis (PSSH) was developed to describe the kinetic behaviors from which the first apparent rate constant, $k_{app,1}$ was experimentally obtained.

2. Experimental

2.1. Materials

All reagents, including n-bromobutane, sodium sulfide (Na$_2$S·3.5H$_2$O), toluene, n-hexane, chloroform, cyclohexane, 1,2-dichloroethane, tetrabutylammonium bromide, tetrahexylammonium bromide (THAB), tetraethylammonium bromide (TEAB), benzyltetrabutylammonium bromide (BTEAB), 4-(tributylammonium) propansultan (QSO$_3$), sodium hydroxide, biphenyl, dialkyl sulfide, and other reagents for synthesis were guaranteed grade (G.R.) chemicals.

2.2. Procedures

2.2.1. Synthesis of di-n-butyl sulfide product (RSR)

Measured quantities of sodium sulfide (7 g, excess agent), n-bromobutane (2 ml, limiting reactant), and THAB (0.1 g) were dissolved in 20 ml of n-hexane (or toluene) and 10 ml of water at 35 °C. The mixed solution was uniformly agitated to start the reaction. After 20 min of reaction, the solution was separated and the portion of the organic solution was washed by deionized water (DI) at least five times to remove THAB catalyst. The solution was concentrated by vacuum evaporation. Transparent liquid di-n-butyl sulfide of over 95% purity was obtained. The product was identified by gas chromatography (GC)-mass for molecular weight, as well as by FTIR and NMR (^{1}H NMR and ^{13}C NMR) for functional groups.

2.2.2. Kinetics of the two-phase reaction

The reaction was carried out in a 150 ml three-necked Pyrex flask, which permitted agitating the solution, inserting thermometer, taking samples, and adding the feed. Known quantities of sodium sulfide and sodium hydroxide were completely dissolved in water. The solution was put into the reactor, which was submerged into a well-controlled temperature water bath within ±0.1 °C. Then, measured quantities of quaternary ammonium bromide (QBr), biphenyl (internal standard) and n-bromobutane dissolved in organic solvent were added to the solution and agitated to start the reaction. The sample (0.5 ml), which was withdrawn from the reactor at each time interval, was put into test tubes containing 4 ml of water and 4 ml of solvent at 4 °C. The samples were analyzed

for *n*-bromobutane, di-*n*-butyl sulfide and others. The contents of *n*-bromobutane and di-*n*-butyl sulfide were measured by gas chromatography (Shimadzu, 17A). The analyzing conditions were

- column: 30 m × 0.525 mm i.d. capillary column containing 100% poly(dimethylsiloxane), increase 5 °C/min;
- injection temperature: 220 °C;
- carrier gas: N$_2$ at a flow rate 30 ml/min;
- detector: FID 250 °C.

## 3. Mechanism and kinetic model

For synthesizing dialkyl sulfide compounds, *n*-bromobutane was added to the aqueous concentrated solution of sodium sulfide/*n*-hexane two-phase medium in the presence of quaternary ammonium bromide as catalyst. Only the di-tetrabutyl-ammonium-substitution product, di-*n*-butyl sulfide, was detected in the organic reaction. The mono-tetrabutylammonium-substitution product, *n*-butyl-tetrabutylammonium sulfide (RSQ) was not observed in the GC analysis procedure. Sodium sulfide of high alkalinity (e.g. pH 12.7 at 100 g of anhydrous Na$_2$S dissolved in 1 l of water) reacts with acid compound to generate hydrogen sulfide. The reaction formula is described as shown in Scheme 1.

Generally, the pairs of quaternary ammonium cation with hydroxide, hydrosulfide, and sulfide anions to produce QOH, QSH, and QSQ are formed. Thus, it is clear that there are, in general, three or four products in the organic phase. However, only one species (QSQ) is generated via phase transfer catalysis. This is due to the fact that the active catalyst, QOH and QSH, are all hydrophilic and difficult to transfer to the organic phase. No *n*-butanol (substitution product of QOH) or *n*-butyl hydrosulfide (substitution product of QSH) were observed from the two-phase reaction in the presence of PTCs, NaOH, and NaSH. Thus, the reaction mechanism is proposed as shown in Scheme 2.

This mechanism is formulated on the basis of Starks' extraction model. The first organic-soluble

$$S^{2-} + H_2O \rightleftharpoons OH^- + HS^-$$

$$S^{2-} + 2H^+ \longrightarrow H_2S_{(g)}$$
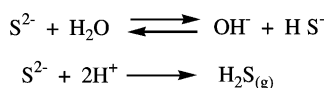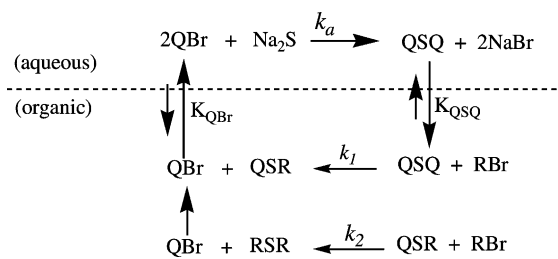
Scheme 1.

Scheme 2.

active catalyst QSQ was produced from the aqueous solution by reacting the catalyst QBr and sodium sulfide. Then, this organic-soluble active catalyst, which transferred to the organic phase, reacted with the organic-phase reactant *n*-bromobutane to produce the second active catalyst (tetrabutylammonium *n*-butyl sulfide, QSR; R: C$_4$H$_9$ and Q: (C$_4$H$_9$)$_4$), which is not detected in the GC analysis procedure because of its high activity. QBr then transferred from the organic phase in preparation for regeneration in the aqueous phase.

Based on the experimental data, no byproducts were produced. Therefore, the total mole of di-*n*-butyl sulfide is twice the consumption of *n*-bromobutane. Several independent experiments were carried out to identify the reaction mechanism. First, no reaction of *n*-bromobutane and sodium sulfide was observed in the absence of tetrabutylammonium salt and water. In the second, the active catalyst (QSQ) was synthesized by reacting tetrabutylammonium salt and Na$_2$S aqueous solution, and then transferred to *n*-hexane. After separating the organic phase from the aqueous phase, the active catalyst (QSQ), which is an unstable compound, could not be isolated from the organic phase. After this, *n*-bromobutane was added to this portion of organic-phase solution, and di-*n*-butyl sulfide was produced after 10 min of this homogenous organic-phase reaction. These experiments confirm that the reaction is catalyzed by TBAB, and that the first active catalyst (QSQ) produced from the aqueous phase exists in the organic phase.

Applying the two-film theory, the material balance of each species can be written as

$$\frac{d[QSQ]_o}{dt} = K_{QSQ}A \left([QSQ]_a - \frac{[QSQ]_o}{M_{QSQ}} \right) - k_1[RBr]_o[QSQ]_o \tag{1}$$

$$\frac{d[QSQ]_a}{dt} = k_a[Na_2S]_a[QBr]_a^2$$
$$- K_{QSQ}Af\left([QSQ]_a - \frac{[QSQ]_o}{M_{QSQ}}\right) \qquad (2)$$

$$\frac{d[QBr]_o}{dt} = k_1[RBr]_o[QSQ]_o + k_2[QSR]_o[RBr]_o$$
$$- K_{QBr}A([QBr]_o - M_{QBr}[QBr]_a) \qquad (3)$$

$$\frac{d[QBr]_a}{dt} = K_{QBr}A([QBr]_o - M_{QBr}[QBr]_a)$$
$$- 2k_{a,2}[Na_2S]_a[QBr]_a^2 \qquad (4)$$

Where K_{QSQ} and K_{QBr}: overall mass transfer coefficients of QSQ and QBr; M_{QSQ} and M_{QBr}: partition coefficient of QSQ and QBr in two phases; A: interfacial area between two phases; f: ratio of the volume of organic phase and aqueous phase.

The rate of consuming the n-bromobutane reactant, and the rate of producing the second active catalyst (QSR) and the product di-n-butyl sulfide are

$$\frac{d[RBr]_o}{dt} = -k_1[RBr]_o[QSQ]_o - k_2[RBr]_o[QSR]_o \qquad (5)$$

$$\frac{d[QSR]_o}{dt} = k_1[RBr]_o[QSQ]_o - k_2[QSR]_o[RBr]_o \qquad (6)$$

$$\frac{d[RSR]_o}{dt} = k_2[QSR]_o[RBr]_o \qquad (7)$$

The subscripts "a" and "o" represent the characteristics of the species in the aqueous and organic phase, respectively. The nomenclature of the species are defined as

- QSQ: $(C_4H_9)_4N^+-S^{2-}-N^+(C_4H_9)_4$;
- QBr: $(C_4H_9)_4N^+Br^-$;
- QSR: $(C_4H_9)_4N^{+-}SR$.

The total initial amount of catalyst Q_0 added is

$$Q_0 = V_o(2[QSQ]_o + [QSR]_o + [QBr]_o)$$
$$+ V_a(2[QSQ]_a + [QBr]_a) \qquad (8)$$

The initial conditions of the species are

$$t = 0, \quad [QBr]_{o,0} = [QSQ]_{o,0} = [QSQ]_{a,0}$$
$$= [QSR]_{o,0} = 0$$
$$[QBr]_{a,0} = Q_0 \qquad (9)$$
$$[RBr]_o = [RBr]_{o,0}$$

where the subscript "0" denotes the condition of species at zero time. In this study, $[QBr]_o$ and $[QSQ]_o$ keep at constant values in using large excess amount of sodium sulfide. It is reasonable to assume that $[QSQ]_o$ remains at a constant value because the activity of QSR is higher than that of QSQ. QSR is not detectable in the organic-phase solution during or after reaction. Thus, by considering n-bromobutane as a limiting component, the pseudo steady-state hypothesis is applied, i.e.

$$\frac{d[QSQ]_a}{dt} = 0; \quad \frac{d[QSQ]_o}{dt} = 0; \quad \frac{d[QSR]_o}{dt} = 0;$$
$$\frac{d[QBr]_a}{dt} = 0; \quad \frac{d[QBr]_o}{dt} = 0 \qquad (10)$$

Combining Eqs. (1)–(4) and (10), the concentration of QBr in organic phase and aqueous phase, and the concentration of the first active catalyst (QSQ) in the aqueous phase are

$$[QBr]_a = \left\{\frac{fk_1[RBr]_o[QSQ]_o}{k_a[Na_2S]_a}\right\}^{1/2} \qquad (11)$$

$$[QBr]_o = \frac{M_{QBr}}{K_{QBr}A}\left(\frac{fk_1[RBr]_o[QSQ]_o}{k_a[Na_2S]_a}\right)^{1/2}$$
$$+ \frac{2k_1[RBr]_o[QSQ]_o}{K_{QBr}A} \qquad (12)$$

$$[QSQ]_a = \left(\frac{1}{M_{QSQ}} + \frac{k_1[RBr]_o}{K_{QSQ}A}\right)[QSQ]_o \qquad (13)$$

Combining Eqs. (8) and (11)–(13), the initial concentration of QBr in aqueous phase is

$$\frac{Q_0}{V_o} = [QSQ]_o$$
$$\times \left(2 + \frac{2k_1[RBr]_o}{K_{QBr}A} + \frac{2}{fM_{QSQ}} + \frac{2k_1[RBr]_o}{fK_{QSQ}A}\right)$$
$$+ [QSR]_o + [QSQ]_o^{1/2}$$
$$\times \left\{\frac{M_{QBr}}{K_{QBr}A}\left(\frac{fk_1[RBr]_o}{k_a[Na_2S]_a}\right)^{1/2}\right.$$
$$\left.+ \left(\frac{k_1[RBr]_o}{fk_a[Na_2S]_a}\right)^{1/2}\right\} \qquad (14)$$

In general, the rate of acid–base neutralization and the rate of ion-exchange in the aqueous phase are all rapid. Thus, the aqueous phase rate constant k_a is

larger than the organic-phase rate constant k_1. Furthermore, Wang and Yang [11], Wang and Chang [12], and Wang and Tseng [13] found that the induced time of the active catalyst is short, so the concentration of QSQ in the organic phase remains at a constant value after 1 min of reaction. Therefore, both $K_{QBr}A$ and $K_{QSQ}A$ are larger than $k_1[RBr]_o$. The concentration of QSR is very close to zero because the activity of QSR is much higher than that of QSQ. For this, Eq. (14) is simplified to

$$[QSQ]_o = \frac{Q_0}{2V_o} \frac{fM_{QSQ}}{1 + fM_{QSQ}} \qquad (15)$$

Combining Eqs. (6) and (9), and applying the PSSH approach, Eq. (5) can be written as

$$\frac{d[RBr]_o}{dt} = -k_{app,1}[RBr]_o - k_2[QSR]_o[RBr]_o$$
$$= -2k_{app,1}[RBr]_o \qquad (16)$$

$$k_2[QSR]_o = k_1[QSQ]_o = k_{app,1} \qquad (17)$$

in which $k_{app,1}$ is the rate coefficient of pseudo-first-order reaction.

$$k_{app,1} = k_1[QSQ]_o = \frac{k_1 fM_{QSQ}}{1 + fM_{QSQ}} \frac{Q_0}{2V_o} \qquad (18)$$

The conversion of n-bromobutane is defined as X,

$$X = 1 - \frac{[RBr]_o}{[RBr]_{o,0}} \qquad (19)$$

where $[RBr]_{o,0}$ is the initial concentration of $1\text{-}C_4H_9Br$. Thus, Eq. (16) is expressed as

$$\ln(1 - X) = -2k_{app,1}t \qquad (20)$$

According to Eq. (18), the value of $k_{app,1}$ is obtained from the rate coefficient of the first reaction in the organic phase and the distribution coefficient of QSQ between two phases. However, $k_{app,1}$ is obtained experimentally from the slope of the straight line by plotting $\ln(1 - X)$ versus time. Therefore, the intrinsic rate constant k_1 is obtained from Eqs. (18) and (20).

4. Results and discussion

In this work, two S_N2 reactions take place in the organic phase. One is the displacing of n-bromobutane

by QSQ, and the other is n-bromobutane being attacked by QSR. Only the final product RSR was observed in the organic phase, because QSR possesses high reactivity in reacting with alkyl halide in the organic phase. The reason for such a higher activity of QSR can be explained by three factors. First, there are two positive charges on the sulfide of QSQ molecule and only one positive charge on the QSR molecule. Therefore, the electron-withdrawing capability of QSQ is stronger than that of QSR. Second, the stereic hindrance due to the molecule radius of quaternary ammonium group is much larger than that of n-butyl group. Thus, it is difficult for QSQ to attack other molecules. Third, the quaternary ammonium group of QSR can leave the sulfide more easily than that of QSQ. This is because the n-butyl group is a weaker electron-withdrawing group compared to the electron-withdrawing group of the quaternary ammonium group. Thus, the electron density on the second quaternary ammonium group is increased. Hence, the secondary apparent rate constant ($k_{app,2}$) cannot be calculated from experiment data due to the high reactivity of QSR.

4.1. Effect of the agitation speed

In the two-phase reaction, mass transfer resistance is an important factor in affecting the reaction rate. In general, either the organic or the aqueous solution can be dispersed in smaller droplet size by agitating the two-phase solution, so, the contact area of two phases is increased with higher agitation speed. The flux of the two-phase mass transfer is also highly dependent on the flow condition (e.g. agitation speed). Fig. 1 shows the dependence of the apparent rate constant ($k_{app,1}$) on the agitation speed. For agitation speeds less than 350 rpm, both mass transfer and reaction resistance are important in determining the overall reaction rate. In this work, the reaction rate does not significantly change for agitation speeds larger than 350 rpm, and the mass transfer resistances of the active catalyst between the two phases are the same for agitation speed over 350 rpm. Hence, it is obvious that the reaction in organic phase is the rate-controlling step for agitation speed larger than 350 rpm under the present conditions. Below 50 rpm, the reaction rate is quite low because the two-phase solutions do not mix well and layering is clearly observed. Over 100 rpm,
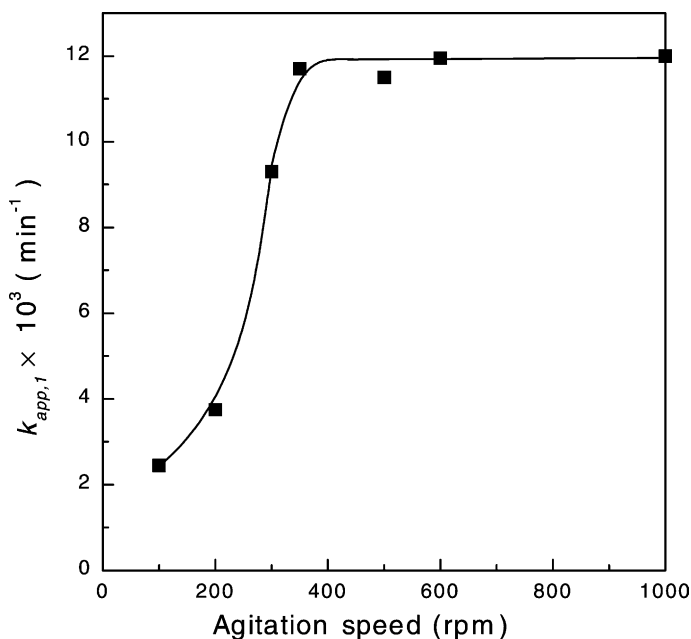
Fig. 1. Effect of the agitation speed on the apparent rate constant ($k_{app,1}$) in the organic phase; 7 g of sodium sulfide, 10 ml of water, 0.15 mmol of TBAB, 4 mmol of n-bromobutane, 40 ml of n-hexane, 40 °C.

the ivory-white dispersion phase occurs. However, the phenomenon of constancy of the reaction rate constant over a certain agitation speed widely exists in PTC reactions, which are formulated based on an extraction model. Do and Chou [14], Wang and Wu [15], Jayachandran et al. [16], Park et al. [17], and Wang and Tseng [18] proposed the agitation speeds from 200 to 800 rpm. This threshold value changes with changes in the reaction parameters, e.g. the two-phase surface tension will be changed using different organic solvents or adding cationic surfactants, so the maximum two-phase mass transfer rate will be changed under different agitation speeds.

4.2. Effect of the temperature

Fig. 2 shows the effect of temperature on the reaction. As expected, the conversion is increased with higher temperatures. The reaction, which follows a pseudo-first-order rate law, is a type of endothermic without any other side-reactions occurring. From Eq. (20), the apparent rate constant is obtained from the slope of the straight line by plotting $\ln(1 - X)$ versus time. According to Arrhenius law, the activation

energy (E_a) is calculated from the plot of $\ln(k_{app,1})$ versus $1/T$. However, in these kinetic experiments, the data of the apparent rate constant data do not fit an Arrhenius equation because the concentration of QSQ changes with temperature. In addition, the solubility of sodium sulfide (anhydrous without hydrate) is seriously affected by temperature (solubility of anhydride Na_2S in water, g of $Na_2S/100$ g of H_2O: 8.1 (−9 °C); 12.4 (0 °C); 18.6 (20 °C); 29.0 (40 °C); 35.7 (48 °C); 39.0 (50 °C) [19]). Thus, from Le Chatelier's principle, the concentration of QSQ in organic solution increases by increasing temperature.

In addition to the solubility of Na_2S, the other reason is the hydrolysis effect of sulfide ions. The sulfide ion will react with water to generate hydrosulfide and hydroxide ion, which both decrease the concentration of QSQ in organic solution. In the absence of the equilibrium constant (K_{eq}) of this hydrolysis reaction, the enthalpy and entropy values are employed to calculate Gibbs free energy (ΔG). As shown in Table 1, the values of ΔG and K_{eq} at 25 °C are 3.1 and 0.29 kJ mol^{-1}, respectively [20]. It is pointed out that ΔG and K_{eq} are decreased and increased, respectively, with the increase in temperature from thermodynamic laws, so
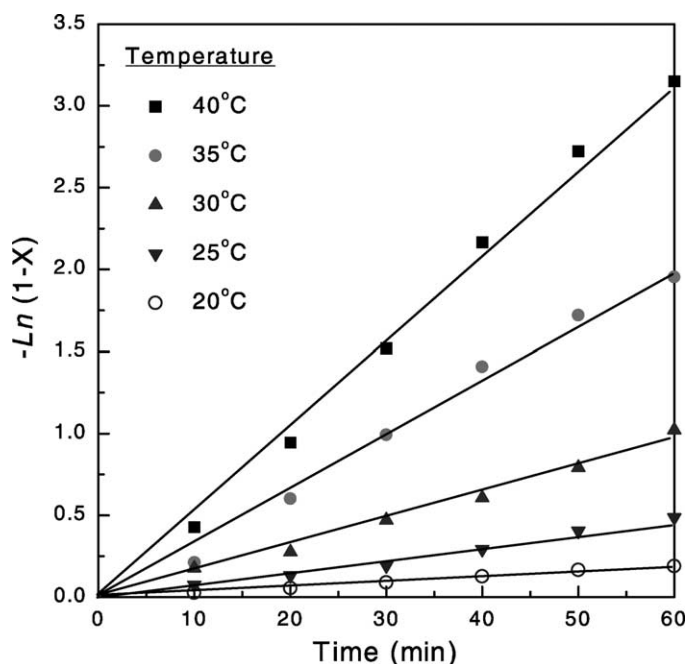
Fig. 2. Effect of the temperature on the conversion of n-bromobutane; 7 g of sodium sulfide, 10 ml of water, 0.31 mmol of TBAB, 4 mmol of n-bromobutane, 40 ml of n-hexane, 500 rpm.

the concentration of sulfide ion in the aqueous phase increases with the increase in temperature. Almost no reaction takes place at low temperatures, and no reaction proceeds at 10 °C or below.

4.3. Effect of the organic solvents

In this work, organic solvents such as: toluene, n-hexane, cyclohexane, chloroform and 1,2-dichloroethane were employed to investigate the effect of their polarities (or dielectric constants) on the synthesis of di-n-butyl sulfide. A plot of $\ln(1 - X)$ versus time with various organic solvents is depicted in Fig. 3 and Table 2. As shown in Table 2, the reactivity order of these organic solvents is: toluene > chloroform > 1, 2-dichloroethane > cyclohexane > n-hexane. However, the reaction rate does not increase with the polarity of organic solvents. The formation of dipole–dipole force from polar solvent and bromide group is favorable for the separation of bromide from the n-butyl group. Also, the higher the polarity of

Table 1
Evaluation of the thermodynamic value of the compounds in the hydrolysis reaction of sulfide ion

Species (298.15 K)	ΔH_f° (kJ mol^{-1}) [20]	ΔS° (J mol^{-1} K^{-1}) [20]
S^{2-} (aq)	35.8	−22.0
H$_2$O (l)	−285.84	69.95
HS$^-$ (aq)	−17.7	56.1
OH$^-$ (aq)	−229.94	−10.5

$\Delta G = \Delta H - T\Delta S = 3.1\,\mathrm{kJ\,mol^{-1}}$; $K_{eq} = k_1/k_{-1} = \exp(-\Delta G/RT) = 0.29$.

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

Organic solvent	Dielectric constant (ε)	$k_{app,1}$ ($\times 10^{-3}$ min^{-1})
Toluene	2.4	12.7
Chloroform	4.8	6.2
1,2-Dichloroethane	10.4	5.5
Cyclohexane	2.02	4.4
n-Hexane	1.88	3.9

7 g of sodium sulfide, 10 ml of water, 0.31 mmol of TBAB, 4 mmol of n-bromobutane, 40 ml of n-hexane, 500 rpm, 30 °C.
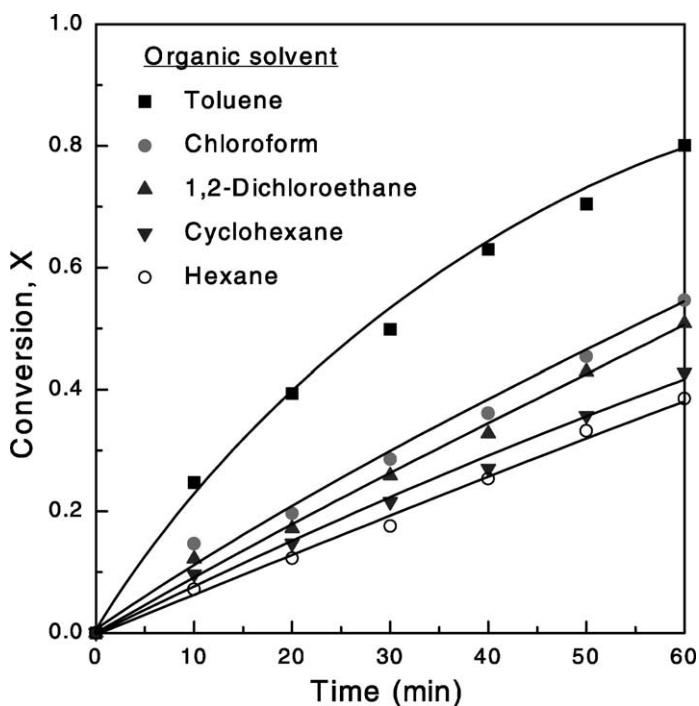
Fig. 3. Effect of the organic solvents on the conversion of *n*-bromobutane; 7 g of sodium sulfide, 10 ml of water, 0.31 mmol of TBAB, 4 mmol of *n*-bromobutane, 40 ml of organic slovent, 500 rpm, 30 °C.

the organic solvent is, the easier it is the Q^+ ion to leave sulfide groups. Hence, it is favorable for the sulfide ion to displace bromide in the S_N2 nucleophilic substitution. Nevertheless, the reactants, both *n*-butyl bromide and QSQ, are also solvated tightly by polar solvent, so those solvents of high polarity hinder collision between reactants. From the competition results of solvation effect and dipole–dipole moment, the relatively medium polar solvent (toluene) is most reactive. Different solvents do not have significant effect on extraction ability to active catalyst because of the large organic-solubility of QSQ. Similar results were also obtained by Wang and Tseng [13].

4.4. Effect of the phase transfer catalysts

In general, there is no universal rule to guide in selecting an appropriate phase transfer catalyst apart from those that determined from experiments. In this work, the Stark's extraction mechanism is employed to explain the reaction characteristics. Five chem-

icals were employed to examine their reactivities: tetrahexylammonium bromide, tetrabutylammonium bromide, tetraethylammonium bromide, benzyltetrabutylammonium bromide, and 4-(tributylammonium) propansultan. The kinetic data are given in Fig. 4. Table 3 depicts the apparent rate constants ($k_{app,1}$) for these five catalysts, of which THAB exhibits the highest reactivity. These results also confirm that the reaction mechanism follows the extraction model.

Table 3
Effect of the catalysts on the apparent rate constants

Catalyst	$k_{app,1}$ ($\times 10^{-3}$ min^{-1})
THAB	17.1
TBAB	11.5
TEAB	3.8
BTEAB	3.1
QSO$_3$	1.8

7 g of sodium sulfide, 10 ml of water, 0.15 mmol of catalyst, 4 mmol of *n*-bromobutane, 40 ml of *n*-hexane, 500 rpm, 40 °C.
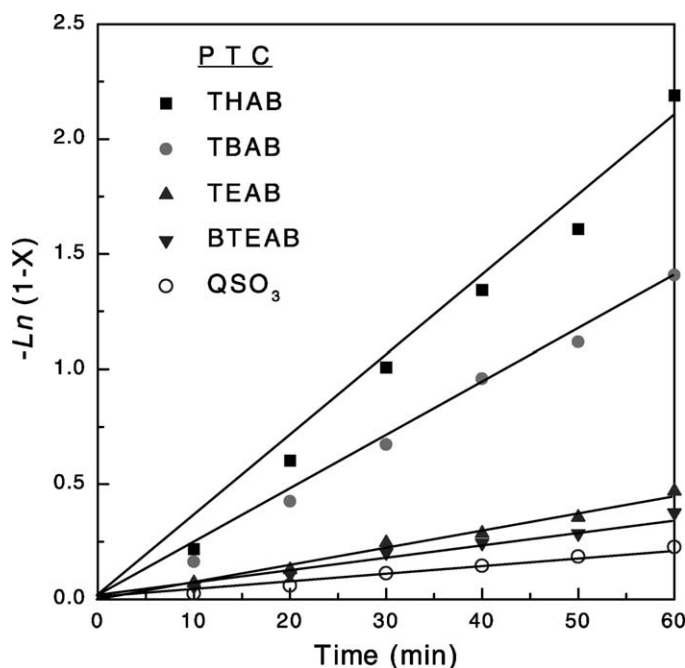
Fig. 4. Effect of the catalysts on the conversion of n-bromobutane; 7 g of sodium sulfide, 10 ml of water, 0.15 mmol of catalyst, 4 mmol of n-bromobutane, 40 ml of n-hexane, 500 rpm, 40 °C.

In general, there are two methods to clarify the mechanism, activation energy and the suitable catalyst. In conclusion, first, the activation energy less than $10 \, \text{kJ} \, \text{mol}^{-1}$ is controlled by diffusion and that larger than $10 \, \text{kJ} \, \text{mol}^{-1}$ is controlled by chemical reaction. Unfortunately, the activation energy is not available with explanation in Section 4.3. Second, the catalyst property in extraction is the ammonium cation with symmetric, long, linear carbon group. The interface reaction (e.g. PTC dichlorocarbene system) is usually against this rule. Comparing the results for THAB, TBAB, and TEAB, indicates that the reactivity of quaternary salt increases with an increase in the total carbon number in the alkyl group of the cation. TEAB is more reactive than BTEAB although the total number of carbon in the cation of TEAB is less than that of BTEAB, in which the benzyl group appears in the unsymmetric cation. The reaction system using the unsymmetric cation easily forms the emulsion solution, which is a retardant state for the regeneration of catalysts. The experimental results verify this reaction mechanism. QSO$_3$ is a Zwitterionic compound and widely applied as bio-cleaner. It tends to be anionic

(Q^-) in a base and cationic (Q^+) in an acid, so the concentration of Q^+ is very low in the alkaline solution. Therefore, the reaction rate of QSO$_3$ and Na$_2$S to produce the active catalyst QSQ is low. It is worthwhile to modify the cation of QSO$_3$ to serve as phase transfer catalyst because of its low price, which is about 1/20 of the price of TBAB.

4.5. Effect of the amount of TBAB catalyst

The effect of the amount of TBAB catalyst on the apparent rate constant is shown in Fig. 5. The reaction follows a pseudo-first-order law using 1-C$_4$H$_9$Br as a limiting component. In the absence of catalyst, the reaction rate is low, and only $7.5 \times 10^{-4} \, \text{min}^{-1}$ for the apparent rate constant is obtained. However, the conversion is increased to 52% after 60 min of reaction after 0.05 g of TBAB catalyst is added. Furthermore, n-bromobutane is completely converted to di-n-butyl sulfide after 60 min of reaction with use of 0.125 g of TBAB. Thus, the apparent rate constant is highly dependent on the amount of TBAB catalyst. As shown in Fig. 5, the apparent rate constant increases linearly
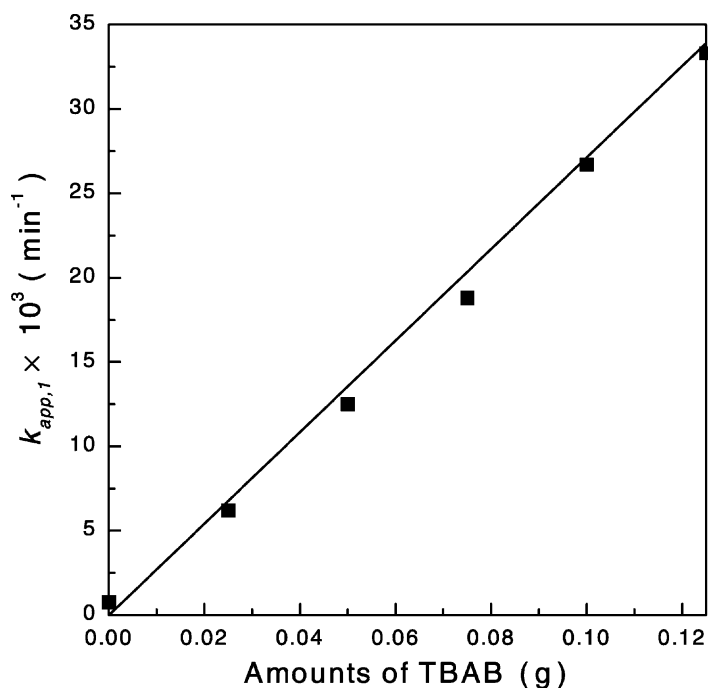
Fig. 5. Effect of the amount of TBAB on the apparent rate constant ($k_{app,1}$) in the organic phase; 7 g of sodium sulfide, 10 ml of water, 4 mmol of *n*-bromobutane, 40 ml of *n*-hexane, 40 °C, 500 rpm.

with the amount of TBAB catalyst. Eq. (18) is simplified for only the partition coefficient M_{QSQ} larger than 1. This result indicates that the apparent rate constant ($k_{app,1}$) was determined only by the amount of the initial addition of the catalyst. These results are very consistent with Eq. (18). Similar observations were made by Starks and Owens [3], Herriott and Picker [21], Sharma and Pradhan [22], and Gaitonde [23] under various phase transfer catalytic reactions.

4.6. Effect of the amount of sodium sulfide

The effect of the amount of sodium sulfide on the reaction rate was studied in the range of 2–20 g, and four interesting reaction periods were observed, as depicted in Fig. 6. First, no reaction takes place in 2–4 g of Na_2S; second, the reaction rate increases rapidly during 4–6.5 g of Na_2S; third, the rate constant is maintained at a constant rate with $k_{app,1} = 11.5 \times 10^{-3} min^{-1}$ in 6.5–14 g of Na_2S; finally, the reaction rate is seriously retarded over 14 g of Na_2S. The reason for first period is hydrolysis of sulfide (Scheme 1), which directly reduces the concentration of sulfide ion. The aqueous solution is rust-colored and similar to the appearance of sodium hydrosulfide solution. The active intermediate, QSQ, is not produced in this range, so reaction does not occur. In the second period, the concentration of sulfide ion increases with the increase in the amount of Na_2S. QSQ is produced in aqueous phase and transferred through interface to react with *n*-bromobutane. The sodium sulfide solution is saturated in 6.5 g of Na_2S (with hydrate) in 10 ml of water, and precipitated over 6.5 g (with hydrate). The concentration of sulfide ion is the highest value and constant in third period, so the rate constant is not changed and remains at a constant value. In fourth period, the amount of precipitation of Na_2S is quickly increased and the volume of water is decreased due to the crystallization of sodium sulfide (with hydrate). The appearance of the precipitate changes from maize color to white-transparent crystals from the third to the fourth period. Both precipitates from these two periods are isolated and analyzed for hydration molecule number by thermogravimetric instrument (TGA). The average
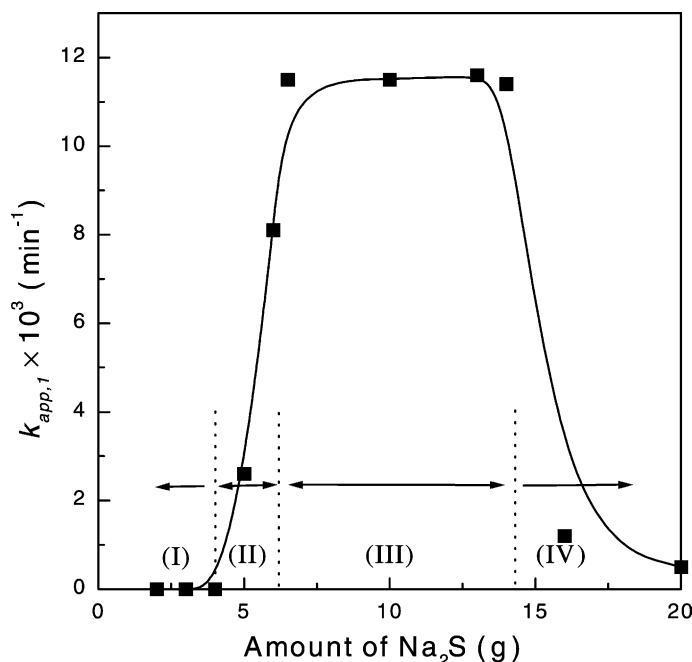
Fig. 6. Effect of the amount of sodium sulfide on the apparent rate constant ($k_{app,1}$) in the organic phase; 10 ml of water, 0.15 mmol of TBAB, 4 mmol of n-bromobutane, 40 ml of n-hexane, 40 °C, 500 rpm.

hydration number of precipitation in the third period is about 3.6, and similar to the initial addition reactant ($Na_2S·3.5H_2O$). The hydration number of precipitation in the final period is 8.9. TGA results indicate the reason for a low rate in the fourth period. Over 14 g of sodium sulfide, $Na_2S·3.5H_2O$ is recrystallized to $Na_2S·9H_2O$ and absorbs aqueous phase for crystallization. Aqueous phase does not exist with using 20 g of Na_2S, and the reaction rate is very slow. In addition, the reaction type changes from a liquid–liquid reaction to a solid–liquid or a solid–liquid–liquid (little aqueous phase) reaction. The reaction rate of 20 g of $Na_2S·3.5H_2O$ is $5 × 10^{-4}$ min^{-1} and is close to the solid–liquid reaction ($4.1 × 10^{-4}$ min^{-1}), in which 25 g of $Na_2S·9H_2O$ is used to react in the same conditions, except in the absence of water.

4.7. Effect of the amount of sodium hydroxide

In principle, the pH value of the aqueous phase affects the distribution of the active catalyst between two phases, and the solubility of sodium sulfide in the aqueous phase. The effect of NaOH, which is added

to the participate reaction, is investigated in this work. As shown in Fig. 7, an optimal value of the amount of NaOH (1.3 g) to obtain a maximum value of $k_{app,1}$ is presented. Below 1.3 g of NaOH, the reaction rate is enhanced by increasing the amount of NaOH. In contrast, the rate constant is decreased with increase in the amount of NaOH over 1.3 g of NaOH. This peculiar phenomenon is caused by the interaction of the three factors. First, the pH value of the aqueous phase is raised with adding alkaline salt. The solvation effect of quaternary ammonium cation is weak in base condition, so the further addition of NaOH reduces the hydration number of QSQ and increases the activity of QSQ. Second, the solubility of sodium sulfide in aqueous phase is much lower than NaOH. Also, the solubility of sodium sulfide decreases with the increase in the concentration of NaOH because of the same cation effect. Thus, the effect of salting out due to the addition of NaOH is not significant using less than 1.3 g of NaOH in this reaction condition. Third, according to Le Chatelier's principle for the reaction, as shown in Scheme 1, with higher concentrations of hydroxide anion, there is higher concentration of
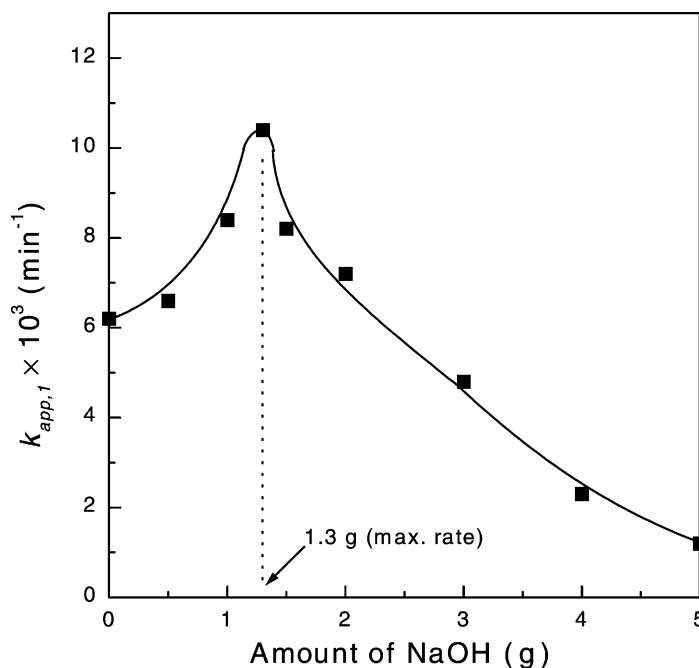
Fig. 7. Effect of the amount of NaOH on the conversion of *n*-bromobutane; 7 g of sodium sulfide, 10 ml of water, 0.08 mmol of TBAB, 4 mmol of *n*-bromobutane, 40 ml of *n*-hexane, 500 rpm, 40 °C.

sulfide anion in the aqueous phase. From this point of view, the reaction rate constant is enhanced with the concentration of NaOH. An optimal amount of NaOH is generated from the competition between three factors. Then, sodium sulfide begins to salt out with the use of 0.5 g NaOH, and a large amount of sodium sulfide is salted out with the addition of 3–5 g of NaOH. As shown in Fig. 7, the reaction rate with addition of 3–5 g NaOH is lower than without this addition. The effect of salting out addition of NaOH is more effective than the others with addition of 3–5 g NaOH. Therefore, the reaction is enhanced with addition property amount of NaOH ($k_{app,1}^{1.3\,g\,of\,NaOH}/k_{app,1}^{none} = 1.68$), but it is clearly retarded by using an excess amount of NaOH ($k_{app,1}^{none}/k_{app,1}^{5\,g\,of\,NaOH} = 5.17$).

4.8. Effect of the volume of 5.56 M sodium sulfide solution

This work also investigates the effect of the volume of sodium sulfide solution (5.56 M) on the reaction, finding that the reaction rate is increased with an increase in the volume of sodium sulfide solution. Al-

though the concentration of QBr in aqueous phase is decreased with the increase in the volume of aqueous solution, the interface contact area is increased by increasing the volume of the aqueous solution. The conversion is increased with the increase of mass transfer area. As shown in Fig. 8, the reaction rate constant using 20 ml of sodium sulfide solution is twice that using 5 ml. The apparent rate constant ($k_{app,1}$) is highly dependent on the volume of sodium sulfide solution.

4.9. Effect of the volume of organic solvent

The effect of the volume of *n*-hexane on the reaction rate was studied in the range 10–60 ml. As shown in Fig. 9, the reaction rate decreases with an increase in the volume of *n*-hexane. Although the interface contact area is increased by increasing the volume of organic solvent, at the same time, the concentrations of active intermediate (QSQ) and *n*-butyl bromide both decrease with the increase in *n*-hexane. The result of Section 4.5 indicates that the partition coefficient (M_{QSQ}) is larger than 1, so the first apparent reaction rate constant increases linearly with the decrease in
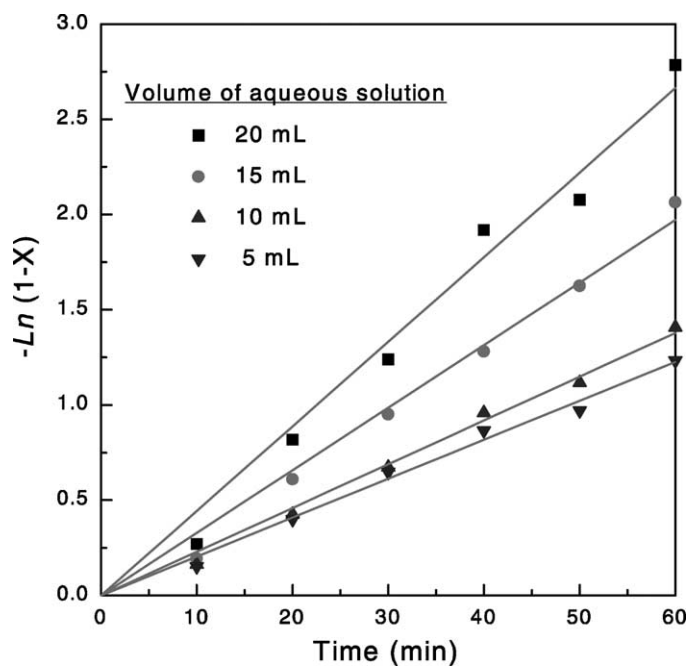
Fig. 8. Effect of the amount of sodium sulfide solution (5.56 M) on the conversion of n-bromobutane; 0.15 mmol of TBAB, 4 mmol of n-bromobutane, 40 ml of n-hexane, 500 rpm, 40 °C.
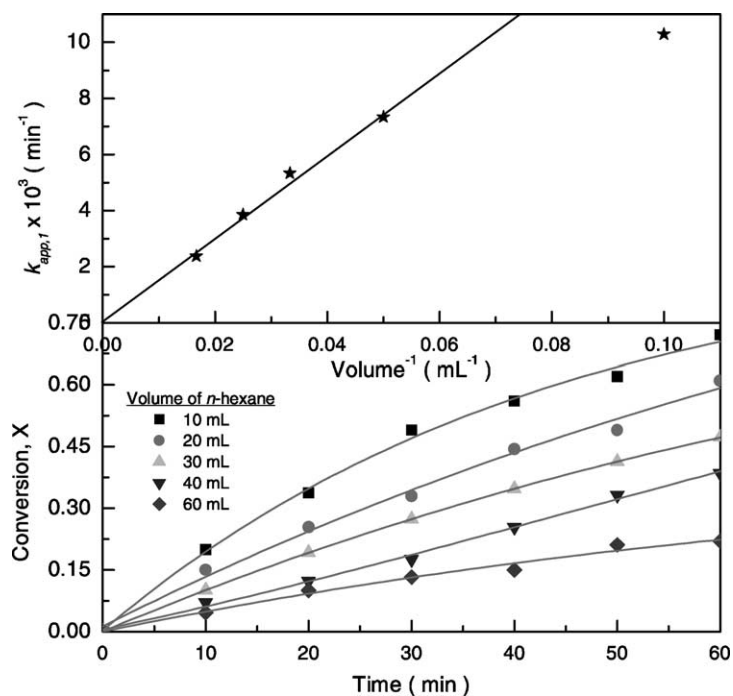

Fig. 9. Effect of the volume of organic solvent on the apparent rate constant ($k_{app,1}$) and conversion of n-bromobutane; 7 g of sodium sulfide, 10 ml of water, 0.31 mmol of TBAB, 4 mmol of n-bromobutane, 500 rpm, 25 °C.
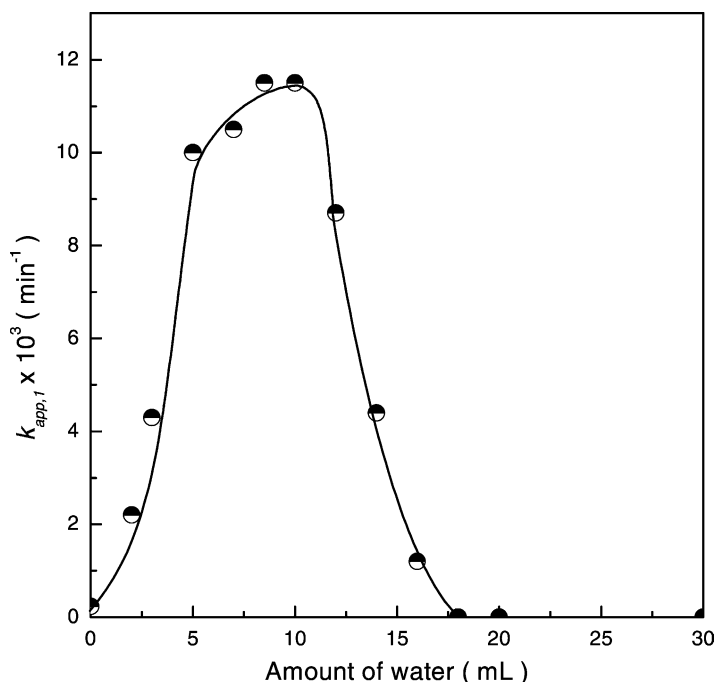
Fig. 10. Effect of the amount of water on the apparent rate constant ($k_{app,1}$) in the organic phase; 7 g of sodium sulfide, 0.15 mmol of TBAB, 4 mmol of n-bromobutane, 40 ml of n-hexane, 40 °C, 500 rpm.

volume of organic solvent due to Eq. (18). The results, as shown in Fig. 9, are very consistent with the inference in the range 20–60 ml (e.g. $k_{app,1}^{20\,ml}/k_{app,1}^{40\,ml} = 1.9$). However, the rate constant was not enhanced as expectedly in the 10 ml of n-hexane due to the effect of interface contact area ($k_{app,1}^{10\,ml}/k_{app,1}^{20\,ml} = 1.4$). Therefore, the effect of mass transfer is not significant over 20 ml of the organic solvent.

4.10. Effect of the amount of water

In general, the effect of the amount of water on the reaction rate of liquid–liquid PTC reactions is usually great [2,3,10–18]. In this work, this effect on the PTC thioetherification reaction was studied in the range of 0–30 ml with 7 g of sodium sulfide. As shown in Fig. 10, an optimal amount of water is 10 ml with $k_{app,1} = 11.5 \times 10^{-3}\,min^{-1}$ (maximum value). The reaction would not proceed in the absence of water, or with using over 16 ml of water, respectively. The reason for a low reaction rate in the anhydrous condition is that the active intermediate (QSQ) is generated with difficulty, and the biphasic contact area is very

small in the solid–liquid reaction. This phenomenon is similar to the case for using 20 g of sodium sulfide in the Section 4.6. No reaction occurred in the excess amount of water (16–30 ml) due to the hydrolysis of sulfide anion. Thus, only hydrosulfide anions present in the aqueous phase and the QSQ was not generated under this condition. This phenomenon is also similar to the case using 2–4 g of sodium sulfide in the Section 4.6. Below 10 ml of water, the precipitation of sodium sulfide clearly occurs, and the amount of water is decreased due to the recrystallization of sodium sulfide. On the contrary, the hydrolysis of sulfide anion is effective to retard the reaction rate. Therefore, an optimal amount of water is generated from the competition between two factors—the hydrolysis of sulfide anion and the decrease of interface contact area.

5. Conclusion

In this work, di-n-butyl sulfide was successfully synthesized by the phase transfer catalytic reaction, which was carried out from the reaction of sodium

sulfide and n-bromobutane in an alkaline solution/organic solvent two-phase medium. The kinetic model was satisfactorily constructed to account for the factors of the reaction. Two sequential reactions of the active catalyst and n-bromobutane in the organic phase for the S_N2 substitution were indicated. However, only the final di-tetrabutylammonium-substituted product was obtained. The second intrinsic rate constant ($k_{app,2}$) in the organic phase is much larger than the first intrinsic rate constant ($k_{app,1}$), so that the first S_N2 reaction is the rate determining step. The reaction is not influenced by an agitation speed larger than 350 rpm. Due to solvation effect, hydrolysis effect, distribution of active catalyst, interface area, as well as the solubility and recrystallization of sodium sulfide; thus, 1.3 g of NaOH, 7 g of Na_2S, and 10 ml of water are the optimum values. The peculiar phenomenon was satisfactorily explained by these effects. In this work, the largest yield was obtained by using THAB as the phase transfer catalyst. The reaction rate is increased with the increase in the volume of Na_2S solution.

Acknowledgements

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