



Selectivity engineering in multiphase transfer catalysis in the preparation of aromatic ethers

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Abstract

Phase transfer catalysis (PTC) is a very mature discipline now. However, there are hardly any studies on the theoretical and experimental analysis of the effect of nature and number of phases on enhancement of rates and selectivities. PTC reactions can be carried out in liquid–liquid (L–L), solid–liquid (S–L), and liquid–liquid–liquid (L–L–L) and solid–liquid–liquid (S–L–L) conditions bringing into picture dominance of mass transfer effects. The current work addresses these issues in the alkylation reaction of β -naphthol with benzyl chloride with the C- and O-alkylation being the competing reactions. The role of various phases in enhancing the selectivity towards benzyl-2-naphthyl ether has been extensively investigated. The L–L–L PTC process has been found to be the most effective and economical route giving only the desired ether within a short reaction times and high catalyst reusability, unlike the L–L PTC process. A mathematical model is developed to establish the rate constant.

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1. Introduction

Phase transfer catalysis (PTC) is now a commercially matured discipline with over 600 applications covering a wide spectrum of industries such as pharmaceuticals, agrochemicals, perfumes, flavors, dyes, speciality polymers, pollution control, etc [1–3]. Alkylation reactions (C, O, N and S) are one of the most widely studied reactions under PTC and some of these may be competing reactions depending on the substrate [4–13]. Aromatic ethers and their substituents are used in a variety of industries and are produced by PTC routes.

The selective preparation of O-alkylated aromatic products from substituted phenol and naphthols is challenging. Liquid–liquid (L–L), solid–liquid (S–L) and

liquid–liquid–liquid (L–L–L) PTC have been used to prepare phenolic ethers from *o*- and *p*-chloronitrobenzene using methanol, ethanol and *n*-butanol in our laboratory [4–6]. The role of omega phase in C-alkylation S–L PTC has been illustrated from fundamental view points by us [7–9]. The L–L–L PTC gives 100% selectivity towards the formation of O-alkylated product and avoids the formation of competing C-alkylation reaction [4,5,11,13]. A variety of ethers can be prepared advantageously by using any of the techniques [14].

Benzyl naphthyl ethers are versatile compounds. The alkylation of β -naphthol with benzyl chloride can lead to both C- and O-alkylated β -naphthol and both these compounds are used as precursors in several industries. The O-alkylated product, benzyl-2-naphthyl ether (2-benzyloxynaphthalene) is used in preparation of thermographic recording materials as additive, as an aromatic sensitizer in heat-sensitive recording material for excellent coloring and printed image stability. Thus, preparation of benzyl-2-naphthyl ether was considered

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Nomenclature

C_{Ao}	feed concentration of benzyl chloride in the organic phase (mol/cm ³)
C_{A-org}	concentration of benzyl chloride in the organic phase (mol/cm ³)
$C_{A-third}$	concentration of benzyl chloride in the third phase (mol/cm ³)
K_A	distribution coefficient of benzyl chloride between the organic phase and the third phase (dimensionless)
k_{inter}	rate of reaction at the interface between the organic and aqueous phases (cm ³ /mol of catalyst)
k_{obs}	observed first-order reaction rate constant (cm ³ /mol of catalyst)
k_{org}	rate of reaction in the organic phase (cm ³ /mol of catalyst)
k_{third}	rate of reaction in the third phase (cm ³ /mol of catalyst)
N_{Ao}	feed mole of benzyl chloride (mol)
N_{A-org}	mole of benzyl chloride in the organic phase (mol)
$N_{A-third}$	mole of benzyl chloride in the third phase (mol)
N_{Qo}	feed mole of catalyst (mol)
N_{Q-aq}	mole of catalyst in the aqueous phase (mol)
N_{Q-org}	mole of catalyst in the organic phase (mol)
$N_{Q-third}$	mole of catalyst in the third phase (mol)
t	time of reaction (min)
v_{third}	volume of third phase per feed mol of catalyst (cm ³ /mol of catalyst)
V_{third}	volume of the third phase (cm ³)
V_{org}	volume of organic phase (cm ³)
ω	concentration of catalyst based on the organic phase (mol/cm ³ of organic)
ψ_{aq}	mole fraction of catalyst in the aqueous phase to the feed of catalyst (dimensionless)
ψ_{org}	mole fraction of catalyst in the organic phase to the feed of catalyst (dimensionless)
ψ_{third}	mole fraction of catalyst in the third phase to the feed of catalyst (dimensionless)

under this study. The L–L–L PTC reaction is far superior to L–L PTC reaction as has been brought out by us in several publications.

The advantages of L–L–L PTC over L–L PTC are:

- increased rate of reaction;
- easier catalyst recovery and reuse; and
- the catalyst need not be bound to solid support as is required for L–L–S PTC.

The L–L–L PTC however suffers from following disadvantages:

- More amount of catalyst (PTC) is required, which is expensive.
- The method is not applicable for the system where a very high temperature is required to carry out the reaction. As the temperature increases, the stability of the third liquid phase decreases. However, if the catalyst is stable then at the end of the reaction it could be easily separated into a third phase at lower temperature for recovery and reuse.

It was therefore thought worth while to study the effect of etherification of β -naphthol with benzyl chloride in L–L–L PTC.

β -Naphthoxide is an ambident anion capable of covalency formation at oxygen or at the α -carbon. Gomberg and Buchler [15] were the first to observe the carbon alkylation. Zagorevsky [16] investigated the alkylation of the solutions of β -naphthoxide salts using a variety of solvents. Kornblum and Laurie [17] studied the importance of solvation in the synthesis of 2-benzyloxynaphthalene; reaction of sodium with benzyl bromide employing DMF solvent resulted in 97% yield of benzyl 2-naphthyl ether while with trifluoroethanol resulted in 85% yield of 1-benzyl-2-naphthol. McKillop et al. [18] developed a simple and efficient process for the synthesis of ethers of both simple and hindered phenols, using PTC, which involves alkylation of the phenoxide ion with an alkyl halide or sulphate esters using quarternary ammonium salts in a methylene chloride–water system at room temperature. Yadav and Bisht [19] developed a simple but general mathematical model for analysing the rate data for displacement type L–L PTC reactions in laboratory reactors under conventional thermal heating and microwave irradiation. Yadav [20] has given an analysis of effect of nature and number of phases in influencing selectivities in PTC alkylation reactions.

This paper discusses the theoretical and experimental investigation of the selective O-alkylation of β -naphthol with benzyl chloride.

2. Experimental

2.1. Materials

Benzyl chloride, β -naphthol, toluene, sodium chloride, and sodium hydroxide, all of AR grade were obtained from M/s s.d. Fine Chemicals Pvt. Ltd., Mumbai, India. Tetrabutylammonium bromide (TBAB) was obtained as a gift sample from M/s Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India.

2.2. Procedure

The reactions were studied in a 5.0 cm (i.d.) fully baffled mechanically agitated contactor of 100 cm³ total capacity, which was equipped with a 6-blade-turbine impeller. The reactor was kept in a constant temperature water bath. Typical runs were conducted by taking 0.01 mol β -naphthol,

Table 1
Characteristics of third phase

Phase	Volume (ml), before reaction	Volume (ml), after reaction
Organic phase	23.0	24.0
Aqueous phase	23.0	22.0
Third phase	5.0	2.0

0.012 mol of NaOH and 0.051 mol of NaCl in water and made upto 25 ml. To this 6.2×10^{-3} mol of TBAB catalyst was added. The organic phase comprised of 0.01 mol of benzyl chloride made upto 25 ml with toluene. All the typical reactions were carried out at 70 °C and 1000 rpm. This composition of the reaction mixture created three distinct and stable phases at the operating conditions.

2.3. Method of analysis

Samples were withdrawn periodically and GC analyses were performed (Chemito Model 8610) by using a stainless steel column (3.25 mm \times 4 m) packed with a liquid stationary phase of 10% OV-17. The conversion was based on the disappearance of benzyl chloride in the organic phase. The melting point of isolated benzyl-2-naphthyl ether (99.0% purity) was found to be 95–96 °C (literature value 99–100 °C) [8]. The products were confirmed by GC–MS.

2.4. Determination of third phase composition

The composition of the third phase was analyzed on gas chromatography using thermal conductivity detector (Chemito Model 8510) by using a stainless steel column (3.25 mm \times 4 m) packed with a liquid stationary phase of 10% OV-17. The third phase at the end of reaction was found to contain 13.0% toluene, 13.0% TBAB, 3.0% β -naphthol, 1.0% benzyl chloride, 1.5% benzyl-2-naphthyl ether and 68.5% water by weight. The amount of the water present in the third phase was analyzed by Karl–Fisher apparatus. The appropriate details are given in Table 1. Composition of the catalyst phase before the reaction and after the completion of the reaction is given in Table 2. The distribution of catalyst at the end of the reaction is given in Table 3.

Table 2
Composition of third phase

Components	Before reaction (wt.%)	After reaction (wt.%)
Water	68.0	68.5
TBAB	21.5	13.0
Toluene	0	13.0
β -Naphthol	10.5	3.0
Benzyl chloride	0	1.0
Benzyl-2-naphthyl ether	0	1.5
Density	0.8254	0.8048

Table 3
Distribution of catalyst

Total catalyst added = 0.0062 mol; third phase = 0.000806 mol
Aqueous phase = 0.005394 mol
ψ_{third} = mole fraction of catalyst in third phase with reference to original amount = $0.000806/0.0062 = 0.13$
ψ_{aq} = mole fraction of catalyst in organic phase with reference to original amount = $0.005394/0.0062 = 0.87$
Amount of benzyl chloride taken = 0.01 mol
Amount of benzyl chloride in third phase = 0.0001 mol
Amount of benzyl chloride in organic phase = 0.0099 mol
$K_A = \frac{N_{A\text{-third}} V_{\text{org}}}{N_{A\text{-org}} V_{\text{third}}} = \frac{0.0001 \times 25}{0.0099 \times 2} = 0.1263$

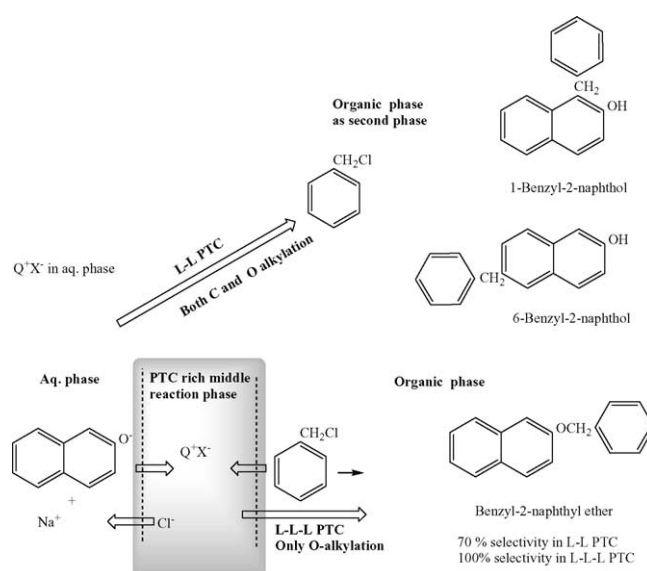
3. Results and discussion

β -naphthol reacts with benzyl chloride in presence of the phase transfer catalyst to give selectively benzyl-2-naphthyl ether in three liquid PTC system whereas it drops down to 70% in two liquid phase PTC (Scheme 1).

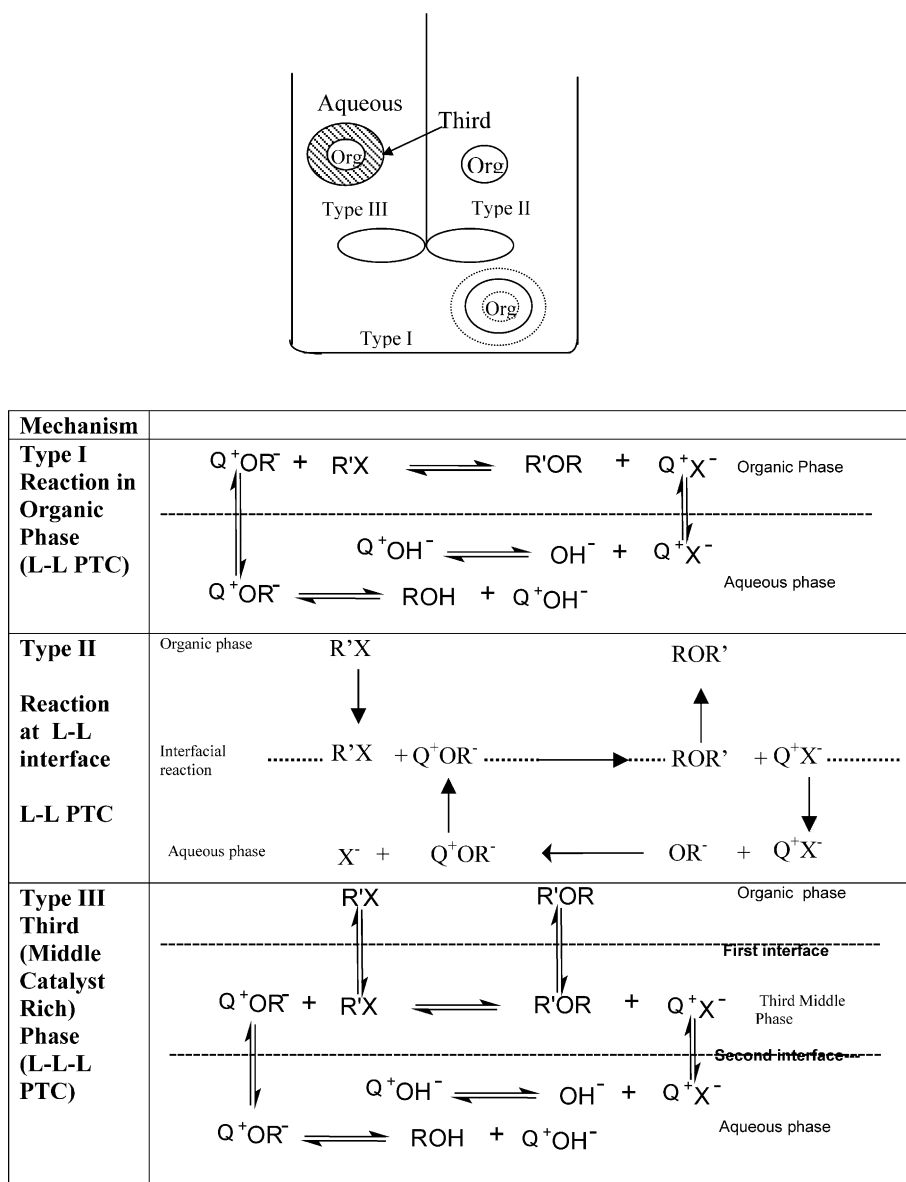
3.1. Kinetics of reaction

For the three-phase system, the organic reactant benzyl chloride (A) is distributed between an organic phase and a third phase but is not in an aqueous phase because of insolubility, Fig. 1. Therefore, the reaction can be classified into three types as proposed by Yadav and Reddy [4], namely: (a) Type I: the reaction in the organic phase (L–L PTC); (b) Type II: the reaction at the interphase between an organic phase and an aqueous phase or in the bulk aqueous phase (L–L inverse PTC); and (c) Type III: the reaction in the third phase. The mole balance for A is:

$$N_{A0} = N_{A\text{-org}} + N_{A\text{-third}} \quad (1)$$



Scheme 1. Effect of number of phases on selectivity in alkylation of β -naphthol with benzyl chloride.

Fig. 1. Mechanism for the O-alkylation of β -naphthol under L-L and L-L-L PTC conditions.

where N_{A0} is the total moles of A, which is distributed between the organic ($N_{A\text{-org}}$) and the third phase ($N_{A\text{-third}}$).

When the distribution of A between an organic phase and a third phase is at equilibrium conditions, the distribution coefficient of A is defined as follows:

$$K_A = \frac{C_{A\text{-third}}}{C_{A\text{-org}}} = \frac{N_{A\text{-third}} V_{\text{org}}}{N_{A\text{-org}} V_{\text{third}}} \quad (2)$$

where C_A stands for concentration of A (benzyl chloride); V_{org} and V_{third} are the volumes of the organic and third phases, respectively.

The following equation can be obtained from Eqs. (1) and (2):

$$N_{A0} = N_{A\text{-org}} \left(1 + K_A \times \frac{V_{\text{third}}}{V_{\text{org}}} \right) \quad (3)$$

Since the reaction rate is assumed to be proportional to the concentration of the A and the amount of catalyst, the overall reaction rate can be expressed by the summation of respective rates for the three types: I, II, III.

$$\begin{aligned} -\frac{dN_A}{dt} &= k_{\text{org}} N_{Q\text{-org}} C_{A\text{-org}} + k_{\text{inter}} N_{Q\text{-aq}} C_{A\text{-org}} \\ &\quad + k_{\text{third}} N_{Q\text{-third}} C_{A\text{third}} = (k_{\text{org}} \psi_{\text{org}} + k_{\text{inter}} \psi_{\text{aq}} \\ &\quad + k_{\text{third}} K_A \psi_{\text{third}}) N_{Q0} C_{A\text{-org}} \end{aligned} \quad (4)$$

where ψ 's are mole fractions of catalyst present in the respective phases, based on the mole of catalyst N_{Q0} , added initially.

When Eq. (4) is integrated, Eq. (5) is obtained:

$$1 - X_A = \frac{N_{A\text{-org}}}{N_{A0}} = \frac{V_{\text{org}}}{V_{\text{org}} + K_A V_{\text{third}}} \exp(-k_{\text{obs}} \omega t) \quad (5)$$

where N_{A0} are the moles of A originally taken and $X_A = (N_{A0} - N_A)/N_{A0}$, is the fractional conversion of A,

$$k_{\text{obs}} = \frac{V_{\text{org}}}{V_{\text{org}} + K_A V_{\text{third}}} (k_{\text{org}} \psi_{\text{org}} + k_{\text{inter}} \psi_{\text{aq}} + k_{\text{third}} K_A \psi_{\text{third}}) \quad (6)$$

and

$$\omega = \frac{N_{Q0}}{V_{\text{org}}} \quad (7)$$

When $K_A V_{\text{third}}$ is negligibly small compared to V_{org} , Eq. (6) can be approximated as follows:

$$k_{\text{obs}} = (k_{\text{org}} \psi_{\text{org}} + k_{\text{inter}} \psi_{\text{aq}} + k_{\text{third}} K_A \psi_{\text{third}}) \quad (8)$$

Taking logarithm of Eq. (5) leads to Eq. (9):

$$-\ln(1 - X_A) = k_{\text{obs}} \omega t \quad (9)$$

For a given concentration of catalyst ω and k_{obs} is constant, therefore,

$$-\ln(1 - X_A) = k_1 t \quad (10)$$

where $k_1 = k_{\text{obs}} \omega$. (11)

For respective types of mechanisms, the following equations are obvious:

$$k_{\text{obs}} = k_{\text{org}} \text{ for Type 1 } (\psi_{\text{org}} = 1.0); \quad (12)$$

it is normal L–L PTC with organic phase as the locale of the main reaction

$$k_{\text{obs}} = k_{\text{aq}} \text{ for Type 2 } (\psi_{\text{aq}} = 1.0); \quad (13)$$

it is inverse L–L PTC with aqueous phase as the locale of the main reaction

$$k_{\text{obs}} = k_{\text{third}} K_A \text{ for Type 3 } (\psi_{\text{third}} = 1.0); \quad (14)$$

it is L–L–L PTC with the middle catalyst rich phase as the locale of the main reaction.

The kinetic parameters k_{org} , k_{aq} and k_{third} ; and K_A can be determined from experiments.

3.2. Effect of speed of agitation

To ascertain the influence of mass transfer resistance of the reactants to the reaction phase, the speed of agitation was varied in the range of 600–1200 rpm under otherwise similar conditions in the presence of TBAB catalyst. The conversion is plotted as a function of time in Fig. 2. The conversion was found to be practically the same at 1000 and 1200 rpm. Further increase in the speed of agitation had practically no effect on the conversion. Thus, further experiments were carried out at 1000 rpm.

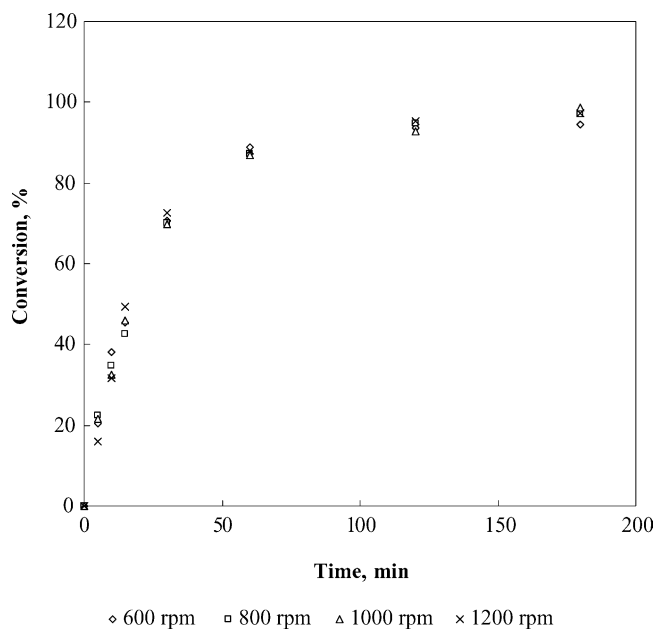


Fig. 2. Effect of speed of agitation. β -Naphthol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, TBAB 0.0062 mol, toluene 25 cm³, water 25 cm³, and temperature 70 °C.

3.3. Effect of catalyst concentration

The concentration of the TBAB catalyst was varied from 0.062×10^{-3} to 0.312×10^{-3} mol/cc. The conversion is plotted against time for different catalyst concentration under otherwise similar reaction conditions. Fig. 3 shows that with the increase in the concentration of the catalyst there is an in-

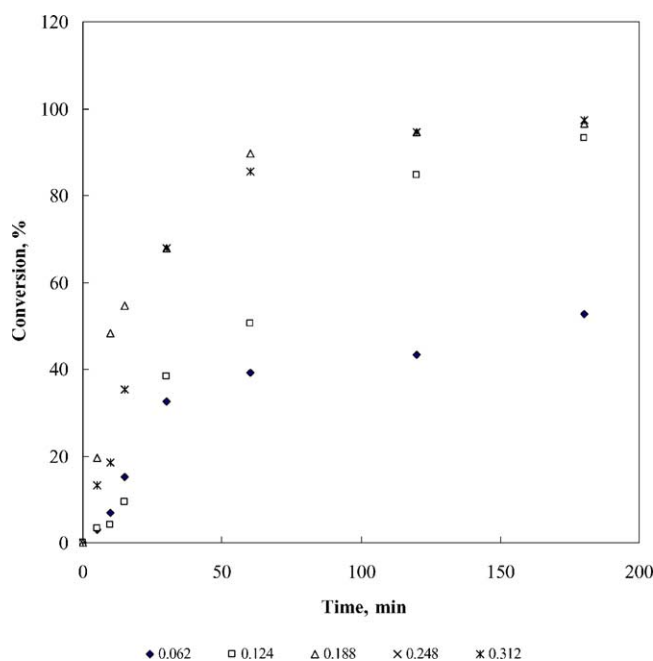


Fig. 3. Effect of catalyst concentration ($\times 10^{-3}$ mol/cc). β -Naphthol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, toluene 25 cm³, water 25 cm³, temperature 70 °C, RPM 1000.

crease in the conversion, which is the characteristic of a PTC reaction. At catalyst concentration of 0.062×10^{-3} mol/cc the selectivity of the benzyl-2-naphthyl ether was 70%. The L–L PTC conditions exist at this catalyst loading. With increase in the catalyst concentration to 0.124×10^{-3} mol/cc the third catalyst rich liquid phase appeared and the 100% selectivity of benzyl-2-naphthyl ether was obtained. For all the reactions 0.248×10^{-3} mol/cc of the catalyst was used as the conversion obtained at this catalyst loading was found to be optimum.

3.4. Effect of NaOH concentration

Sodium hydroxide concentration was varied from 0.4×10^{-3} to 0.8×10^{-3} mol/cc under otherwise similar reaction conditions (Fig. 4). In these experiments, NaOH concentration was kept at 0.4, 0.48, 0.6 and 0.8×10^{-4} mol/cc. The conversion was low at low concentrations of NaOH because the formation of ion-pair between the β -naphthol and catalyst does not proceed unless the HCl is neutralized and the equilibrium is distributed. The best conversion was obtained with 0.48×10^{-4} mol/cc of NaOH. Further increase in the NaOH concentration did not have any effect on the conversion and selectivity pattern. The mechanism of the reaction shows that so long as NaOH is taken in excess over the stoichiometric amount, all catalyst is in the form Q^+OR^- (aq) which is transferred across the interface for the reaction to take place in the middle phase with R'X. Thus Fig. 4 shows that the conversions are independent of NaOH concentration.

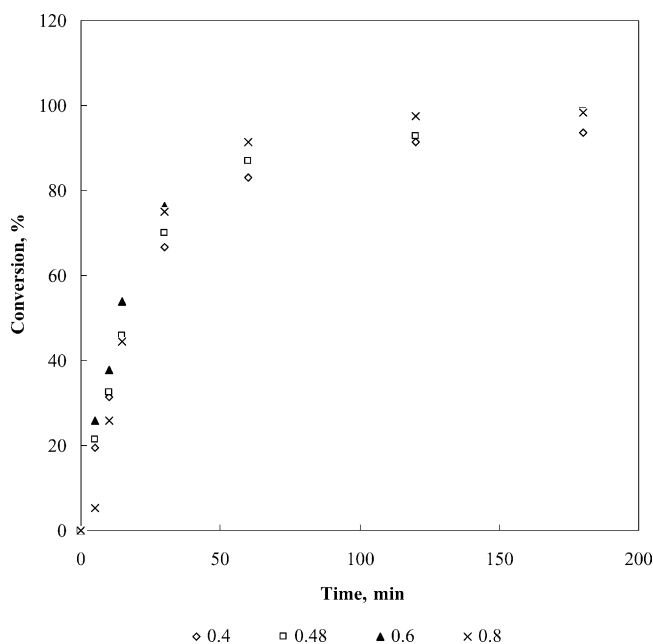


Fig. 4. Effect of NaOH concentration ($\times 10^{-3}$ mol/cc). β -Naphthol 0.01 mol, Benzyl chloride 0.01 mol, TBAB 0.0062 mol, toluene 25 cm^3 , water 25 cm^3 , temperature 70°C , RPM 1000.

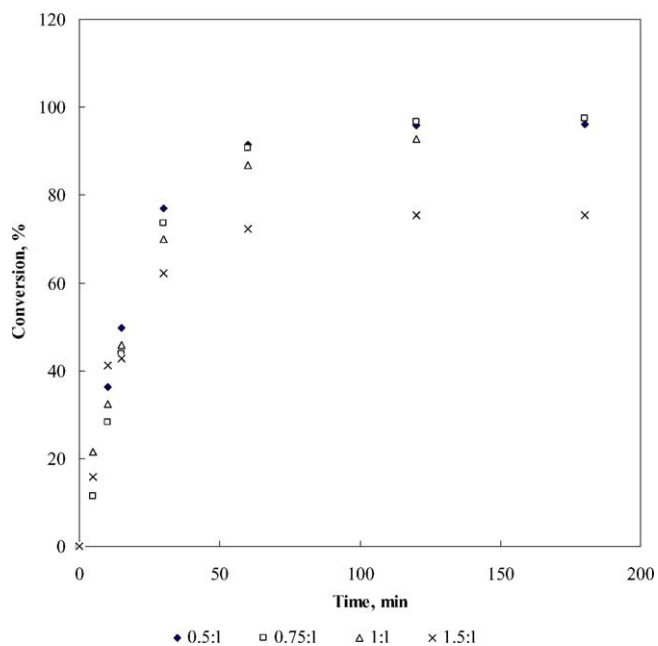


Fig. 5. Effect of mole ratio of benzyl chloride to β -naphthol on conversion of limiting reactant. β -Naphthol:NaOH 1:1.2, TBAB 0.0062 mol, toluene 25 cm^3 , water 25 cm^3 , temperature 70°C , RPM 1000.

3.5. Effect of mole ratio

Effect of change in mole ratio of reactants benzyl chloride: β -naphthol was studied by varying it in the range of 0.5:1–1.5:1. The conversion remained practically the same with increase in the benzyl chloride concentration, except

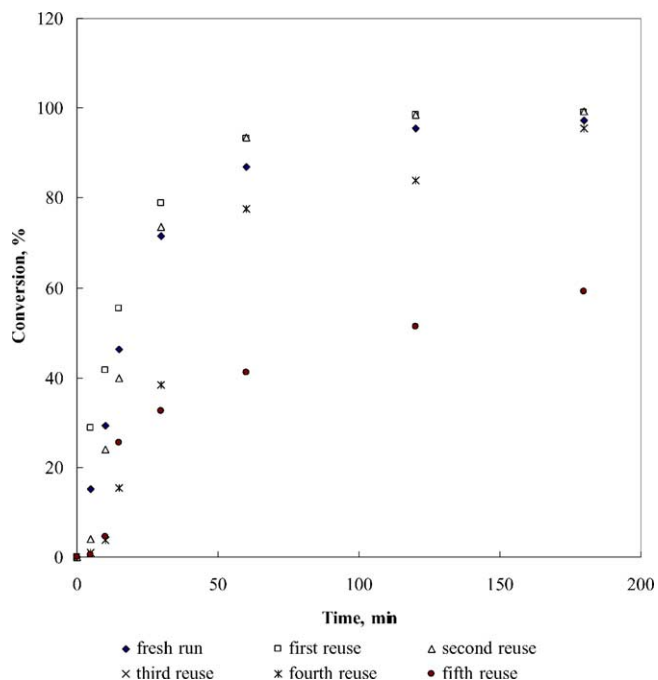


Fig. 6. Reusability of catalyst. β -Naphthol 0.01 mol, benzyl chloride 0.01 mol, TBAB 0.0062 mol, toluene 25 cm^3 , water 25 cm^3 , temperature 70°C , RPM 1000.

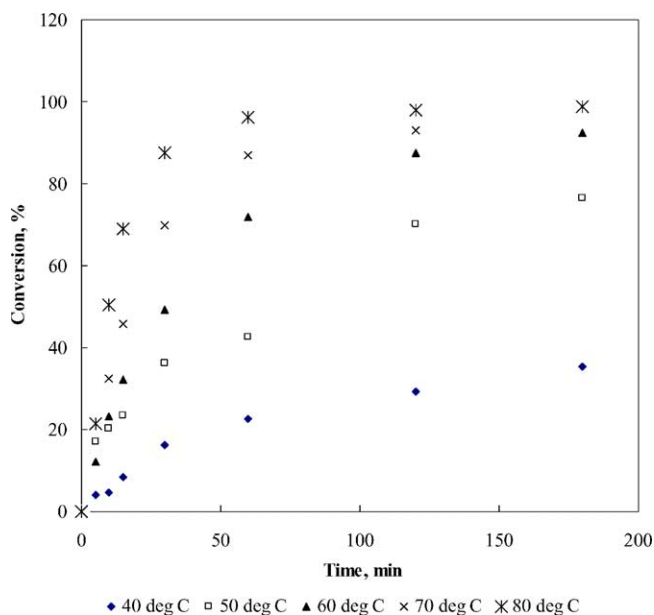


Fig. 7. Effect of temperature. β -Naphthol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, TBAB 0.0062 mol, toluene 25 cm³, water 25 cm³, RPM 1000.

for the 1.5:1 mole ratio, as shown in Fig. 5. This could be attributed to the fact that as the concentration of benzyl chloride increased, the triphase disappeared, leading to the decrease in conversion of the reaction.

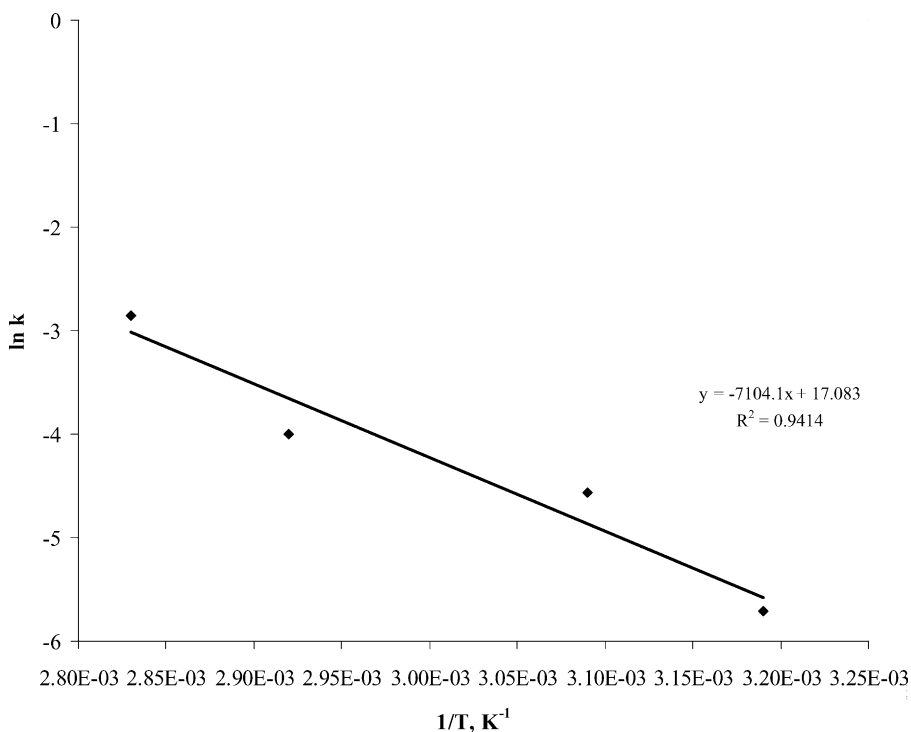


Fig. 9. Arrhenius plot.

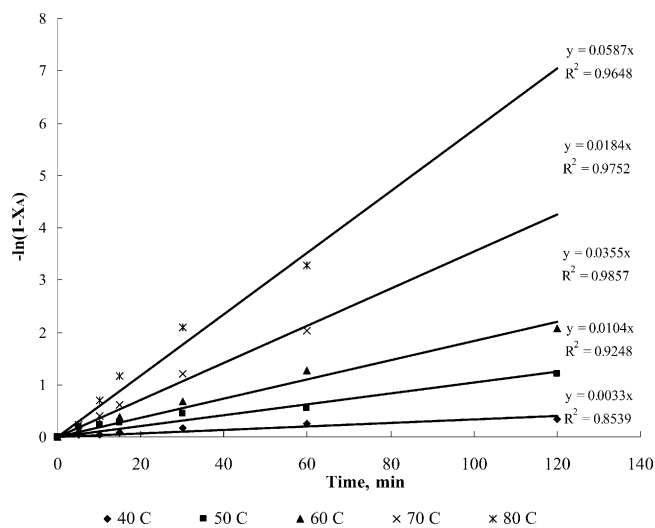


Fig. 8. Pseudo-first order kinetic plot for effect of temperature. β -Naphthol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, TBAB 0.0062 mol, toluene 25 cm³, water 25 cm³, temperature 70 °C, RPM 1000.

3.6. Reusability of catalyst

After completion of the kinetic run the phases reappeared. When the phases were clearly separated, the organic phase containing the product was removed. The reusability studies can be done in two ways, either by using the catalyst rich phase alone or by using the catalyst rich and the aqueous phase together. It was observed that when only the catalyst

rich phase was used, the third phase disappeared leading to lower conversion even for the first reuse. This is because the catalyst gets dissolved in the aqueous phase. Thus, the second method was adopted wherein the aqueous phase and the catalyst phase were reused five times and the organic phase along with the aqueous reactants was replenished every time (Fig. 6). The reusability was found to be good up to four uses and there was a loss in conversion during the fifth time since the amount of third phase was less in comparison with the previous runs. The formation of the sodium salt of β -naphthol was incomplete in the absence of enough quantity of the third phase.

3.7. Effect of temperature

The effect of temperature on the reaction between β -naphthol and benzyl chloride was studied under otherwise similar conditions. The temperature was varied from 40 to 80 °C. Experiments were conducted at 40, 50, 60, 70 and 80 °C. It was observed that at 40 °C, the reaction rate was slow. With increase in the temperature the reaction rate intensified as expected (Fig. 7). The kinetic plot for the effect of temperature (Fig. 8) were made by using Eq. (10) and it shows that the reaction follows the first order rate of reaction and the Arrhenius plot (Fig. 9) was made to determine energy of activation. The energy of activation has been found out to be 14.00 kcal/mol.

4. Conclusion

The reaction between β -naphthol and benzyl chloride in the presence of NaOH in a triphasic system, employing tetrabutylammonium bromide (TBAB) as the catalyst, occurs under L–L–L triphasic system. The best results were obtained employing 0.01 mol each of β -naphthol and benzyl chloride, 0.012 mol of NaOH and 0.0062 mol of TBAB catalyst.

The results of reaction conducted in L–L–L PTC are much better compared with the L–L PTC. The third liquid phase rich in catalyst appears only after a critical amount of catalyst

has been added to the reaction mixture. It has been found that the formation of the third phase increases the reaction rate sharply. The catalyst-rich phase was separated and reused five times to check the utility of the L–L–L PTC to the industrial applications. The detailed mechanism for the reaction has been suggested and a kinetic model accounting for the observed rates has been proposed and validated.

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