Selective engineering in O-alkylation of *m*-cresol with benzyl chloride using liquid–liquid–liquid phase transfer catalysis

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ABSTRACT

Selective O-alkylation or etherification of phenolic substances is attractive to make pharmaceuticals and fine chemicals. Liquid–liquid phase transfer catalysis (L–L PTC) is used to make such ethers but it always leads to byproduct formation and wastage of catalyst. On the contrary, liquid–liquid–liquid (L–L–L) PTC is an excellent strategy for waste reduction and improving profitability, in which a catalyst-rich middle (or third) phase is formed between aqueous and organic phases. The reaction takes place in the middle phase, which intensifies the rates and offers better selectivity including catalyst reusability unlike the bi-liquid PTC. Selective O-benzylation of *m*-cresol was studied with benzyl chloride by using L–L–L PTC at 50 °C. It gives 100% selectivity to 3-benzyloxytoluene. The catalyst-rich third phase was recycled many times, thereby leading to profitability and waste minimization. A kinetic model is developed and validated against experimental data. The reaction follows a pseudo-first order rate law. The studies were also extended to the benzylation of *o*- and *p*-cresol. The energy of activation for the benzylation of *o*-, *m*- and *p*-cresols were found to be 12.84, 10.00 and 12.12 kcal/mol, respectively. The results are novel.

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1. Introduction

Phase transfer catalysis (PTC) has been applied to several industrial processes in a variety of industries such as pharmaceuticals, agrochemicals, perfumes, flavors, dyes, specialty polymers [1–3]. PTC has been quite successful for C, N, O and S alkylations involving SN_2 type of reactions in fine chemical industries, apart from dehydrohalogenations. The multiphase system of phase-transfer catalysis can be divided into liquid–liquid, solid–liquid, gas–liquid, solid–liquid–liquid, and liquid–liquid–liquid phases, among which the reuse of catalyst in tri-liquid phase-transfer catalysis can overcome drawbacks of other systems. Among the various phase transfer catalysts used, quaternary ammonium salts are less expensive, highly effective and stable in alkaline medium. Recently, third-liquid phase-transfer catalysis has received widespread attention because of its ability to greatly augment the reaction rate and to provide a relatively uncomplicated means of recovery and reuse of catalysts. The third-liquid phase would be formed when the catalyst has limited solubility in both the organic phase and the aqueous phase, and there is a proper hydrophilic–liphophilic balance [4–16].

Liquid–liquid (L–L) PTC has been the most widely used technique, where mainly the organic phase is the reaction phase with associated transfer of species and many nucleophilic substitution reactions are reported under neutral and basic conditions under L–L PTC. One of the drawbacks of the L–L PTC process from the environmental aspect is that the catalyst is normally not recovered and reused, since the cost of the catalyst per kg product is paltry. In industrial practice, the catalyst is extracted with large quantities of water from the organic phase and sent as a waste to the effluent treatment plant. Thus, catalyst recovery and reuse will be very important in today's emphasis on green chemistry. The separation of phase-transfer catalysts from the reaction mixture can be achieved by extraction, distillation and adsorption [1,17]. In extraction, an additional solvent is required which has to be distilled off to recover the catalyst. Distillation becomes feasible if the catalyst has a lower boiling point than the reactants, products and the solvents. Otherwise, it becomes an energy intensive process to recover catalysts from dilute solutions. In the case of adsorption, the catalyst has to be eluted. Because of these practical difficulties, the phase transfer catalyst is not recovered in industrial practice. To solve this problem, the conversion of L–L PTC into a liquid–liquid–liquid (L–L–L) PTC reaction has demonstrated to be beneficial. The L–L–L PTC gives 100% selectivity towards the formation O-alkylated product. Once the third-phase rich in catalyst appear, the reaction rate increases spectacularly. The organic phase does not come in contact with the aqueous phase in L–L–L PTC and therefore side reactions, such as hydrolysis can avoided and selectivity of the desired product

Nomenclature

A	benzyl chloride
C_A^{org}	concentration of benzyl chloride in the organic phase (mol/cm³ of organic phase)
C_A^{th}	concentration of benzyl chloride in the third phase (mol/cm³ of third phase)
C_{QOR}^{aq}	concentration of RO^-Q^+ (also QOR) in aqueous phase (mol/cm³ aqueous phase)
C_{QCl}^{aq}	concentration of Q^+Cl^- (also QCl) in aqueous phase (mol/cm³ aqueous phase)
C_{QOR}^{th}	concentration of RO^-Q^+ (also QOR) in third phase (mol/cm³ third phase)
C_{QCl}^{th}	concentration of Q^+Cl^- (also QCl) in third phase (mol/cm³ third phase)
C_{QOR}^{org}	concentration of RO^-Q^+ (also QOR) in organic phase (mol/cm³ organic phase)
C_{QCl}^{org}	concentration of Q^+Cl^- (also QCl) in organic phase (mol/cm³ organic phase)
K_1	$\dfrac{C_{QCl}^{th}}{C_{QCl}^{aq}}$
K_2	$\dfrac{C_{QOR}^{th}}{C_{QOR}^{aq}}$
K_3	$\dfrac{C_{RONa}^{th}}{C_{RONa}^{aq}}$
K_4	$\dfrac{C_{NaCl}^{aq}}{C_{NaCl}^{th}}$
K_5	$\dfrac{C_{QOR}^{org}}{C_{QOR}^{th}}$
K_7	$\dfrac{C_{R'Cl}^{th}}{C_{R'Cl}^{org}}$
K_8	$\dfrac{C_{R'OR}^{th}}{C_{R'OR}^{org}}$
k_{app}	apparent first-order reaction rate constant (cm³/(mol of catalyst s))
k_{th}	rate of reaction in the third phase (cm³/(mol of catalyst s))
N_{Qtot}	total moles of catalyst added to the system (mol)
N_A^{th}	moles of A in third phase (mol)
N_A^{org}	moles of A in organic phase (mol)
N_{QOR}^{th}	moles of QOR in third phase (mol)
R'Cl	benzyl chloride
ROH	p-hydroxybiphenyl
R'OR	benzyloxytoluene
t	time of reaction (s)
V^{aq}	volume of aqueous phase (cm³)
V^{org}	volume of organic phase (cm³)
V^{th}	volume of the third phase (cm³)
$X_A = \dfrac{N_{A0}-N_A}{N_{A0}}$	fractional conversion

Greek letters

$\alpha = \dfrac{V^{th}}{V^{aq}}$	ratio of third to aqueous phase volumes
$\beta = \dfrac{V^{th}}{V^{org}}$	ratio of third to organic phase volumes
$\eta = \dfrac{C_{QOR}^{th}}{C_{QOR}^{th}+C_{QCl}^{th}}$	molar ratio of Q^+ in the form of QOR at any time in the third-phase.

is improved. The current work is centered around the novelties of etherification of *m*-cresol with benzyl chloride with under L–L–L PTC to get 1-methyl-3-(phenylmethoxy)benzene. The product is used as an intermediate for the preparation of a resin which is used for synthesis of Υ ray-resistant polycarbonates [18]. It is also used in the preparation of dyeing or printing hydrophobic fibers [19]. This paper covers the theoretical and experimental details of L–L–L PTC.

2. Experimental

2.1. Chemicals and catalyst

Benzyl chloride, toluene, *m*, *p*, and *o*-cresol, sodium hydroxide, sodium chloride, and diphenyl ether, all AR grade, were obtained from M/S s.d. Fine. Chem. Pvt. Ltd. Mumbai, India. Tetrabutylammonium bromide (TBAB) of pure grade was obtained as gift sample from M/s Dishman Pharmaceuticals and Chemicals Ltd., Ahemdabad, India.

2.2. Experimental procedure

The reaction was studied in a 5 cm i.d. fully baffled mechanically agitated glass reactor of 100 cm³ total capacity which was equipped with a 6 blade-pitched turbine impeller and a reflux condenser. The entire reactor assembly was immersed in a thermostatic oil bath, which was maintained at a desired temperature with an accuracy of $\pm 1\,^\circ$C and the reaction mixture was agitated mechanically with the help of an electric motor. Typical L–L–L PTC runs were conducted by taking 0.02 mol *m*-cresol, 0.025 mol sodium hydroxide, 0.17 mol sodium chloride and 0.016 mol TBAB in 30 cm³ water. The organic phase comprised of 0.02 mol of benzyl chloride in 30 cm³ toluene. These concentrations led to the formation of third liquid phase at 50 °C (Fig. 1). All typical runs were conducted at 50 °C and 1000 rpm.

2.3. Method of analysis

Samples of the organic phase were withdrawn periodically and analyzed by gas chromatography on a Chemito 8510 model. A 2 m × 3.25 mm internal diameter stainless steel column packed with 10% SE-30 on chromosorb WHP was used for analysis in conjunction with a flame ionization detector. In L–L–LPTC, only 3-benzyloxytoulene was produced. The conversion was based on the disappearance of benzyl chloride in organic phase. The product was confirmed by GC-MS.

2.4. Determination of composition of third phase

The composition of third phase was analyzed by gas phase chromatography using thermal conductivity detector and a stainless steel column (3.25 mm × 2 m) packed with a liquid stationary phase of 10% SE-30. The third phase contained 18.16% toluene, 41.35% TBAB, 1.04% benzyl chloride, 1.36% *m*-cresol, 0.86% 1-methyl-3-(phenylmethoxy)benzene, 37.23% water. Karl-Fischer apparatus was used to analyze the amount of water present in the third phase.

2.5. Reaction scheme

The overall reaction is shown in Scheme 1. It was observed that there was no formation of any byproduct at any conversion levels in L–L–L PTC.

3. Results and discussion

Several experiments were done to understand the critical parameters of maintaining three immiscible phases at 50 °C as well
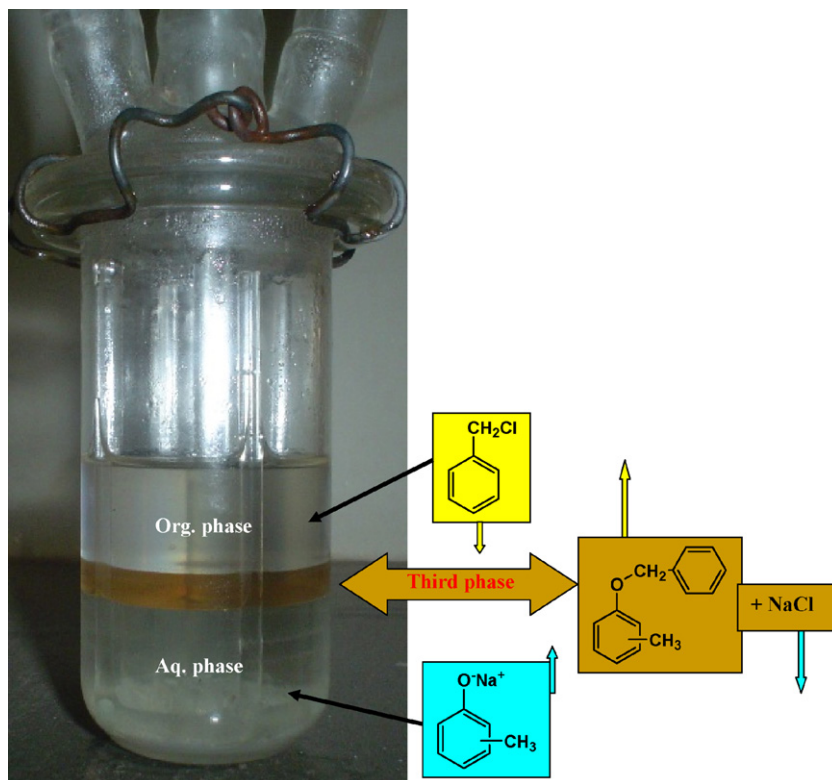
Fig. 1. Photograph of the L–L–L PTC at 50 °C.

as at room temperature under agitation. In all cases, three distinct liquid phases were created as shown in Fig. 1. The nature of triphase system depends on nature of substrate and solvent, type and amount of the catalyst, composition of aqueous phase and temperature.

For the three-phase system, the organic reactant benzyl chloride is distributed between organic phase and third phase but it is not in aqueous phase. Scheme 2 illustrates the mechanism of L–L–L PTC reaction in which different reactions take place in different phases and the products are transferred across the interfaces. Thus, the magnitudes of rates of mass transfer and individual reaction rates must be considered. The locale of the rate controlling reaction (reaction b) is the third phase and no side reactions occur since benzyl chloride does not transfer to the aqueous phase-third phase interface.

3.1. Effect of speed of agitation

To determine the influence of mass transfer resistance to the transfer of the reactants to the reaction phase, the speed of agitation was varied in the range of 800–1200 rpm under otherwise similar conditions in the presence of TBAB as the catalyst while maintaining the three phases at 50 °C (Fig. 2). The conversion was found to be practically the same at 1000 and 1200 rpm. Further increase in the speed of agitation to 1200 rpm had no effect on conversion. So there was no mass transfer resistance at and beyond 1000 rpm and all further experiments were conducted at 1000 rpm. A typical calculation was also done for mass transfer rates and overall reaction rates by using theoretical correlations on overall mass transfer coefficients also to demonstrate that there were no mass transfer effects beyond 1000 rpm. This is further bolstered by
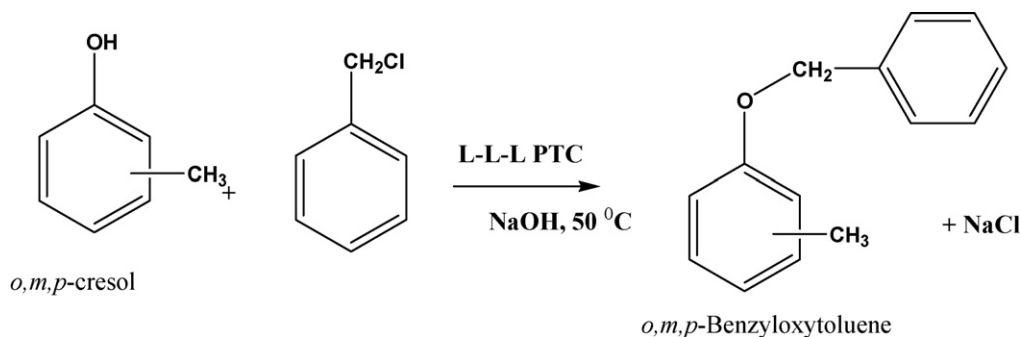
Scheme 1. Reaction scheme for O-benzylation of cresols with benzyl chloride.

Scheme 2. L–L–L PTC mechanism for etherification of cresols.
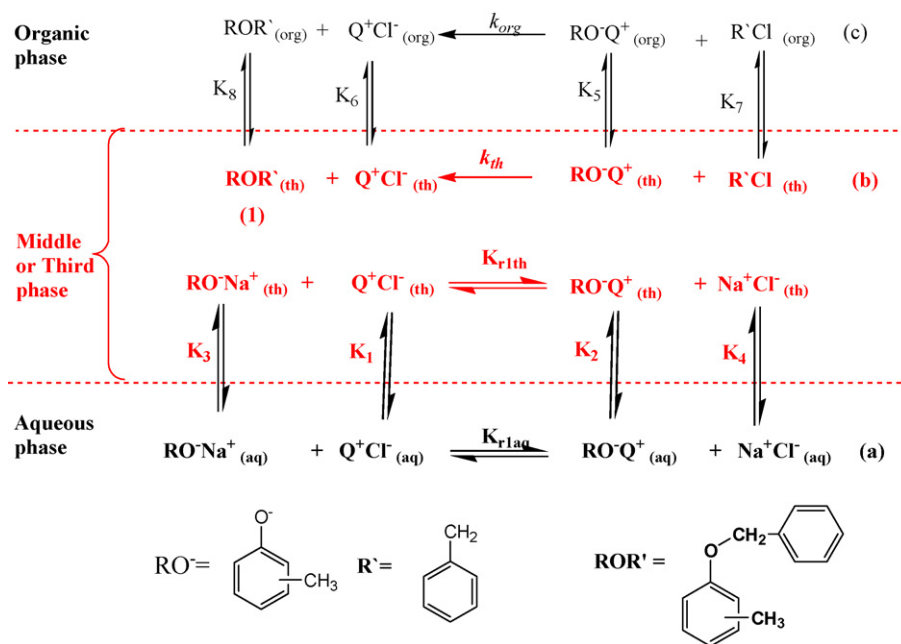
studying the effect of temperature and evaluation of energy of activation for the reaction; a value greater than 7.00 kcal/mol shows complete absence of mass transfer resistance. This is discussed in Section 3.7. Hence all further experiments were done at this speed.

3.2. Effect of catalyst loading

The catalyst amount was varied from 1.6×10^{-3} to 3.0×10^{-2} mol under otherwise similar conditions. The formation of third phase would occur only after a certain critical amount of catalyst was added to the reaction mixture. In the present case, the formation of third phase took place at a catalyst concentration of 1.6×10^{-2} mol TBAB and it was a critical value. At any quantities of catalyst below the critical, the third phase disappeared and the system would convert itself into bi-liquid PTC system thereby decreasing the conversion (Fig. 3). Only at all higher amounts of catalyst beyond the critical value of 1.6×10^{-2} mol, the third phase formation was observed. The rate of reaction would then shoot up dramatically. It would suggest that the locale of reaction had
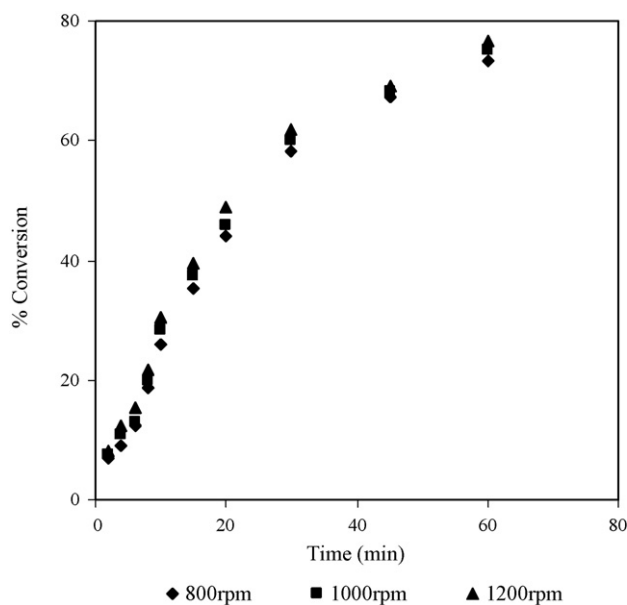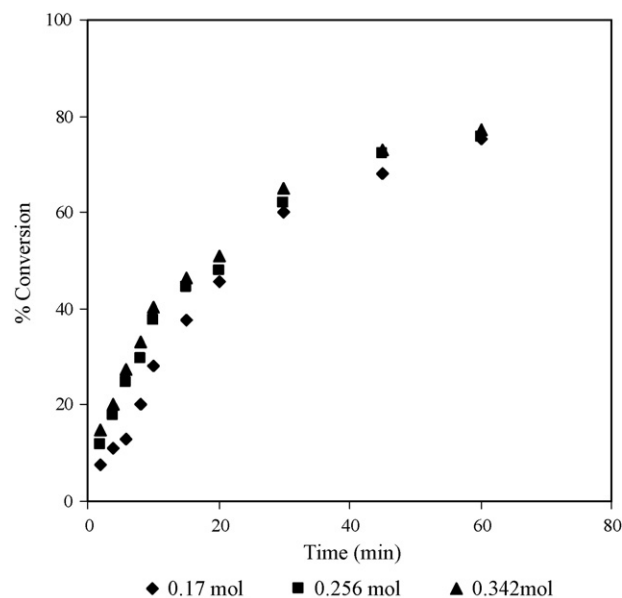

Fig. 2. Effect of speed of agitation on conversion of benzyl chloride. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm³ with toluene, m-cresol: 0.02 mol, TBAB: 16×10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm³ with water, NaCl: 0.17 mol, temperature: 50 °C.
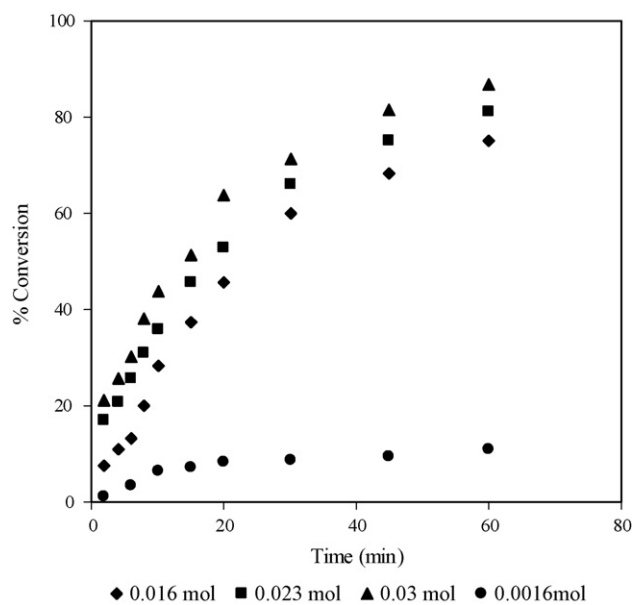
Fig. 3. Effect of catalyst loading on conversion of benzyl chloride. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm³ with toluene, m-cresol: 0.02 mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm³ with water, NaCl: 0.17 mol, temperature: 50 °C, speed of agitation: 1000 rpm.
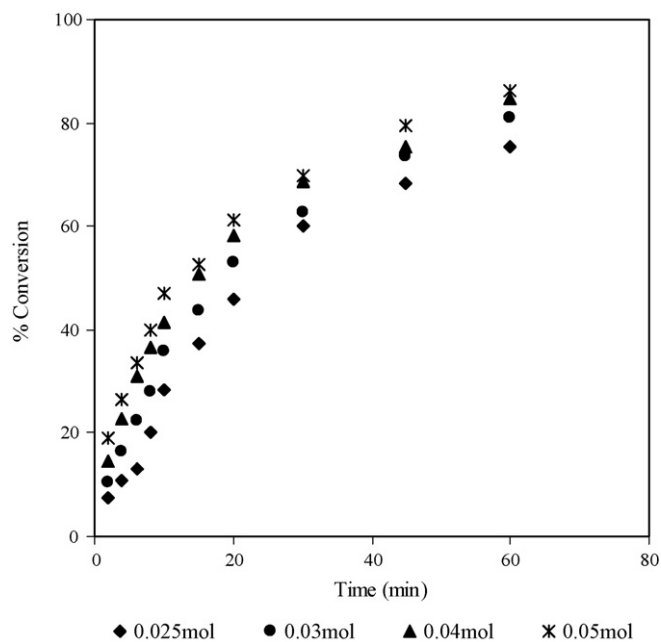
Fig. 4. Effect of NaOH on conversion of benzyl chloride. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm^3 with toluene, m-cresol: 0.02 mol, TBAB: 16×10^{-3} mol, aqueous phase made up-to 30 cm^3 with water, NaCl: 0.17 mol, temperature: 50 °C, speed of agitation: 1000 rpm.

mainly shifted to the middle phase, unlike the L–L PTC where it is typically the organic phase. It is not the quantity of catalyst alone which enhanced the rate, but the microscopic environment of the reacting species. When the catalyst quantity was increased from 1.6×10^{-2} to 3.0×10^{-2} mol, the rate of reaction increased substantially. The initial rate increased proportionately to the increase in catalyst concentration.

3.3. Effect of concentration of NaOH

The concentration of sodium hydroxide has a pronounced effect on formation of third liquid (catalyst-rich) phase as well as on the rate of reaction. The effect of NaOH concentration was studied from 0.025 to 0.05 mol (Fig. 4). As the concentration of NaOH was increased, the rate of the reaction also increased. As the NaOH concentration increases, the aqueous phase becomes saturated and more amount of the ion-pair Q$^+$RO$^-$ goes into the third phase (due to salting-out effect) leading to increase in the reaction rates. One of the reasons why there is no formation of any byproducts is that the third phase does not have any free OH$^-$ ion concentration.

3.4. Effect of sodium chloride concentration

The amount of sodium chloride was varied from 0.17 to 0.34 mol under otherwise similar reaction conditions (Fig. 5). As the concentration of sodium chloride was increased, the initial rate of the reaction increased since the aqueous phase was saturated with NaCl and a greater amount of TBAB was driven into the third phase. Consequently, the concentration of quaternary phenate, RO$^-$Q$^+$ increases resulting into higher rates of reaction in the third phase. However, the conversions at 0.256 and 0.342 mol are practically the same, since the aqueous phase was completely saturated. The role of NaCl is to salt out the catalyst along with the nucleophile in the form of the RO$^-$Q$^+$ ion-pair from the aqueous phase into the third phase as well as to increase the rate of aqueous phase ion-exchange reaction, which leads to equilibrium. There are already Na$^+$ ions

Fig. 5. Effect of sodium chloride on conversion of benzyl chloride. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm^3 with toluene, m-cresol: 0.02 mol, TBAB: 16×10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm^3 with water, temperature: 50 °C, speed of agitation: 1000 rpm.

from NaOH which also increase the ionic strength of the aqueous phase which enhances the rate in that phase. When the concentration of sodium chloride was much less, the volume of the third phase was also less because the aqueous phase was not saturated with sodium chloride and there was no salting out of TBAB.

3.5. Effect of mole ratio

Effect of mole ratio of m-cresol to benzyl chloride was studied in the range of 1:1 to 2:1 (with a fixed m-cresol to NaOH mole ratio of 1:1.25). It was found that increasing the concentration of sodium salt of m-cresol increases the rate of reaction and conversion (Fig. 6). Increasing the concentration of sodium salt of m-cresol leads to an increase in the concentration of RO$^-$Q$^+$ which in turn increases the rate of reaction.

3.6. The kinetic model for L–L–L PTC reaction

The reaction mechanism is shown in Scheme 2. Since the selectivity to the ether (R′OR) (**1**) was 100%, the mechanism is straight forward. Sodium salt of m-cresol (RO$^-$Na$^+$) is generated in aqueous phase. Sodium alkoxide ion-pair (RO$^-$Na$^+$) generated in-situ in the aqueous phase is equivalent to moles of m-cresol due to excess of sodium hydroxide. The anion exchange takes place between the quaternary salt (Q$^+$X$^-$) and RO$^-$Na$^+$ to form an ion-pair (RO$^-$Q$^+$), which is then transferred into the third liquid phase. This is an equilibrium reaction and all the species involved have equilibrium concentrations. The substrate benzyl chloride R′Cl is transferred from the organic phase to the third phase and it reacts with RO$^-$Q$^+$ to produce the desired product R′OR (**1**), which is subsequently transferred to the organic phase.
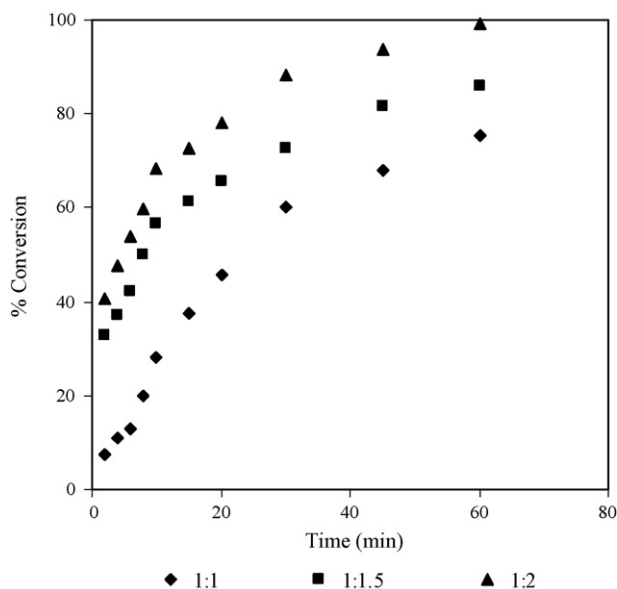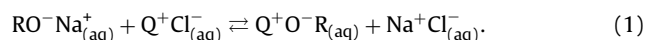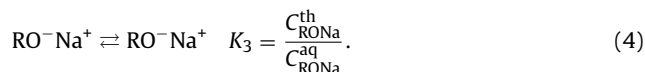
Thus, the overall reaction is:

$$RONa_{(aq)} + R'Cl_{(org)} \xrightarrow{L-L-LPTC} R'OR_{(org)} + NaCl_{(aq)}$$
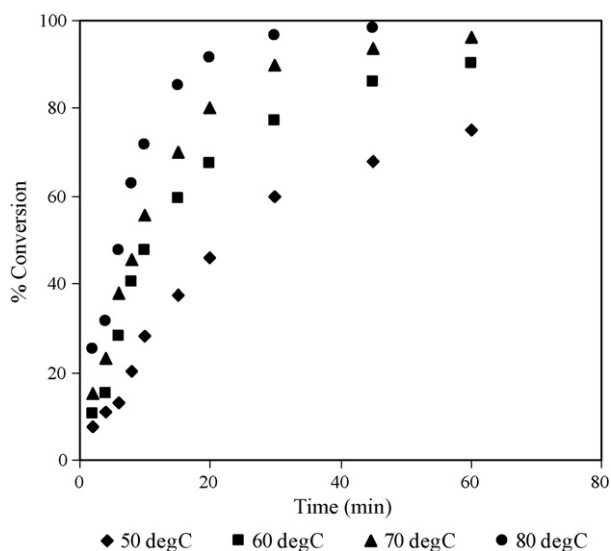
The steps involved are as follows:

Fig. 7. Effect of temperature on conversion of benzyl chloride for benzylation of *m*-cresol. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm^3 with toluene, *m*-cresol: 0.02 mol, TBAB: 16 × 10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm^3 with water, NaCl: 0.17 mol, speed of agitation: 1000 rpm.

$$\frac{-dN_A}{dt} = \frac{k_{th}K_7N_{QOR}^{th}N_A}{(V^{org} + K_7V^{th})}$$

$$= \frac{k_{th}K_7N_A}{(V^{org} + K_7V^{th})}$$

$$\times \frac{N_{Qtot}V^{th}/V^{aq}}{[((1/K_2)+(V^{th}/V^{aq}))+((1/K_1)+(V^{th}/V^{aq}))((1-\eta)/\eta)]} \tag{21}$$

$$\frac{-dN_A}{dt} = \frac{\alpha k_{th}K_7N_AN_{Qtot}}{V^{org}(1+K_7\beta)[((1/K_2)+\alpha)+((1/K_1)+\alpha)((1-\eta)/\eta)]} \tag{22}$$
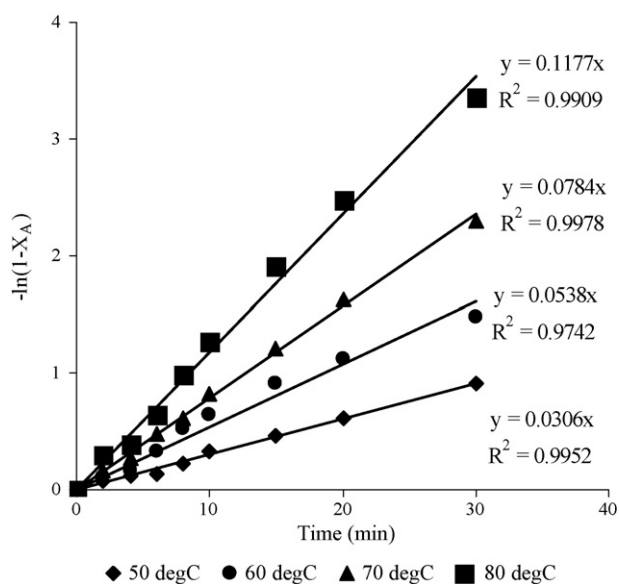

Fig. 8. Validity of kinetic plot at various temperatures for benzylation of *m*-cresol. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm^3 with toluene, *m*-cresol: 0.02 mol, TBAB: 16 × 10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm^3 with water, NaCl: 0.17 mol, speed of agitation: 1000 rpm.
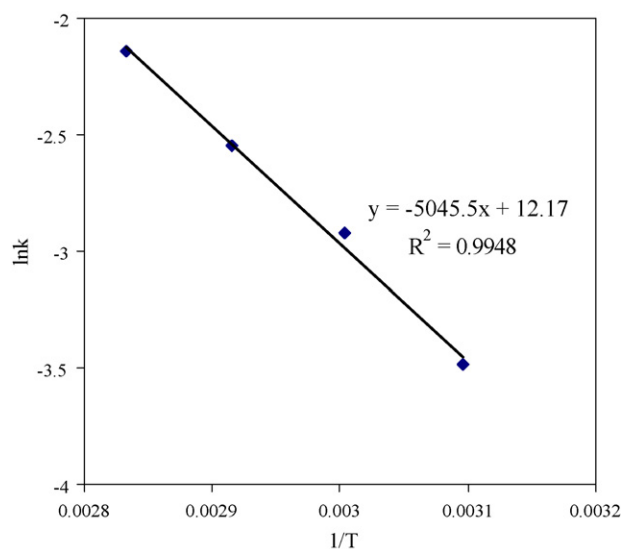

Fig. 9. Arrhenius plot for benzylation of *m*-cresol.

where

$$\alpha = \frac{V^{th}}{V^{aq}} \qquad \beta = \frac{V^{th}}{V^{org}} \tag{23}$$

In Eq. (22) above, α, β, K_7 and k_{th} are constants and hence can be suitably combined as an apparent rate constant k_{app}. The catalysts quantity added, N_{Qtot} is also constant.

In terms of fractional conversion, now Eq. (22) can be written as follows:

$$\frac{dX_A}{dt} = k_{app}(1 - X_A)N_{Qtot} \tag{24}$$

By integrating Eq. (24) gives,

$$-\ln(1 - X_A) = k_{app}N_{Qtot}t \tag{25}$$

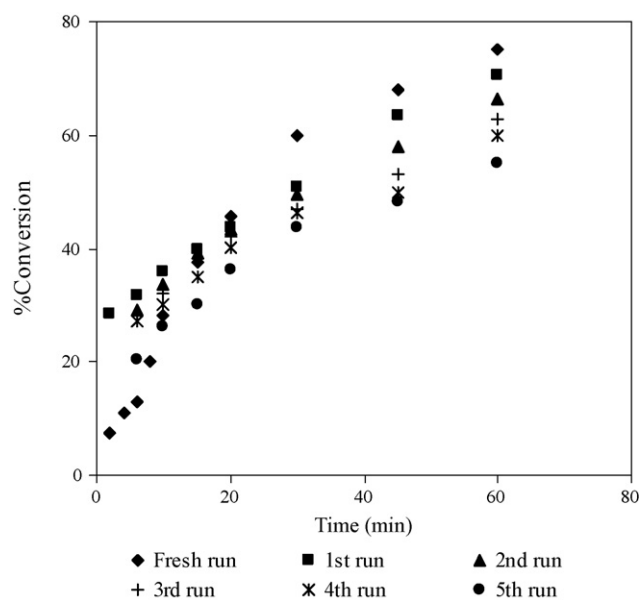The above model can be fitted to the collected data.

Fig. 10. Reusability of catalyst and aqueous phase only for *m*-cresol. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm^3 with toluene, temperature: 50 °C, speed of agitation: 1000 rpm.
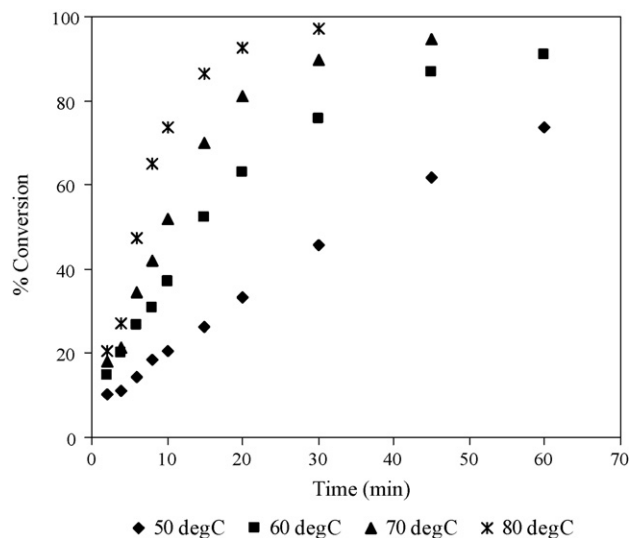
Fig. 11. Effect of temperature on conversion of benzyl chloride for benzylation of o-cresol. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm³ with toluene, o-cresol: 0.02 mol, TBAB: 16×10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm³ with water, NaCl: 0.17 mol, speed of agitation: 1000 rpm.

3.7. Effect of temperature

The effect of temperature on rate of reaction between m-cresol and benzyl chloride was studied under otherwise similar conditions. The temperature was varied from 50 to 80 °C. The conversion of benzyl chloride was observed to increase with increase in reaction temperature. The effect of temperature on conversion of benzyl chloride is given in Fig. 7. At all temperatures, the three phases were maintained. The kinetic plot for the effect of temperature was made by using Eq. (25) and it shows that the reaction follows the first order rate of reaction (Fig. 8). The model fits very well at all temperatures. The Arrhenius plot was made to determine the apparent energy of activation as 10.00 kcal/mol (Fig. 9). This value also confirms that the reaction is kinetically controlled.
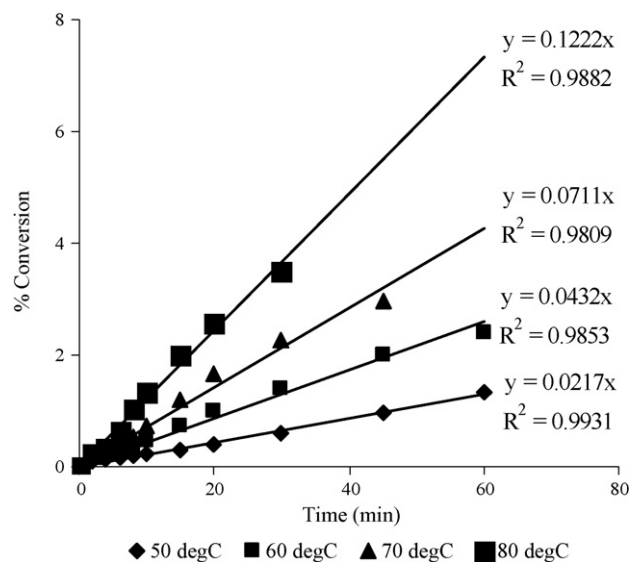

Fig. 12. Kinetic plot for benzylation of o-cresol. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm³ with toluene, o-cresol: 0.02 mol, TBAB: 16×10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm³ with water, NaCl: 0.17 mol, speed of agitation: 1000 rpm.
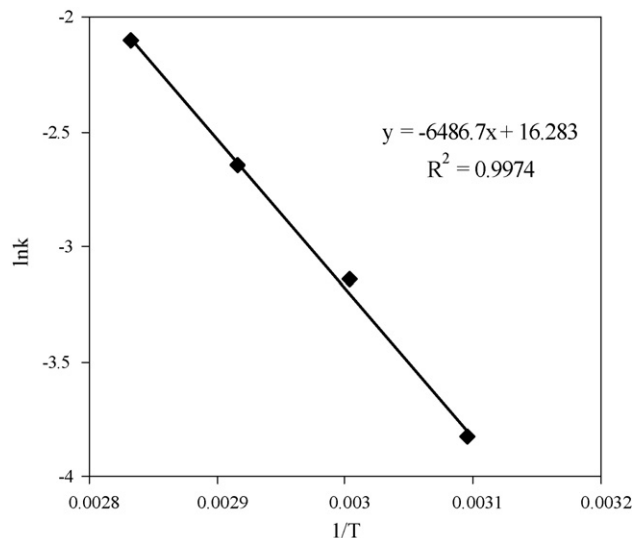

Fig. 13. Arrhenius plot for benzylation of o-cresol.

3.8. Reusability study

After completion of the kinetic run, the agitation was stopped and the phases were allowed to separate into three layers. The organic phase containing the product was removed. The reusability studies could 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 after the first reuse. This is because the catalyst gets redistributed in the aqueous phase. Thus, the second method was adopted. 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. 10). The reusability was found to be excellent up to four uses. There was a loss in conversion during the fifth time since the amount of third phase formed was less in comparison
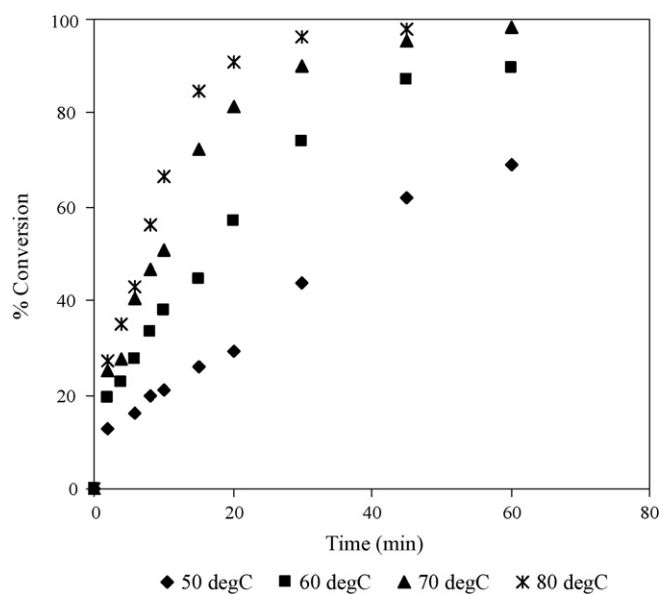

Fig. 14. Effect of temperature on conversion of benzyl chloride for benzylation of p-cresol. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm³ with toluene, p-cresol: 0.02 mol, TBAB: 16×10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm³ with water, NaCl: 0.17 mol, speed of agitation: 1000 rpm.
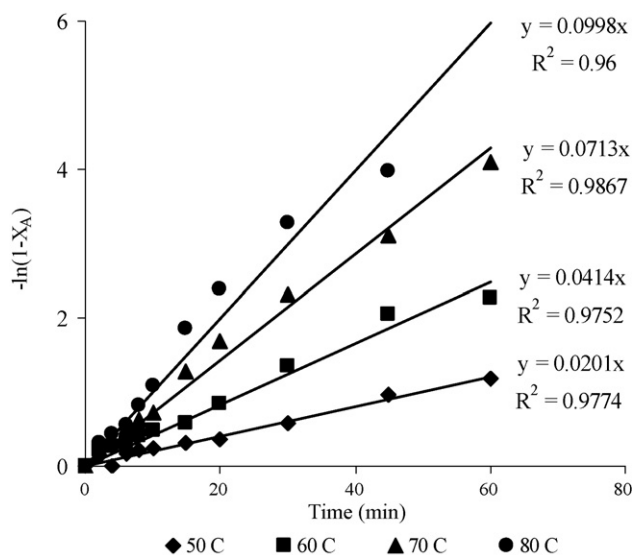
Fig. 15. Kinetic plot for benzylation of *p*-cresol. Benzyl chloride: 0.02 mol, organic phase made up-to 30 cm³ with toluene, *p*-cresol: 0.02 mol, TBAB: 16×10^{-3} mol, NaOH: 0.025 mol, aqueous phase made up-to 30 cm³ with water, NaCl: 0.17 mol, speed of agitation: 1000 rpm.
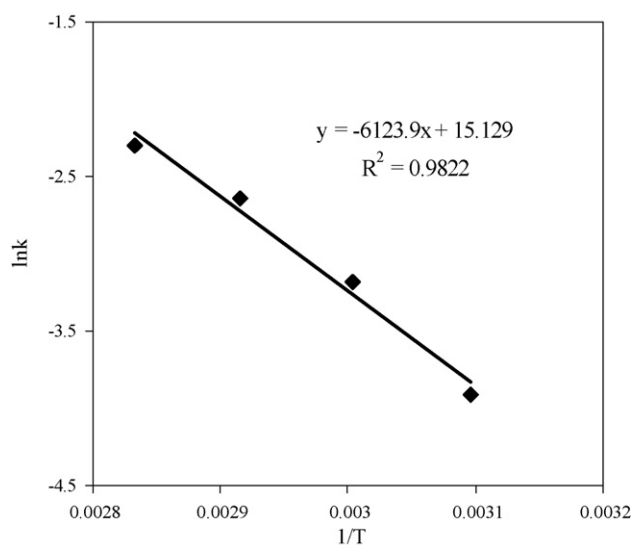

Fig. 16. Arrhenius plot for benzylation of *p*-cresol.

with the previous runs. The formation of the sodium salt of *m*-cresol was incomplete in the absence of enough quantity of the third phase.

3.9. Effect of different cresol isomers

The etherification of *o*-cresol and *p*-cresol was also studied with benzyl chloride by using TBAB as a catalyst, under otherwise similar reaction conditions. The effect of temperature on rate of reaction of benzyl chloride was studied from 50 to 80 °C. The conversion of benzyl chloride was observed to increase with

increase in reaction temperature. The effect of temperature on conversion of benzyl chloride is given for *o*-cresol in Fig. 11. Fig. 12 shows that the reaction follows the first order kinetics as modeled earlier. The Arrhenius plot for *o*-cresol gave activation energy of 12.84 kcal/mol (Fig. 13). Corresponding data were collected for *p*-cresol (Fig. 14). The kinetic model fitting and Arrhenius plot are given in Figs. 15 and 16, respectively. The energy of activation was found to be 12.12 kcal/mol for *p*-cresol. Activation energy for the benzylation of *m*-cresol found to be lower than that for benzylation of *o*-cresol and *p*-cresol. This shows that benzylation of *m*-cresol is faster than benzylation of *o*-cresol and *p*-cresol.

4. Conclusion

Benzylation of cresols leads to very valuable products. The present study brings out the novelties of benzylation of *m*-cresol in liquid–liquid–liquid phase transfer catalysis. The effects of speed of agitation, temperature, catalyst loading, salt concentration and mole ratio in L–L–L PTC were also studied. It has been found that the formation of third phase increases the reaction rate sharply. It would suggest that the locale of reaction has mainly in middle phase. The third phase was separated and reused. A mathematical model has been proposed to account for the calculation of the rate constant. The studies were also extended to the benzylation of *o*- and *p*-cresol. The energy of activation for the benzylation of *o*-, *m*- and *p*-cresols were found to be 12.84, 10.00 and 12.12 kcal/mol, respectively.

Acknowledgments

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