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Phase Transfer Catalyzed Extraction of Phenolic Substances from Aqueous Alkaline Stream

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Abstract

Experimental investigations are presented on the extraction/removal of such phenolic compounds as phenol, *m*-cresol, and resorcinol from alkaline medium via reaction with benzoyl chloride dissolved in toluene as the solvent under two-phase conditions using hexadecyltributyl phosphonium bromide as a phase transfer catalyst. Two types of experiments were performed in order to assess the utility of the reaction scheme for treatment of industrial wastewater. The results of stirred cell experiments revealed that the reactions of phenolics conform to a diffusion-limited fast pseudo-first-order regime. The rate enhancement of the reaction was found to be reasonably low as compared to that reported when Aliquat 336 was used as the catalyst. The specific rate of extraction decreases for the phenolics in the order phenol > *m*-cresol > resorcinol. Batch experiments conducted in a baffled agitated reactor with individual phenolic compounds as well as mixtures of all components, representing compositions typical of industrial wastewater, revealed that the volumetric rate of extraction is dependent on the stirring speed under otherwise identical conditions. Conversion of phenolics in a batch agitated reactor was found to be more than 99.5% under suitable conditions of stirring speed and reaction time, and the products of reaction, essentially esters, are completely partitioned to the organic phase. Some aspects of product recovery, solvent, and catalyst recycle are discussed.

INTRODUCTION

Phenol, *m*-cresol, and resorcinol are the major constituents of phenolic wastewater generated in coal conversion industries. Stringent pollution control regulations call for lowering the phenolic content in the wastewater down to around 1 part per million (ppm) from several thousand ppm. In general, two types of treatment processes are available, one based on the

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destructive process principle and the other based on a recovery or regenerative scheme. When the phenolic content of the wastewater exceeds 1000 ppm, the recovery scheme becomes an attractive proposition. Solvent extraction and solid absorption methods are usually practiced as recovery schemes. Chemical conversion of phenol (present in wastewater) to a useful product has also been found to be feasible. A process based on catalytic aerobic coupling reactions of phenol has been developed on a pilot-plant scale (*1*) at North Carolina State University, USA. More recently, a novel concept on recovery of phenolic substances from wastewater has been established through a study of phase transfer catalyzed reactions of phenols with benzoyl and *p*-toluene sulfonyl chloride under two-phase conditions (*2*). As reviewed by the author (*3*), various phase transfer catalyzed reactions of phenolic compounds may be exploited for recovery schemes. The phase transfer reactions are effective under alkaline condition of the aqueous stream, in which case phenols exist in a highly dissociated form. It may be noted that the percentage of molecular phenol in a buffered alkaline solution decreases drastically with an increase of pH between 9 and 11 (*4*). The phenolate anion under the above conditions can be transferred into an organic phase where it can be easily reacted with a suitable reagent by exploiting the principle of phase transfer catalysis (*5*). The products of reactions with benzoyl chloride and *p*-toluene sulfonyl chloride are organic soluble esters which are valuable intermediates for the manufacture of certain costly pesticides. Thus, the reaction scheme may well serve as a basis for the development of a novel regenerative process for the treatment of alkaline wastewater such as those generated in coal gasification and carbonization industries.

To be highly effective for two-phase displacement reactions, as in the case of reactions of phenolate ion with benzoyl chloride, the catalyst cation should be strongly associated with the aqueous anion and the cation pair should be strongly partitioned into the organic phase where the reaction necessarily takes place. Aliquat 336 (tricaprylmethyl ammonium chloride) and hexadecyl tributyl phosphonium bromide (HTPB) are ideal choices as the phase transfer catalysts (PTCs) since they are insoluble in water and they will completely partition toward the organic phase in the presence of a nonpolar solvent.

While Aliquat 336 was evaluated to be a successful catalyst for the reactions of phenol, *m*-cresol, and resorcinol with benzoyl chloride and *p*-toluene sulfonyl chloride, the purpose of the present paper is to examine the suitability of HTPB as the PTC for the reaction with benzoyl chloride in particular. Our interest was drawn to this reaction since this compound is readily available in India and its product has good marketing potential as well. The selection of this catalyst was motivated by the fact that the quaternary phosphonium salts are more lipophilic than Aliquat 336, and it is possible to achieve stronger organic phase solvation of the catalyst cation than aqueous phase solvation of the anion because of the larger organic structure. The need for this study of the catalyst is further justified because polymer supported phosphonium salts are thermally more stable and reactive than the ammonium salt counterpart.

EXPERIMENTAL

Materials and Method of Analysis

Analytical grade phenol, *m*-cresol, and resorcinol were obtained from CDH (Pvt) Ltd., India, while GPR grade toluene and benzoyl chloride were procured from E. Merck (India) Ltd., BDH Chemical Division. The catalyst hexadecyl tributyl phosphonium bromide was obtained from Aldrich Chemical Co., USA. Benzoyl chloride was distilled under reduced pressure before use. Other reagents used for chemical analysis were obtained from reputed firms. Synthetic solutions of phenolics were taken in all experiments to simulate compositions typical of coal carbonization wastewater. The phenolic solutions were made alkaline by adding a stoichiometric amount of alkali.

The aqueous phase concentrations of phenol, *m*-cresol, and resorcinol at the ppm level were estimated by the spectrophotometric method reported by Whitlock et al. (*6*). Phenols in the aqueous phase were coupled with diazotized sulfanilic acid to form colored azo dyes. The absorbance at different concentrations was measured in a Beckman UV/visible spectrophotometer. The Volhard method (*7*) was used to estimate the chloride ion formed in the aqueous phase. The esters formed in the organic phase were analyzed in a CCI (India) Gas Chromatograph.

Stirred Cell Experiments

A 6.8-cm i.d. glass cell was used for the stirred cell assembly (see Fig. 1). The two phases were stirred separately without causing dispersion of the phases. The lower aqueous phase was stirred with a magnetic stirrer while the organic phase was stirred with a flat-bladed Teflon stirrer. In order to avoid dispersion and vortex formation, it was necessary to locate the aqueous phase stirrer slightly off-center. A flat interface was maintained between the two phases by regulating the speed of the two stirrers. The interfacial area can reasonably be assumed to be the i.d.-based geometric cross-sectional area of the glass cell. An aqueous phase (100 mL) containing phenolic substances of known concentration was initially taken in the cell. Toluene (100 mL) containing known concentrations of the catalyst and benzoyl chloride was added along the side of the cell, taking care that the organic phase was not dispersed into the aqueous phase. The reaction was

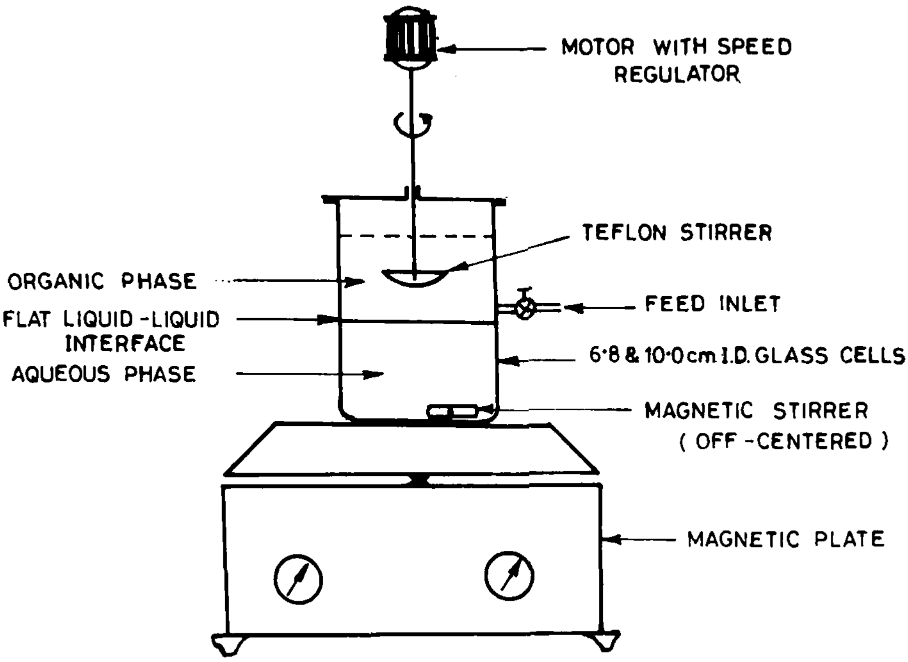


FIG. 1. Schematic diagram of the stirred cell assembly.

conducted at around 30°C. The batch times in all experiments were manipulated in such a way that the conversion level was maintained at around 20%. The range of stirring speed was maintained within 20–50 rpm. In order to see the effect of the interfacial area, an experiment was also performed in a large diameter (10 cm i.d.) stirred cell while maintaining a flat interface and a conversion of about 20%.

Batch Experiments in an Agitated Contactor

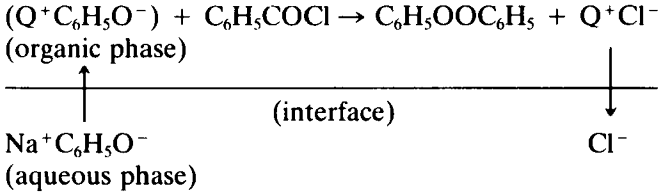
Batch experiments were carried at around 30°C in a cylindrical glass vessel (250 mL capacity) provided with a suitable baffle arrangement. The reaction mass stirred with a moon-shaped Teflon stirrer of 3 cm diameter. An aqueous alkaline phase (120 or 225 mL) containing phenolic substances at a concentration of 6000 ppm and 60 or 75 mL of toluene containing a stoichiometric amount of benzoyl chloride (aqueous to organic phase volume ratio of 2:1 or 3:1, respectively) and the catalyst (15×10^{-6} g·mol/cm^3) were taken in the flask. The agitation speed, as measured by a digital tachometer, was maintained at around 1500 rpm. The aqueous phase was made alkaline by adding NaOH in a stoichiometrically equivalent amount to form the phenolate ion. It was observed that the pH of the medium varied between 9.5 to 10.0 in all cases when the phenolic substances were used. The reactions were independently conducted for different time periods in order to assess the reaction time for optimum conversion. At the end of each run, the stirrer was stopped and the phases were separated for analysis. The coalescence and phase separation time was always less than 20 s, and it is assumed that this time will not influence the overall conversion. The percent phenol conversion was cross-checked from a material balance made from chromatographic and spectrophotometric analyses of the organic and aqueous phases, respectively.

In order to see the effect of stirring speed on the volumetric rate of extraction, R_Aa [expressed as g·mol/cm^3(dispersion)·s], the speed was varied between 500 and 1500 rpm, a range where extractive equilibrium for the two-phase reaction may be assumed (5). In these experiments the reactions were performed for 3 min. The catalyst concentration in the organic phase was maintained at 15×10^{-6} g·mol/cm^3.

A few experiments were carried out (with an aqueous to organic phase volume ratio of 3:1) with a mixture of phenol, *m*-cresol, and resorcinol at different proportions and containing stoichiometric and 3 times stoichiometric quantities of benzoyl chloride and PTC at a concentration of 10×10^{-6} g·mol/cm^3. Reaction times were between 10 and 20 min, and the stirring speed was around 1450 rpm. The percent conversion was estimated from a material balance made on the basis of a chromatographic analysis of the ester formed in the reaction and was cross-checked from a spectrophotometric analysis of the aqueous phase.

RESULTS AND DISCUSSION

Values of the specific rate of extraction, R_A (expressed as g·mol/cm^2·s), evaluated in the stirred cell experiment are quite reasonable since a material balance made from both aqueous and organic phase analyses checked well. As shown in Fig. 2, R_A is proportional to the PTC concentration in the range up to 15×10^{-6} g·mol/cm^3 studied here. While this finding conforms to the theory of phase transfer catalysis (5), the values of R_A are relatively low (by a factor of 1.2 on average) in comparison to those reported for the reaction fo phenol using Aliquat 336 as the catalyst (2) under identical conditions of reactant and catalyst concentrations. This lowering of R_A while using HTPB as the catalyst is justifiable if one considers the mechanism of the reaction:



$$(Q^+C_6H_5O^-) + C_6H_5COCl \rightarrow C_6H_5OOC_6H_5 + Q^+Cl^-$$

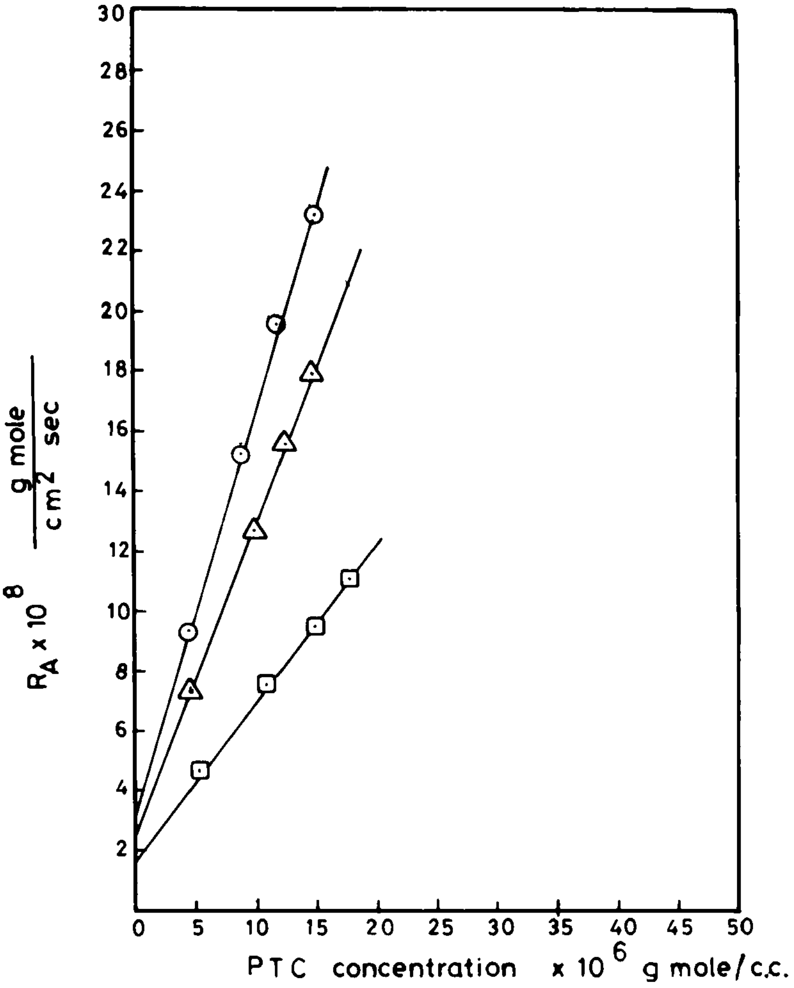


FIG. 2. Effect of PTC concentration of specific rate of extraction, R_A. (○) Phenol, (△) *m*-cresol, (□) resorcinol, and [sodium phenolates] = [benzoyl chloride] ≈ 2.2 × 10^{-4} g·mol/cm^3.

where Q^+Cl^- represents the PTC and the parentheses represent ion pairs. Since the catalyst is insoluble in the aqueous phase, the ion transfer step is shown as a liquid-ion exchange step. When HTPB is used as the PTC, the catalyst anion differs from the transported aqueous phase anion. An additional ion-exchange step is involved in the overall reaction, and as a result, overall R_A measured in the stirred cell experiment is lowered in the reaction studied. However, this type of behavior caused by different anions cannot be generalized but will depend on the type of reaction and reactants involved (5). Figure 3 presents log-log plots of the concentration of the reactants vs the specific rates of the extraction. From these data, the dependence of R_A on reactants concentration has been calculated (summarized in Table 1).

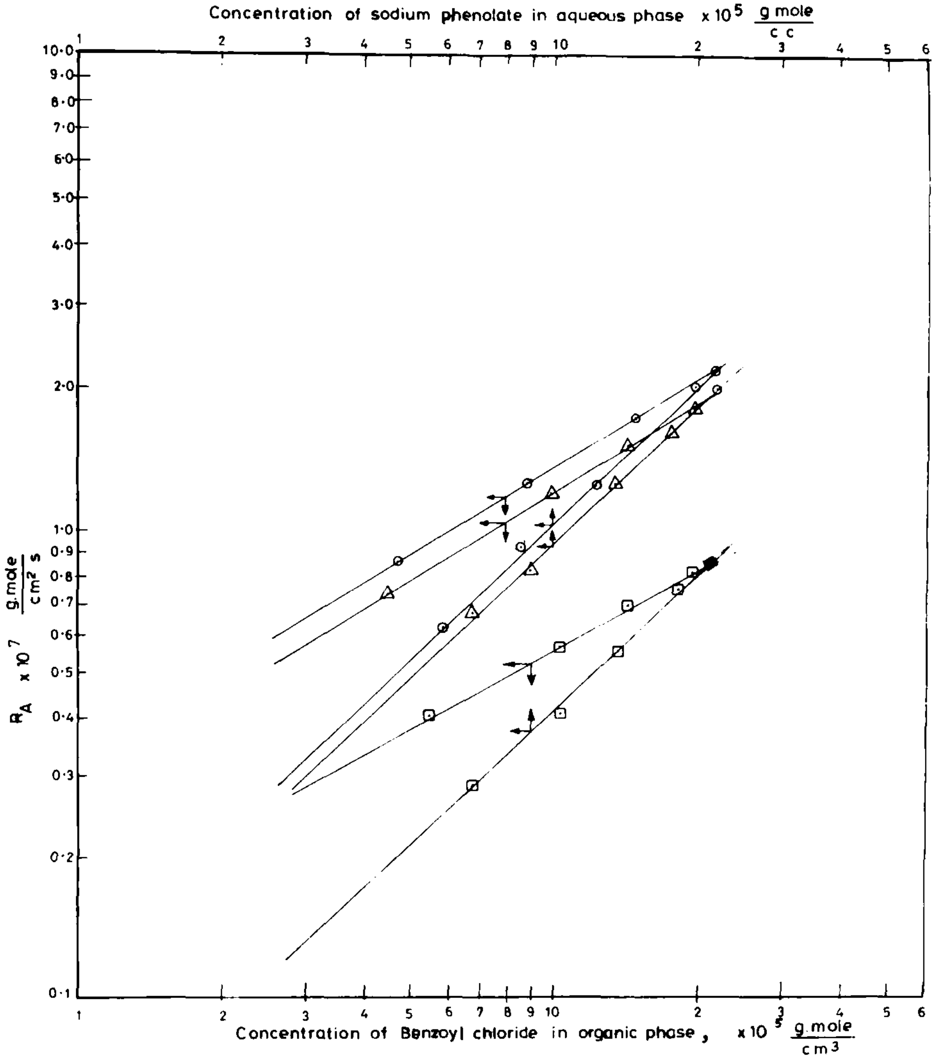


FIG. 3. Effect of concentration of phenolate {[benzoyl chloride] = 2.2 × 10^{-4} g·mol/cm^3} and of benzoyl chloride concentration {[sodium phenoate] = 2.3 × 10^{-4} g·mol/cm^3} on R_A. (○) Phenol, (△) *m*-cresol, and (□) resorcinol, all at [PTC] = 15 × 10^{-6}.

TABLE 1
Dependence of R_A on Reactant Concentration

Phenolic substance	Organic reagent	Order with respect to concentration of	
		Phenolate ion	Benzoyl chloride
Phenol	Benzoyl chloride	1.0390	0.503
m-Cresol	Benzoyl chloride	0.9839	0.532
Resorcinol	Benzoyl chloride	0.9817	0.533

The values of R_A obtained with both stirred cells were comparable under otherwise identical conditions. For example, at a PTC concentration of 15×10^{-6} g·mol/cm^3 and equal concentrations of sodium phenoate in g·mol/cm^3, R_A values were 1.95×10^{-7} and 1.98×10^{-7} g·mol/cm^2·s for the 6.8 and 10 cm i.d. stirred cells, respectively. Therefore, it may be inferred that R_A is independent of interfacial area. Further, within the range of stirring speed studied, the effect of the hydrodynamic boundary layer on R_A can be neglected. The results of the stirred cell experiments indicate that R_A is directly proportional to the phenolate ion concentration and to the square root of the benzoyl chloride concentration. This also implies that the two-phase reaction conforms to the fast pseudo-first-order reaction regime for which the volumetric rate of extraction (R_Aa) may be expressed as (*8*)

$$R_Aa = a[A^*]\sqrt{D_Ak_2[B_0]} \tag{1}$$

where a = effective liquid–liquid interfacial area, cm^2/cm^3 of dispersion; $[A^*]$ = interfacial concentration of Reactant A (sodium phenoate) in Phase B′ where the reaction takes place, g·mol/cm^3; B_0 = concentration of Reactant B (benzoyl chloride) in bulk phase B′, g·mol/cm^3; D_A = diffusivity of A in Phase B′, cm^2/s; and k_2 = second-order rate constant, cm^3/mol·s. It will be shown later than R_Aa varies linearly with the stirring speed in the agitated contactors, indicating the dependence of R_Aa on the interfacial area. In this case, the overall reaction may be represented as

$$Q^+Y^- + RX \rightarrow \text{product} \tag{2}$$

Therefore, the volumetric rate of extraction is given by

$$R_Aa = a[Q^+Y^-)\sqrt{Dk_2[RX]} \tag{3}$$

where $[Q^+Y^-]$ = interfacial concentration of the ion-pair; [RX] = concentration of the organic reactant (benzoyl chloride) in the organic phase;

D = molecular diffusivity of Q^+Y^- in the organic phase; Q^+ = quaternary phosphonium ion of the PTC; and Y^- = aqueous anion, i.e., phenolate. The validity of the reaction scheme is supported by the observation that for many substitution reactions, the ion-pair Q^+Y^-, rather than the aqueous anion, is often the reactive species, in which case the ion-pair diffusivity and its interfacial concentration become the parameters for rate expression (*9*). The lower values of R_Aa for cresol and resorcinol are possibly realized through low values of their respective ion-pair diffusivities and interfacial concentrations.

The results of percent conversion versus reaction time from the batch agitated reaction experiments are given in Fig. 4. The percentage conversion under identical conditions with respect to the phenolic substances changes in the order phenol > *m*-cresol > resorcinol. Chromatographic analysis of the organic phase and spectrophotometric analysis of the aqueous phase revealed that the product of the reaction, i.e., an ester, is completely extracted to the organic phase. The effect of the aqueous to organic phase volume ratio on conversion can be seen from the data of

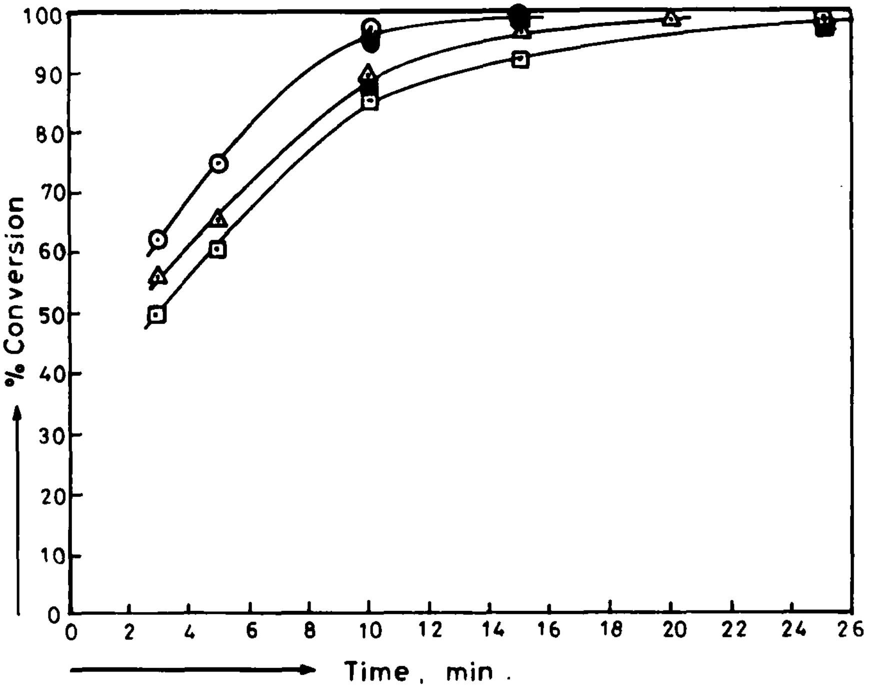


FIG. 4. Effect of reaction time on percent conversion at 2:1 phase volume ratio. (○) Phenol, (△) *m*-cresol, and (□) resorcinol. Shaded symbols represent data for 3:1 ratio.

TABLE 2
Conversion of Phenolic Substances at Two-Phase Volume Ratios (A:O). Initial Concentration of Phenolics: 6000 ppm

Phenolics	A:O[a]	Reaction time (min)	% Conversion	Final concentration (ppm)
Phenol	2:1	10	98.55	87.0
Phenol	2:1	15	99.85	9.0
m-Cresol	2:1	10	98.50	90.0
m-Cresol	2:1	15	98.90	66.0
m-Cresol	2:1	20	99.70	18.0
Resorcinol	2:1	10	85.50	870.0
Resorcinol	2:1	15	91.25	525.0
Resorcinol	2:1	25	99.75	15.0
Phenol	3:1	10	96.22	226.8
Phenol	3:1	15	99.70	18.0
m-Cresol	3:1	15	97.75	135.0
m-Cresol	3:1	20	99.72	16.8
Resorcinol	3:1	15	87.00	780.0
Resorcinol	3:1	20	99.70	18.0

[a] A = aqueous phase, O = organic phase.

Table 2. It is noteworthy that an essentially comparable degree of conversion can be obtained at both 2:1 and 3:1 ratios under otherwise identical experimental conditions. A ratio of 3:1 is very likely to prove economical in an industrial treatment process. However, at this ratio, a certain degree of emulsification in the separated aqueous phase is obtained with a concommitant observation of lowering of solvent phase volume, reflected in a certain loss of solvent (less than 1%) as well as some product in the aqueous phase.

However, the data of Table 2 show that it is possible to remove phenolic substances from wastewater to 9, 16.8, and 15 ppm of phenol, *m*-cresol, and resorcinol, respectively, under certain conditions.

The effect of stirring speed on R_Aa is shown in Fig. 5. The linear increase of R_Aa within the range of 500 to 1500 rpm might be attributed to the increase of interfacial area over a wide range. This observation is in agreement with that reported for diffusion-limited phase transfer catalyzed alkaline hydrolysis of formate esters (*10*). The finding is of practical relevance since industrial reactors can be designed for the known interfacial areas.

In Table 3, the results of batch experiments involving a mixture of phenolic substances in the aqueous phase are reported. The percentage conversion when using a stoichiometric amount of benzoyl chloride is reasonably low in comparison with the results of experiments with a single

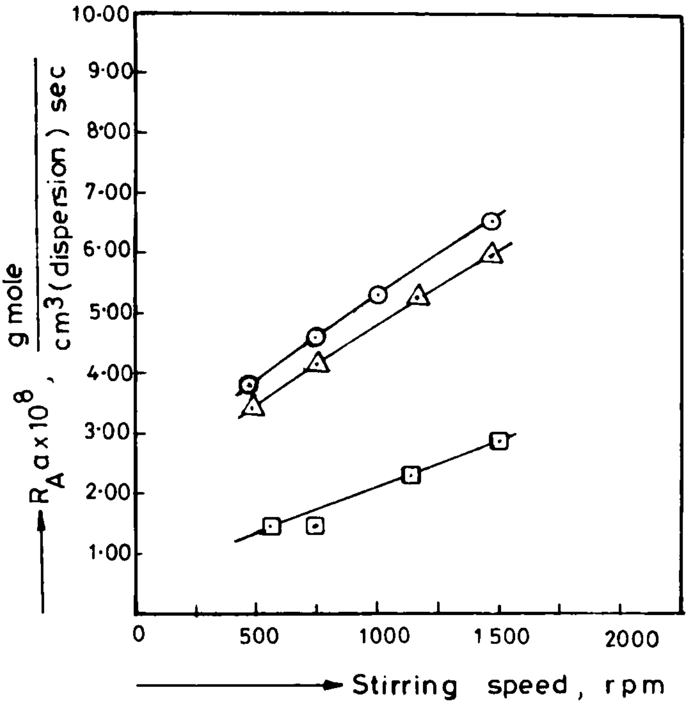


FIG. 5. Effect of stirring speed on R_Aa. (○) Phenol, (△) *m*-cresol, and (□) resorcinol with PTC concentration = 15×10^{-6} g·mol/cm^3; reaction time = 3 min; initial phenolic concentration = 5000 ppm.

phenolic component. Further, chromatographic analysis of the product indicates the presence of a number of trace impurities. This implies that rather tedious product purification and recovery steps are likely to be involved in any commercial process. However, by increasing the amount of benzoyl chloride to threefold over the stoichiometric amount, an increase in conversion is achieved, perhaps through enhancement of R_A due to an increase of the organic reactant concentration. In this case the product purity is also high, i.e., of the order of 90%, as was evident from a chromatographic analysis of the product. Further experiments with a fourfold increase of PTC and the reactant concentration did not show any improvement over the results reported in the preceding section. It is inferred from the above results that Aliquat 336 is a better PTC (2) than HTPB for the conversion of phenol to phenyl benzoate. To further reduce the phenol concentration, two experiments were carried out with 15 ppm phenol, and it was possible to reduce the phenol concentration to 6 ppm. These results

TABLE 3
Conversion of Phenolics from Mixture Component in Batch Experiments

Reaction time (min)	Initial concentration (ppm)			Quantity of benzoyl chloride	% Conversion		
	Phenol	*m*-Cresol	Resorcinol		Phenol	*m*-Cresol	Resorcinol
PTC Concentration: 15 × 10^{-6} g·mol/cm^3							
10	2000	1000	1000	Stoichiometric	46.5	38.5	26.5
20	2000	2000	1000	"	80.5	60.6	40.7
10	2000	1000	1000	3.5 mol/mol phenolics	90.1	71.3	55.6
20	2000	1000	1000	"	98.1	85.4	75.5
25	2000	1000	1000	"	99.5	96.8	98.3
PTC Concentration: 60 × 10^{-6} g·mol/cm^3							
10	2000	1000	1000	Stoichiometric	65.6	61.5	55.5
10	2000	1000	1000	3.5 mol/mol phenolics	99.5	96.7	94.2

indicate that it may not be possible to use this reaction scheme for the treatment of phenolic wastewater in a single step to meet industrial wastewater disposal requirements. In view of this, recycling of the effluent as a process water after the reaction with HTPB and subsequent recovery of the product is proposed. Alternately, it may be necessary to degrade the phenol biologically after recovery of the product through the proposed reaction scheme. However, in the latter case the combined technoeconomics of product recovery and the processing cost for biological treatment should be worked out before such a scheme can be suggested for phenolic wastewater.

Some Aspects of Product Recovery, Solvent, and Catalyst Recycle

Product recovery from the organic phase through the usual procedure of distillation cum evaporative crystallization has met with partial success, i.e., the product is contaminated with PTC and solvent recovery for recycle is always less than 95%. While the degree of solvent recovery achieved may be considered reasonable, undesirable product contamination with PTC implies loss of the costly PTC compound. It is recognized that by using PTC immobilized on solid supports such as polymers or inorganic oxides (triphase catalyst), catalyst recovery and recycling problems may be solved (*11*). The generally observed low activity of polymer-supported catalyst has been improved by utilizing long-spacer chain bonding the catalyst to the polymer matrix (*11*). A fixed-bed reactor (*12*) is suitable for use with a polymer-supported catalyst.

Preliminary work has been carried out by the authors on the use of some supported PTC for the reaction scheme. Supported catalysts were prepared by treating macroporous polystyrene beads with tri-*n*-butylphosphine by refluxing in 1,2-dichloropropane following the procedure reported by Ford et al. (*13*). Conversion around 80% could be achieved in 1 h by using the catalyst prepared under suitably manipulated conditions. It appears that rate enhancement of the reaction is very low compared to the results of experiments with soluble catalyst. Further work aimed at enhancing the triphase catalyzed reaction rate is in progress.

CONCLUSION

A phase transfer catalyzed reaction may be exploited for development of a process for recovery of a significant amount of phenols as useful products from industrial wastewater. Product recovery, solvent, and catalyst recovery or recycle need to be investigated in detail before the commercial application of such a reaction scheme can be exploited.

Acknowledgments

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