Theoretical and experimental analysis of capsule membrane phase transfer catalysis: selective alkaline hydrolysis of benzyl chloride to benzyl alcohol

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Intensification of and selectivity in multiphase reactions catalysed by phase transfer catalysts can be greatly improved by the use of the so-called capsule membrane-PTC (CM-PTC) technique in comparison with the L-L PTC. We report here the theoretical and experimental analysis of the CM-PTC and inverse CM-PTC for exclusively selective formation of benzyl alcohol from the alkaline hydrolysis of benzyl chloride. The theoretical analysis shows that it is possible to simultaneously measure the rate constant and equilibrium constant under certain conditions. The effects of speed of agitation, catalyst concentration, substrate concentration, nature of catalyst cation, membrane structure, nucleophile concentration, surface area for mass transfer and temperature on the rate of reaction are discussed.

Keywords: Phase transfer catalysis; alkaline hydrolysis of benzyl chloride

1. Introduction

Selectivity engineering refers to the engineering aspects of multiphase reactions that could be manipulated through the use of several techniques such as use of an additional immiscible liquid phase, porous inert solids, particles smaller than diffusion film thickness, etc. in order not only to intensify the rates of reaction but also to improve greatly the selectivity of the desired product. Under this ambit, shape selective catalysts, immobilized enzymes and phase transfer catalysts can be embraced. We are particularly concerned in this paper with the selectivity engineering aspects of the capsule membrane phase transfer catalysis, which has interesting attributes, for the preparation of benzyl alcohol by selective alkaline hydrolysis of benzyl chloride.

In the industrial process, benzyl alcohol is normally manufactured by refluxing

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benzyl chloride with an alkali over a very long period (~ 24 h). However, this process leads to significant formation of the byproduct benzyl ether [1]. Several attempts have been reported in the literature to suppress the yields of the ether. Thus, it was thought desirable to employ the technique of capsule membrane phase transfer catalysis [2] to enhance the rate of reaction and particularly the selectivity of benzyl alcohol.

Phase transfer catalysts, despite their many advantages in liquid–liquid and solid–liquid systems, suffer from the disadvantage that the catalyst cannot be recovered easily and reused and, in fact, on industrial scale they are a major source of pollution. In order to overcome this problem, triphase catalysts, which are bound to a polymer matrix, were introduced in the late 1970s. However, binding a phase transfer ammonium, phosphonium or polyethylene glycol catalyst to the solid phase, leads to loss in activity and thus to an increase in reaction times.

In their pioneering work in 1985, Okahata et al. [2] introduced the concept of capsule membrane supported phase transfer catalysis (CM-PTC), wherein the phase transfer catalyst is grafted onto the surface of a porous ultrathin nylon capsule membrane. The chief advantage of this technique is that the hydrophobic onium salt or polyethylene glycol grafted on the capsule membrane physically separates the organic and aqueous phase reactants because the inner phase contains the organic substrate in a suitable solvent and the outer phase is an aqueous phase containing the nucleophile. This technique changes the selectivity drastically because the phase transfer catalyst attached to long graft polymer chains can move freely between the inner organic and the outer aqueous phase. Problems associated with emulsification due to the surface active properties of the phase transfer catalyst are eliminated in the capsule grafted technique. The pore size distribution of the membrane also plays a very vital role in getting favourable selectivity.

INVERSE CAPSULE MEMBRANE PHASE TRANSFER CATALYSIS (ICM-PTC)

The literature on CM-PTC so far reveals that no attempt has been made to exploit this technique in terms of the reusability of the capsule. The normal practice of digesting the capsule with the organic phase reactant (substrate) suffers from the disadvantage that the capsules have to be either releached with organic solvents to extract the organic phase or to be broken totally to recover the product. Therefore, the same capsules cannot be reused. Thus, there is a merit in having the aqueous phase nucleophile inside the capsule and the organic phase substrate as the bulk outside phase. This way, the capsule can be reused several times and the process can be made economical. The aqueous phase byproduct salt could be washed easily with water, or digested with fresh aqueous solution of the substrate. We have named this process as inverse capsule membrane phase transfer catalysis (ICM-PTC) wherein the locale of the reaction is likely to be outer surface of the capsule. Some aspects of ICM-PTC are also reported in this paper.

2. Experimental

Large, semipermeable ultrathin nylon capsules were prepared from amines and acid chloride by interfacial polymerisation by using a drop technique. However, a small amount of crosslinking agent (trimesoyl chloride) was added to obtain a strong and hard capsule membrane [2]. 2 ml volume of an aqueous solution containing 0.8 M NaOH and a suitable amine (such as ethylenediamine/diethylenetriamine/triethylenetetramine = 0.38/0.6/0.75 M was added dropwise from a syringe to a mixture of chloroform (75 ml), cyclohexane (25 ml), terephthaloyl chloride (1 mmol) and trimesoyl chloride (0.03 mmol). Nylon capsules having ultrathin thickness (7.625 μm) and small diameter (1.74 mm), as measured by using a high performance image analyser model (TN 8502, Tracor-Northen, USA) were obtained. Three different types of capsules, with different amines were prepared with ethylenediamine, diethylenetriamine and triethylenetetramine.

2.1. SUPPORTING PTC ON CAPSULE

The nylon capsules prepared with different amines were used to graft a suitable phase transfer catalyst (PTC). Initially, capsules prepared with ethylenediamine were chosen to support the following PTCs:

(i) Aliquat-336 (trioctylmethylammonium bromide),

(ii) tetrabutylammonium bromide (TBAB),

(iii) cetyltrimethylammonium chloride (CTMAC).

A saturated solution of the desired catalyst was prepared in acetone, into which a known number and weight of capsules were added, stirred for 30 min and then allowed to soak for additional 3 h. Finally the capsules were filtered off and dried at 70°C for 2 h. An isopropanol wash was given to the capsule to remove any unbound PTC followed by drying. The difference in the weight of the capsule denoted the amount of catalyst bound onto the capsule. Thereafter the same capsules were digested with benzyl chloride for about 12 h to allow its diffusion inside the capsules. The time for digestion was based on a number of previous trials. After digestion, the capsules were filtered off and washed carefully from outside with isopropanol and dried gently. Once again they were weighed to determine the actual amount of the reactant benzyl chloride that had penetrated the capsules. In order to minimise errors associated with weighing, etc., a large number of capsules were employed for each experiment and utilised for the reaction.

In the case of ICM-PTC, after the phase transfer catalyst was grafted on them, the capsules were digested with the aqueous phase containing the substrate.

2.2. REACTION PROCEDURE

The reactions were studied in a 5 cm i.d. fully baffled mechanically agitated con-

tactor, of 250 cm^3 of total capacity and equipped with a six-bladed pitched turbine impeller and reflux condenser. The aqueous phase containing NaOH was added to the reactor and agitated at the reaction temperature, following which the requisite number of capsule containing benzyl chloride was added. In a typical experiment, 50 cm^3 of the outer phase was used with the desired concentration. The reaction was allowed to proceed to the desired time period and a few capsules were sampled out, washed, cooled and broken in chloroform to expose its organic content which was analysed by GC (Perkin Elmer, 8350). The concentration profiles were determined as a function of time for each case, from the chromatograms which were quantitatively analysed with reference to synthetic samples. 5% OV-17 on Chromosorb WHP (2 m, 1/8″) column was used for the analysis.

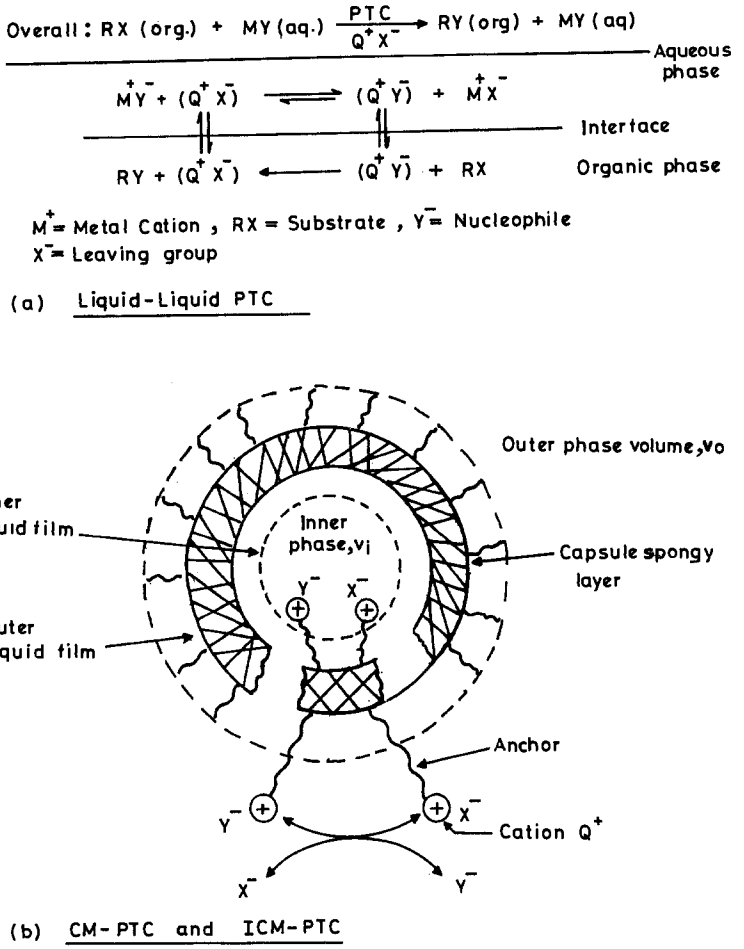

Fig. 1. Mechanism of capsule membrane phase transfer catalysis.

3. Results and discussion

3.1. MODELS OF CM-PTC AND ICM-PTC

Okahata et al. [2] have presented a mechanistic model for CM-PTC wherein the organic phase reactant resides inside the capsule membrane and aqueous phase reactants outside. A generalised model for both CM-PTC and ICM-PTC is depicted in fig. 1, along with the liquid–liquid PTC [3,4].

The interface between the inner and outer phases would lie in the spongy layer of the capsule, wherein the PTC polymer is grafted. The exact location of the interface inside the thin layer of the membrane would depend on several factors, including the preferential wettability of the membrane, its pore size distribution, the external pressure exerted by the outside phase in the agitated mixture, etc. Since the reaction mechanism is of S_N2 type, there should be an exchange of ions via the PTC on spacer chains or anchors which are dangling across the aqueous and organic phases. The reaction is interfacial. Furthermore, the said hypothesis which discusses the microscopic phenomenon can only be tested by macroscopic observations. Additionally the length of anchors, the thickness of the membrane and the thickness of the liquid films adjacent to the interface ought to be considered. Since the membranes are hydrophobic, there is a possibility of formation of a micellar-like oil–water interface in the spongy layer but it can be discounted on the basis of other observations that are characteristics of true PTC, one of them being the linear dependence of rate on the concentration of the PTC. It appears that the reaction occurs either at the interface or at the immediate vicinity of the interface in the organic phase upto which the anchors are mobile. In view of the very small thickness of the membrane and small lengths of the anchors, for all practical purposes, the surface area of the capsule can be assumed to be the locale of the reaction.

With reference to fig. 2, a simple picture of the various steps can be depicted. At steady state, the following specific rates based on unit surface area (gmol/cm^2 min) hold:

rate of transfer of Y^- from the bulk exterior phase to the outer capsule surface

$$= r_Y \tag{1}$$

$$= \text{rate of exchange of } [Y^-_{so}] \text{ with } [Q^+X^-_{so}] \text{ at the anchor dangling outside the surface} \tag{2}$$

$$= \text{rate of transfer of } [\ ]\text{–}Q^+Y^-_{so} \text{ from outer phase anchor to the inner phase} \tag{3}$$

$$= \text{rate of transfer of substrate RX from inside bulk phase to the inside capsule surface} \tag{4}$$

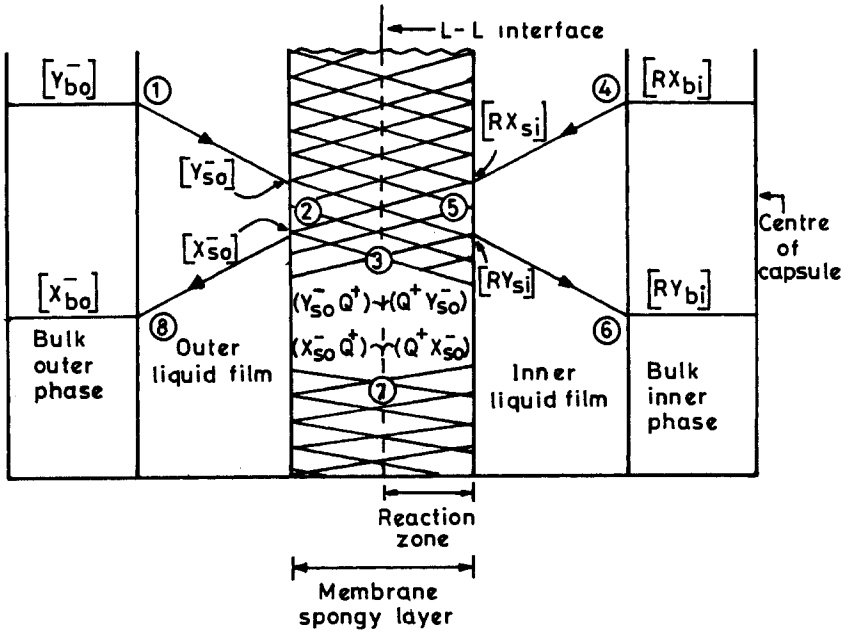

Fig. 2. Capsule membrane PTC: concentration profiles.

= rate of reaction at interface to generate RY (5)

= rate of transfer of product RY from the inner surface to the inside bulk phase of capsule (6)

= rate of transfer of $]\text{–}Q^+X^-_{si}$ generated at the anchorlocated inside, to the outer surface of capsule (7)

= rate of transfer of X^-_{so} at the anchor at the outer surface of capsule to the outside bulk phase. (8)

In the above equations the second subscript refers to the inner (i) or outer (o) phase; b refers to bulk and s to surface. Any of the above (eight) steps could control or, for that matter, more than one step may control the overall rate.

Resistance due to steps (1) and (8) can be eliminated by using high speeds of agitation. It can be argued that except step (5) all other steps are fast and therefore, the specific rate of reaction in the spongy layer can be calculated.

The overall rate can be arrived at by eliminating the unknown concentration terms and the total resistance would thus comprise of several resistance in series. A detailed analysis of the theory is presented elsewhere [5].

For step (5) as the rate determining step the specific rate of reaction for n capsules (diameter d) was found to be

$$-\frac{\mathrm{d}[\mathrm{RX_{si}}]}{\mathrm{d}}t = n(\pi d^2)\left(\frac{k_\mathrm{R}[\mathrm{RX_{si}}]}{V_\mathrm{i}}\right)\left(\frac{K[\mathrm{Q_t}][\mathrm{Y^-_{so}}]}{[\mathrm{X^-_{so}}]+K[\mathrm{Y^-_{so}}]}\right), \tag{9}$$

where $[\mathrm{Q_t}]$ = gmol of catalyst anchored on capsule/cm^2, V_i = volume of inner phase of capsule. The above equation was integrated to get the values of K and k_R under certain conditions [5].

3.2. SELECTIVITY

It was found that the capsule membrane technique was exclusively selective, in that the hydrolysis reaction led to the formation of only benzyl alcohol. Furthermore, the rates of reaction were substantially enhanced. For a liquid–liquid PTC hydrolysis, there is a substantial formation of the byproduct dibenzyl ether. This exclusive selectivity was possible because of the occurrence of the reaction in the spongy layer of the capsule, which avoids the solvolytic reactions which normally occur in other L-L PTC cases.

The kinetic data were interpreted by employing the theoretical model, under the various assumptions outlined before, because there were no complications arising out of formation of different byproducts.

3.3. EFFECT OF SPEED OF AGITATION

The preliminary experiments were run at different speeds of agitation of the reaction mixture, under otherwise similar conditions. Typically 100 capsules were used at a temperature 100°C and the conversions were monitored as a function of time. It was interesting to note that the conversions increase substantially with speed below 500 rev/min, because the reactions are controlled by mass transfer. It was also observed that beyond 750 rev/min the speed had no effect on conversion and hence on the rates of reaction, thereby indicating absence of liquid-to-membrane surface mass transfer resistance both inside and outside the capsules. The reaction could be taken as kinetically controlled and governed by eq. (5). This was further confirmed by studying the effect of temperature and the values of activation energy, which will be discussed later. Further experiments were conducted beyond these speeds which were safe to maintain the fidelity of the capsules.

3.4. MEASUREMENT OF EQUILIBRIUM CONSTANTS AND RATE CONSTANTS

As delineated earlier, by careful manipulation of variables, it was possible to calculate the rate constant k_R and the equilibrium constant K. For the alkaline hydrolysis of benzyl chloride, the typical molar ratio of NaOH to benzyl chloride was 20.4 when 100 capsules were used. It was observed that upto 85% conversions the

experimental data could be correlated by the pseudo-first. It was possible to obtain K and k_R values, under certain conditions. Table 1 summarises the individual values of k_R and K by changing the different variables. It can be seen that the average values obtained from the plots are consistent. The k_R are reported in cm^3/gmol min and K values are dimensionless. It is interesting to know that the equilibrium constant values for the]–Q^+OH^- are around 0.5 which are almost ten times higher than that for the L-L PTC. This explains the enhancement in CM-PTC reactions.

3.5. EFFECT OF CATALYST CONCENTRATION

The observed rates of reaction should be proportional to the catalyst concentration in the true PTC unlike the micellar catalysis. The initial rates of reaction were plotted against the catalyst concentration under otherwise similar conditions as shown in fig. 3, which confirms that the reaction is true PTC, because of the linear dependence of rate on catalyst concentration.

3.6. EFFECT OF DIGESTION TIME OR CONCENTRATION OF SUBSTRATE

Different amounts of concentrations of benzyl chloride were introduced into the capsules by varying the digestion period to study the effect of concentration of benzyl chloride on the rate under otherwise similar conditions. Fig. 4 shows the effect of concentration, where rates are directly proportional to the concentration of benzyl chloride under otherwise similar conditions.

3.7. EFFECT OF STRUCTURE OF PTC CATION

Three different phase transfer catalysts, namely, TBAB, Aliquat-336 and CTMAC were evaluated under otherwise similar conditions (fig. 5). The anchored TBAB was found to be superior to others in the following orders (k_R, K). TBAB (700, 0.4) > Aliquat-336 (269.2, 17.05) > CTMAC (145.2, 17.17). It appears that, although K values for the more bulky catalyst are higher than TBAB, the less bulky TBAB anchor is more mobile across the interface, thereby resulting into higher rates of reaction because anion exchange is very high. The low K values for the TBAB are thus of no consequence because the anion exchange taking place in the aqueous phase across the interface is much faster for TBAB than the other two catalysts.

3.8. EFFECT OF STRUCTURE OF MEMBRANE POLYMER

The capsules prepared with EDA, DETA and TETA which were anchored with TBAB as PTC were used to compare the effect of polymer structure on the rate of hydrolysis reaction. The k_R are 700, 641.2 and 575.7 respectively. This could

Table 1
Rate constant and equilibrium constants for CM-PTC hydrolysis of benzyl chloride

Variables	k_R (cm^3/gmol min)	K
effect of temp.		
100°C	700.1	0.500
75°C	250.1	0.500
60°C	90.3	0.484
catalyst loading (gmol)		
6.713E − 5	700.1	0.318
4.805E − 5	657.5	0.318
2.884E − 5	463.1	0.389
number of capsules		
100	700.1	0.628
200	774.0	0.628
500	798.0	0.773
effect of digestion time (effect of conc. of benzyl chloride) (gmol)		
2.449E − 3 (12 h)	700.1	0.499
2.133E − 3 (9 h)	696.0	0.499
1.683E − 3 (6 h)	689.8	0.446
effect of concentration of nucleophile (gmol)		
0.05	700.1	0.292
0.10	755.0	0.292
0.25	762.0	0.366
effect of addition of NaCl (gmol)		
0.0000	700.1	0.400
0.1709	700.0	0.400
0.3418	700.0	0.400
effect of surface area of capsules (dia in mm)		
1.74	700.1	0.320
1.10	791.4	0.320
4.92	610.9	0.280
effect of different catalysts		
TBAB	700.1	0.500
Aliquat-336	315.0	17.050
CTMAC	213.0	17.170
effect of different capsule membranes		
EDA	700.1	0.500
DETA	641.0	17.040
TETA	575.6	16.020
inverse CM-PTC	220.1	0.261

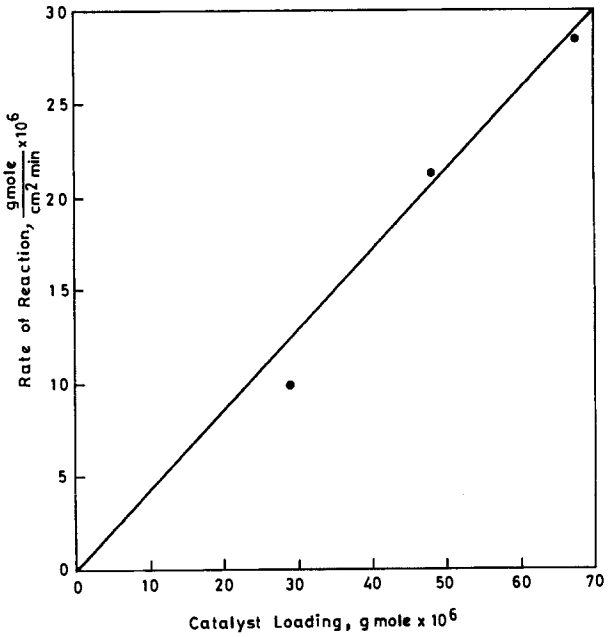

Fig. 3. Effect of catalyst loading; catalyst, TBAB; temperature, 100°C; number of capsules, 100; [BnCl], 2.449E – 03 gmol; [NaOH], 0.05 gmol; V_i, 0.27 cm^3; V_o, 50 cm^3; speed of agitation, 750 rpm.

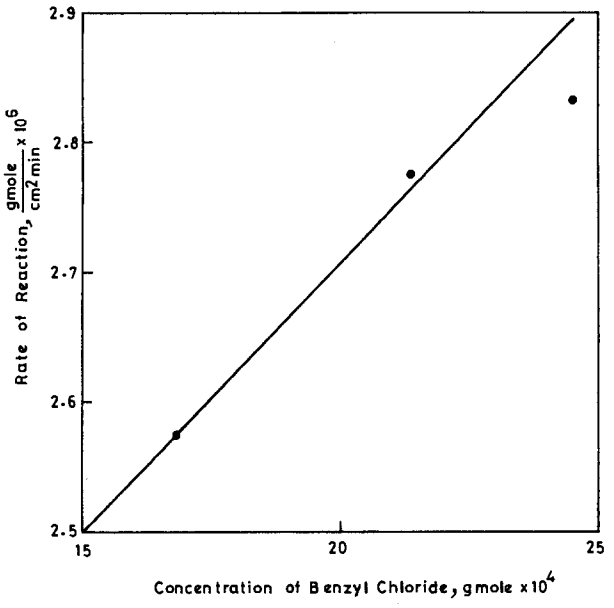

Fig. 4. Effect of concentration of benzyl chloride; catalyst, TBAB; temperature, 100°C; number of capsules, 100; Q_t, 7.076E – 06 gmol/cm^2; [NaOH], 0.05 gmol; V_i, 0.27 cm^3; V_o, 50 cm^3; speed of agitation, 750 rpm.

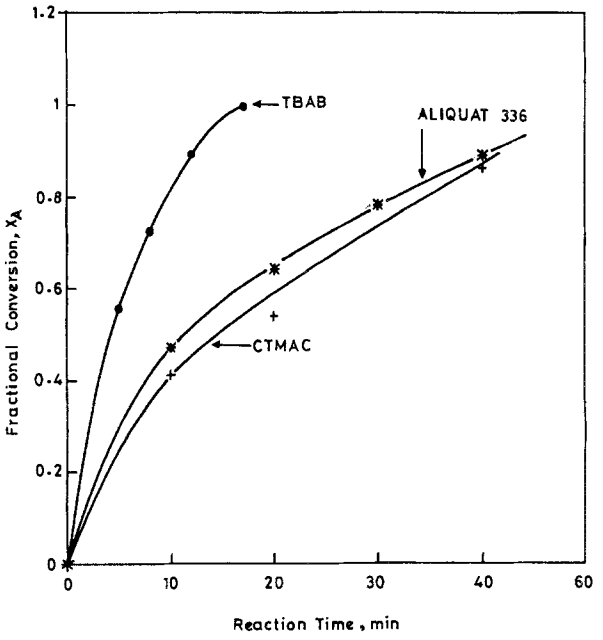

Fig. 5. Effect of different catalysts; temperature, 100°C; number of capsules, 100; Q_t, 7.076E – 06 gmol/cm^2; [BnCl], 2.449E – 03 gmol; [NaOH], 0.05 gmol; V_i, 0.27 cm^3; V_o, 50 cm^3; speed of agitation, 750 rpm.

be attributed to better mobility of anchors in the porous network of EDA membranes.

3.9. EFFECT OF CONCENTRATION OF NUCLEOPHILE IN AQUEOUS PHASE

Fig. 6 shows the effect of concentration of aqueous phase nucleophile Y^- in the aqueous phase under otherwise similar conditions. The ionic strength of the solution was also calculated. It was found that the ionic strength of aqueous phase in the alkaline hydrolysis case was varied from 1.0×10^{-3} to 5×10^{-3} gion/ℓ. This was further confirmed by adding NaCl salt (10 and 20 g) to the aqueous phase in the beginning to vary the ionic strength as well as to study the effect of Cl^- on K. It is interesting to note that the conversions were unaffected thereby indicating that the K values were also not influenced, unlike the regular L-L PTC. There was no effect on the rate of reaction and hence rate constant. K is dependent on ionic strength among other factors for L-L PTC but binding the PTC to the anchor results into enhanced rates.

3.10. EFFECT OF SURFACE AREA

Here three different capsule sizes (1.1, 1.74 and 4.92 mm) were taken and the number of capsules were chosen in order to have the same concentration of the sub-

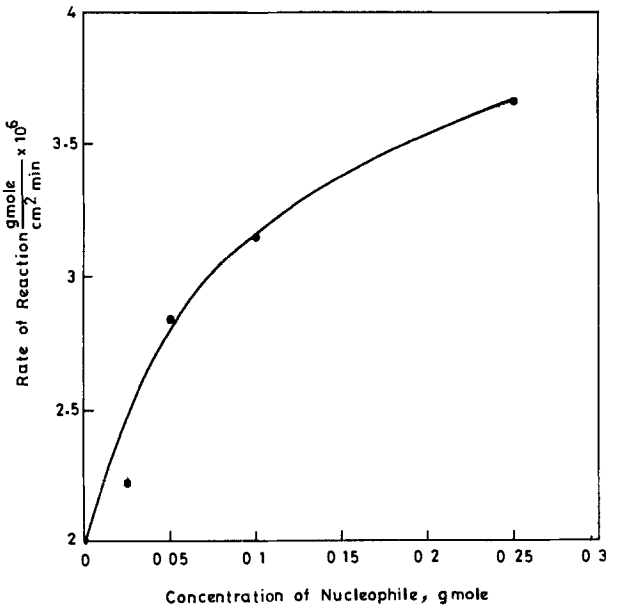

Fig. 6. Effect of concentration of NaOH; catalyst, TBAB; temperature, 100°C; number of capsules, 100; Q_t, 7.076E – 06 gmol/cm^2; [BnCl], 2.449E – 03 gmol; V_i, 0.27 cm^3; V_o, 50 cm^3; speed of agitation, 750 rpm.

strate, nucleophile and the catalyst. The rate of reaction is directly proportional to surface area, which supports the arguments put forward before that the reaction occurs in the spongy layer of the capsule surface.

3.11. EFFECT OF TEMPERATURE

The Arrhenius type plot was made to study the effect of temperature on rate constant (k_R). The activation energy was found to be 12.54 kcal/gmol. This value also suggests that there was no influence of mass transfer and the reaction occurs at the capsule surface.

3.12. INVERSE-CM-PTC

The ICM-PTC reactions were conducted by taking the aqueous phase nucleophile inside and the substrate in organic phase outside, wherein the organic phase was diluted with toluene to maintain same volume of outer phase for 100 capsules. The values of k_R and K obtained were less than the CM-PTC (table 1) although the selectivity was 100%. The lower rates could be attributed to the change in polarity of the organic phase, change in K values due to deficiency of nucleophile, etc. The reusability of capsule was found to be much better in the ICM-PTC. Further work is in progress.

4. Conclusions

A complete experimental analysis of capsule membrane phase transfer catalysis has been done for the alkaline hydrolysis of benzyl chloride. Further support to the theoretical model has been generated by the reaction of benzyl chloride with aqueous sodium acetate and aqueous chromate to give benzyl acetate and benzaldehyde, respectively [5,6]. It is possible to determine both rate constant and equilibrium constant for the same data. There is 100% selectivity to benzyl alcohol with no formation of any byproduct, both for CM-PTC and ICM-PTC. There is a tremendous scope for research on various aspects of the CM-PTC and ICM-PTC techniques to be exploited for the intensifications of rates of a variety of multiphase reactions and the selectivity of desired products.

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References

[1] R.E. Kirk and D.F. Othmer, *Encyclopedia of Chemical Technology*, Vol. 3, 3rd Ed. (Wiley–Interscience, New York, 1979) p. 795.
[2] Y. Okahata, K. Ariga and T. Seki, J. Chem. Soc. Chem. Commun. 51 (1985) 920.
[3] E.V. Dehmlow and S.S. Dehmlow, *Phase Transfer Catalysis*, 2nd Ed. (Verlag Chemie, Weinheim, 1983).
[4] C.M. Starks and C. Liotta, *Phase Transfer Catalysis: Principles and Techniques* (Academic Press, New York, 1978).
[5] G.D. Yadav and P.H. Mehta, Langmuir, submitted.
[6] G.D. Yadav and B.V. Haldavanekar, Langmuir, submitted.