# Alkaline Hydrolysis of *n*-Butyl Acetate with Phase Transfer Catalyst Aliquat 336

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*A reasonable analytical procedure of the overall reaction rate for the phase transfer catalysis with mass transfer is discussed. Alkaline hydrolysis of n-butyl acetate with a phase transfer catalyst Aliquat 336 (tricaprylmethylammonium chloride, $Q^+Cl^-$) was chosen as a model system and carried out in an agitated vessel with a flat interface. Overall reaction rates observed were proportional to the interfacial concentration of the actual reactant $Q^+OH^-$ (the ion pair consisting of quaternary ammonium cation $Q^+$ and $OH^-$) for the hydrolysis in the organic phase. The interfacial concentration of $Q^+OH^-$ was a unique function of bulk concentrations of the catalyst and NaOH, and the ionic strength of the aqueous solution. This behavior of the overall reaction rates was explained by the proposed model solution. The reaction rate constant, evaluated by fitting the rate data to the model prediction, was 47 $m^3/kmol \cdot s$ at 298 K. It was 70 or more times greater than that of conventional alkaline hydrolysis in the aqueous phase.*

## Introduction

In many heterogeneous liquid-liquid reaction systems, where the reactions seldom take place substantially in either phase due to very low reactivity caused by the sparing mutual solubility, the reaction rates could be promoted by adding the quaternary onium salts or crown ethers. Since these phenomena were systematized by Starks (1971) as phase transfer catalysis, their catalysts have been found to offer many benefits, such as high product yield and high selectivity under rather mild reaction conditions (Weber and Gokel, 1977; Starks and Liotta, 1978; Dehmlow and Dehmlow, 1983; Keller, 1986). Therefore, the use of their catalysts has become increasingly important in such fields as organic synthesis, polymer chemistry, inorganic chemistry, and photo chemistry.

In most of the reaction systems previously studied, the main chemical reactions were still very slow even in the presence of phase transfer catalysts, and the mass transfer resistance of relevant species was negligibly small. The use of a phase transfer catalyst, however, may be effective also for moderately slow reactions, shifting the reaction regime to a fast reaction regime, as demonstrated by Lele et al. (1983) for the alkaline hydrolysis of formic esters with various quaternary ammonium salts (cetyltrimethylammonium bromide, tricaprylmethylammonium chloride, lauryltrimethylammonium chloride) and laurylpyridinium chloride as phase transfer catalysts. The analysis of not so slow reactions requires a comprehensive understanding of the effect of mass transfer on the overall reaction rate.

Evans and Parmer (1981) suggested from numerical experiments of simple reactions in a pseudo-first-order and an instantaneous irreversible reaction regime that mass transfer plays an important role in the overall reaction rate. The validity of their theory, however, has not been proved experimentally. Lele et al. (1983) demonstrated how the overall reaction rates depend on the catalyst concentration. Although they claimed that the reaction rates fit qualitatively conventional theoretical predictions for the fast pseudo-first-order reaction, they did not make the analysis in view of the phase transfer catalysis. Therefore, they did not describe the evaluation procedure of the interfacial concentration of the actual reactant $Q^+OH^-$, the ion pairs consisting of lipophilic group (quaternary ammonium cations) of phase transfer catalyst and hydroxyl ion, reacting directly with ester in the organic phase, nor the value of the reaction rate constant. They also did not consider the effect of alkaline hydrolysis in the aqueous phase, which occurs simultaneously with hydrolysis in the organic phase.

In this work, the alkaline hydrolysis of *n*-butyl acetate was adopted as a test reaction system to develop a reasonable analytical procedure of overall reaction rates for relatively rapid

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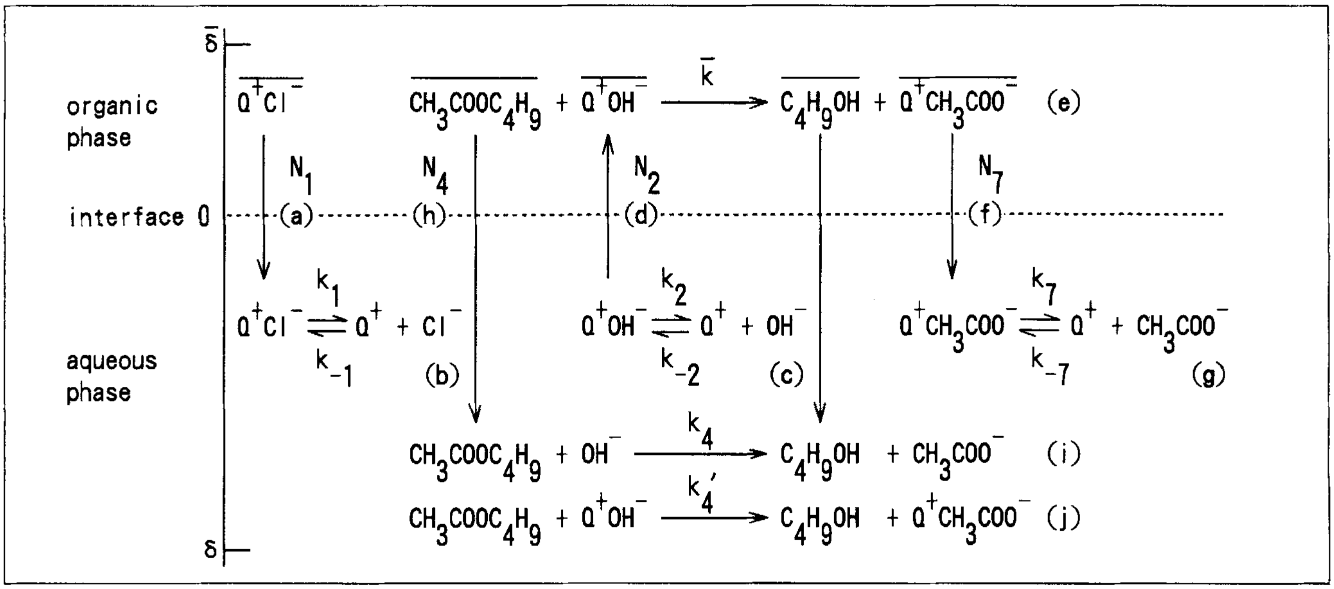

**Figure 1. Reaction-diffusion model.**

reactions. Aliquat 336 (tricaprylmethylammonium chloride) was used as the phase transfer catalyst. Overall reaction rates were measured as a heterogeneous liquid-liquid system and were analyzed by comparing them with the theoretical predictions considering the diffusion of relevant reaction species.

## Experimental Studies

The experimental apparatus used in this study was an agitated vessel, similar to that used in a previous work (Asai et al., 1983). The upper organic phase was *n*-butyl acetate containing 0.02-0.16 kmol/m$^3$ Aliquat 336 ($Q^+Cl^-$, General Mills Co. Ltd.), while the lower aqueous phase consisted of the mixed solution of NaOH and NaCl to give 0.05-2.0 kmol/m$^3$ and 0-1.9 kmol/m$^3$, respectively. NaCl was used to adjust the ionic strength of the solutions.

Samples of $1.0\times10^{-6}$-$2.0\times10^{-6}$ m$^3$ were withdrawn at intervals of 5-30 minutes. The concentration of $OH^-$ was determined by titration with a standard 0.1 kmol/m$^3$ aqueous HCl solution using phenolphthalein as an indicator. The concentration of $Q^+$ was measured by means of an ultraviolet spectrophotometer, by which the concentration of the $Q^+$-orange II complex in chloroform was determined (Scott, 1968). The concentration of $Cl^-$ was measured by mercury (II) thiocyanate method with an ultraviolet spectrophotometer (Tomonari, 1962). The initial concentration of $Q^+Cl^-$ in the organic phase was measured directly by an ultraviolet spectrophotometer.

The overall reaction rates of hydrolysis and mass transfer rates of $Q^+Cl^-$ across the interface were evaluated from the concentration variations of $OH^-$ and $Cl^-$, respectively, with time. The experiments were carried out at agitation speeds of 2.5 1/s for each phase, temperature of 298 K, and the ionic strength of 0.1-2.0 kmol/m$^3$.

## Reaction Model and Theory

The reaction-diffusion model for the present heterogeneous reaction system is shown in Figure 1. Aliquat 336 ($Q^+Cl^-$), existing initially in the organic phase, transfers to the aqueous phase (step a) and dissociates into two ions, $Q^+$ and $Cl^-$ (reaction b). The dissociated quaternary ammonium cation $Q^+$ reacts with $OH^-$ existing originally in the aqueous phase to form other ion pair $Q^+OH^-$, according to reaction c. The lipophilic ion pair $Q^+OH^-$ moves to the organic phase (step d). The ion pair $Q^+OH^-$ in the organic phase reacts with *n*-butyl acetate existing there originally (reaction e). This main reaction can be regarded as a pseudo-first-order with respect to $Q^+OH^-$, because *n*-butyl acetate is usually present excessively. The formed ion pair $Q^+CH_3COO^-$ transfers to the aqueous phase (step f) and dissociates partially into the quaternary ammonium cation $Q^+$ and acetate ion $CH_3COO^-$, according to reaction g. The resulting ion $Q^+$ produces again ion pair $Q^+OH^-$ (reaction c). This catalytic reaction cycle is repeated. *n*-Butyl acetate, dissolved partially in the aqueous phase (step h), undergoes a (1, 1)th-order, irreversible reaction with $OH^-$ and $Q^+OH^-$, according to reactions i and j, respectively.

To simplify the analysis, the effect of reaction j was assumed to be negligible compared with that of reaction i, because the bulk concentration of $Q^+OH^-$ was very small compared with that of $OH^-$ in the present reaction system. Then, the differential equations, based on the film theory describing the diffusion of each species, can be expressed as:

*For the organic phase,*

$$\bar{D}_1 \frac{d^2\overline{[Q^+Cl^-]}}{dx^2} = 0 \tag{1}$$

$$\bar{D}_2 \frac{d^2\overline{[Q^+OH^-]}}{dx^2} = \bar{D}_4 \frac{d^2\overline{[CH_3COOC_4H_9]}}{dx^2} = -\bar{D}_7 \frac{d^2\overline{[Q^+CH_3COO^-]}}{dx^2} = \bar{k}'\overline{[Q^+OH^-]} \tag{2}$$

where

$$\overline{k}' = \overline{k}[\overline{CH_3COOC_4H_9}]_b \tag{3}$$

*For the aqueous phase,*

$$D_1 \frac{d^2[Q^+Cl^-]}{dx^2} = -D_6 \frac{d^2[Cl^-]}{dx^2} = k_1[Q^+Cl^-] - k_{-1}[Q^+][Cl^-] \tag{4}$$

$$D_2 \frac{d^2[Q^+OH^-]}{dx^2} = k_2[Q^+OH^-] - k_{-2}[Q^+][OH^-] \tag{5}$$

$$D_3 \frac{d^2[Q^+]}{dx^2} = -k_1[Q^+Cl^-] + k_{-1}[Q^+][Cl^-] - k_2[Q^+OH^-] + k_{-2}[Q^+][OH^-] - k_7[Q^+CH_3COO^-] + k_{-7}[Q^+][CH_3COO^-] \tag{6}$$

$$D_4 \frac{d^2[CH_3COOC_4H_9]}{dx^2} = k_4[CH_3COOC_4H_9][OH^-] \tag{7}$$

$$D_5 \frac{d^2[OH^-]}{dx^2} = -k_2[Q^+OH^-] + k_{-2}[Q^+][OH^-] + k_4[CH_3COOC_4H_9][OH^-] \tag{8}$$

$$D_7 \frac{d^2[Q^+CH_3COO^-]}{dx^2} = k_7[Q^+CH_3COO^-] - k_{-7}[Q^+][CH_3COO^-] \tag{9}$$

$$D_8 \frac{d^2[CH_3COO^-]}{dx^2} = -k_7[Q^+CH_3COO^-] + k_{-7}[Q^+][CH_3COO^-] - k_4[CH_3COOC_4H_9][OH^-] \tag{10}$$

The boundary conditions for these equations are:

at $x=0$,

$$\begin{gathered}
[\overline{Q^+Cl^-}] = [\overline{Q^+Cl^-}]_i \\
[\overline{Q^+OH^-}] = [\overline{Q^+OH^-}]_i \\
[\overline{CH_3COOC_4H_9}] = [\overline{CH_3COOC_4H_9}]_i \\
[\overline{Q^+CH_3COO^-}] = [\overline{Q^+CH_3COO^-}]_i \\
[Q^+Cl^-] = [Q^+Cl^-]_i \\
[Q^+OH^-] = [Q^+OH^-]_i \\
[Q^+] = [Q^+]_i \\
[CH_3COOC_4H_9] = [CH_3COOC_4H_9]_i \\
[OH^-] = [OH^-]_i \\
[Cl^-] = [Cl^-]_i \\
[Q^+CH_3COO^-] = [Q^+CH_3COO^-]_i \\
[CH_3COO^-] = [CH_3COO^-]_i
\end{gathered} \tag{12}$$

at $x=\delta$,

$$[Q^+Cl^-] = [Q^+Cl^-]_b,\ [Q^+OH^-] = [Q^+OH^-]_b,\ [Q^+] = [Q^+]_b,\ [CH_3COOC_4H_9] = 0,\ [OH^-] = [OH^-]_b,\ [Cl^-] = [Cl^-]_b,\ [Q^+CH_3COO^-] = [Q^+CH_3COO^-]_b,\ [CH_3COO^-] = [CH_3COO^-]_b \tag{13}$$

where the conditions of $[\overline{Q^+OH^-}]=0$ in Eq. 11 and $[CH_3COOC_4H_9]=0$ in Eq. 13 reflect the assumption that resistances of the main reaction e and reaction i are very small compared with mass transfer resistances of $Q^+OH^-$ in the organic phase and of *n*-butyl acetate in the aqueous phase, respectively.

Mass balances at the interface ($x=0$) result in:

$$N_1 = -D_1 \frac{d[Q^+Cl^-]}{dx}\bigg|_{x=0} - D_6 \frac{d[Cl^-]}{dx}\bigg|_{x=0} \tag{14}$$

$$N_2 = D_2 \frac{d[Q^+OH^-]}{dx}\bigg|_{x=0} + D_5 \frac{d[OH^-]}{dx}\bigg|_{x=0} \tag{15}$$

$$N_4 = -D_4 \frac{d[CH_3COOC_4H_9]}{dx}\bigg|_{x=0} \tag{16}$$

$$N_7 = -D_7 \frac{d[Q^+CH_3COO^-]}{dx}\bigg|_{x=0} - D_8 \frac{d[CH_3COO^-]}{dx}\bigg|_{x=0} \tag{17}$$

$$D_3 \frac{d[Q^+]}{dx}\bigg|_{x=0} - D_6 \frac{d[Cl^-]}{dx}\bigg|_{x=0} - D_5 \frac{d[OH^-]}{dx}\bigg|_{x=0} - D_8 \frac{d[CH_3COO^-]}{dx}\bigg|_{x=0} = 0 \tag{18}$$

Here, Eqs. 14, 15 and 17 are obtained expecting that reactions b, c and g are instantaneous (Asai et al., 1991). Equation 18 comes from the requirement of electroneutrality.

From the distribution equilibria of the relevant species between both phases,

$$[Q^+Cl^-]_i = \alpha_1[\overline{Q^+Cl^-}]_i,\ [Q^+OH^-]_i = \alpha_2[\overline{Q^+OH^-}]_i,\ [Q^+CH_3COO^-]_i = \alpha_7[\overline{Q^+CH_3COO^-}]_i \tag{19}$$

The dissociation equilibria of $Q^+Cl^-$, $Q^+OH^-$, and $Q^+CH_3COO^-$ may be expected to hold at any place in the aqueous phase. Thus,

$$\begin{gathered}
K_1 = \frac{[Q^+]_i[Cl^-]_i}{[Q^+Cl^-]_i} = \frac{[Q^+]_b[Cl^-]_b}{[Q^+Cl^-]_b} \\
K_2 = \frac{[Q^+]_i[OH^-]_i}{[Q^+OH^-]_i} = \frac{[Q^+]_b[OH^-]_b}{[Q^+OH^-]_b} \\
K_7 = \frac{[Q^+]_i[CH_3COO^-]_i}{[Q^+CH_3COO^-]_i} = \frac{[Q^+]_b[CH_3COO^-]_b}{[Q^+CH_3COO^-]_b}
\end{gathered} \tag{20}$$

Solving Eqs. 1-20 simultaneously, one obtains the following expression for the overall rate of reaction e, that is, the mass transfer rate $N_2$ of $Q^+OH^-$ across the interface:

$$N_2 = \bar{\beta}_2 \bar{k}_{L2} [\overline{Q^+OH^-}]_i \qquad (21)$$

The reaction factor $\bar{\beta}_2$ and the interfacial concentration of $Q^+OH^-$ in the organic phase are given by:

$$\bar{\beta}_2 = \frac{\bar{\gamma}}{\tanh \bar{\gamma}} \qquad (22)$$

$$[\overline{Q^+OH^-}]_i = \frac{[OH^-]_b + \frac{k_{L2}}{k_{L5}} [Q^+OH^-]_b - \frac{k_{L4}}{k_{L5}} (\beta_4 - 1)[CH_3COOC_4H_9]_i}{\alpha_2 \left\{ \frac{K_2[Cl^-]_i}{K_1 \alpha_1 [\overline{Q^+Cl^-}]_i} + \frac{k_{L2}}{k_{L5}} \right\} + \frac{\bar{k}_{L2}}{k_{L5}} \frac{\bar{\gamma}}{\tanh \bar{\gamma}}} \qquad (23)$$

where

$$\bar{\gamma} = \frac{\sqrt{\bar{k}' \bar{D}_2}}{\bar{k}_{L2}}, \quad k_{Lj} = \frac{D_j}{\delta}, \quad \bar{k}_{Lj} = \frac{\bar{D}_j}{\bar{\delta}} \qquad (24)$$

The interfacial concentrations and interphase mass transfer rates of the relevant species are evaluated from the simultaneous solution of Eqs. 19-24 and the following equations:

$$N_1 = \bar{k}_{L1}([\overline{Q^+Cl^-}]_b - [\overline{Q^+Cl^-}]_i) = k_{L1}([Q^+Cl^-]_i - [Q^+Cl^-]_b) + k_{L6}([Cl^-]_i - [Cl^-]_b) \qquad (25)$$

$$N_4 = \beta_4 k_{L4} [CH_3COOC_4H_9]_i \qquad (26)$$

$$N_2 + N_4 = \bar{k}_{L2}[\overline{Q^+OH^-}]_i + \bar{k}_{L4}([\overline{CH_3COOC_4H_9}]_b - [\overline{CH_3COOC_4H_9}]_i) \qquad (27)$$

$$\begin{aligned} -N_2 + N_7 &= -\bar{k}_{L2}[\overline{Q^+OH^-}]_i + \bar{k}_{L7}([\overline{Q^+CH_3COO^-}]_b - [\overline{Q^+CH_3COO^-}]_i) \\ &= k_{L2}([Q^+OH^-]_i - [Q^+OH^-]_b) + k_{L5}([OH^-]_i - [OH^-]_b) \\ &\quad + k_{L7}([Q^+CH_3COO^-]_i - [Q^+CH_3COO^-]_b) + k_{L8}([CH_3COO^-]_i - [CH_3COO^-]_b) \end{aligned} \qquad (28)$$

$$N_4 + N_7 = k_{L4}[CH_3COOC_4H_9]_i + k_{L7}([Q^+CH_3COO^-]_i - [Q^+CH_3COO^-]_b) + k_{L8}([CH_3COO^-]_i - [CH_3COO^-]_b) \qquad (29)$$

$$k_{L3}([Q^+]_i - [Q^+]_b) - k_{L5}([OH^-]_i - [OH^-]_b) - k_{L6}([Cl^-]_i - [Cl^-]_b) - k_{L8}([CH_3COO^-]_i - [CH_3COO^-]_b) = 0 \qquad (30)$$

In Eqs. 23 and 26, $\beta_4$ refers to the reaction factor of *n*-butyl acetate, which reacts with $OH^-$ according to reaction i. Although $OH^-$ is consumed by both reaction i and reverse reaction c, $\beta_4$ may be approximated by the reaction factor $\beta_4^*$, which corresponds to the value in the absence of a phase transfer catalyst (Asai et al., 1992), owing to $[Q^+] \ll [CH_3COOC_4H_9]$. Thus,

$$\beta_4 \simeq \beta_4^* = \gamma\eta + 0.474715/(\gamma\eta)^2 \text{ for } \gamma\eta \geq 2.4$$

$$\beta_4 \simeq \beta_4^* = 1 + \sum_{j=1}^{\infty} b_j(\gamma\eta)^2 \text{ for } \gamma\eta < 2.4$$

$$\eta = \sqrt{(\beta_{4\infty}^* - \beta_4^*)/(\beta_{4\infty}^* - 1)}$$

$$\beta_{4\infty}^* = 1 + \frac{k_{L5}[OH^-]_b}{k_{L4}[CH_3COOC_4H_9]_i}$$

$$\gamma = \frac{\sqrt{k_4[OH^-]_b D_4}}{k_{L4}} \qquad (31)$$

Mass transfer rates $N_2$ of $Q^+OH^-$ were calculated from the difference between the observed decrease $\Delta[OH^-]_{obs}$ in the $OH^-$ concentration in the aqueous phase and the predicted mass transfer rate $N_4$ of $CH_3COOC_4H_9$ toward the aqueous phase.

The value of the only adjustable parameter, dimensionless number $\bar{\gamma}$, can be evaluated from observed mass transfer rates $N_2$, or the overall reaction rates in the organic phase by using Eqs. 19-31. Thus, one can determine the reaction rate constant $\bar{k}'$ or $\bar{k}$ from the evaluated value of $\bar{\gamma}$ by means of Eq. 24.

## Physical Properties

Relevant physical properties were measured or predicted as follows. Densities and viscosities of the solutions used in all the experiments were measured by the conventional procedure. The interfacial tensions between the upper and lower phases were determined by the capillary method for the combination of a fictitious organic solution not containing $Q^+Cl^-$ and the actual aqueous solution, since $Q^+Cl^-$ is a kind of surface-active agent. The validity of this procedure was explained in a previous article (Asai et al., 1991).

The diffusivity $D_{1w}$ of ion pair $Q^+Cl^-$ in water was taken as $1.90 \times 10^{-9}$ m$^2$/s at 298 K (Asai et al., 1991). Diffusivities $D_{2w}$ and $D_{7w}$ of ion pairs $Q^+OH^-$ and $Q^+CH_3COO^-$ in water were predicted to be $2.58 \times 10^{-9}$ and $1.33 \times 10^{-9}$ m$^2$/s, respectively, at 298 K, by using the Nernst-Planck equation with the ionic diffusivity of $Q^+$ ($1.71 \times 10^{-9}$ m$^2$/s) (Asai et al., 1991). The diffusivity $\bar{D}_1$ of ion pair $Q^+Cl^-$ in *n*-butyl acetate was taken as $3.60 \times 10^{-9}$ m$^2$/s at 298 K (Asai et al., 1991). Since this value was about 5 times higher than the estimated one from the correlation of Wilke and Chang (1955), diffusivities $\bar{D}_2$ and $\bar{D}_7$ of ion pairs $Q^+OH^-$ and $Q^+CH_3COO^-$ in *n*-butyl acetate were predicted to be $3.56 \times 10^{-9}$ and $3.42 \times 10^{-9}$ m$^2$/s, respectively, at 298 K, by multiplying the estimated value from the correlation of Wilke and Chang by this factor. The diffusivity $D_{4w}$ of *n*-butyl acetate in water was taken to be $0.97 \times 10^{-9}$ m$^2$/s at 298 K (Chandrasekaran and King, 1972). Diffusivities $D_4$ of the *n*-butyl acetate in the mixed electrolyte solutions were predicted from the following expression on the basis of the correlation of Hikita et al. (1979):

$$\frac{D_4}{D_{4w}} = 1 - (0.129[NaOH] + 0.081[NaCl]) \qquad (32)$$

The aqueous-phase concentrations of $Q^+$, $Q^+OH^-$, $Q^+Cl^-$, $CH_3COOC_4H_9$, $C_4H_9OH$, $CH_3COO^-$, and $Q^+CH_3COO^-$ were too small to affect the physical properties of the aqueous phase during the time of experiment, in which the initial rates of the reactions were measured. The diffusivities $D_3$ of $Q^+$, $D_5$ of $OH^-$, $D_6$ of $Cl^-$, and $D_8$ of $CH_3COO^-$ in the electrolyte solutions were predicted from the equation of Vinograd and McBain (1941).

Physical solubilities of the *n*-butyl acetate in the aqueous reactive solutions were estimated from the following equation based on the correlation of Danckwerts and Gillham (1966), using the observed salting-out parameter of NaOH (Asai et al., 1992) and the estimated one of NaCl:

$$\log\frac{[CH_3COOC_4H_9]_i}{[CH_3COOC_4H_9]_w}=-(0.247[NaCl]+0.287[NaOH]) \qquad (33)$$

where $[CH_3COOC_4H_9]_w=4.60\times10^{-2}$ kmol/m³ at 298 K (Asai et al., 1992).

The dissociation constants $K_1$ of $Q^+Cl^-$ and $K_2$ of $Q^+OH^-$ were taken as $K_1=K_2=0.0047$ kmol/m³ (Asai et al., 1991), and the value of $K_7$ was determined to be 0.0051 kmol/m³, independent of the ionic strength, by the present equilibrium experiment. The distribution coefficients $\alpha_1$ of $Q^+Cl^-$, $\alpha_2$ of $Q^+OH^-$ and $\alpha_7$ of $Q^+CH_3COO^-$ were evaluated from the following relations, which were given by Asai et al. (1991) or evaluated in this work:

$$\log\frac{\alpha_1}{\alpha_{1w}}=-(0.294\ [NaCl]+0.334\ [NaOH]) \qquad (34)$$

$$\log\frac{\alpha_2}{\alpha_{2w}}=-(0.261\ [NaCl]+0.301\ [NaOH]) \qquad (35)$$

$$\log\frac{\alpha_7}{\alpha_{7w}}=-(0.331\ [NaCl]+0.371\ [NaOH]) \qquad (36)$$

where $\alpha_{1w}=0.0064$, $\alpha_{2w}=0.46$, $\alpha_{7w}=0.043$.

The mass transfer coefficients $k_L$ and $\bar{k}_L$ of the relevant species in the aqueous and organic phases, respectively, were predicted from the empirical correlation of Asai et al. (1983).

## Results and Discussions

The experiments of the catalytic reaction were carried out under various concentrations of $Q^+Cl^-$ and NaOH in the organic and aqueous phases, respectively, at the ionic strength of 1.0 kmol/m³ and temperature of 298 K. Figure 2 shows mass transfer rates $N_2$ of $Q^+OH^-$, that is, the overall reaction rate of the main reaction e in the organic phase, which is plotted against $Q^+Cl^-$ concentration in the organic phase with a parameter of NaOH concentration. The overall reaction rates may be seen to increase with the concentrations of $Q^+Cl^-$ and NaOH. This may be attributed to an increase in the interfacial concentration of reactant $Q^+OH^-$ for the main reaction. Figure 3 shows overall reaction rates $N_2$ vs. the interfacial concentration $[\overline{Q^+OH^-}]_i$ of $Q^+OH^-$ in the organic phase. The data for different initial concentrations $[\overline{Q^+Cl^-}]_0$ of the catalyst $Q^+Cl^-$ in the organic phase fall on a single straight line. Figure 4 shows a similar plot with the NaOH concentration in the aqueous phase as a parameter. The data for the different initial concentration $[NaOH]_0$ of NaOH also fall on a single straight line. Thus, overall reaction rates $N_2$ are a unique function of $[\overline{Q^+OH^-}]_i$.

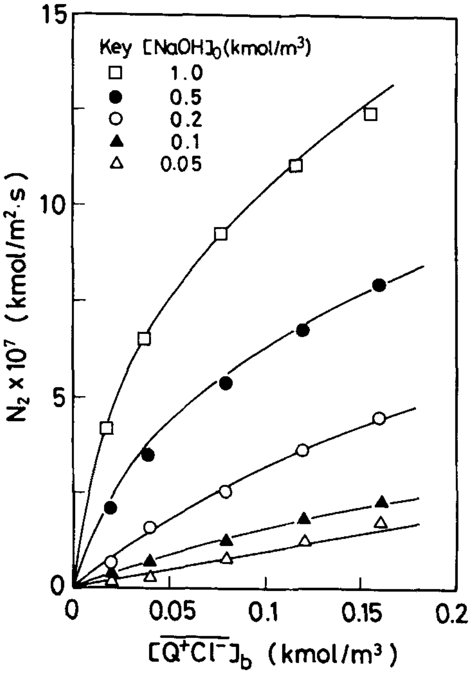

**Figure 2. Effects of bulk concentration of $Q^+Cl^-$ in organic phase and initial concentration of NaOH in aqueous phase on observed overall reaction rates of reaction e at 298 K and ionic strength of 1.0 kmol/m³.**

When the main reaction e in the organic phase occurs in the fast reaction regime ($\bar{\gamma}>3$), tanh $\bar{\gamma}$ may be approximated by unity. Then, Eqs. 21, 22 and 24 can be written as:

$$N_2=\sqrt{\bar{k}'\bar{D}_2}\,[\overline{Q^+OH^-}]_i \qquad (37)$$

Hence, the overall reaction rate $N_2$ is proportional to the interfacial concentration $[\overline{Q^+OH^-}]_i$. Therefore, the behavior of the experimental data in Figures 3 and 4 is consistent with Eq. 37. The slopes of the straight lines in both figures were the same, and from the slopes the second-order reaction rate constant $\bar{k}$ was determined to be 47 m³/kmol·s.

Figure 5 shows the effect of the ionic strength of the aqueous solution on the overall reaction rate $N_2$ of $Q^+OH^-$. Reaction rates $N_2$ decrease with an increase in the ionic strength for the same NaOH concentration, because with an increase in the ionic strength, the solubility of $Q^+Cl^-$ in the aqueous phase decreases due to the enhanced salting-out effect, and then the interfacial concentration of the $Q^+OH^-$, which is formed by ion exchange between $Cl^-$ and $OH^-$, also decreases. This leads to decreased reaction rates according to Eq. 37. Figure 6 shows observed overall reaction rates $N_2$ against the interfacial concentration $[\overline{Q^+OH^-}]_i$ of $Q^+OH^-$. The reaction rates are independent of the ionic strength at the constant interfacial concentration of $Q^+OH^-$, lending support to the foregoing

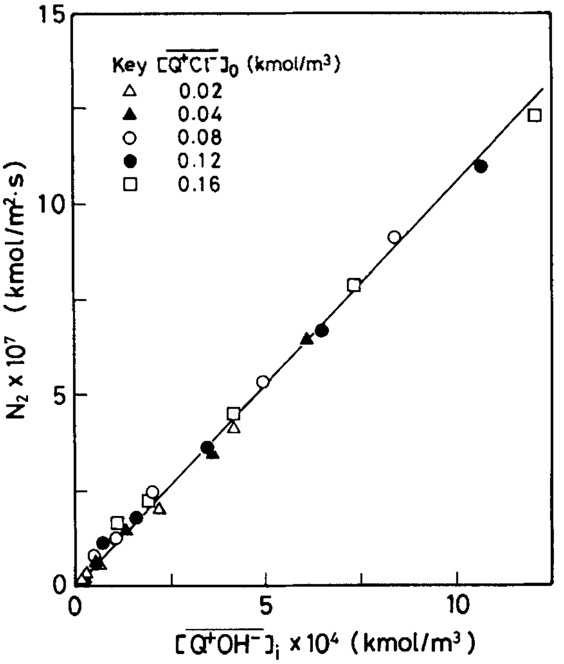

**Figure 3. Effect of interfacial concentration of $Q^+OH^-$ in organic phase on observed overall reaction rates of reaction e at 298 K and ionic strength of 1.0 kmol/m³.**

inference. From the slope of the straight line, the reaction rate constant $\bar{k}$ was evaluated to be 47 m³/kmol·s, which is independent of the ionic strength and in agreement with the values evaluated from Figures 3 and 4.

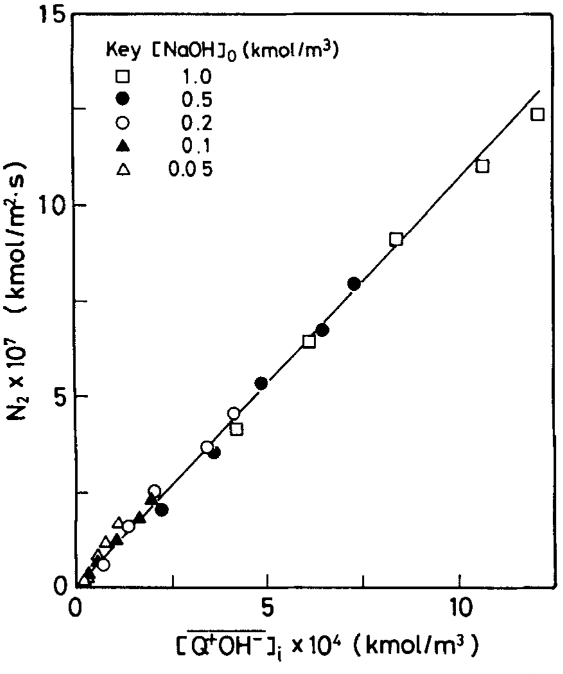

**Figure 4. Effect of interfacial concentration of $Q^+OH^-$ in organic phase on observed overall reaction rates of reaction e at 298 K and ionic strength of 1.0 kmol/m³.**

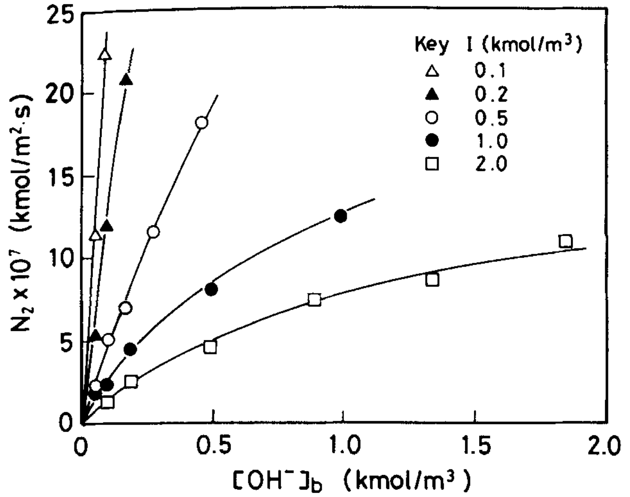

**Figure 5. Effect of bulk concentration of $OH^-$ in aqueous phase and ionic strength on observed overall reaction rates of reaction e at 298 K and initial catalyst concentration of 0.16 kmol/m³.**

We have given attention to the reaction rate $N_2$ of the main reaction e in the organic phase. Thus, the findings that the reaction rate or reaction rate constant does not depend on the NaOH concentration and the ionic strength in the aqueous phase, apart from dependency on the interfacial concentration of $Q^+OH^-$, justify the validity of the proposed model solution for the phase transfer catalytic reaction with mass transfer. In most of the runs under the present experimental conditions, the mass transfer of $Q^+OH^-$ with chemical reaction and $Q^+Cl^-$ without chemical reaction in the organic phase, and of $OH^-$ and *n*-butyl acetate with chemical reaction between themselves in the aqueous phase played an important role on the overall reaction rates, and the ion exchange reactions b, c, and g could be regarded as occurring at the interface. However, when the

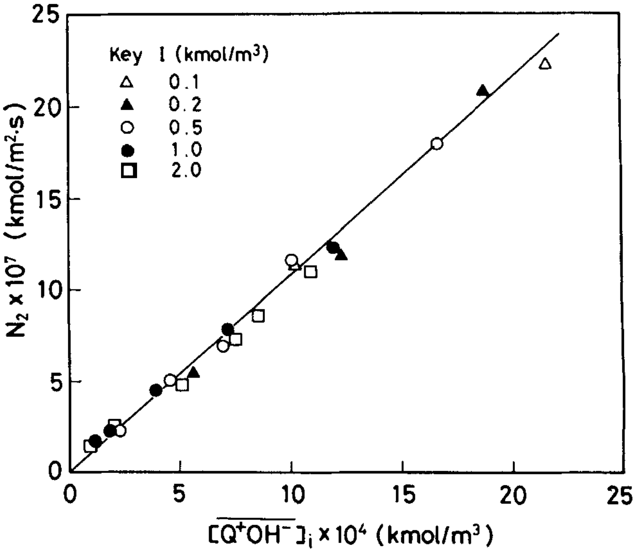

**Figure 6. Effect of interfacial concentration of $Q^+OH^-$ in organic phase on observed overall reaction rates of reaction e at 298 K and initial catalyst concentration of 0.16 kmol/m³.**

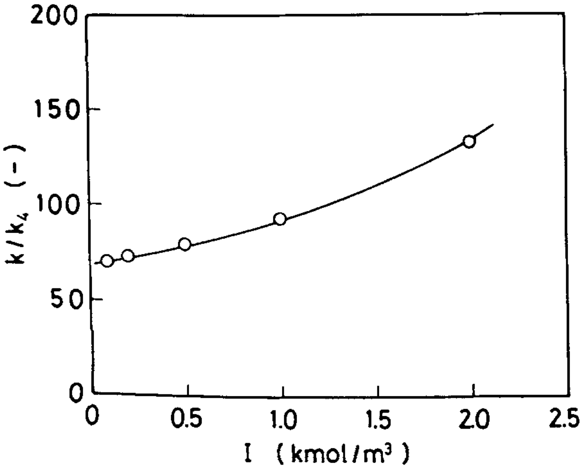

Figure 7. Reaction rate constants of alkaline hydrolysis with and without a phase transfer catalyst Aliquat 336.

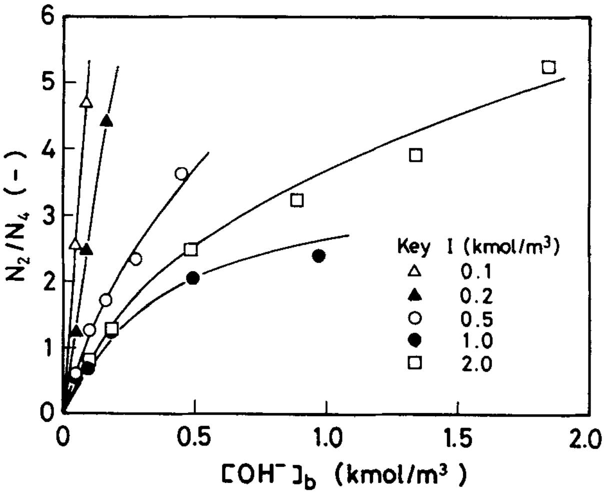

Figure 8. Overall reaction rate of alkaline hydrolysis with and without a phase transfer catalyst Aliquat 336.

concentration of the catalyst $Q^+Cl^-$ and ionic strength are high and $OH^-$ concentration is low, the effect of the aqueous-phase mass transfer of $Q^+Cl^-$ with the dissociation became substantial.

Figure 7 shows reaction rate constants in the organic phase vs. in the aqueous phase at 298 K (Asai et al., 1992). The reaction rate constant in the organic phase is 70 to 140 times larger than those in the aqueous phase, which depend on the ionic strength.

Figure 8 shows hydrolysis rates $\overline{N_2}$ in the organic phase with the catalyst concentration $\overline{[Q^+Cl^-]_0} = 0.16$ kmol/m³ vs. reaction rates $N_4$ in the aqueous phase without catalysis, at 298 K. This ratio is less than what is expected from Figure 7. This may be attributed to the fact that the interfacial concentration of $Q^+OH^-$ in the organic phase is less than that of the *n*-butyl acetate in the aqueous phase.

## Conclusion

The alkaline hydrolysis of *n*-butyl acetate using Aliquat 336 as a phase transfer catalyst was carried out. The main reaction e in the organic phase took place in a fast reaction regime. Then, observed overall reaction rates were proportional to the interfacial concentration of $Q^+OH^-$. This interfacial concentration was a unique function of the concentrations of $Q^+Cl^-$ in the organic phase and of NaOH in the aqueous phase, and of the ionic strength of the aqueous phase, but the evaluated reaction rate constant (47 m³/kmol·s at 298 K) was independent of these concentrations and the ionic strength. This verifies the validity of the proposed model for the phase transfer catalysis with mass transfer.

The reaction rate constant $\bar{k}$ obtained was 70 to 140 times larger than the values without a phase transfer catalyst. Therefore, the use of a phase transfer catalyst may be very effective also for relatively rapid reactions.

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## Notation

$D$ = diffusivity, m²/s
$I$ = ionic strength, kmol/m³
$k$ = reaction rate constant (Figure 1), 1/s or m³/kmol·s
$\bar{k}'$ = pseudo-first-order reaction rate constant defined by Eq. 3, 1/s
$k'_4$ = reaction rate constant of reaction j, m³/kmol·s
$k_L$ = mass transfer coefficient, m/s
$K$ = dissociation constant, kmol/m³
$N$ = mass transfer rate, kmol/m²·s
$x$ = distance from interface, m
[ ] = concentration, kmol/m³

### Greek letters

$\alpha$ = distribution coefficient
$\beta$ = reaction factor
$\gamma$ = dimensionless number defined by Eq. 31
$\bar{\gamma}$ = dimensionless number defined by Eq. 24
$\delta$ = film thickness, m
$\eta$ = dimensionless parameter defined by Eq. 31

### Subscripts

$b$ = bulk
$i$ = interface
obs = observed value
$w$ = water
$\infty$ = instantaneous reaction
0 = initial value
1 = $Q^+Cl^-$
2 = $Q^+OH^-$
3 = $Q^+$
4 = $CH_3COOC_4H_9$
5 = $OH^-$
6 = $Cl^-$
7 = $Q^+CH_3COO^-$
8 = $CH_3COO^-$

### Superscripts

— = organic phase
* = without catalyst

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