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Micellar-catalyzed alkaline hydrolysis of *n*-butyl acetate by cetyltrimethylammonium bromide

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Abstract

The overall reaction rates of alkaline hydrolysis of *n*-butyl acetate by aqueous sodium hydroxide solutions, with cetyltrimethylammonium bromide (CTMAB) as a micellar catalyst, were measured in an agitated vessel with a flat interface. The overall reaction rates observed with respect to various liquid compositions could be reasonably explained by the theoretical model, allowing for reactions in the micellar and bulk phases and the distribution of the relevant species between the micellar and bulk phases. This alkaline hydrolysis was accelerated by the solubilization of *n*-butyl acetate and OH^- ions to the micelles, but not by an increase in the reaction rate constant in the micellar phase. The maximum catalytic effect of CTMAB micelles at 298 K occurred at 0.07 kmol m^{-3} CTMAB and 0.2 kmol m^{-3} NaOH. The maximum value of the ratio of the overall reaction rates of *n*-butyl acetate with and without micellar catalyst was about 6.

The evaluated apparent reaction rate constants were dependent on the concentration of CTMAB micellar catalyst and the ionic strength of the aqueous solution. © 1997 Elsevier Science S.A.

Keywords: Alkaline hydrolysis; *n*-Butyl acetate; Cetyltrimethylammonium bromide; Mass transfer; Micellar catalyst

1. Introduction

In many heterogeneous liquid–liquid reaction systems, where reactions seldom occur owing to the sparing mutual solubility, the reaction rates can be accelerated by adding a phase transfer catalyst or a micellar catalyst [1–4]. Such catalysts are therefore useful in the field of organic synthesis. In a previous paper [3], we carried out the alkaline hydrolysis of *n*-butyl acetate using Aliquat 336 as phase transfer catalyst, and revealed that the use of this catalyst is very effective even for the relatively fast reactions in which the mass transfer resistance of relevant species is not negligible. A similar catalytic effect may be expected for the alkaline hydrolysis of *n*-butyl acetate using a micellar catalyst.

Micellar catalysts incorporating the micelles of surfactants with both hydrophobic and hydrophilic groups can enhance reaction rates in the aqueous solutions by the solubilization of solute and/or by electrostatic interaction near the polar group. Except for the studies of Janakiraman and Sharma [5] and Asai et al. [4], however, many previous studies on micellar catalysis have dealt primarily with very slow reactions, where there is no effect of mass transfer. Janakiraman and Sharma [5] studied the oximation of cycloalkanone accompanied by mass transfer in the aqueous phase containing sodium dodecyl sulfate (SDS) micelles, and found that the apparent pseudo first-order reaction rate constants for the reaction in the micellar phase are much larger than those in the bulk phase. In their analysis, however, it was assumed that a dissolving solute (cycloalkanone) and another reacting solute (hydroxylammonium) existing originally in the aqueous phase diffuse only through the bulk phase, maintaining the solubilization equilibrium of their solutes between the bulk and the stationary micellar phases.

In previous work [6], we clarified the mass transfer mechanism of a solute solubilized in an aqueous micellar solution to enable a reasonable analysis of micellar catalysis with mass transfer. Furthermore, we carried out the oximation of cyclohexanone using SDS micellar catalyst and demonstrated that its overall reaction rate could be explained quantitatively by the proposed model [4].

In this work, we investigated quantitatively the effect of the micellar catalyst on the overall reaction rates in a heterogeneous liquid–liquid reaction system for the alkaline hydrolysis of *n*-butyl acetate with sodium hydroxide using a micellar catalyst, cetyltrimethylammonium bromide (CTMAB).

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2. Modelling of micellar catalysis

The analysis was made by extending our mass transfer model [6] of solubilized solute in the aqueous micellar solution without chemical reaction. In this model, it was assumed that very tiny micelles disperse uniformly in the aqueous phase and the concentrations of the relevant species are at equilibrium between the micellar and the bulk phases.

n-Butyl acetate is hydrolyzed in the presence of sodium hydroxide to produce *n*-butyl alcohol and sodium acetate

$$\mathrm{CH_3COOC_4H_9\ (A) + NaOH\ (B) \rightarrow CH_3COONa + C_4H_9OH} \quad (1)$$

This alkaline hydrolysis has been shown to be irreversible and first order with respect to both reactants, and the reaction kinetics were clarified by Asai et al. [7].

The model of the micellar-catalyzed reaction for the present heterogeneous reaction system is shown in Fig. 1. When the concentration of the surfactant CTMAB is larger than the critical micelle concentration, the micelles are formed in the aqueous phase. It is assumed that *n*-butyl acetate, which dissolves partially in this aqueous micellar solution phase, undergoes an irreversible (1,1)th-order reaction with OH^- ions in both the micellar and the bulk phases, according to the reactions (a) and (b) respectively (as shown in Fig. 1). *n*-Butyl acetate and OH^- ions transfer between the micellar and the bulk phases, in which their solutes are assumed to be at equilibrium.

The analysis is based on the Lévêque model, which is applicable to the present experimental apparatus, an agitated vessel with a flat interface [8]. The differential equations for relevant species in the aqueous micellar solution are set up in parallel to those in the previous study [4] and are expressed as follows

For the micellar phase

$$D_{\mathrm{A_m}}\partial^2\mathrm{A_m}/\partial x^2 - ax\partial\mathrm{A_m}/\partial y = k_\mathrm{m}\mathrm{A_m}\mathrm{B_m} + R_{\mathrm{A_m}} \quad (2)$$

$$D_{\mathrm{B_m}}\partial^2\mathrm{B_m}/\partial x^2 - ax\partial\mathrm{B_m}/\partial y = k_\mathrm{m}\mathrm{A_m}\mathrm{B_m} + R_{\mathrm{B_m}} \quad (3)$$

For the bulk phase

$$D_{\mathrm{A_b}}\partial^2\mathrm{A_b}/\partial x^2 - ax\partial\mathrm{A_b}/\partial y = k_\mathrm{b}\mathrm{A_b}\mathrm{B_b} + R_{\mathrm{A_b}} \quad (4)$$

$$D_{\mathrm{B_b}}\partial^2\mathrm{B_b}/\partial x^2 - ax\partial\mathrm{B_b}/\partial y = k_\mathrm{b}\mathrm{A_b}\mathrm{B_b} + R_{\mathrm{B_b}} \quad (5)$$

where a is the interfacial velocity gradient in the aqueous micellar solution, k_m and k_b are the reaction rate constants in the micellar and the bulk phase, respectively, and $R_{\mathrm{A_m}}$ and $R_{\mathrm{B_m}}$ are the mass transfer rates of *n*-butyl acetate and OH^- ions, respectively, from the micellar phase to the bulk phase per unit volume of micellar phase. Also, $R_{\mathrm{A_b}}$ and $R_{\mathrm{B_b}}$ are the corresponding mass transfer rates from the bulk phase to the micellar phase per unit volume of bulk phase. Here, the following relationships hold for the respective mass transfer rates

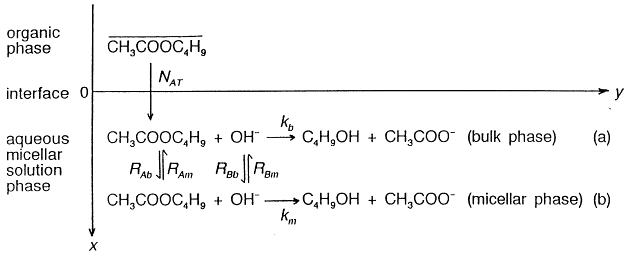

Fig. 1. Reaction model.

$$R_{\mathrm{A_b}} = -\epsilon R_{\mathrm{A_m}}/(1-\epsilon) \quad (6)$$

$$R_{\mathrm{B_b}} = -\epsilon R_{\mathrm{B_m}}/(1-\epsilon) \quad (7)$$

where ϵ is the volume fraction of micelles in the aqueous micellar solution.

The total concentrations $\mathrm{A_T}$ and $\mathrm{B_T}$ of *n*-butyl acetate and OH^- ions, respectively, in the aqueous micellar solution are shown by

$$\mathrm{A_T} = -\epsilon\mathrm{A_m} + (1-\epsilon)\mathrm{A_b} \quad (8)$$

$$\mathrm{B_T} = -\epsilon\mathrm{B_m} + (1-\epsilon)\mathrm{B_b} \quad (9)$$

Furthermore, on the assumption that the distribution equilibria of the species are established between the micellar and bulk phases, the distribution coefficients m_A and m_B of *n*-butyl acetate and OH^- ions, respectively, are defined by

$$m_\mathrm{A} = \mathrm{A_m}/\mathrm{A_b} \quad (10)$$

$$m_\mathrm{B} = \mathrm{B_m}/\mathrm{B_b} \quad (11)$$

Arranging Eqs. (2)–(5) with Eqs. (6)–(11), the following equations are derived

$$D_{\mathrm{A_T}}\partial^2\mathrm{A_T}/\partial x^2 - ax\partial\mathrm{A_T}/\partial y = k_\mathrm{app}\mathrm{A_T}\mathrm{B_T} \quad (12)$$

$$D_{\mathrm{B_T}}\partial^2\mathrm{B_T}/\partial x^2 - ax\partial\mathrm{B_T}/\partial y = k_\mathrm{app}\mathrm{A_T}\mathrm{B_T} \quad (13)$$

where $D_{\mathrm{A_T}}$ and $D_{\mathrm{B_T}}$ are the total diffusivities of *n*-butyl acetate and OH^- ions, respectively, in the aqueous micellar solution, and k_app is the apparent reaction rate constant, that is, an overall reaction rate constant on the basis of the total concentrations $\mathrm{A_T}$ and $\mathrm{B_T}$ of *n*-butyl acetate and OH^- ions, respectively, in the aqueous micellar solution. They are given by

$$D_{\mathrm{A_T}} = D_{\mathrm{A_b}}(1-\epsilon+\epsilon r_\mathrm{A} m_\mathrm{A})/(1-\epsilon+\epsilon m_\mathrm{A}) \quad (14)$$

$$D_{\mathrm{B_T}} = D_{\mathrm{B_b}}(1-\epsilon+\epsilon r_\mathrm{B} m_\mathrm{B})/(1-\epsilon+\epsilon m_\mathrm{B}) \quad (15)$$

$$r_\mathrm{A} = D_{\mathrm{A_m}}/D_{\mathrm{A_b}} \quad (16)$$

$$r_\mathrm{B} = D_{\mathrm{B_m}}/D_{\mathrm{B_b}} \quad (17)$$

$$k_\mathrm{app} = \frac{k_\mathrm{m} m_\mathrm{A} m_\mathrm{B}\epsilon + k_\mathrm{b}(1-\epsilon)}{[(m_\mathrm{A}-1)\epsilon+1][(m_\mathrm{B}-1)\epsilon+1]} \quad (18)$$

The boundary conditions are given by

$$\left.\begin{array}{l} x=0,\ y>0;\ \ \mathrm{A_T}=\mathrm{A}_{\mathrm{T}_i},\ \partial\mathrm{B_T}/\partial x=0 \\ x=\infty,\ y\geq 0;\ \ \mathrm{A_T}=0,\ \mathrm{B_T}=\mathrm{B}_{\mathrm{T_l}} \\ y=0,\ x>0;\ \ \mathrm{A_T}=0,\ \mathrm{B_T}=\mathrm{B}_{\mathrm{T_l}} \end{array}\right\} \quad (19)$$

Here, it is assumed that *n*-butyl acetate disappears completely in the bulk of aqueous phase.

The aqueous phase can be regarded as homogeneous when the unique reaction rate constant k_app is used. So an analysis may be made in view of the mass transfer with a conventional heterogeneous liquid–liquid reaction. Eqs. (12) and (13) with the boundary conditions of Eq. (19) were solved numerically by Hikita et al. [8]. The reaction factor (enhancement factor) β_{A_T} of *n*-butyl acetate is given by

$$\beta_{A_T} = \gamma\eta + 0.474715/(\gamma\eta)^2 \text{ for } \gamma\eta \geq 2.4 \tag{20}$$

$$\beta_{A_T} = 1 + \sum_{j=1}^{\infty} b_j(\gamma\eta)^{2j} \text{ for } \gamma\eta < 2.4 \tag{21}$$

$$\eta = \sqrt{(\beta_{A_{T\infty}} - \beta_{A_T})/(\beta_{A_{T\infty}} - 1)} \tag{22}$$

$$\beta_{A_{T\infty}} = 1 + (D_{B_T}/D_{A_T})^{2/3} B_{T_l}/A_{T_i} \tag{23}$$

$$\gamma = \sqrt{k_{app} B_{T_l} D_{A_T}}/k_{LA_T} \tag{24}$$

where b_j are the numerical constants and are given in the literature [8].

In the present system, the mass transfer resistance in the organic phase was absent owing to the use of pure *n*-butyl acetate. So the observed reaction factors β_{A_T} were evaluated from the following expression, by using the observed total overall reaction rate N_{A_T} of alkaline hydrolysis, and the mass transfer coefficients k_{LA_T} and solubilities A_{T_i} of *n*-butyl acetate in the aqueous micellar solution

$$N_{A_T} = \beta_{A_T} k_{LA_T} A_{T_i} \tag{25}$$

Furthermore, one can evaluate the apparent reaction rate constants k_{app} by a comparison of this observed reaction factor with the theoretical one, which is calculated from Eqs. (14)–(17) and Eqs. (20)–(24) with the relevant system parameters. The values of the parameters k_m and m_B, which were difficult to measure, were taken as adjustable parameters. The Simplex method was used to determine these adjustable parameters from Eq. (18) with the apparent reaction rate constants k_{app} evaluated under various conditions.

3. Experimental

The apparatus used in this work is the same type of agitated vessel with a flat interface as that used in a previous study [9]. The diameter of the agitated vessel was 0.083 m, yielding an interfacial area of 5.41×10^{-3} m^2 and a liquid volume of 4.30×10^{-4} m^3 for each phase. The upper organic phase was pure *n*-butyl acetate. The lower aqueous phase consisted of mixed solutions to give 0.05–0.5 kmol m^{-3} of sodium hydroxide, 0.01–0.1 kmol m^{-3} of the cationic surfactant cetyltrimethylammonium bromide (CTMAB), and 0–2.95 kmol m^{-3} of sodium chloride. Sodium chloride was used to adjust the ionic strength of the aqueous solutions.

Samples of 0.5×10^{-6}–2×10^{-6} m^3 were taken from the lower phase at intervals of 10–20 min for the determination of the concentration of OH$^-$ ion. The overall reaction rates were evaluated from the variation of OH$^-$ concentration over time. The OH$^-$ ion concentration was determined by titration with a standard aqueous 0.05–0.5 kmol m^{-3} HCl solution after adding phenolphthalein as indicator.

The experiments were carried out at agitation speeds of 2.5 s^{-1} for both the upper and lower phases, at a temperature of 298 K and an ionic strength of 0.2–3.0 kmol m^{-3}.

4. Physical properties and system parameters

The viscosities and densities of the relevant solutions were measured by conventional techniques. The interfacial tensions of the solution without CTMAB, which were used in the evaluation of mass transfer coefficients k_{LA_b} of *n*-butyl acetate in the bulk phase, were measured by the capillary rise method.

The volume fraction ϵ of CTMAB micelles in the aqueous micellar solution was predicted from the following equation

$$\epsilon = (C_t - C_{CMC}) V_M \tag{26}$$

where C_t is the concentration of the surfactant CTMAB, C_{CMC} is the critical micelle concentration, and V_M is the molar volume of CTMAB micelles. The value of V_M was taken as approximately 0.36 m^3 kmol^{-1}, according to the procedure of Janakiraman and Sharma [5]. The critical micelle concentration C_{CMC} of CTMAB in water and in aqueous electrolyte solution was taken as 9.9×10^{-4} kmol m^{-3}, independent of the ionic strength of the solution [6].

The aqueous bulk phase diffusivities D_{A_b} of *n*-butyl acetate in the aqueous mixed electrolyte solutions were predicted from the following expression on the basis of the correlation of Hikita et al. [10]

$$D_{A_b}/D_{A_w} = 1 - (0.081[\text{NaCl}] + 0.138[\text{NaOH}]) \tag{27}$$

where the diffusivity D_{A_w} of *n*-butyl acetate in water was taken as 0.97×10^{-9} m^2 s^{-1} at 298 K [7].

The bulk phase diffusivities D_{B_b} of OH$^-$ ion in the aqueous electrolyte solutions were predicted from the equation of Vinograd and McBain [11].

The total diffusivities D_{A_T} and D_{B_T} of *n*-butyl acetate and OH$^-$ ions, respectively, in the aqueous micellar solution were evaluated from Eqs. (14)–(17). In evaluating the diffusivity ratios r_A and r_B, the apparent diffusivities D_{A_m} and D_{B_m} of CTMAB micelles incorporating *n*-butyl acetate and OH$^-$ ions, respectively, in equilibrium with their concentrations at interface of organic and aqueous phases, were taken to be identical, as *n*-butyl acetate and OH$^-$ ions coexist in micelles and they move together with the micelles. However, these diffusivities, and also the distribution coefficients m_A of *n*-butyl acetate, could not be measured directly owing to the occurrence of reaction between themselves. Therefore, the values for the system of toluene–aqueous NaOH micellar solution, $m_A = 126$–677 and $r_A = 0.31$–0.5, depending on the experimental conditions [6] were used as those for the system of *n*-butyl acetate–aqueous NaOH micellar solution. This was because the system of toluene–aqueous NaCl (0–3.0 kmol m^{-3}) micellar solution yields the diffusivity ratio D_{A_m}/D_{A_b} and the distribution coefficient m_A, approximately equal to those for the system of *n*-butyl acetate–aqueous NaCl micellar solution. The values of r_B were predicted to be 0.080–0.099, depending on the experimental conditions, from Eqs. (16) and (17) by using the known bulk phase diffusivities D_{A_b} and D_{B_b} and the relationship $D_{A_m} = D_{B_m}$.

The total physical solubilities A_{T_i} of *n*-butyl acetate in the aqueous micellar solution were evaluated from the following equation, which is derivable from Eqs. (8) and (10), using the evaluated distribution coefficient m_A of *n*-butyl acetate

$$A_{T_i} = A_{b_i}[(m_A - 1)\epsilon + 1] \tag{28}$$

The physical solubilities A_{b_i} of *n*-butyl acetate in the bulk phase at 298 K were estimated from the following correlation in accordance with the previous paper [7]

$$\log A_{b_i}/A_w = -(0.247[\mathrm{NaCl}] + 0.287[\mathrm{NaOH}]) \tag{29}$$

where $A_w = 0.046$ kmol m^{-3}.

The total mass transfer coefficients k_{LA_T} of *n*-butyl acetate in the aqueous micellar solution were obtained from the following relationship [6]

$$k_{LA_T} = k_{LA_b}[(1-\epsilon+\epsilon r_A m_A)/(1-\epsilon+\epsilon m_A)]^{2/3} \tag{30}$$

where the mass transfer coefficient k_{LA_b} of *n*-butyl acetate in the aqueous bulk phase was predicted from the empirical correlation of Asai et al. [9], using the fictitious interfacial tensions of the solution without CTMAB. This procedure for prediction of the mass transfer coefficient for the aqueous surfactant solution was justified empirically [6].

The reaction rate constants k_b for the alkaline hydrolysis of *n*-butyl acetate in the bulk phase were taken to be equal to those in the conventional aqueous solution without micelles and were calculated from the following expression [7]

$$\ln k_b = 25.9 - 7830/T - 0.275I - 0.0248I^2 \tag{31}$$

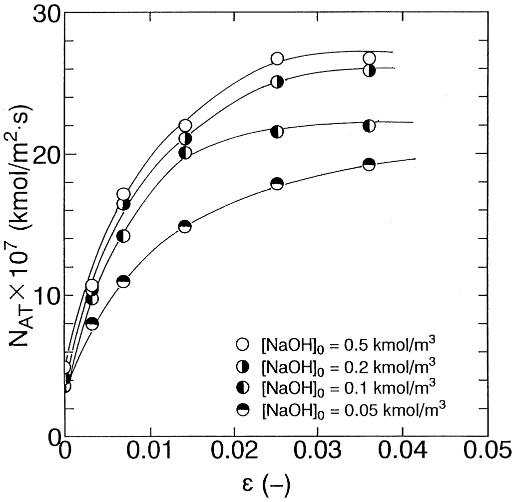

Fig. 2. Effect of volume fraction ϵ of CTMAB micelles on total overall reaction rates N_{A_T} of *n*-butyl acetate at 298 K and $I = 1.0$ kmol m^{-3}.

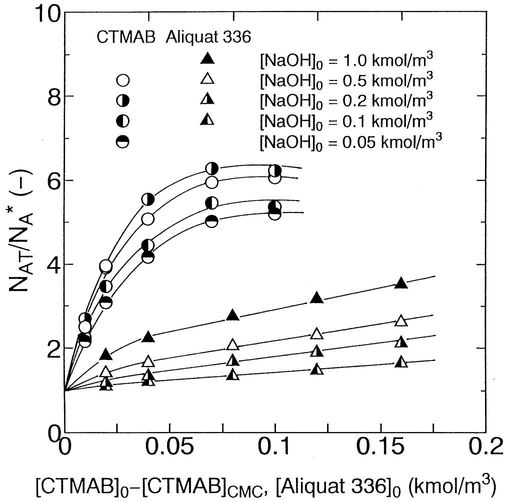

Fig. 3. Relative overall reaction rate N_{A_T}/N_A^* for alkaline hydrolysis of *n*-butyl acetate with and without catalysts at 298 K and $I = 1.0$ kmol m^{-3}.

5. Experimental results and discussion

Fig. 2 shows the effect of the volume fraction ϵ of CTMAB micelles on the total overall reaction rates N_{A_T} of *n*-butyl acetate at $I = 1.0$ kmol m^{-3}, with a parameter of the initial NaOH concentration. The total overall reaction rates N_{A_T} for each NaOH concentration may be seen to increase with the volume fraction ϵ of micelles, reducing the extent of the increase. This is because the enhancement of the total overall reaction rates due to the solubilization of *n*-butyl acetate are counteracted in part by the decrease in the apparent reaction rate constants k_{app}, as will be described later.

Fig. 3 represents the ratios of the total overall reaction rate N_{A_T} with CTMAB micellar catalyst to the overall reaction rate N_A^* without micellar catalyst at $I = 1.0$ kmol m^{-3}. The values of N_{A_T}/N_A^* are seen to increase with the micelle concentration $[\mathrm{CTMAB}]_0 - [\mathrm{CTMAB}]_{\mathrm{CMC}}$, but the degree of the increase diminishes with an increase in the micelle concentration, reflecting the behavior of the total overall reaction rates N_{A_T} shown in Fig. 2. Moreover, as noted, the values of N_{A_T}/N_A^* increase with the initial NaOH concentration in the range 0.05–0.2 kmol m^{-3}, yielding a maximum value for the ratio of ≈6. However, further increase in NaOH concentration reduces the ratios, demonstrating that the degree of increase of N_{A_T} is smaller than that of N_A^* with NaOH concentration. In Fig. 3, the data of the phase transfer catalyst Aliquat 336 [3] are also illustrated. It is seen that the catalytic effect of CTMAB is much larger than that of Aliquat 336, which continues to increase with the concentrations of catalyst and NaOH.

Fig. 4 represents the plot of the apparent reaction rate constants k_{app} against the volume fraction ϵ of CTMAB micelles at $I = 1.0$ kmol m^{-3}. The values of k_{app} decrease with an increase in the volume fraction ϵ in the range $\epsilon = 0.0033$–0.036, although the values are larger than the apparent reaction rate constant k_{app}^* without micellar catalyst ($\epsilon = 0$), which is equal to the reaction rate constant k_b ($= 0.507$ m^3 kmol^{-1} s^{-1}) in the bulk phase. This behavior is in qualitative agreement with the expectation from Eq. (18). Fig. 5 shows the apparent reaction rate constants k_{app} plotted against the ionic

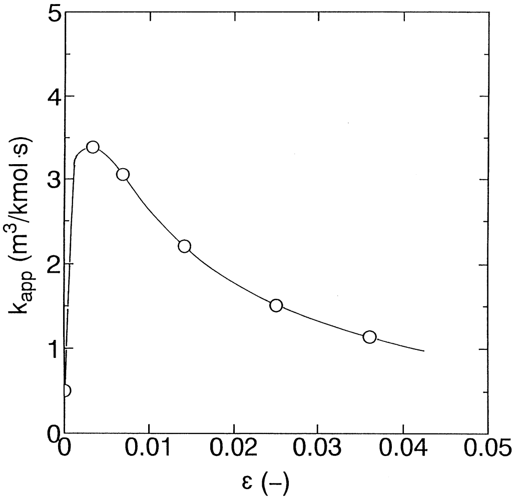

Fig. 4. Relationship between apparent reaction rate constants k_{app} and volume fraction ϵ of CTMAB micelles at 298 K and $I = 1.0$ kmol m^{-3}.

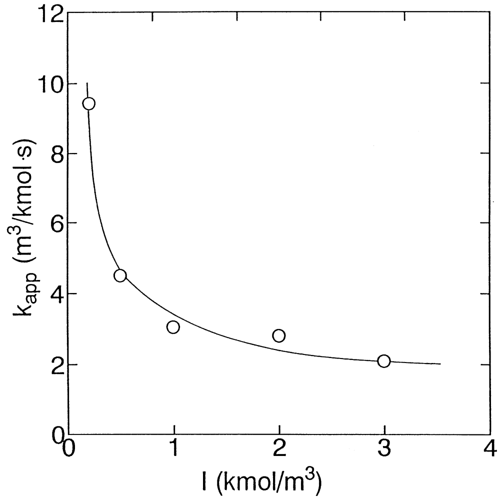

Fig. 5. Relationship between apparent reaction rate constants k_{app} and ionic strength I at 298 K and $\epsilon = 0.007$.

strength I of the aqueous phase at $\epsilon = 0.007$. The values of k_{app} decrease with an increase in the ionic strength. This is due to the decrease of the reaction rate constants k_m and k_b in the micellar and the bulk phase, respectively, as will be described later.

Using these evaluated apparent reaction rate constants k_{app}, the reaction rate constant k_m in the micellar phase and the distribution coefficient m_B of OH$^-$ ions were determined from Eq. (18) by the Simplex method. Fig. 6 shows a semi-logarimthmic plot of the reaction rate constants k_m and k_b at 298 K in the micellar and the bulk phase, respectively. It is noted that the values of k_m are much smaller than those of k_b. The values of k_m and k_b decrease with an increase in the ionic strength of the aqueous solution. The values of k_m could be correlated by the following expression

$$\ln k_m = -1.50 - 1.62I + 0.321I^2 \text{ at 298 K} \qquad (32)$$

The solid line represents the correlation line of Eq. (32), and may be seen to correlate well with the experimental data.

The effect of the ionic strength of the aqueous solution on the estimated distribution coefficient m_B of OH$^-$ ions is shown in Fig. 7. The value of m_B was 240, independent of the ionic strength. In Fig. 7, the dependence of the distribution coefficient m_A of *n*-butyl acetate on the ionic strength is also illustrated [6]. The values of m_A increase with the ionic strength.

The total overall reaction rate N_{A_T} increases with the volume fraction ϵ of micelles as shown in Fig. 2, but the enhancement of the reaction rates was not as large as expected from the considerable solubilization of *n*-butyl acetate. It may be explained by the competing effects between the enhanced effect of the reaction rates due to the solubilization of *n*-butyl acetate and OH$^-$ ions in the micelles, and the reduced effect due to the decrease in the reaction rate constant k_m in the micellar phase and the decrease in the total mass transfer coefficients k_{LA_T} of *n*-butyl acetate in the aqueous micellar solution, with an increase in the micelle concentration. This

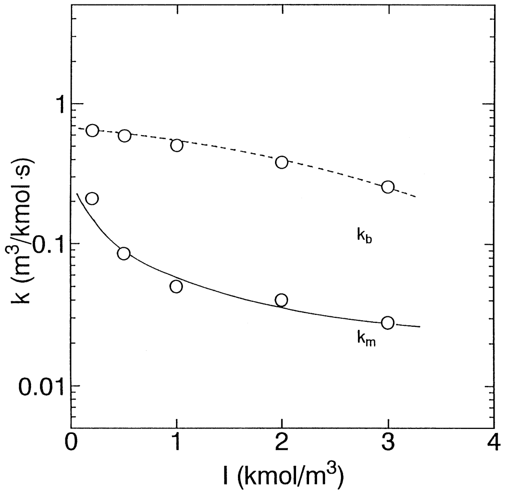

Fig. 6. Effect of ionic strength I on reaction rate constants k in the micellar and the bulk phase at 298 K.

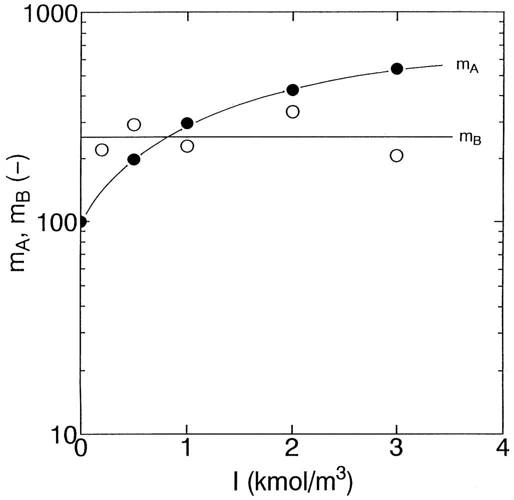

Fig. 7. Effect of ionic strength I on distribution coefficients m_A and m_B of *n*-butyl acetate and OH$^-$ ions, respectively, between the micellar and the bulk phases at 298 K.

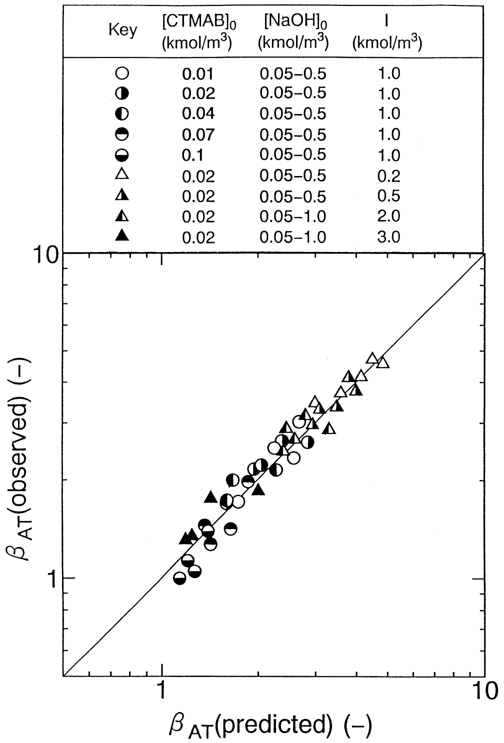

Fig. 8. Comparison between observed and predicted reaction factors β_{A_T} in the presence of CTMAB micellar catalyst.

decrease in the total mass transfer coefficients was caused by the increased solubilization of *n*-butyl acetate and OH^- ions to the micelles with lower diffusivity.

The present experimental results differ from those for oximation of cyclohexanone [4], in which k_m is much larger than k_b. As suggested by Menger and McCreery [12] for the alkaline hydrolysis of *p*-nitrophenyl esters, the finding that k_m is smaller than k_b in the present system may be explained by the fact of rate inhibition arising when the *n*-butyl acetate is solubilized in the micellar core [6], such that the hydrophobic micelle interior dissolving *n*-butyl acetate is less conducive to attack by the strongly hydrophilic OH^- ions. On the other hand, cyclohexanone is solubilized in the palisades layer and is vulnerable to attack by hydroxylammonium ions.

Fig. 8 shows a comparison between all observed values of the reaction factors β_{A_T} and the values predicted from Eqs. (14)–(18), Eqs. (20)–(24), Eqs. (26)–(32) and m_B in Fig. 7. All experimental data could be correlated with an average error of 20%. This justifies the validity of the proposed analytical procedure for micellar-catalyzed heterogeneous reactions.

6. Conclusions

The hydrolysis of *n*-butyl acetate by aqueous NaOH solution containing CTMAB micellar catalyst was studied in an agitated vessel with a flat interface. The measured overall reaction rates could be explained quantitatively by a proposed model allowing for the reactions in the micellar and the bulk phase and the distribution equilibria of the relevant species between the phases. The overall reaction rates for this reaction system were likely to be enhanced by the solubilization of *n*-butyl acetate and OH^- ions, but not by the increase of the reaction rate constant in the micellar phase. However, the enhancement of the reaction rates was not as large as expected from the considerable solubilization of *n*-butyl acetate because of the decrease of the reaction rate constant in the micellar phase and of the total mass transfer coefficient k_{LA_T} of *n*-butyl acetate. The observed apparent reaction rate constants were dependent on the volume fraction of micelles and the ionic strength of the aqueous phase.

The maximum value of the ratio of the overall reaction rates with and without micellar catalyst was ≈6. Thus, the use of CTMAB micellar catalyst is effective even for the relatively fast reactions in which the mass transfer resistance of relevant species is not negligible.

Acknowledgements

The authors thank Daicel Chemical Ind., Ltd. Japan for providing the *n*-butyl acetate.

Appendix A. Nomenclature

A	*n*-butyl acetate, or its concentration (kmol m^{-3})
a	interfacial velocity gradient in aqueous micellar solution (s^{-1})
B	sodium hydroxide ion, or its concentration (kmol m^{-3})
C_t	concentration of surfactant (kmol m^{-3})
C_{CMC}	critical micelle concentration (kmol m^{-3})
D	diffusivity ($m^2\ s^{-1}$)
I	ionic strength of solution (kmol m^{-3})
k	reaction rate constant ($m^3\ kmol^{-1}\ s^{-1}$)
k_{app}	apparent reaction rate constant ($m^3\ kmol^{-1}\ s^{-1}$)
k_L	mass transfer coefficient (m s^{-1})
m	distribution coefficient between micellar and bulk phases (–)
N	overall reaction rate (kmol $m^{-2}\ s^{-1}$)
R_b	mass transfer rate of species from bulk phase to micellar phase per unit volume of bulk phase (kmol $m^{-3}{}_{\text{bulk phase}}\ s^{-1}$)
R_m	mass transfer rate of species from micellar phase to bulk phase per unit volume of micellar phase (kmol $m^{-3}{}_{\text{micellar phase}}\ s^{-1}$)
r	ratio of diffusivity of solute incorporated with micelles to that of solute in bulk phase (–)
T	thermodynamic temperature (K)
V_M	molar volume of micelles ($m^3\ kmol^{-1}$)
x	distance normal to interface (m)
y	distance measured toward center from wall of agitated vessel (m)
[ ]	concentration (kmol m^{-3})

Greek letters

β	reaction factor (–)
γ	dimensionless number defined by Eq. (24) (–)
η	dimensionless number defined by Eq. (22) (–)
ϵ	volume fraction of micelles (–)

Subscripts

A	*n*-butyl acetate
A′	toluene
B	sodium hydroxide
b	bulk phase
i	interface
l	very far from interface
m	micellar phase
T	total values
w	water
∞	instantaneous reaction
0	initial value

Superscripts

—	organic phase (Fig. 1)
*	without catalyst

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