

## ESTERIFICATION OF LAURIC ACID WITH ISOPROPYL ALCOHOL BY TRICAPRYLYLMETHYLAMMONIUM CHLORIDE AS A CATALYST IN A LIQUID-LIQUID HETEROGENEOUS SYSTEM

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**Abstract**—Experiments were performed on the esterification of lauric acid with isopropyl alcohol by tricaprylylmethylammonium chloride in a stirred vessel with a flat liquid-liquid interface. The observed initial rate of reaction was used to analyze the reaction mechanism combined with the catalyst, and to evaluate the several kinds of reaction rate constant, from which equilibrium constants were expressed as a function of reaction temperature. The analysis of reaction kinetics indicated that the reaction was between a very slow and slow reaction regime.

**Key words** : Esterification, Lauric Acid, Isopropyl Alcohol, Heterogeneous Reaction, Tricaprylylmethylammonium Chloride

### INTRODUCTION

Organic esters are a very important class of chemicals having applications in a variety of areas such as perfumery, flavors, pharmaceuticals, plasticizers, solvents and intermediates. Obviously different approaches have been employed on both laboratory and commercial scales to prepare esters.

The most widely employed and supposedly cleaner production technique for esters involves the reaction of the appropriate carboxylic acid with an alcohol in the presence of a mineral acid catalyst.

Sulfuric acid is more commonly used, but it has various problems: formation of undesirable products, byproducts, and polymerization products due to secondary reactions with the double bonds of the molecule [Al-Saadi and Jeffreys, 1981], as well as problems in the separation of the ester from the catalyst.

The typical catalysts used for direct esterification as mentioned in the literature include a sulfuric acid [Chanodalia et al., 1977; Leyes and Othmer, 1945], molecular sieves [Santacesaria et al., 1983], and acidic ion exchange resins [Moore et al., 1979].

Indu et al. [1993] expressed the chemical equilibrium constants as a function of sulfuric acid, sodium sulfate and sodium nitrate in the esterification of formic acid with methanol. The sulfuric acid and sodium salts shift equilibrium in favor of methyl formate. The enzymes can also be used as catalysts in the formation of esters from alcohols and fatty acids in the heterogeneous phases. Lima et al. [1995] studied the esterification of lauric acid with geraniol catalyzed by commercially immobilized lipase. Singh et al. [1994] also used the lipase

as a catalyst in the esterification of oleic acid with glycerol.  $\text{Ph}_3\text{P}/\text{CCl}_4$  [Ramaiah, 1985] was used as a catalyst for synthesis of several esters. *p*-Toluenesulfonic acid [Vieville et al., 1993; Okamoto et al., 1994] was used for esterification of oleic acid by methanol or ethanol. Lewis acid [Senatlar et al., 1994] was used for esterification of castor oil with oleic acid. Cobalt chloride [Sanchez et al., 1992] was used for esterification of oleic acid and oleyl alcohol.

Previous workers [McCracken and Dickson, 1967] studied the kinetics of the reaction of esterification, mostly the presence of excess of alcohol, and came up with a suggestion that the reaction may be second order with respect to the acid.

One encounters the problem of bringing together two mutually insoluble reagents, carboxylic acid and alcohol, in sufficient concentration to attain conveniently rapid reaction rates. The traditional solution to this problem, and by far the one most frequently used in the laboratory, is simply to use a solvent which can dissolve both reagents. Use of solvents is not always convenient, and it is expensive on an industrial scale. The use of phase-transfer catalysts (PTC) to accelerate the rate of two-phase reactions by bringing together chemical reactions has become common practice in recent years [Starks and Liotta, 1978].

Information about the analysis and kinetic modeling of esterification using phase-transfer catalyst is very rare and limited to particular conditions [Cainelli and Manescalchi, 1975; Loupy et al., 1986]. These authors studied only the yield of ester from the carboxylic acid and alkyl halide using phase-transfer catalyst such as quaternary ammonium salts or a macromolecular resin containing quaternary ammonium groups.

In view of the fact that the circumstances of reaction condition in a heterogeneous reaction such as reaction between lauric acid dissolved in toluene and isopropyl alcohol miscible with water are different from those in a homogeneous

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reaction, it was considered worthwhile to investigate the kinetics of a phase-transfer catalyzed reaction together with the mechanism of mass transfer with chemical reaction, i.e., the diffusion effect of solutes across the interface of the heterogeneous phases [Park and Suh, 1994; Park et al., 1997].

The present paper is concerned with the kinetic studies on esterification of lauric acid with isopropyl alcohol in the liquid-liquid heterogeneous phases based on our experimental data using different quantities of tricaprylmethylammonium chloride (Aliquat336 or QCl). The conversions of acid measured in a flat agitated vessel were used to analyze the reaction mechanism of esterification and to evaluate the kinetic parameters.

## THEORY

A carboxylic acid is converted directly into an ester when heated with an alcohol in the presence of a mineral acid in a homogeneous phase.

Esterification reactions are



This reaction is reversible, and generally reaches equilibrium when there are appreciable quantities of both reactants and products present.

In case lauric acid is insoluble in water, but soluble in an organic solvent such as toluene (on the other hand, isopropyl alcohol is miscible with water), reaction (1) occurs in the toluene phase with lauric acid and isopropyl alcohol transferred into toluene phase from the aqueous phase.

The reaction equation of esterification in the toluene phase is represented as follows:



where, A, B and E represent isopropyl alcohol, lauric acid, and isopropyl laurate, respectively.

In case the rate of reaction between the dissolved A and B is very much slower than the rate of transfer of A into the B phase, the reaction is a very slow reaction, and the B phase, in which the reaction occurs, will be saturated with the solute A at any moment and the rate of formation of ester will be determined by the kinetics of the homogeneous chemical reaction. The diffusional factors are unimportant in this reaction.

The transfer rate of A is given by [Doraiswamy and Sharma, 1984].

$$R_A = k_2[A_i][B] - k_2'[E] \quad (3)$$

And the condition for the validity of this mechanism can be expressed as

$$k_2a \gg k_2[B]_\phi \quad (4)$$

In case the rate of reaction between A and B is faster than the rate at which A is transferred to the B phase, the reaction then occurs uniformly throughout the B phase, but the rate is controlled by the transfer of A into the phase containing B.

The rate of transfer of A is given by

$$R_A = k_L[A_i] \quad (5)$$

And the conditions for Eq. (5) to be satisfied are given by the following expressions.

$$\frac{\sqrt{D_A k_2}[B]_\phi}{k_L} \ll 1 \quad (6)$$

$$k_2a \ll k_2[B]_\phi \quad (7)$$

For some systems, the condition given by expression (6) may be satisfied, whereas the condition given by expression (7) may not be. Under these conditions, the concentration of dissolved A in the bulk B phase is a finite quantity, [A].

The following equations hold for this case:

$$R_A = k_2[A_i][B] - k_2'[E] = k_La([A_i] - [A]) \quad (8)$$

$R_A$  is given by the following equation, if [A] is eliminated using the 2nd and 3rd term of Eq. (8).

$$R_A = \frac{k_2k_La[A_i][B] - k_Lak_2'[E]/K_2}{k_2[B] + k_La} \quad (9)$$

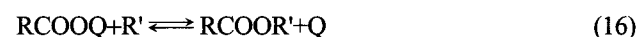
where,  $K_2$  is defined as the equilibrium constant as follows:

$$K_2 = \frac{k_2}{k_2'} \quad (10)$$

Because the concentration of ester, [E], is equal to 0 at the initial reaction time, the following equation can be obtained using the initial rate of transfer of A,  $R_{A0}$ , and the feed concentration of B,  $[B]_\phi$ .

$$\frac{[A_i]}{R_{A0}} = \frac{1}{k_La} + \frac{1}{k_2[B]_\phi} \quad (11)$$

An esterification reaction by the catalyst such as a quaternary ammonium salt is assumed to occur as the following reaction mechanism.



Eqs. (12), (13) and (14) are the dissociation of reactants and catalyst, and these rates of reaction are assumed to be very much faster than those of reactions (15) and (16).

Therefore, the above reactions are simplified as the following expression.



where, B', Q and A' represent RCOO, quaternary ammonium ion, and R', respectively.

The equilibrium constants of Eq. (17) and (18) are defined as follows:

$$K_1 = \frac{k_1}{k_1'} \quad (19)$$

$$K_3 = \frac{k_3}{k_3'} \quad (20)$$

The rate of reaction of A in Eq. (2) is expressed using Eq. (17) as follows:

$$R_A = -\frac{[A]}{dt} = -\frac{[B]}{dt} = k_1[B'][Q] - k'_1[B'Q] \quad (21)$$

The rate of disappearance of component B'Q is

$$-\frac{[B'Q]}{dt} = -k_1[B'][Q'] + k'_1[B'Q] + k_3[B'Q][A'] - k'_3[E][Q] \quad (22)$$

Because  $-[B'Q]/dt$  is equal to 0 at pseudo-steady state, the rate of reaction of A in Eq. (21) is rearranged as the following equation:

$$R_A = \frac{(k_1 k_3 [A'] [B'] - k'_1 k_3 [E]) [Q]_r}{k'_1 + k_3 [A'] + k_1 [B'] + k'_3 [E]} \quad (23)$$

where,  $[Q]_r$  is the feed concentration of component Q, and the following expression can be obtained from the mass balance of catalyst:

$$[Q]_r = [B'Q] + [Q] \quad (24)$$

The initial rate of reaction of A, where the concentration of component of A' and B' becomes to be  $[A]_i$  and  $[B]_0$ , respectively, is expressed as follows:

$$R_{Ao} = \frac{[QCl]_0}{\frac{k'_1}{k_1 k_3 [A]_i [B]_0} + \frac{1}{k_1 [B]_0} + \frac{1}{k_3 [A]_i}} \quad (25)$$

In order to analyze the kinetics of the esterification based on the effect of the catalyst, Eq. (25) can be arranged as the following equation,

$$\frac{[QCl]_0}{R_{Ao}} = \left( \frac{k'_1}{k_1 k_3 [A]_i} + \frac{1}{k_1} \right) \frac{1}{[B]_0} + \frac{1}{k_3 [A]_i} \quad (26)$$

At the initial state, the relationship among  $K_1$ ,  $K_2$  and  $K_3$  is expressed as follows:

$$K_2 = K_1 K_3 \quad (27)$$

## EXPERIMENTAL

All chemicals in this study were reagent grade and used without further purification. A reactor was used for experimental studies of esterification reaction and mass transfer. The reactor was a stirred vessel with a flat liquid-liquid interface. The vessel was composed of a Pyrex cylinder, two bladed glass disk turbine stirrers 1.5 cm in diameter and a reflux condenser. The vessel was 7 cm in diameter and 12 cm in length. Four vertical baffles, 0.5 cm wide, were oriented  $\pi/2$  rad and fitted from 0.5 cm to 7 cm above the bottom. Two stirrers were used to agitate the organic and the aqueous phase, respectively, positioned at the middle of each phase, and set at 80, 120, and 150 rev/min. The vessel was kept in a constant temperature bath with a temperature control of  $\pm 0.5$  °C.

An aqueous solution of 150 cm<sup>3</sup> having dissolved isopropyl alcohol was placed in the vessel, and a toluene solution of 150 cm<sup>3</sup> having dissolved lauric acid and Aliquat 336 was then added into the vessel slowly so as not to disturb the aqueous solution. The reaction mixture was heated to a desired

temperature and then stirred at a given speed of agitation. Samples were withdrawn from the toluene solution at a regular interval and analyzed by gas chromatography to measure the concentrations of lauric acid and isopropyl laurate. The stoichiometric analysis for esterification was confirmed by the comparison of the measured concentrations of lauric acid with those of ester.

The measured conversions of lauric acid to ester as a function of reaction time were used to get the initial rate of reaction at the reaction time equal to 0.

During the experiment in this study, the ranges of concentration of isopropyl alcohol, lauric acid and Aliquat 336 were 0.5-2.0 kmol/m<sup>3</sup>, 0.5-3.0 kmol/m<sup>3</sup> and 0.01-0.2 kmol/m<sup>3</sup>, respectively; those of reaction temperature, 25-55 °C; and those of speed of agitation, 80, 120 and 150 rev/min.

## RESULTS AND DISCUSSION

### 1. Physicochemical Properties

Physicochemical properties such as diffusivity ( $D_A$ ) of isopropyl alcohol in toluene phase, distribution coefficient ( $D$ ) of isopropyl alcohol between toluene and water, mass transfer coefficient ( $k_L$ ) of isopropyl alcohol transferred from the aqueous phase to toluene phase, and chemical equilibrium constant ( $K_2$ ) were obtained as follows for the kinetic analysis of esterification of lauric acid with isopropyl alcohol in the liquid-liquid heterogeneous system.

Diffusivity of isopropyl alcohol in toluene was estimated from the Wilke-Chang equation [Treybal, 1980],

$$D_A = \frac{117.3 \times 10^{-18} (\chi M)^{0.5} T}{\mu V_A^{0.6}} \quad (28)$$

where,  $\chi$  is an association factor and 1 in the case of toluene,  $M$ , the molecular weight of the solvent,  $T$ , temperature,  $\mu$ , the viscosity of the solvent and obtained from a reference [Perry, 1984],  $V_A$ , the molecular volume of the solute, and  $9.25 \times 10^{-2}$  m<sup>3</sup>/kmol in case of isopropyl alcohol. The diffusivities estimated using Eq. (28) at 25, 35, 45 and 55 °C were 2.57, 2.78, 3.11 and  $3.58 \times 10^{-9}$  m<sup>2</sup>/s, respectively.

The distribution coefficient of isopropyl alcohol between toluene and water was measured using a method reported previously [Park et al., 1996]. The mass balance of isopropyl alcohol in terms of equilibrium concentration in toluene-water system can be formulated as follows:

$$[A]_0 = [A_i] + [A_w] \quad (29)$$

Distribution coefficient ( $D$ ) is defined as follows,

$$D = \frac{[A_w]}{[A_i]} \quad (30)$$

The following equation is obtained by combining Eqs. (29) with (30)

$$[A]_0 = \frac{1+D}{D} [A_w] \quad (31)$$

The equilibrium concentrations of isopropyl alcohol in aqueous phase were measured by varying the feed concentration from 0.2 to 2.0 kmol/m<sup>3</sup>. A plot of  $[A]_0$  against  $[A_w]$  was

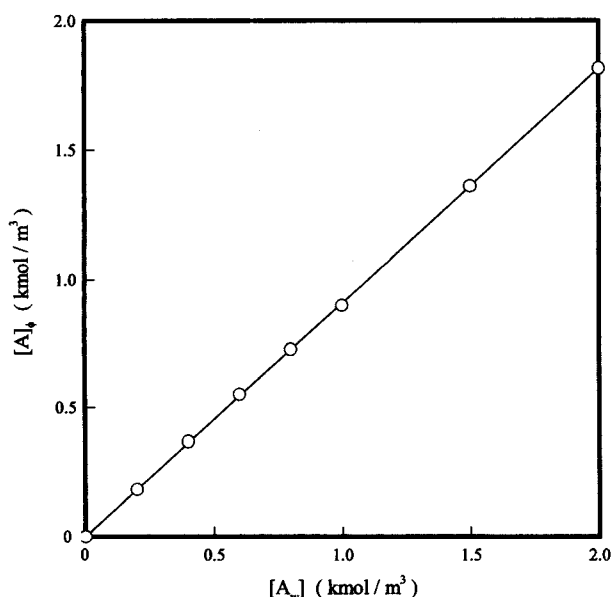


Fig. 1. The feed concentration of isopropyl alcohol as a function of its equilibrium concentration in aqueous phase at 25°C.

typically shown in Fig. 1 at 25°C, which shows that the experimental data coincide with Eq. (31) passing through origin. The value of the distribution coefficient obtained from the slope of the straight line was 9.852. The distribution coefficients at 25, 35, 45 and 55°C were 9.85, 6.25, 3.7 and 2.46, respectively.

If the isopropyl alcohol dissolved in distilled water contacts the toluene phase, the differential mass balance of isopropyl alcohol transferred into the toluene phase can be expressed as follows:

$$\frac{d[A]}{dt} = k_t a - ([A_i] - [A]) \quad (32)$$

where  $[A_i]$  is the solubility of isopropyl alcohol in toluene phase, and  $a$ , the interfacial area of the toluene-aqueous phase per unit volume of toluene phase, is 0.252 in this case. Eq. (32) was integrated with an initial condition such as  $[A]=0$  at  $t=0$ ,

$$\ln \frac{[A_i] - [A]}{[A_i]} = -k_t a t \quad (33)$$

An isopropyl alcohol aqueous solution of 150 cm<sup>3</sup>, whose concentration was 1.0 kmol/m<sup>3</sup>, and a toluene solution of 150 cm<sup>3</sup> were placed in the stirred vessel described in the EXPERIMENTAL section. Under a given speed of agitation, the concentration of isopropyl alcohol in toluene phase was measured at regular intervals by gas chromatography. The terms of the left-hand side of Eq. (33) were plotted against the contact time using the measured concentrations of isopropyl alcohol. As shown in Fig. 2, a linear relationship was observed. The mass transfer coefficients of isopropyl alcohol obtained from the slope of the straight line were  $1.68 \times 10^{-5}$ ,  $1.98 \times 10^{-5}$  and  $2.95 \times 10^{-5}$  m/s at agitation speed of 80, 120 and 150 rev/min, respectively.

At an equilibrium state of Reaction (2), the equilibrium constant,  $K_2$ , can be arranged as follows:

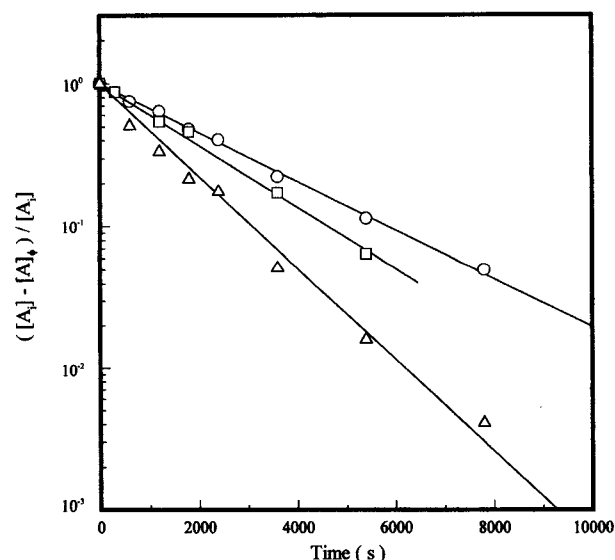


Fig. 2. Plot of  $([A_i] - [A]) / [A_i]$  vs. time at 25°C. ( $\circ$ : 80,  $\square$ : 120,  $\triangle$ : 150 rev/min)

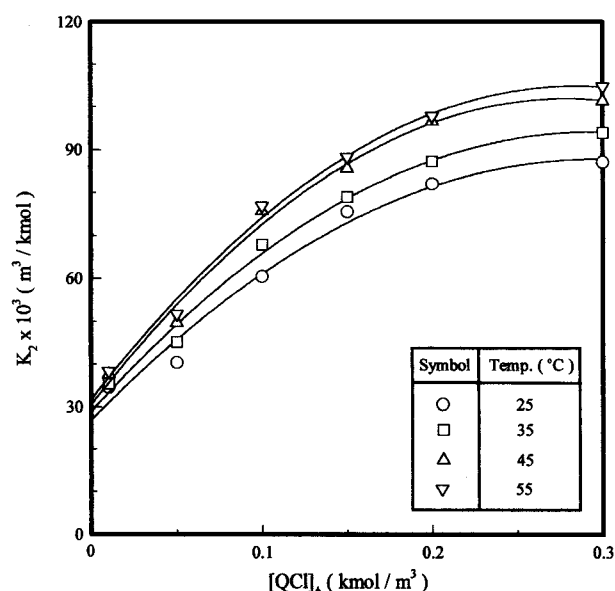


Fig. 3. Effect of concentration of catalyst and reaction temperature on chemical equilibrium constant. ( $[A]_e$ : 1.0 kmol/m<sup>3</sup>,  $[B]_e$ : 1.0 kmol/m<sup>3</sup>, and speed of agitation: 120 rev/min)

$$K_2 = \frac{X_{de}}{[A_i](M - X_{de})(1 - X_{de})} \quad (34)$$

where,  $M$  is  $[B]_e / [A_i]$ .

The concentration of isopropyl alcohol in the toluene phase was measured at a regular interval. The reaction conditions were kept as follows: concentration of isopropyl alcohol, lauric acid, 1.0 kmol/m<sup>3</sup>, and 1.0 kmol/m<sup>3</sup>, respectively; speed of agitation, 120 rev/min, the concentration of Aliquat 336 between 0.01 and 0.3 kmol/m<sup>3</sup>.

It was assumed that the reaction arrived at an equilibrium state when the measured concentration of isopropyl alcohol was held constant. The equilibrium constant,  $K_2$ , was obtained

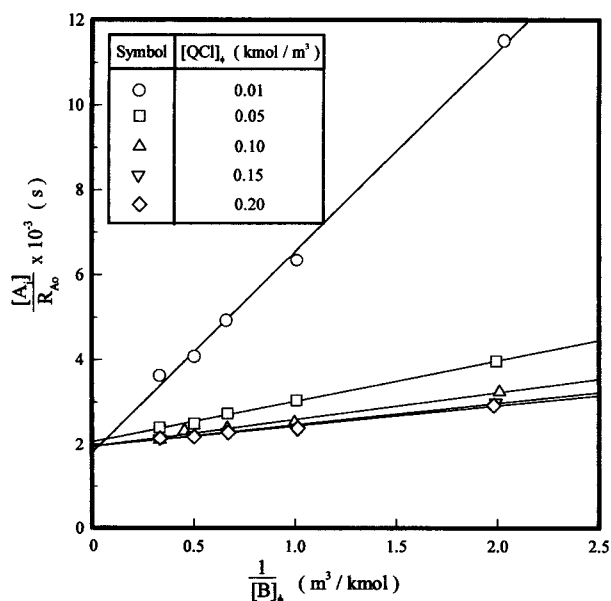


Fig. 4. Plot of  $[A]_0/R_{a0}$  vs.  $1/[B]_0$  for various concentration of Aliquat 336 at 25°C.

using the equilibrium conversion of isopropyl alcohol and Eq. (34).

Fig. 3 shows the plots of the equilibrium constant against the concentration of Aliquat 336 at various reaction temperatures of 25–55°C. As shown in Fig. 3, the equilibrium constant was increased as the reaction temperature and the concentration of catalyst were increased.

## 2. Reaction Regime

It is necessary to decide the scope of the reaction regime in the heterogeneous reaction of the esterification of lauric acid with isopropyl alcohol in order to obtain the proper rate expression.

The initial rate of reaction obtained from the experimental data of the acid conversion versus the reaction time was plotted against the reciprocal values of the feed concentration of lauric acid. Fig. 4 shows a plot of  $[A]_0/R_{a0}$  against  $1/[B]_0$  obtained typically at the following reaction conditions, feed concentration of isopropyl alcohol, 1.0  $\text{kmol}/\text{m}^3$ , those of catalyst, 0.01–0.2  $\text{kmol}/\text{m}^3$ , speed of agitation, 120 rev/min, the concentration of lauric acid from 0.5 to 3.0  $\text{kmol}/\text{m}^3$  at 25°C. As shown in Fig. 4, a linear relationship between the plots was satisfied, and then the values of the slope and the intercept could be obtained from the straight line. Also as shown in Fig. 4, the value of the slope increased as the concentration of Aliquat 336 decreased; the other hand, the values of the intercept were held constant and independent of the concentration of the catalyst. The slopes correspond to the value of  $1/k_2$ , the intercept,  $1/k_1a$  from the comparison of these linear relationships with Eq. (11).

Therefore, the values of  $k_2$  and  $k_L$  obtained from the values of the slope and the intercept of the straight line were plotted against the concentration of the catalyst in Fig. 5 and 6. The result plotted in Fig. 5 shows that  $k_2$  was increased as the concentration of catalyst was increased according to the following empirical equation with the regression coefficient of 99.8%.

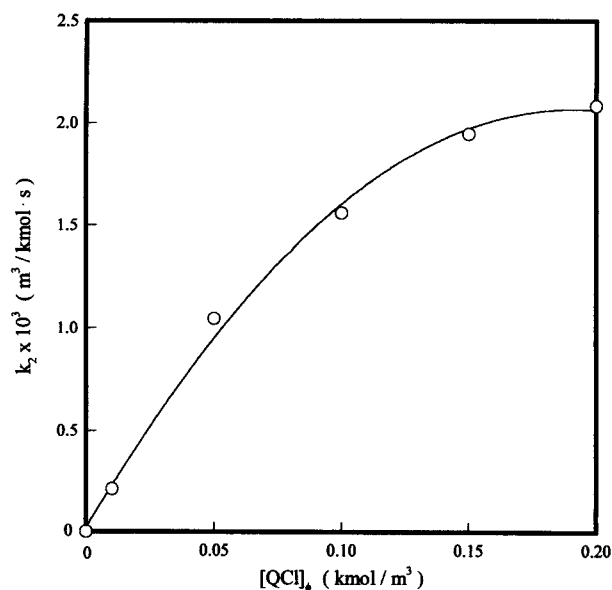


Fig. 5. Effect of concentration of catalyst on the forward reaction rate constant ( $k_2$ ) at 25°C.

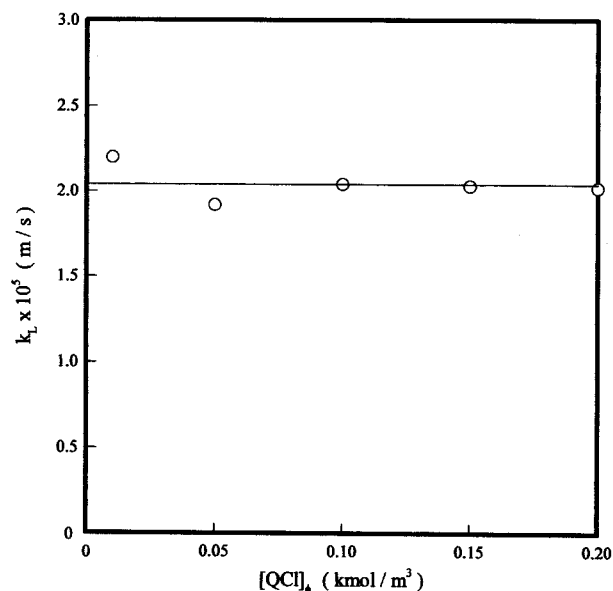


Fig. 6. Effect of concentration of catalyst on the mass transfer coefficient ( $k_L$ ) at 25°C.

$$k_2 = 0.0218[QCl]_0 - 0.0578[QCl]_0^2 \quad (35)$$

As shown in Fig. 6,  $k_L$  was held constant, and the mean value of  $k_L$  was  $2.04 \times 10^{-5}$  m/s, which approached reasonably to the value,  $1.98 \times 10^{-5}$  m/s, measured in the previous section.

Eqs. (4), (6) and (7) were checked by using the values of  $k_2$ ,  $k_L$ , and  $D_A$  estimated in the range of the concentration of lauric acid from 0.5 to 3.0  $\text{kmol}/\text{m}^3$  in order to find the reaction regime. As a result, Eq. (6) was satisfied, but Eqs. (4) and (7) were not satisfied. Moreover, the condition,  $k_1a < k_2[B]_0$ , was satisfied. A similar trend was also obtained in the other experimental variables such as speed of agitation and the re-

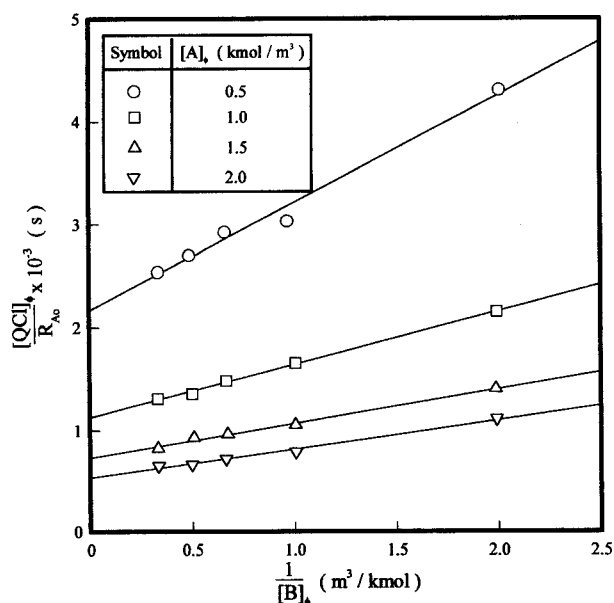


Fig. 7. Plot of  $[QCl]_0/R_{A_0}$  vs.  $1/[B]_0$  for various concentration of isopropyl alcohol at 25°C.

action temperature. Therefore, it was concluded that the reaction regime of the esterification of lauric acid with isopropyl alcohol belonged to the regime between very slow and slow reaction, and Eq. (8) could be used to estimate the rate of the reaction,  $R_A$ .

### 3. Kinetics of Esterification

In order to analyze the kinetics of esterification of lauric acid with isopropyl alcohol by using Aliquat 336 in the heterogeneous liquid-liquid system, the initial rates of reaction were measured in the range of the concentrations of lauric acid, isopropyl alcohol and Aliquat 336, 0.5-3.0, 0.5-2.0 and 0.01-0.2 kmol/m³, respectively, and reaction temperature, 25-55°C at the speed of agitation, 120 rev/min.

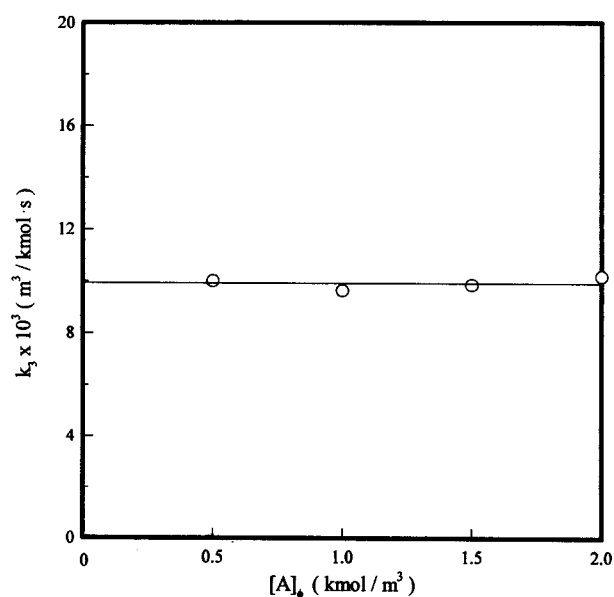


Fig. 8. Effect of the fed concentration of isopropyl alcohol on the forward reaction rate constant ( $k_3$ ) at 25°C.

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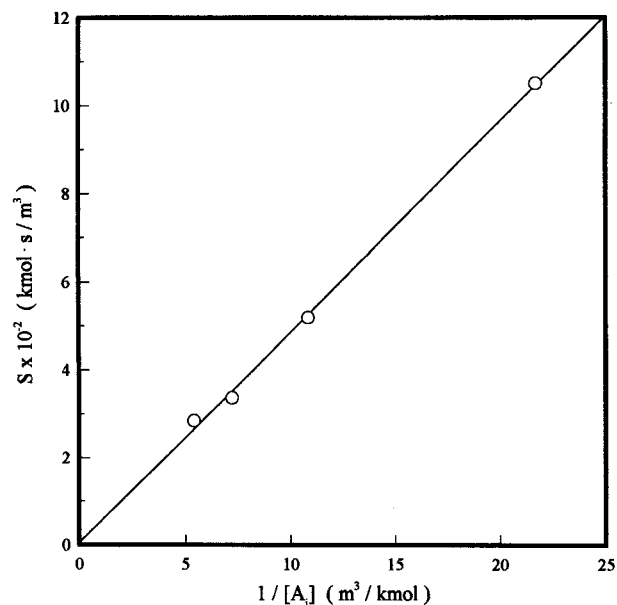


Fig. 9. A plot of  $S$  vs.  $1/[A]_0$ .

The values of  $[QCl]_0/R_{A_0}$  were plotted against the reciprocal values of the feed concentration of lauric acid. Fig. 7 show the plots of  $[QCl]_0/R_{A_0}$  against  $1/[B]_0$  typically in the range of the concentration of lauric acid and isopropyl alcohol, 0.5-3.0 kmol/m³ and 0.5-2.0 kmol/m³, respectively, and the concentration of the catalyst, 0.05 kmol/m³ at 25°C. As shown in Fig. 7, the linear relationship was satisfied with a correlation coefficient of more than 98%, and then the values of the slope and the intercept could be obtained from the straight line.

The forward reaction rate constant in Eq. (18),  $k_3$ , was obtained from the value of the intercept in Eq. (26). The values of  $k_3$  obtained for the feed concentration of isopropyl alcohol, 0.5, 1.0, 1.5 and 2.0 kmol/m³ were  $10.018 \times 10^{-3}$ ,  $9.659 \times 10^{-3}$ ,

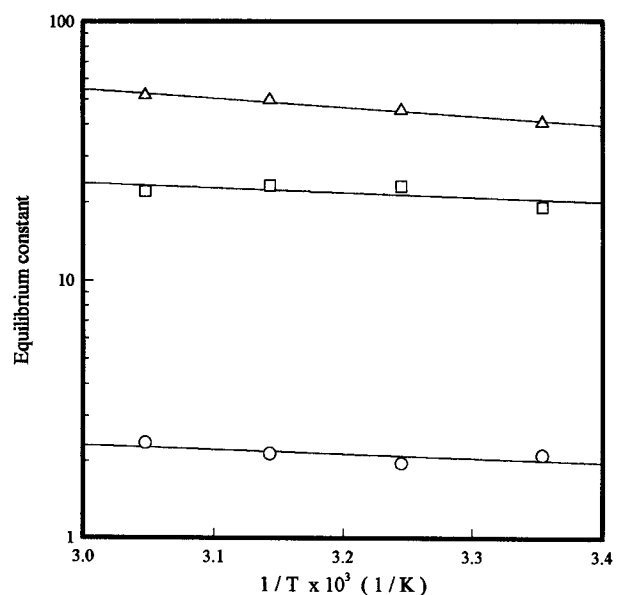


Fig. 10. Effect of reaction temperature on the equilibrium constant.

○ :  $K_1$ , △ :  $K_2$ , □ :  $K_3$

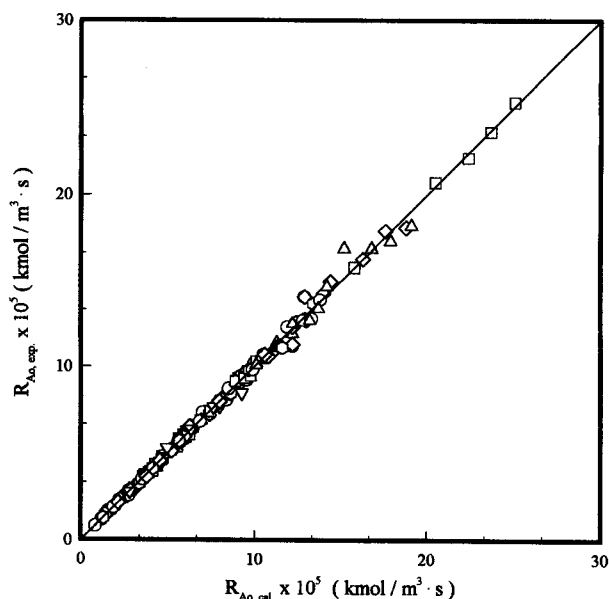


Fig. 11. Comparison of the observed initial rate of reaction with the calculated value at  $[QCl]_0$ , 0.05 kmol/m<sup>3</sup> and speed of agitation, 120 rev/min.

$[A]_0$ : 0.5-2.0 kmol/m<sup>3</sup>,  $[B]_0$ : 0.5-3.0 kmol/m<sup>3</sup>, reaction temperature: 25-55°C

$9.870 \times 10^{-3}$  and  $10.209 \times 10^{-3}$  m<sup>3</sup>/kmol·s, respectively. As shown in Fig. 8,  $k_3$  was held constant and independent of the concentration of isopropyl alcohol as  $9.94 \times 10^{-3}$  m<sup>3</sup>/kmol·s.

The following equation is obtained from a comparison of the slope in Fig. 7 with Eq. (26).

$$S = \frac{k'_1}{k_1 k_3 [A_i]} + \frac{1}{k_1} \quad (36)$$

where,  $S$  is the value of the slope in Fig. 7.

The values of the slope in Fig. 7 were plotted against the reciprocal values of the concentration of isopropyl alcohol in Fig. 9. As shown in Fig. 9, a linear relationship between the plots was observed and the values of the slope and the intercept could be obtained from the straight line, which were 47.651 kmol·s/m<sup>6</sup> and 8.01 kmol·s/m<sup>3</sup>, respectively. The  $k_1$  and  $k'_1$  obtained from these values and Eq. (36) were 0.125 m<sup>3</sup>/kmol·s, and 0.059/s, respectively. Therefore, the value of  $K_1$  was obtained as 2.11 m<sup>3</sup>/kmol, and  $K_3$  was obtained from  $K_1$ ,  $K_2$  and Eq. (27) as 19.13. The values of the equilibrium constant at the other reaction temperature were obtained with the same procedure carried out at 25°C.

The Arrhenius plot was shown in Fig. 10. As shown in Fig. 10, the linear relationship between plots was satisfied. The relationships between the equilibrium constant and the reaction temperature for the catalyst concentration of 0.05 kmol/m<sup>3</sup> were expressed as follows:

$$K_1 = 7.6 \exp(-784/RT) \quad (37)$$

$$K_2 = 649.3 \exp(-1636/RT) \quad (38)$$

$$K_3 = 85.9 \exp(-649/RT) \quad (39)$$

The observed initial rates of reaction were plotted against those calculated from Eq. (25) with  $k_1$ ,  $k'_1$  and  $k_3$  obtained in order to confirm the validity of the reaction mechanism as described in Eq. (17) and (18). As shown in Fig. 11, the calculated initial rates of reaction approached reasonably to the observed values within the standard error with 3.9%.

## CONCLUSION

Esterification of lauric acid with isopropyl alcohol by tri-n-propylmethylammonium chloride was carried out in a stirred vessel with a flat liquid-liquid interface. The initial rate of reaction was measured with varying concentration of reactants and catalyst, reaction temperature and speed of agitation. The observed initial rate of reaction was used to analyze the reaction kinetics combined with the catalyst and to evaluate the reaction kinetics.

The forward overall reaction rate constant was empirically expressed as a function of the concentration of catalyst as follows:

$$k_2 = 0.0218[QCl]_0 - 0.0587[QCl]_0^2$$

The equilibrium constants in Eqs. (17), (2) and (18) were expressed as follows:

$$K_1 = 7.6 \exp(-784/RT)$$

$$K_2 = 649.3 \exp(-1636/RT)$$

$$K_3 = 85.9 \exp(-649/RT)$$

The analysis of the reaction kinetics indicated that the reaction of lauric acid with isopropyl alcohol was between a very slow and slow reaction regime.

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## NOMENCLATURE

- $a$  : interfacial contact area of organic and aqueous phase per unit volume of organic phase [1/m]
- $A$  : isopropyl alcohol
- $[A]$  : concentration of isopropyl alcohol in the bulk body of the organic phase [kmol/m<sup>3</sup>]
- $[A_i]$  : saturated concentration of isopropyl alcohol in the organic phase [kmol/m<sup>3</sup>]
- $[A_w]$  : saturated concentration of isopropyl alcohol in the aqueous phase [kmol/m<sup>3</sup>]
- $B$  : lauric acid
- $[B]$  : concentration of lauric acid in the bulk body of the organic phase [kmol/m<sup>3</sup>]
- $D$  : distribution coefficient defined as in Eq. (30)
- $D_A$  : diffusivity of isopropyl alcohol in the organic phase [m<sup>2</sup>/s]
- $E$  : ester

- [E] : concentration of ester in the bulk body of the organic phase [kmol/m<sup>3</sup>]  
 $K_1$  : equilibrium constant defined as in Eq. (19) [m<sup>3</sup>/kmol]  
 $K_2$  : equilibrium constant defined as in Eq. (10) [m<sup>3</sup>/kmol]  
 $K_3$  : equilibrium constant defined as in Eq. (20)  
 $k_1$  : forward reaction rate constant in Eq. (17) [m<sup>3</sup>/kmol·s]  
 $k_1'$  : backward reaction rate constant in Eq. (17) [1/s]  
 $k_2$  : forward reaction rate constant in Eq. (2) [m<sup>3</sup>/kmol·s]  
 $k_2'$  : backward reaction rate constant in Eq. (2) [1/s]  
 $k_3$  : forward reaction rate constant in Eq. (18) [m<sup>3</sup>/kmol·s]  
 $k_3'$  : backward reaction rate constant in Eq. (18) [1/s]  
 $k_L$  : mass transfer coefficient of isopropyl alcohol in the organic phase [m/s]  
 $Q$  : quaternary ammonium ion  
 $R_A$  : rate of reaction of A [m<sup>3</sup>/kmol·s]  
 $R_{A0}$  : initial rate of reaction of A [m<sup>3</sup>/kmol·s]  
 $S$  : value of the slope in Fig. 7 [kmol/m<sup>3</sup>]  
 $t$  : reaction time [s]  
 $T$  : reaction temperature [K]  
 $X_e$  : equilibrium conversion of isopropyl alcohol at the equilibrium reaction of lauric acid with isopropyl alcohol

### Subscript

- $\phi$  : initial value

## REFERENCES

- Al-Saadi, A. N. and Jeffreys, G. V., "Esterification of Butanol in a Two-Phase Liquid-Liquid System," *AIChE J.*, **27**, 754 (1981).  
 Cainelli, G. and Manescalchi, F., "The Use of Anion-Exchange Resins in the Synthesis of Esters from Carboxylic Acids and Alkylating Agents," *Synthesis*, 723 (1975).  
 Chanodalia, S. B., Dhanuka, V. R. and Malshe, V. C., "Kinetics of the Liquid Phase Esterification of Carboxylic Acids with Alcohols in the Presence of Acid Catalysts," *Chem. Eng. Sci.*, **32**, 551 (1977).  
 Doraiswamy, L. K. and Sharma, K. K., "Heterogeneous Reactions," John Wiley & Sons, New York, **2**, 17 (1984).  
 Indu, B., Ernst, W. R. and Gelbaum, L. T., "Methanol-Formic Acid Esterification Equilibrium in Sulfuric Acid Solutions: Influence of Sodium Salts," *Ind. Eng. Chem. Res.*, **32**, 981 (1993).  
 Leyes, C. E. and Othmer, D. F., "Esterification of Butanol and Acetic Acid," *Ind. Eng. Chem.*, **37**, 968 (1945).  
 Lima, F. V., Ryle, D. L. and Asenjo, J. A., "Factors Affecting the Esterification of Lauric Acid Using an Immobilized Biocatalyst: Enzyme Characterization and Studies in a Well-Mixed Reactor," *Biotech. Bioeng.*, **46**, 69 (1995).  
 Loupy, A., Pedoussaut, M. and Sansoulet, J., "Solid-Liquid Phase-Transfer Catalysis without Solvent: Mild and Efficient Conditions for Saponifications and Preparations of Hindered Esters," *J. Org. Chem.*, **51**, 740 (1986).  
 McCracken, D. J. and Dickson, P. F., "Reaction Kinetics of Cyclohexanol-Acetic Acid Esterification," *Ind. Eng. Chem. Process Des. Rev.*, **6**, 286 (1967).  
 Moore, G. G., Foglia, T. A. and McGaham, T. J., "Preparation of Hindered Esters by the Alkylation of Carboxylate Salts with Simple Alkyl Halides," *J. Org. Chem.*, **44**, 2425 (1979).  
 Okamoto, K., Yamamoto, M., Noda, S., Semoto, T., Otsoshi, Y., Tanaka, K. and Kita, H., "Vapor-Permeation-Aided Esterification of Oleic Acid," *Ind. Eng. Chem. Res.*, **33**, 849 (1994).  
 Park, S. W. and Suh, D. S., "Absorption of O<sub>2</sub> into Aliquat 336-Dephenylmethane Heterogeneous System," *HWAHAK KONG-HAK*, **32**, 700 (1994).  
 Park, S. W., Kaseger, C. F., Moon, J. B. and Kim, J. H., "Mass Transfer of Phenol Through Supported Liquid Membrane," *Korean J. Chem. Eng.*, **13**, 596 (1996).  
 Park, D. W., Park, S. W., Kaseger, C. F., Moon, J. Y. and Moon, J. B., "Absorption and Reaction of CO<sub>2</sub> with 2,3-Epoxypropyl Phenyl Ether Using Aliquat 336 as Catalyst," *React. Kinet. Catal. Lett.*, **62**, 243 (1997).  
 Perry, R. H., "Perry's Chemical Engineers' Handbook," 4th ed., McGraw-Hill Book Co., New York, 3251 (1984).  
 Ramaiah, M., "A New Convenient Method for Esterification Using Ph<sub>3</sub>CCl<sub>4</sub> System," *J. Org. Chem.*, **50**, 4991 (1985).  
 Sanchez, N., Coteron, A., Martinez, M. and Aracil, J., "Kinetic Analysis and Modeling Using Cobalt Chloride as Catalyst," *Ind. Eng. Chem. Res.*, **31**, 1985 (1992).  
 Santacesaria, E., Gelosa, D., Danise, F. and Cerra, S., "Vapor-Phase Esterification Catalyzed by Decationized Y Zeolites," *J. Catal.*, **80**, 427 (1983).  
 Senatalar, A. E., Erencsek, E., Tuter, M. and Erciyes, A. T., "Effect of Lewis Acid Catalysts on the Esterification Kinetics of Castor Oil with Oleic Acid," *J. Am. Oil Chem. Soc.*, **71**, 1035 (1994).  
 Singh, C. P., Skagerlind, P., Holmberg, K. and Shah, D. O., "A Comparison Between Lipase-Catalyzed Esterification of Oleic Acid with Glycerol in Monolayer and Microemulsion Systems," *J. Am. Oil Chem. Soc.*, **71**, 1405 (1994).  
 Starks, C. M. and Liotta, C., "Phase Transfer Catalyst: Principles and Techniques," Academic Press, New York (1978).  
 Treybal, R. E., "Mass Transfer Operation," McGraw-Hill Book Co., New York, 35 (1980).  
 Vieville, C., Mouloungui, Z. and Gaset, A., "Esterification of Oleic Acid by Methanol Catalyzed by *p*-Toluenesulfonic Acid and the Cation-Exchange Resins K2411 and K1481 in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **32**, 2065 (1993).