

Short communication

Saponification Reaction System: a Detailed Mass Transfer Coefficient Determination

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Abstract

The saponification of an aromatic ester with an aqueous sodium hydroxide was studied within a heterogeneous reaction medium in order to determine the overall kinetics of the selected system. The extended thermo-kinetic model was developed compared to the previously used simple one. The reaction rate within a heterogeneous liquid-liquid system incorporates a chemical kinetics term as well as mass transfer between both phases. Chemical rate constant was obtained from experiments within a homogeneous medium, whilst the mass-transfer coefficient was determined separately. The measured thermal profiles were then the bases for determining the overall reaction-rate.

This study presents the development of an extended kinetic model for considering mass transfer regarding the saponification of ethyl benzoate with sodium hydroxide within a heterogeneous reaction medium. The time-dependences are presented for the mass transfer coefficient and the interfacial areas at different heterogeneous stages and temperatures. The results indicated an important role of reliable kinetic model, as significant difference in $k_L a$ product was obtained with extended and simple approach.

Keywords: Kinetics; mass transfer; saponification; heterogeneous system

1. Introduction

Industrial applications such as reactions, extractions, and emulsifications are often conducted within heterogeneous systems. Proper knowledge about kinetics and mass transfer between phases is essential, especially when any changes in operating conditions (temperatures, compositions, stirring speed) and equipment need to be taken into account.

It should be noted that special concern has to be focused on safety analyses regarding those runaway reactions that involve two immiscible liquid-liquid phases, one being mainly organic and the other aqueous. The important heterogeneous reactions where chemical reaction and mass transfer occur simultaneously are sulfonations, saponifications, nitrations, hydrochlorations, esterifications, hydrolyses, and oxidations.^{1,2}

In heterogeneous systems the overall reaction rate and conversion depend, not only on the chemical and physical properties of the studied system, but also on the mechanical and geometrical characteristics of the used

equipment. Those properties that affect the reaction rate are the densities and viscosities during each phase, interfacial surface properties, diffusion coefficients of the reagents and products, and the reaction rate constants. From amongst the mechanical features of the equipment, the geometry of the reactor, type and diameter of the stirrer, flow rates of each phase, and stirrer speed are important.³ The influence of the afore-mentioned parameters has to be determined experimentally. Due to the complexity of heterogeneous liquid-liquid reactions' modeling, a lot of effort should be invested in experimental, theoretical, and computational work.

Mass-transfer is often a rate-limiting process, thus much of the research is oriented towards its intensification. Because mass transfer efficiency also depends on the process equipment mini or micro-reactors are very often used, which can be especially competitive for fast and exothermal reactions.⁴⁻⁶

After saponification reactions, the products become species with surface-active properties having influence on interfacial properties, and alcohols that usually act as co-

solvents changing the solubility properties of the reagents. Altogether they can greatly modify the mass-transfer and affect the overall reaction rate.⁷

An extended kinetic model for sodium benzoate synthesis within heterogeneous media was developed during this work. Although some saponification reactions have been reviewed by other researchers,^{7–9} no data about our selected system has yet been published. During this study we turned our attention towards extending a previously-simplified thermo-kinetic model valid for heterogeneous liquid-liquid reaction systems, where several assumptions were used for mass transfer estimation.¹⁰ In this work the mass transfer coefficient, interfacial area, and the $k_L a$ product were estimated precisely using experimentally determined thermal power profiles.

2. Experimental

2.1. Experimental Procedure

The experimental procedure, equipment, and materials used are described in our previous study.¹⁰ Only a brief description will be given here. All chemicals, ethyl benzoate, ethanol, sodium benzoate and sodium hydroxide are commercially available and were used as received without further purification. The experiments were conducted within a RC1 reaction calorimeter (Mettler Toledo), which measures the heat flow that corresponds to the temperature difference between the temperature of the reactor's content and the temperature of the reactor's jacket. The reactor ($V = 2$ L) was equipped with an anchor glass stirrer, a glass AP01 temperature sensor, and a 25 W glass calibration heater. RC1 is a double walled glass-made automatic laboratory batch reactor. Heat flow was further used for calculating the heat during the reaction. The individual experiment was started by charging the reactor with ethyl benzoate, ethanol, and water. The reaction was triggered by the addition of sodium hydroxide solution. The reaction was performed at fixed rotational frequency of the stirrer, $N = 80 \text{ min}^{-1}$, and reaction media temperatures of $\vartheta = (22, 26, 30, 34, \text{ and } 38) \text{ }^\circ\text{C}$. Ethanol was added to the ethyl benzoate as a co-solvent. For studying different stages of heterogeneity different ethanol mole fractions ($x_{\text{EtOH}} = 0.1, 0.2, 0.3$) were applied. The experiments were performed at equimolar initial concentrations of ethyl benzoate and sodium hydroxide, $c_0 = (1.17, 1.14, 1.11) \text{ mol/L}$ depending on ethanol mole fraction.

2.2. Kinetic Model

The kinetic model was presented in detail in our previous study,¹⁰ only the major points are highlighted here. The overall rate expression regarding the base-hydrolysis of ethyl benzoate with sodium hydroxide in a heterogeneous medium incorporates two rate steps in series – mass

transfer of sodium hydroxide to the surface of ethyl benzoate droplets, followed by reaction on the surface. The chemical kinetic term for this second order reaction is:

$$-r_{\text{AK}} = -\frac{dc_{\text{A}}}{dt} = k c_{\text{A}}^2 \quad (1)$$

where c_{A} is the concentration of sodium hydroxide on the surface of ethylbenzoate droplets, t time and k the reaction rate constant.

The rate expression considering mass transfer among two liquid phases is:

$$-r_{\text{AM}} = -\frac{dc_{\text{A}}}{dt} = k_L a (c_{\text{AL}} - c_{\text{A}}) \quad (2)$$

where $k_L a$ is the mass transfer coefficient multiplied by the interfacial area, and c_{AL} the concentration of sodium hydroxide in the bulk liquid.

By the assumption of two steps in the series relating to the overall rate of reaction ($-r_{\text{AK}} = -r_{\text{AM}}$) and after rearrangements the final form of the rate equation becomes:

$$-r_{\text{A}} = \frac{k_L a}{2k} \left(2k c_{\text{AL}} + k_L a - \sqrt{(k_L a)^2 + 4k k_L a c_{\text{AL}}} \right) \quad (3)$$

where k_L is the mass transfer coefficient, and a the interfacial area.

The interfacial area within a heterogeneous liquid-liquid media is crucial for determining the kinetic parameters when considering mass transfer between phases, and is important for any further designing and developing of a process. From amongst several parameters affecting the interfacial area, the composition of the reaction mixture, stirrer type, and stirrer speed are the more important ones. The interfacial area per continuous phase volume unit was calculated using a Sprow's type correlation as:⁸

$$a = \frac{6 \varepsilon_d}{D \alpha \text{We}^{-0.6}} \quad (4)$$

where D is the stirrer diameter, α the dimensionless parameter (it was set to 0.2, numerical values vary between 0.04 and 0.4⁸), We the Weber number, and ε_d the volume ratio between the dispersed and continuous phases:

$$\varepsilon_d = \frac{V_d}{V_c} \quad (5)$$

The volume of the dispersed phase V_d , was calculated from:

$$V_d = \frac{V_{\text{B0}}}{n_{\text{B0}}} n_{\text{B}} \quad (6)$$

where V_{B0} is the initial volume of ethyl benzoate, n_{B0} the

initial mole number of ethyl benzoate, and n_b the mole number of ethyl benzoate.

When calculating the volume of the continuous phase V_c , all the instantly present components (i) of the continuous phase were taken into account:

$$V_c = \sum_i \frac{V_{i0}}{n_{i0}} n_i \quad (7)$$

Weber's number can be obtained from:

$$We = \frac{\rho_c N^2 D^3}{\sigma} \quad (8)$$

where ρ_c is the density of the continuous phase, N the stirrer speed, and σ the interfacial tension.

Good and Girifalco's model was used for the calculation of interfacial tension:

$$\sigma = \gamma_c + \gamma_d - 2\varphi \sqrt{\gamma_c \gamma_d} \quad (9)$$

where γ_c is the surface tension in the continuous phase, γ_d the surface tension of the dispersed phase, and φ the interaction parameter, calculated as:

$$\varphi = \frac{4(V_{md} V_{mc})^{1/3}}{(V_{md}^{1/3} + V_{mc}^{1/3})^2} \quad (10)$$

where V_{md} is the molar volume of the dispersed phase and V_{mc} the molar volume of the continuous phase.

3. Results and Discussion

The calculation procedure for obtaining the reaction rates from calorimetric data has been explained in our previous work.¹⁰ Mass transfer has to be avoided in order to study sodium benzoate's effect on chemical kinetics. Ethanol was added to the reaction media for reaching the homogeneity.

The concentration of sodium hydroxide within the bulk liquid, as obtained from the calorimetric data, was used for surface area determination. Throughout the reaction's progress the volume of the dispersed phase regarding ethyl benzoate decreased whilst the volume of the continuous phase increased. Both volumes were calculated by considering their concentration profiles. The den-

sity of the continuous phase was calculated for each heterogeneous stage, and was assumed to be constant during the reaction (Table 1).

The surface tensions for both phases were measured using a Krüss tension-meter (Table 2).

Table 2: Surface tensions of the dispersed and continuous phases at the temperature, $\vartheta = 30$ °C. Concentration dependence was not perceived.

| phase | $\gamma/\text{mN m}^{-1}$ |
|------------|---------------------------|
| dispersed | 34.8 |
| continuous | 29.6 |

Four solutions of different concentrations were prepared, according to reaction progress for determining the surface tension of the continuous phase. There was no clear concentration dependence therefore the average value was taken. The surface tension of the dispersed phase corresponded to pure ethyl benzoate.

For calculating the overall reaction rate the interfacial area versus time has to be known. The mass transfer coefficients, k_L , during the reaction were calculated using Matlab software (eq. (3)). This values were compared only with that of similar reaction system⁴ (alkaline hydrolysis of methyl benzoate) and are the same order of magnitude ($5 \cdot 10^{-6} \text{ m s}^{-1}$). The simulation results at a temperature of $\vartheta = 30$ °C, and the ethanol mole fraction $x_{\text{EtOH}} = 0.3$, are presented in Figure 1. The reaction rate constants, k , were previously determined from the data regarding the homogeneous mixture.¹⁰

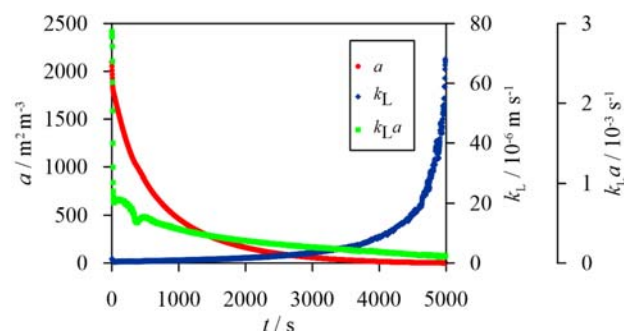


Figure 1. Relationship between interfacial area, mass transfer coefficient and $k_L a$ product at the temperature, $\vartheta = 30$ °C and ethanol mole fraction, $x_{\text{EtOH}} = 0.3$. Rotational frequency of the stirrer was constant for all experiments, $N = 80 \text{ s}^{-1}$.

For our reaction system we presumed the reaction is taking place on the surface of the ethyl benzoate droplets and it starts when sodium hydroxide diffuses to the surface. Figure 1 shows that during the progress of the reaction, the droplets of ethyl benzoate slowly disappear and consequently the interfacial area decreases. The

Table 1: Densities of the continuous phase for different heterogeneous stages. Constant densities were assumed during the reaction.

| x_{EtOH} | $\rho_c / \text{kg dm}^{-3}$ |
|-------------------|------------------------------|
| 0.1 | 0.96 |
| 0.2 | 0.93 |
| 0.3 | 0.90 |

mass transfer coefficients increase whilst the $k_L a$ products decrease. Temperature and concentration dependence of the mass transfer coefficients, is presented in Figure 2.

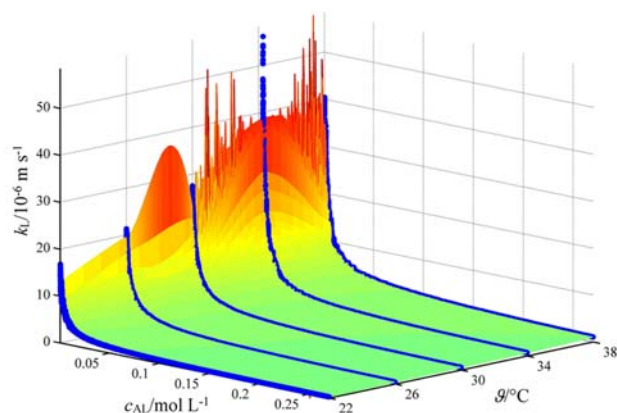


Figure 2. Surface plot of mass transfer coefficients, k_L , as a function of temperature and sodium hydroxide concentration in the bulk liquid, at mole fraction of ethanol, $x_{\text{EtOH}} = 0.1$.

It is evident from the surface plot (Figure 2) that a larger increase occurred in the values for mass transfer coefficient at the end of the reaction, where the mass transfer was no longer within the rate-limiting process. The mass transfer coefficients also increased with increasing temperature.

The dependence of the mass transfer coefficients on the ethanol mole fraction, is presented in Figure 3.

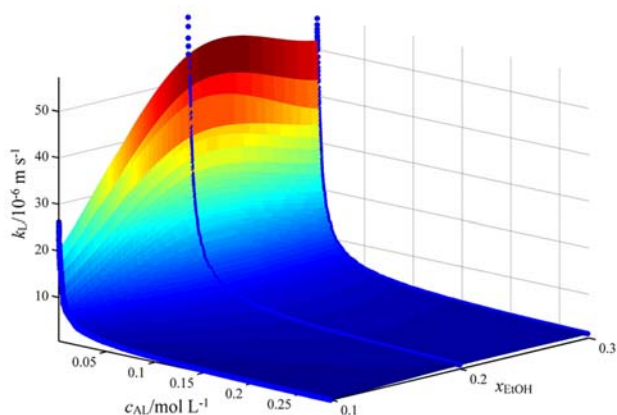


Figure 3. Surface plot of mass transfer coefficients, k_L , as a function of sodium hydroxide concentration in the bulk liquid and mole fraction of ethanol, at the temperature, $\vartheta = 30\text{ }^\circ\text{C}$.

Figure 3 shows that when approaching a more homogeneous mixture at the end of the reaction, the values of the mass transfer coefficients increased steeply, as they also increased with increasing initial mole fractions of ethanol.

Using the simple kinetic model, the $k_L a$ product was determined without any time-dependence. For the purpose of comparison we calculated the average values of $k_L a$ products for the extended model (Table 3). They were calculated considering $k_L a$ products from complete time range at a certain temperature and heterogeneity stage.

Table 3: Comparisons between the $k_L a$ products, at different heterogeneity stages, calculated for both the simple (S)¹⁰ and extended (EM) kinetic models at the temperature, $\vartheta = 30\text{ }^\circ\text{C}$.

| x_{EtOH} | $k_L a$ (S)/ 10^{-4} s^{-1} | $k_L a$ (EM)/ 10^{-4} s^{-1} |
|-------------------|--------------------------------------|---------------------------------------|
| 0.1 | 2.9 | 1.8 |
| 0.2 | 9.4 | 3.6 |
| 0.3 | 19.4 | 4.4 |

It is evident from Table 3, that the values obtained from the extended model are in general lower compared to the ones obtained from the simple one. This difference was expected because many assumptions were used in the simple model. Nevertheless, it can be seen that the values for the $k_L a$ product increase with any increasing mole fraction of ethanol when the reactive mixture becomes more homogeneous.

Finally, knowing mass transfer coefficient and chemical kinetic term, the overall reaction rate can be calculated according to Eq. (3). The comparison of experimental and calculated values of reaction rate is presented in Figure 4.

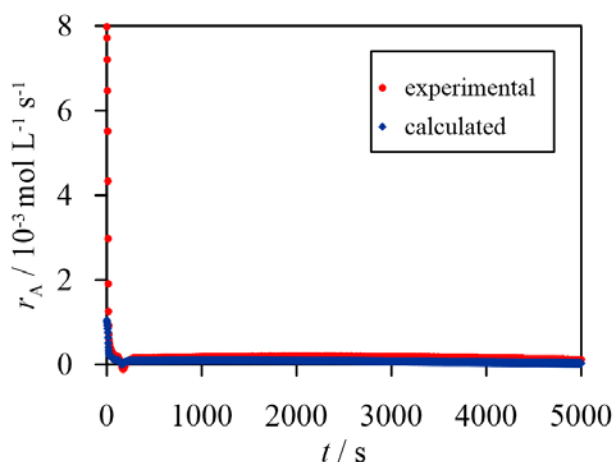


Figure 4. Experimental and calculated reaction rates, $-r_A$, as a function of time, at the temperature, $\vartheta = 30\text{ }^\circ\text{C}$ and mole fraction of ethanol, $x_{\text{EtOH}} = 0.1$.

As we can see in Figure 4 the agreement between experimental and calculated values of reaction rate is good. Only at the beginning of the reaction the discrepancies among both data sets are larger, which is due to the significant changes of the reaction rate.

4. Conclusions

The saponification of ethyl benzoate with sodium hydroxide in heterogeneous liquid-liquid reaction mixture was used to test an extended thermo-kinetic model, by taking into account mass transfer between both phases.

The results show that during the reaction in the heterogeneous liquid-liquid mixture the interfacial area decreases whilst the mass transfer coefficient increases. The product of the mass transfer coefficient and interfacial area, $k_L a$, decreases during the reaction because any decrease in the interfacial area prevails over any increase in the mass transfer coefficient.

The obtained results lead us to the conclusion that for any prediction by a reliable kinetic model it is obligatory to evaluate the rate steps, the chemical kinetics, and the mass transfer precisely, using minimum assumptions. This is extremely important for industrial applications and safety studies.

5. Nomenclature

- a = interfacial area ($\text{m}^2 \text{m}^{-3}$)
 c_{AL} = concentration of sodium hydroxide in the bulk liquid (mol L^{-1})
 D = stirrer diameter (m)
 k = reaction rate constant ($\text{L mol}^{-1} \text{s}^{-1}$)
 k_L = mass transfer coefficient (m s^{-1})
 $k_L a$ = $k_L a$ product (s^{-1})
 n_A = number of moles which corresponds to the component A (mol)
 N = rotational frequency of the stirrer (s^{-1})
 r_A = overall reaction rate ($\text{mol L}^{-1} \text{s}^{-1}$)
 t = time (s)
 V = volume (m^3)
 We = Weber number
 x = mole fraction
 α = dimensionless parameter
 γ = surface tension (mN m^{-1})
 ε_d = volume ratio between dispersed and continuous phase
 ϑ = temperature ($^{\circ}\text{C}$)

- ρ_c = density of continuous phase (kg m^{-3})
 σ = interfacial tension (mN m^{-1})
 φ = interaction parameter
 A = component A
 B = component B
 c = continuous phase
 d = dispersed phase
 EtOH = ethanol
 i = component i
 m = molar
 0 = initial (at time $t = 0$)

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Povzetek

Umiljenje aromatskega estra v vodni raztopini natrijevega hidroksida smo preučevali v heterogenem reakcijskem mediju z namenom razvoja kinetičnega modela. Za primerjavo s predhodno uporabljenim preprostim modelom je bil razvit razširjen termo-kinetični model. Proizvodnost v heterogenem tekoče-tekoče sistemu smo opisali z izrazom, ki upošteva tako kemijsko kinetiko, kakor tudi prenos snovi med obema fazama. Konstanta proizvodnosti je bila pridobljena iz poskusov v homogenem mediju, medtem ko je bil koeficient snovnega prenosa določen posebej. Izmerjeni termični profili so bili osnova za določitev proizvodnosti reakcije. Prikazane so časovne odvisnosti koeficienta snovnega prenosa in medfazne površine pri različnih stopnjah heterogenosti in temperaturah. Iz rezultatov je razvidno, da razlika v $k_L a$ produktu, dobljenim z razširjenim in enostavnim modelom obstaja, kar potrjuje pomembnost izbire zanesljivega kinetičnega modela.