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Marcel Schmidt, Johannes Deckwerth, Reinhard Schomaecker, and Michael Schwarze J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.8b00247 • Publication Date (Web): 15 May 2018 Downloaded from http://pubs.acs.org on May 18, 2018

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Alkaline Hydrolysis of Methyl Decanoate in Surfactant based Systems

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KEYWORDS: Surfactant, Hydrolysis, Triton X-100

ABSTRACT:

Surfactant-modified reaction systems are one approach to perform organic reactions with water as the solvent involving hydrophobic reactants. Herein, the alkaline hydrolysis of the long-chain methyl decanoate in cationic and nonionic surfactant-modified systems is reported. The physicochemical behavior of the reaction mixture and the performance of the alkaline hydrolysis were systematically investigated. In water as the solvent, the reaction is slow, but at elevated temperatures, the alkaline hydrolysis of methyl decanoate is accelerated because the reaction product sodium decanoate acts as an ionic surfactant, leading to an increased solubility of methyl decanoate in the aqueous phase. The rate can be significantly increased by the addition of surfactants as solubilizers. In nonionic TX-100 solutions, the reaction rate can be increased by a factor of about 100 for a surfactant concentration of 5 wt%. If cationic surfactants are applied, the reaction rate can be further increased by a factor of 30 due to the electrostatic interaction between the hydroxide ions in solution and the charged head-groups of the cationic micelles.

INTRODUCTION

Surfactant-based reaction media have attracted much attention during the last years as alternatives to conventional organic solvents. Their outstanding properties, such as water as solvent, increased interfacial area, and advanced separation concepts, have classified them as green solvents. Manifold stoichiometric, noble-metal- as well as bio-catalyzed reactions were successfully performed in these media.¹⁻³ Above the critical micelle concentration (CMC), surfactant monomers spontaneously aggregate into micelles that act as nano-sized carriers able to solubilize hydrophobic reactants in water. In many stoichiometric reactions involving surfactants, a significant increase in the reactions rate is observed for which the term *micellar catalysis* was introduced.⁴ Mubofu and Engberts studied Diels-Alder reactions and in comparison to pure water as the solvent, the rate increased by a factor of about 80 using SDS (10 mM, pH 2) as the surfactant.⁵ Bahrami et al. synthesized benzimidazoles and got almost quantitative yield using SDS whereby in pure water the yield was only 23%.⁶ The main reason for the higher reaction rate is the locally higher concentration of reactants. In both examples, the hydrophobic reactants are solubilized in the core of the micelles, where they accumulate and react. In other examples, especially hydrolysis reactions involving OH⁻ ions, one reactant accumulates at the surface of the micelles, if cationic surfactants are applied.^{7–10} One group of reactants where this phenomena can be followed visually are triarylmethane dyes, where the solution at full conversion becomes colorless. Several studies for hydrolysis reactions catalyzed by cationic micelles are shown in the literature.¹¹⁻¹³ The effects that surfactants can have on the rate of chemical reactions are reviewed by Samiey et al.¹⁴ From the huge number of commercially available surfactants, sodium dodecyl sulfate (SDS), linear alkyl sulfononate (LAS), cetyltrimethylammonium bromide (CTAB), and (tert-Octylphenoxy) Polyethoxyethanol (TX-100) are most frequently used. In addition, new so-called designer surfactants, e.g. PTS, PQS or TPGS-750, have been synthesized by the group of Prof. Lipshutz at the University of California, Santa Barbara. These surfactants possess higher solubilization capacity and show good performance, e.g. in noble-metal catalyzed coupling^{15,16} or metathesis^{17,18} reactions. Besides the solubilization of hydrophobic reactants, micellar reaction media allow for the recycling of expensive noble-metal catalyst complexes in their active state, e.g. by micellar enhanced ultrafiltration^{19,20} or phase separation.^{21,22} Recently it was shown that such advanced

separation concept can be applied on a technically relevant scale in a continuously operated mini plant, e.g. for the hydroformylation of long-chained olefins.²³

In this contribution, we study the hydrolysis of methyl decanoate in aqueous-micellar solutions of various cationic and nonionic surfactants. The investigations on the alkaline hydrolysis are part of collaborative research project called InPROMPT "Integrated Chemical Processes in Liquid Multiphase Systems". A strong focus of InPROMPT is catalytic reactions in multiphase systems to recycle the homogeneously dissolved catalyst by a simple phase separation under simultaneously discharge of the product.^{24–26} The formation of long chained acids like decanoic acid can be carried out with a one-step sequence (hydroxycarbonylation) or with a two-step sequence (methoxycarbonylation with consecutive hydrolysis) (see Figure 1).



Figure 1. Reaction network for the synthesis of decanoic acid.

To evaluate the advantages and disadvantages of the two reaction pathways, investigations on the alkaline hydrolysis are indispensable. The reaction can be catalyzed by a base, involving only irreversible reaction steps. Generally, water is used as the solvent for the alkaline hydrolysis process to dissolve both the ester and the base. However, methyl decanoate is poorly soluble in water and the obtained two-phase system provides only a small interfacial area, resulting in low reaction rates. The addition of surfactants as solubilizers will lead to an increased solubility of methyl decanoate in water. But for the micellar system, the properties of the surfactant and the reaction rate depend on the composition of the reaction mixture and the temperature; therefore,

we determined first the impact of the reaction conditions on the CMC and the phase behavior. Thereafter, we investigated the hydrolysis of methyl decanoate using TX-100 and alkyl trimethylammonium bromide surfactants with variable alkyl chain length $(CH_3(CH_2)_nN(CH_3)_3Br, n = 9 - 15)$. Detailed investigations of the reaction rate as a function of surfactant type and concentration were performed to select the minimum concentration of surfactant for the reaction mixture and to facilitate the subsequent product isolation.

RESULTS AND DISCUSSION

Reaction

The alkaline hydrolysis is an important reaction for the synthesis of carboxylic acids from the corresponding esters. We selected the poorly water-soluble long chained methyl decanoate as a model substrate which reacts with sodium hydroxide as the base to sodium decanoate (Figure 2).



Figure 2. Reaction scheme for the alkaline hydrolysis of methyl decanoate with sodium hydroxide (NaOH) to sodium decanoate.

With aqueous NaOH solutions, methyl decanoate will form a two-phase system where the reaction will slowly take place at the interphase. To increase the reaction rate, we applied different surfactants. The main surfactant characteristics needed to select an appropriate additive to the reaction mixture is the CMC of the surfactant and the phase behavior of the reaction mixture. Both were evaluated prior to the stoichiometric reaction to relate the observed kinetics to the properties of the reaction system.

Determination of the critical micelle concentration (CMC)

Since TX-100 is frequently investigated as a solubilizer for organic reactions in water, e.g. for coupling reactions^{15,27}, and available with high purity, it was chosen as the benchmark surfactant. The CMC of the surfactant is a crucial parameter for organic reactions in water. Hence, the CMC of the applied surfactant TX-100 has been measured with a bubble pressure tensiometer at room temperature. In addition, the CMC of sodium decanoate and mixtures of sodium decanoate and Triton X-100 have been determined, since the alkaline hydrolysis of methyl decanoate forms sodium decanoate. Because of its amphiphilic structure, the sodium decanoate may act as a surfactant, leading to the formation of single micelles or mixed micelles with TX-100. Consequently, the CMC could vary significantly, depending on the conversion of methyl decanoate hydrolysis. For TX-100, the determined CMC in water is 4.1 · 10⁻⁴ mol/L, which is in accordance with the literature.²⁸⁻³⁰ The pure sodium decanoate, which can be classified as an ionic surfactant, has a CMC of 0.1 mol/L, which is significantly higher compared to TX-100. The CMC of a mixture of sodium decanoate and Triton X-100 with a mole fraction of 0.5 is $5.8 \cdot 10^{-4}$ mol/L. With lower mole fraction of TX-100 (x=0.25) the CMC is further increased to $6.9 \cdot 10^{-4}$ mol/L. As expected, the CMC values of the mixtures are between the values of the pure components (see Figure 3). However, the CMC of the mixtures resemble predominantly the CMC of the nonionic surfactant TX-100, which is typical for mixed micelles consisting of an ionic and nonionic surfactant.^{31,32} The electrostatic repulsion of the anionic head groups of sodium decanoate is drastically reduced with the addition of TX-100, causing micellization and a significant decrease in the CMC value already for low mole fractions of TX-100. The results show that the formed sodium decanoate molecules aggregate with TX-100 molecules in aqueous solutions. In summary, the formation of sodium decanoate leads to an increase of the CMC. especially at low mole fractions of TX-100, which has to be kept in mind for the evaluation of the reaction performance for the alkaline hydrolysis of methyl decanoate.



Figure 3. CMC of TX-100, sodium decanoate and mixtures of TX-100 and sodium decanoate at room temperature, standard deviation 3%.

Investigation on phase behavior

Besides the impact of aqueous mixtures on the CMC, knowledge about the phase behavior, especially the cloud point, is essential for the investigation of the alkaline hydrolysis in aqueous TX-100 solutions, particularly for the separation of the applied surfactant TX-100. Since the hydrolysis takes place under alkaline conditions, the impact of the sodium hydroxide concentration and additionally, the impact of the formed sodium decanoate on the cloud point of TX-100 has been investigated. Figure 4 (left) shows the cloud point of aqueous TX-100 solutions (5 wt%) as a function of the concentration of sodium hydroxide in a range of 0 to 1 mol/L. The cloud point of TX-100 (5 wt%) in an aqueous solution without sodium hydroxide was determined to be 67.2°C and is in good agreement with the literature.³³ With increasing concentration of sodium hydroxide, the cloud point decreases linearly to 36.8°C at 1 mol/L of

sodium hydroxide. As expected, sodium hydroxide act as an electrolyte and leads to a salting out process decreasing the cloud point with increasing electrolyte concentration. The sodium hydroxide molecules are cosmotropic ions, binding strongly to water and thus belonging to the "water-structure-making" ions. Hence, the strong interaction of the electrolyte molecules with water molecules leads to a dehydration of the polyethylene glycol chains of the applied surfactant, resulting in a lower cloud point, which is known as salting out effect.³⁴ Based on these findings the sodium hydroxide concentration for all further experiments was fixed to 0.2 mol/L.

Next, the effect of sodium decanoate on the cloud point has been investigated (Figure 4, right). Interestingly, sodium decanoate strongly influences the cloud point of the mixtures. The cloud point increases drastically from 58.1°C to 93.6°C with only 0.03 mol/L of sodium decanoate, showing a linear tendency. The sodium decanoate act as an anionic cosurfactant forming mixed micelles with TX-100. The incorporation of the anionic molecules into the micelles, formed by TX-100, leads to a negative surface charge of the micelles. Thus, the incorporation of charged cosurfactants forces a repulsion between the micelles, resulting in an increased water solubility, which makes the micelles more hydrophilic.³⁵ Consequently, the cloud point of the mixtures is drastically increased. We have to mention that a full conversion of methyl decanoate corresponds to a sodium decanoate concentration of 0.2 mol/L. In Figure 4 (right), the concentration of methyl decanoate in the alkaline hydrolysis between 0 and 15%. As the cloud point is increased to very high temperatures with increasing conversion of methyl decanoate, a one-phase solution is expected after the reaction.



Figure 4. Effect of sodium hydroxide (left) and sodium decanoate (right) on the cloud point of an aqueous TX-100 solution. Experimental conditions: V=20 mL, c_{TX100} =5 wt%, right: c_{NaOH} =0.2 mol/L.

Alkaline hydrolysis of methyl decanoate in water

Initially, the alkaline hydrolysis of methyl decanoate in an aqueous sodium hydroxide solution has been studied at different temperatures, which is shown in Figure 5. For 40 °C and 60 °C the conversion after 20 h reaction time is 3% and 5%, respectively. As expected, the low solubility of methyl decanoate in water causes the low reaction rates, resulting in low conversions. Surprisingly, the conversion obtained after 20 h reaction time at a reaction temperature of 80°C is 82%, although no further additives were used. Furthermore, the slope of the conversion plot for the reaction temperature of 80°C increases with proceeding reaction time, which is an untypically trend for a second order reaction. Apparently, the conversion of methyl decanoate to sodium decanoate accelerates the reaction. The determined CMC of sodium decanoate at room temperature is 0.1 mol/L, which is equal to 50% conversion of methyl decanoate. Hence, the formation of micelles, initiated by the formation of sodium decanoate during the reaction, increases the solubility of methyl decanoate, resulting in an enhancement of the reaction rate with proceeding reaction time. Obviously, the slope of the conversion plot is slightly increasing at a conversion of 40% (see Figure 5), which confirms this assumption, since the CMC of sodium decanoate is reached. We have to keep in mind that the CMC of sodium decanoate is slightly temperature dependent, which could lead to a small mismatch.



Figure 5. Effect of the temperature on the conversion plot of the alkaline hydrolysis of methyl decanoate in water. Experimental conditions: V=20 mL, c_{methyl} decanoate=0.2 mol/L, c_{NaOH} =0.2 mol/L.

Alkaline hydrolysis of methyl decanoate in aqueous TX-100 solution

Based on the findings of the critical micelle concentration and the phase behavior, the alkaline hydrolysis of methyl decanoate was performed at three different temperatures. To perform the reaction below and above the cloud point of the reaction mixture, we decided to operate at 40°C, 60°C and 80°C. The twofold amount of the determined CMC for TX-100, which was measured at room temperature, has been used as TX-100 concentration for the temperature variation. As seen in Figure 6 the addition of TX-100 is crucial for the reaction performance of the alkaline hydrolysis of methyl decanoate comparing both reaction systems, with and without phase transfer agent (Figure 5). Already the addition of small amounts of TX-100 leads to a significant increase in the reaction rate. Comparing the reaction at 80°C with and without added TX-100, the reaction rate, which is proportional to the slope of the conversion plot, is increased by a factor of 30. Moreover, the conversion reaches 100% after 8 h reaction time. If the temperature is lowered to 60 or 40°C, the reaction is still much faster than in the absence of the surfactant. Even for the reaction performed at 40°C noticeable conversions of 40% are obtained after 20 h reaction time. Since the added TX-100 forms micelles above the CMC, methyl decanoate can be solubilized in the aqueous phase and the reaction rate is significantly enhanced. If hydrolysis reactions are performed under conventional two-phase conditions, the rate is often influenced by film diffusion, resulting in apparent low activation energies. The application of surfactants with concentrations above the CMC will not only increase the solubility of the hydrophobic reactants in the aqueous phase; moreover, it will provide a high interfacial area for mass transport. In this case, the temperature dependency of the reaction using the Arrhenius law should result in much higher apparent activation energy. The activation energy of the alkaline hydrolysis of methyl decanoate was calculated from Figure 6 to be 56.4 KJ/mol, which indicates a kinetic control of the reaction in aqueous TX-100 solution that results in a stronger acceleration of the reaction at elevated temperature.



Figure 6. Effect of the temperature on the conversion plot of the alkaline hydrolysis of methyl decanoate in aqueous TX-100 solution. Experimental conditions: V=20 mL, $c_{methyl decanoate}=0.2 \text{ mol/L}$, $c_{NaOH}=0.2 \text{ mol/L}$, $c_{TX-100}=2xCMC$.

Additionally, the impact of the TX-100 concentration has been studied with regard to the reaction performance, especially the initial rate of reaction. As it can be seen in Figure 7 the amount of surfactant plays a crucial role for the reaction rate of the alkaline hydrolysis of methyl decanoate in aqueous systems. The reaction temperature was kept constant at 80°C. As expected, the reaction rate increases substantially with increasing concentration of the phase transfer agent, for instance an increase of the surfactant concentration from 4.1 mmol/L, which is equal to 10xCMC, to 133.3 mmol/L (5 wt%) leads to an enhancement of the reaction rate by a factor of 5. On the one hand, the higher the concentration of TX-100, the higher is the concentration of methyl decanoate in the aqueous phase since more micelles can be formed. As a result the reaction rate is enhanced. On the other hand the amount of surfactant increases the interface

Page 13 of 28

between water and oil, which could result in higher reaction rates. However, the increase of the reaction rate is not proportional to the increase of the surfactant concentration. Obviously, the reaction rate converge a maximum rate with increasing surfactant concentration since the rate is limited by the concentration of methyl decanoate in the aqueous phase. At high TX-100 concentrations all of the substrate can be solubilized in the micelles. A further increase of the surfactant concentration could lead to a decrease of the reaction rate since the methyl decanoate is diluted with higher amount of surfactant. This trend was also shown by other researchers, e.g. for the fading of dyes.^{36,37}

Moreover, no correlation can be found between the reaction rate and the phase behavior of the systems. Starting above the cloud point (80°C), indicated by a white and turbid reaction mixture after injecting of the substrate, the mixture turns into a clear solution at the end of the reaction, indicating a micellar solution below the cloud point. As mentioned, the formed sodium decanoate has a strong impact on the cloud point of the mixture, leading to an increase of the cloud point with increasing conversion of methyl decanoate. However, no change in the conversion plot can be observed, concluding no correlation between reaction performance and phase behavior. This is another indication that no mass transfer limitation is involved in the reaction kinetics.



Figure 7. Effect of the TX-100 concentration on the initial rate of the alkaline hydrolysis of methyl decanoate. Experimental conditions: T=80°C, V=20 mL, $c_{methyl decanoate}$ =0.2 mol/L, c_{NaOH} =0.2 mol/L, initial rate determined at a conversion of 10%.

Interestingly, the electrical conductivity of the reaction mixture drops drastically using high concentrations of Triton X-100 (5 wt%), resulting in an unexpected minimum at the beginning of the reaction. Figure 8 shows the conductivity and the calculated conversion over time for a Triton X-100 concentration of 5 wt%. Starting above the cloud point (Figure 9, **A**), the reaction mixture passes through different phase states with increasing conversion, herein expressed by the proceeding reaction time. Firstly, a blue transparent reaction mixture can be observed after 12 minutes reaction time (Figure 9, **B**), indicating a phase transition to a lamellar phase. Due to the bilayer structure of the lamellar phase, the movement of the ions is restricted, which explains the minimum in the conductivity plot.³⁸ The distance of the surfactant layers is in the range of the wavelength of visible light, which describes the blue color of the solution. After that, the reaction

mixture turns back into a turbid biphasic reaction mixture, leading to an increase of the conductivity (Figure 9, \mathbf{C}). At the end, with increasing conversion the solutions are transparent, since the cloud point increases strongly due to the formation of sodium decanoate (Figure 9, \mathbf{D}). Due to these overlapping effects of the concentration of ionic reactants and phase behavior of the system, the conductivity measurement has to be corrected to monitor the progress of the reaction. Hence, the minimum of the electrical conductivity, due to the formation of a lamellar phase, was not considered to calculate the conversion of methyl decanoate.



Figure 8. Conversion and conductivity plot of the alkaline hydrolysis of methyldecanoate. Experimental conditions: T=80°C, V=20 mL, $c_{TX100}=5$ wt% $c_{NaOH}=0.2$ mol/L, $c_{methyl decanoate}=0.2$ mol/L.



Reaction time

Figure 9. Reaction mixture with proceeding reaction time, **A**=0 min, **B**=12 min, **C**=15 min, **D**=180 min.

Effect of the type of surfactant

Besides the widely used TX-100, several nonionic and cationic surfactants for the alkaline hydrolysis of methyl decanoate have been tested (see Figure 10). To increase the hydrophobicity of the surfactant, TX-114 has been chosen which has a lower amount of ethoxy units as the polar head group, but the same hydrophobic alkyl chain as TX-100. Furthermore, the nonionic surfactants Marlipal 24/70 and Marlosol TA3070 have been tested, which have a linear alkyl chain without any aromatic groups as hydrophobic part. In addition to the nonionic surfactants, alkyltrimethylammonium bromides with an alkyl chain length from 10 to 16 have been investigated as cationic surfactants to evaluate the impact of the hydrophobicity of the surfactant on the reaction performance. The cationic surfactants have been applied as they frequently show the potential to increase the reaction rate of hydrolysis reactions.^{39–41}



Marlipal 24/70: i=10-12, j=7 Marlosol TA3070: i=11, j=7



Triton X-100: j=9-10 Triton X-114: j=7-8

⊂ Br

DeTAB: i=8 DTAB: i=10 TTAB: i=12 CTAB: i=14

Figure 10. Chemical structures of the applied surfactants.

As seen in Figure 11 (left), the type of nonionic surfactant has only a minor impact on the reaction performance since the conversion plots are nearly identical. Interestingly, the same reaction rate is observed using TX-100 and Marlipal 24/70 as phase transfer agents, which have the same cloud point around 60°C and thus, almost an identical hydrophobicity. In contrast, the more hydrophobic surfactants TX-114 and Marlosol TA3070, indicated by their lower cloud points around room temperature, show a slightly lower reaction rate compared to TX-100 and Marlipal 24/70. Apparently, the hydrophobicity of the surfactant has a low impact on the reaction performance. Since the more hydrophobic surfactants TX-114 and Marlosol TA3070 exhibit a lower cloud point, the solubility of methyl decanoate is lower, resulting in a lower reaction rate compared to TX-100 and Marlipal 24/70. However, the more or less equal reaction profiles clarify that the surfactants are utilized as phase transfer agents as the substrate is non-charged and non-aromatic further interactions between the substrate and the surfactant are not expected.



Figure 11. Variation of the type of surfactant. Experimental conditions: $T=80^{\circ}C$, V=20 mL, $c_{NaOH}=0.2 \text{ mol/L}$, $c_{methyl \ decanoate}=0.2 \text{ mol/L}$, left: nonionic surfactants (5wt%), right: cationic surfactants (10xCMC).

Additionally, several cationic surfactants have been investigated (see Figure 11, right). Compared to the nonionic surfactants, much less surfactant is needed to obtain similar reaction rates. Since the head groups of the alkyltrimethylammonium bromides carry a positive charge, an electrostatic attraction of the hydroxide ions is obtained, increasing the local concentration of hydroxide ions at the water-oil interface and enhancing the reaction rate.

Since the CMC of cationic surfactants is much higher compared to the applied nonionic surfactants, the effect of the CMC towards the reaction performance has to be investigated. Therefore, the amount of surfactant was varied in two series of experiments, in which firstly the tenfold CMC and secondly a constant c-CMC value of 10 mM was used. The results are given in

Page 19 of 28

The Journal of Organic Chemistry

Table 1 expressed as the initial rates which were calculated from the conversion plots. For a better comparison, also the normalized rates (based on CTAB with the lowest observed reaction rate) are given. Additionally, the CMC values were determined by bubble pressure tensiometer and conductivity measurements. As expected, with increasing chain length of the alkyl chain from 10 to 16, the CMC decreases significantly from 60 mmol/L to 1 mmol/L (see Table 1), indicating a higher hydrophobicity of the cationic surfactant. Using the tenfold CMC, the initial rate decreases from 3839 mmol/($L \cdot h$) with DeTAB to 322 mmol/($L \cdot h$) with CTAB as surfactant. Since the CMC increases from CTAB to DeTAB, the amount of surfactant in the reaction mixture increases drastically using the tenfold CMC, resulting in higher solubilization of methyl decanoate and thus, in a much higher initial reaction rate. Hence, experiments were carried out using the same concentration of the surfactant but corrected with the determined CMC (c-CMC=10 mM). As a result, the molar concentration for micellization is constant which allows for a fairer comparison of the used cationic surfactants. Interestingly, the same trend can be observed whereby the initial rate decreases from 1023 mmol/(L·h) for DeTAB to 291 mmol/($L\cdot h$) for CTAB. From the normalized reaction rates it is obvious that for the same micellar concentration, the rates are closer together, showing that the CMC can't be neglected in the screening of ionic surfactants. After correction of the surfactant concentration by its CMC, the more hydrophilic cationic surfactant still shows a higher reaction rate. Two more effects have to be considered to discuss the observed reactions rates: a) the solubilization of methyl decanoate and b) the local concentration of hydroxide ions at the water-oil interface. Considering the aggregation number for the investigated surfactants, which decreases from CTAB to DeTAB by a factor of about two,^{42,43} the number of micelles for DeTAB as the phase transfer agent is higher. Hence, the concentration of methyl decanoate is higher in the water phase which explains the higher initial reaction rate. Nevertheless, to understand the role of the surfactant in detail, investigations of the aggregation behavior, solubilization capacity and phase behavior is essential.

Surfactant	CMC ^b [mmol/L]	CMC ^c [mmol/L]	Initial rate r ₀ ^d [mmol/(L·h)] 10xCMC	Normalized rate	Initial rate r ₀ ^d [mmol/(L·h)] c-CMC=10 mM	Normalized rate
DeTAB	61.1	62.1	3839	11.9	1023	3.5
DTAB	14.4	14.5	2813	8.7	632	2.2
TTAB	5.8	4.6	703	2.2	461	1.6
CTAB	1.4	1.0	322	1	291	1
-	-	-	5	0,015	-	-

Table 1. CMC values and initial reaction rates for the cationic surfactants.^a

^a CMC was measured at 25°C.

^b Determined by bubble pressure tensiometer, standard deviation 3%.

^c Determined by conductivity measurements, standard deviation 3%.

^d Determined at a conversion of 10% from the conversion plot. Experimental conditions: T=80°C, V=20 mL, c_{NaOH} =0.2 mol/L, $c_{methyl \ decanoate}$ =0.2 mol/L.

CONCLUSION

In summary, the presented results show the impact of the surfactant type and concentration on the reaction performance of the alkaline hydrolysis of methyl decanoate in surfactant modified systems. The surfactant is needed to increase the water-oil interface, resulting in higher reaction rates compared to system without additive. The physical properties of the mixtures like phase behavior and CMC are essential to understand the role of the surfactant. Interestingly, the formation of sodium decanoate has a strong influence on the phase behavior and CMC due to its surface active properties. Hence, an autocatalytic effect of the product can be observed.

EXPERIMENTAL SECTION

Chemicals

The substrate methyl decanoate (99%), sodium decanoate (98%) for the calibration to evaluate the reaction progress and the surfactants (tert-Octylphenoxy) Polyethoxyethanol degree of ethoxylation (EO)=9-10 (Triton X-100), (tert-Octylphenoxy) Polyethoxyethanol EO=7-8 (Triton X-114), dodecyltrimethylammonium bromide (DTAB, 98%), and tetradecyltrimethylammonium bromide (TTAB, 99%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) as base with a purity of 99% and the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) with a purity of 99% were acquired from Roth. ABCR has delivered the cationic surfactant decyltrimethylammonium bromide (DeTAB, 99%). The technical grade nonionic surfactants Marlipal 24/70 and Marlosol TA3070 were purchased from Sasol. Deionized water was used in all experiments. All chemicals were used without further purification.

CMC determination

The electrical conductivity method and the bubble pressure tensiometer were used to determine the critical micelle concentration (CMC) of the alkyltrimethylammounium bromides. Aqueous solutions with different concentrations of the corresponding surfactants were prepared and measured with both methods. For the electrical conductivity method the conductivity was plotted versus the concentration of the surfactant and the CMC was obtained from the intersection of the two resulting linear slopes. In addition, the surface tension of the solution was measured using a bubble pressure tensiometer, depending on the surface age of the produced bubbles. At a surface age of 14000 ms, when the surface tension remains constant, the surface tension value was taken and plotted versus the concentration of the surfactant to determine the CMC. Also, the CMC of Triton X-100, sodium decanoate and 1:1 mixture of Triton X-100 and sodium decanoate was determined with the bubble tensiometer. All reported values were measured at 25°C and are indicated as moles of surfactant per volume.

Investigation on the cloud point

The influence of sodium hydroxide and the surface active product sodium decanoate on the cloud point of the aqueous TX-100 solution was investigated in a temperature range from 25°C to 95°C. The concentration of TX-100 was fixed at 5 wt% and the concentration of sodium hydroxide was varied in the range from 0.1 to 1.0 mol/L. In addition, the cloud points of the nonionic surfactants Triton X-114, Marlipal 24/70 and Marlosal TA3070 were examined. To determine the impact of sodium decanoate on the cloud point, the concentration of sodium hydroxide and TX-100 was fixed at 0.2 mol/L and 5 wt%, respectively and the amount of sodium decanoate was varied between 0 and 0.04 mol/L. The mixtures, prepared in graduated cylinders, were added to a water bath and the temperature was raised in one degree steps waiting one minute to reach the equilibrium for each temperature step. The resulting phase behavior was observed, mainly indicated by the turbidity of the solution.

General procedure of the alkaline hydrolysis

The main part of the setup for the alkaline hydrolysis is a 40 mL double-wall reactor to adjust the temperature via a thermostat. The substrates can be injected with a two-way valve at reaction temperature, whereby the mixture is mechanically stirred. To follow the reaction progress the conductivity is measured *in-situ* using a conductivity electrode from the company WTW. The thermostat and the conductivity probe are connected to a computer to monitor the reaction progress. To perform the reaction, a stock solution containing the surfactant and sodium hydroxide (4 mmol, 1 eq.) was filled into the reactor, stirred mechanically and heated up to the desired reaction temperature. Immediately after reaching the reaction temperature, the substrate methyl decanoate (4 mmol, 1 eq.) was injected via a syringe into the reactor. The bulk volume was 20 mL for each experiment. The reaction was stopped when the conductivity remains constant, or latest after 24 hours.

Evaluation of reaction progress

Since the conversion depends linear on the conductivity of the mixture, the conductivity was measured to determine the conversion of methyl decanoate to sodium decanoate. For that, sodium hydroxide, which mainly contributes to the conductivity of the mixture, and the product sodium decanoate were mixed, adapted to the concentrations from the previous section, simulating different conversions between 0% and 100%. After waiting four minutes for temperature equilibrium, the corresponding conductivity was measured for 40°C, 60°C and 80°C and plotted versus the associated conversion. A two-point calibration was done for the cationic surfactants, mixing the tenfold critical micelle concentration (CMC) of the corresponding surfactant, sodium hydroxide, and sodium decanoate and measuring the conductivity at 80°C.

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Author Contributions

The manuscript was written through contributions of all authors.

ACKNOWLEDGMENT

This work is part of the Collaborative Research Center "Integrated Chemical Processes in Liquid Multiphase Systems" (subproject A2) coordinated by the Technische Universität Berlin. Financial support by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) is gratefully acknowledged (TRR 63).

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