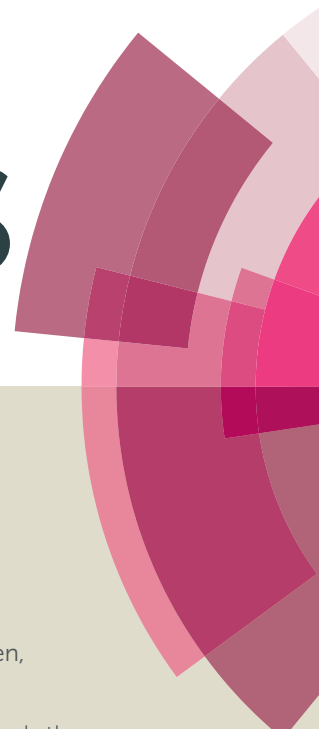


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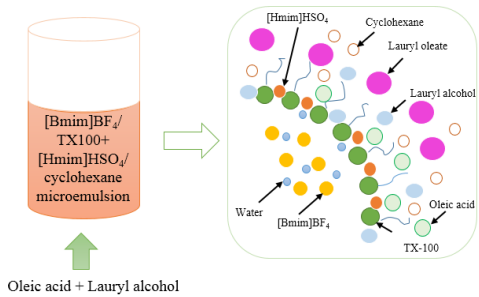
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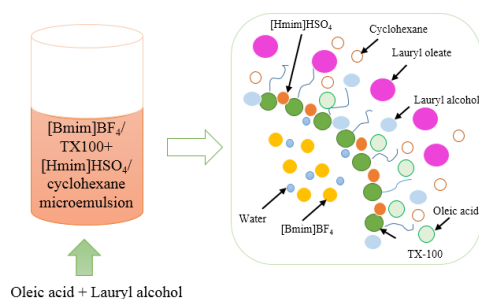
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[Hmim]HSO₄-based microemulsion is an efficient catalyst system for esterification; it provides large interface areas, the resultant water enters [Bmim]BF₄ microdomain.

Abstract: Esterification of oleic acid was carried out in 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄)/Triton X-100+1-hexyl-3-methylimidazolium hydrogen sulfate ([Hmim]HSO₄)/cyclohexane microemulsion. A pseudo ternary phase diagram of the designed systems was drawn to investigate the phase behavior of the microemulsion, with the surfactant [Hmim]HSO₄ acting as a catalyst. The effects of various reaction parameters were explored. Results showed that the maximum yield of lauryl oleate reaches 91.17% and its selectivity reaches 98.55% under optimum reaction conditions. The reaction was carried out with 8 wt.% catalyst at 373 K for 6 h. The molar ratios of [Bmim]BF₄ to surfactant and of oleic acid to lauryl alcohol were 0.24 and 0.2, respectively. Comparison reactions between different alcohols and oleic acid were also performed, and results showed that long alkyl chain alcohols promote the reaction rate. UV–vis absorption spectra demonstrated that the generated water enters the [Bmim]BF₄ microdomain of the ionic liquid microemulsions. A possible mechanism of the reaction was also presented. All results indicate that the [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane microemulsion is a very efficient catalyst system for esterification reactions.

Keywords: Ionic Liquid; Oleic acid; Microemulsion; Esterification

1. Introduction

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Esterification reaction, as a dehydration reaction, is of major importance in synthetic organic chemistry.^{1, 2} The traditional catalysts used in esterification are sulfuric acid and phosphoric acid, but they have several drawbacks such as side reactions, low reaction activity, low selectivity, equipment corrosion, and environmental pollution. Generally, direct esterification is carried out in organic solvents and needs either of two methods to shift the equilibrium between reactants and products.³⁻⁵ One method is by removing the generated water azeotropically or using dehydrating agents, and the other is by overdosing one reactant.

Ionic liquids (ILs) have received much attention as green media for reactions and separations because of their unique physicochemical properties.⁶ A concept relating to ionic liquid microemulsions (ILMs) was put forward to expand the application of ILs.⁷⁻⁹ The IL-based microemulsions show potential in the synthesis of metal nanomaterial¹⁰, biodiesel production¹¹, and enzymatic reaction¹². Microemulsion is a thermodynamically stable, homogeneous, isotropic, and optically transparent solution formed by two or more immiscible liquids, which are stabilized by a surfactant and occasionally, a co-surfactant film at the liquid-liquid interface.^{13,14} Moreover, microemulsion is an excellent media for organic reactions because it can provide a very large interfacial area and overcome the incompatibility of reagents.¹⁵⁻¹⁸ Research studies on esterification catalyzed by microemulsions have been reported.¹⁹⁻²² The results of these studies showed that esterification occurs in the interface area, and the resultant water enters the water microdomain of the microemulsion, making the esterification equilibrium shift towards product generation. Esterification in traditional microemulsions needs more than 24 h at low temperature of 318 K to reach equilibrium. The product yield decreases with increasing reaction temperature because traditional microemulsions should be kept at low temperature to remain stable. However, ILMs have relatively higher temperature-independence compared with traditional aqueous systems.²³ The microstructure of ILMs remains stable over a wide range of temperature, increasing the range of application for the ILM systems in

many fields. ILMs acting as media in esterification may have more advantages owing to the unique features of the ionic liquids and microemulsions.

In this study, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄)/Triton X-100+1-hexyl-3-methylimidazolium hydrogen sulfate ([Hmim]HSO₄)/cyclohexane microemulsion was formulated and investigated to determine its phase behavior. Pseudo ternary phase diagrams were used to design a more reasonable system for esterification. Esterification reactions between oleic acid and different alcohols were carried out in these ILM system. [Hmim]HSO₄ was used as a surfactant-type Brønsted-acid catalyst. Based on the pseudo ternary phase diagrams of ILMs, the effects of ILM composition and reaction parameters were investigated. The UV-vis spectrograms obtained indicated that the resultant water could enter the [Bmim]BF₄ microdomain of the ILMs. A possible mechanism of the reaction was also demonstrated. This work may provide an efficient method for preparing oleates.

2. Results and Discussion

2.1 Pseudo ternary phase diagrams

The phase diagram of [Bmim]BF₄/[Hmim]HSO₄/cyclohexane system at 298 ± 1 K is shown in Fig. 1(a). The blank region was the single-phase microemulsion, and the shadow region marked the multi-phase, which was a cloudy region. The fact that [Bmim]BF₄, [Hmim]HSO₄, and cyclohexane can formulate the microemulsion proves the surfactant function of [Hmim]HSO₄. However, the formation of ILMs requires large amounts of the surfactant [Hmim]HSO₄, which is expensive. Therefore, in view of this economic problem, we used a combination of [Hmim]HSO₄ and TX-100 surfactants to reduce the dosage of [Hmim]HSO₄. Fig. 1(b) shows the phase diagram of [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane system at 298 ± 1 K. The pseudo ternary phase diagram showed the consistent formation of single-phase microemulsion over [Bmim]BF₄ or cyclohexane content range of 0–100 wt.%. The single-phase region area of [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane microemulsion is larger than that of [Bmim]BF₄/[Hmim]HSO₄/cyclohexane

microemulsion. In this research, [Hmim]HSO₄ acted as a surfactant-type Brønsted-acid catalyst, and the [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane microemulsion was chosen as the media for the preparation of lauryl oleate.

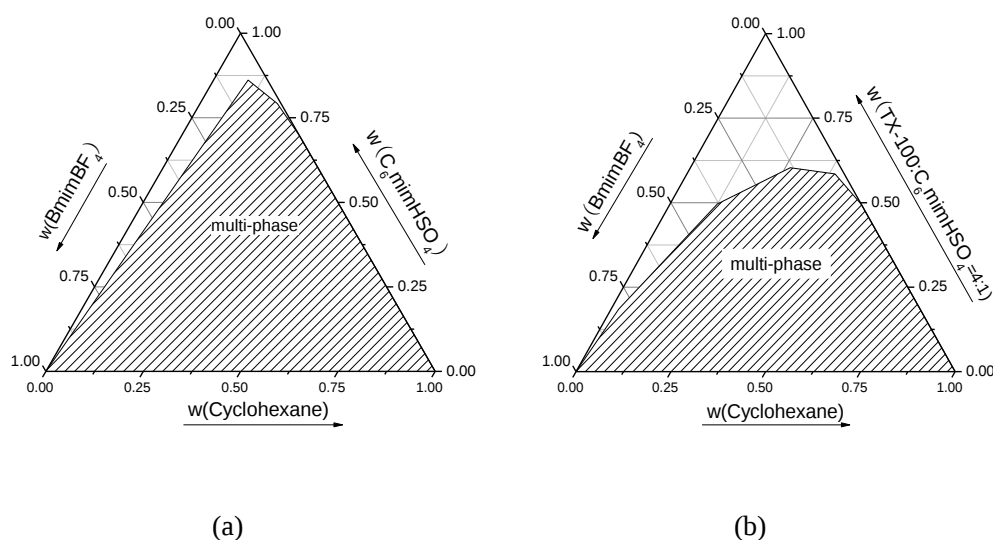


Fig. 1 Phase diagrams of [Bmim]BF₄/[Hmim]HSO₄/cyclohexane system (a) and [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane system (b) at 298 ± 1 K

2.2 Catalytic activity of [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane microemulsion

To investigate the catalytic properties of different catalysts, esterification of oleic acid and lauryl alcohol was introduced. Table 1 presents the comparison of the catalytic activities of different catalysts. Results showed that [Hmim]HSO₄ in the ILM system revealed much higher catalytic activity than other catalysts. By contrast, [Bmim]BF₄ had almost no catalytic activity. The yield decreased to 9.06% when the reaction was carried out in the [Bmim]BF₄/TX-100/cyclohexane system because the microemulsion separated the reactants from the [Bmim]BF₄. Esterification can't gain good product yield in microemulsion without catalyst. After formulating [Hmim]HSO₄-based microemulsion, the esterification carried out in the ILM system attained better product yield and selectivity than when [Hmim]HSO₄ is used as a

direct catalyst. In addition, [Hmim]HSO₄-based microemulsion revealed much higher catalytic activity than [Hmim]HSO₄ and cyclohexane without formulation of ILMs. These results can be ascribed to the large interface area of the ILMs.²⁴ The reaction was also studied in the absence of catalyst, obtaining 12.35% yield and 85.35% selectivity. These results indicate the significant role of [Hmim]HSO₄-based ILM systems as a catalyst media for esterification.

Table 1 Catalytic activity of the catalysts^a

Entry	Catalyst	Reaction media	Yield/(%) ^b	Selectivity/(%)
1	Without catalyst	/	12.35	85.35
2	[Bmim]BF ₄	/	13.68	90.72
3	[Hmim]HSO ₄	/	82.56	94.82
4	Without catalyst	[Bmim]BF ₄ /TX-100 /cyclohexane	9.06	89.03
5	[Hmim]HSO ₄	cyclohexane	84.25	97.88
6	[Hmim]HSO ₄	[Bmim]BF ₄ /TX-100+[Hmim]HSO ₄ /cyclohexane	91.17	98.55

^a Reaction conditions: oleic acid: lauryl alcohol = 1:5 molar ratio, T = 373 ± 1 K, reaction time: 6 h, catalyst amount: 8 wt.%. ^b Determined by HPLC using external standard method

2.3 Effect of the *R* values of ILMs

A series of reverse ILM samples with different *R* values ($R = n_{([Bmim]BF_4)}/n_{(TX-100+[Hmim]HSO_4)}$) was prepared to characterize the effect of [Bmim]BF₄ concentration of the ILMs, expressed as *R* values, on esterification. The results are shown in Table 2. The yield of lauryl oleate attained a maximum value at *R* = 0.24. In general, esterification occurred at the interface of the microemulsion.¹² The large interface area provided more opportunity of contact between the reactants and allowed the completion of the reaction. The interface area increased with increasing *R* values, varying from 0.12 to 0.24, and the lauryl oleate maximum yield was achieved

at $R = 0.24$. Esterification is a dehydration reaction, and the generated water can easily access the [Bmim]BF₄ microdomain in the ILM system because of the hydrophily of [Bmim]BF₄.²⁵ With the increase in R values, the product yield decreased. An excess in [Bmim]BF₄ caused the microemulsion to become unstable, hence decreasing the phase interface area. This phenomenon led the esterification equilibrium to move toward the reverse direction, thereby facilitating ester hydrolysis and reducing product yield.

Table 2 The effect of ILM with different R values on the esterification^a

Entry	R value	Yield of product/(%) ^b	Selectivity/(%)
1	0.12	74.13	98.07
2	0.18	81.68	98.91
3	0.24	91.05	98.02
4	0.30	88.56	97.89
5	0.36	87.08	97.55
6	0.48	86.72	96.91

^a Reaction conditions: oleic acid: lauryl alcohol = 1:5 molar ratio, $T = 373 \pm 1$ K, reaction time: 6

h. ^b Determined by HPLC using external standard method

2.4 Effect of reaction conditions

The effects of reaction conditions including the reaction temperature and time, the molar ratio of oleic acid to lauryl alcohol, and the catalyst amount were investigated.

Fig. 2 presents the effects of the reaction temperature and time on product yield. The yield of lauryl oleate increased and the equilibrium time became shorter as the reaction temperature increased. High temperature gave rise to more frequent and successful collisions for high conversion of reactants to ester products.²⁶ Ionic liquid microemulsions revealed relatively high temperature-independence resulting in shorter esterification equilibrium time. In addition, ILM can remain stable at

relatively high temperature. The lauryl oleate yield increased distinctly with increasing temperature, which indicated a similar characteristic with esterification catalyzed by acid.²⁷ However, the color of the product became darker at temperatures higher than 373 K, and therefore, the optimal reaction temperature for esterification in ILMs was 373 K. In addition, the yield of lauryl oleate increased as the reaction time increased. Within 6 h, the reaction approached equilibrium, and the yield of lauryl oleate did not increase anymore when the reaction time was extended. Hence, the optimal reaction time for esterification in ILMs was 6 h. Results show that the participation of ILM system as a media in esterification reduces the reaction time compared with results in previous studies.^{13–15,19} In addition, because large surface areas were employed, [Hmim]HSO₄ exhibited high activity under mild conditions.

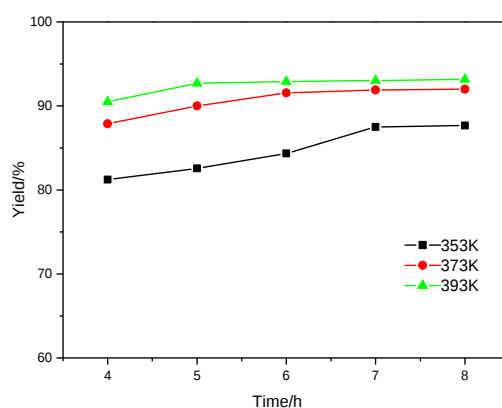


Fig. 2 The effect of temperature and time on esterification, oleic acid: lauryl alcohol = 1:5 molar ratio, catalyst amount = 8 wt.%

Given that the esterification reaction is reversible, excess amounts of lauryl alcohol use favor the conversion of oleic acid. Fig. 3 shows the product yields at decreasing molar ratio of oleic acid to lauryl alcohol, varying from 1:1.1 to 1:7. Low molar ratios are required to allow the reaction to proceed until completion.^{28,29} The yield increased rapidly from 73.53% to 91.17% with the decrease in oleic acid to lauryl alcohol ratio from 1:1.1 to 1:5. Further decreases in ratio led to only a slight increase in yield probably because the ILM system was diluted with excess lauryl alcohol. Therefore,

1:5 oleic acid to lauryl alcohol ratio was the most appropriate molar ratio for esterification in the present work.

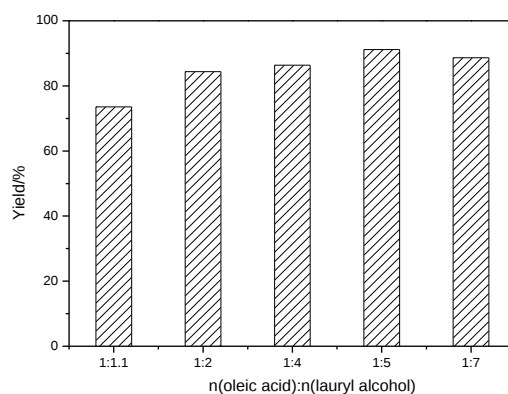


Fig. 3 Effect of molar ratio of oleic acid to lauryl alcohol on esterification, $T = 373 \pm 1$ K, $t = 6$ h, catalyst amount = 8 wt.%

The amount of [Hmim]HSO₄ used was also found to affect esterification; relevant results are presented in Fig. 4. The greater the amount of catalyst used, the more the active site promotes the transformation of the reactant.³⁰ The yield increased with the increment of [Hmim]HSO₄ concentration. On the one hand, this result can be ascribed to the availability of large surface area and acid sites, which favored the dispersion of more active species.²⁷ On the other hand, the amount of hydrogen ions may increase with increasing [Hmim]HSO₄ concentration, which causes rapid attainment of equilibrium for the reaction.²⁷ This increasing yield trend slowed down quickly when the concentration of [Hmim]HSO₄ exceeded 8 wt.% (based on reactants). Hence, the appropriate concentration of [Hmim]HSO₄ for esterification was 8 wt.%.

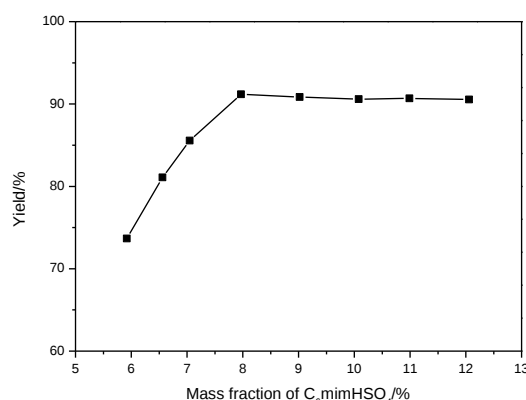


Fig. 4 Effect of [Hmim]HSO₄ concentration on esterification, oleic acid: lauryl alcohol = 1:5 molar ratio, $T = 373 \pm 1$ K, $t = 6$ h

To study the influence of different alcohols as raw materials, various alcohols (methanol, ethanol, 1-butanol, 1-hexanol, 1-octanol, and lauryl alcohol) were selected, and their esterification activities were compared under the same reaction conditions. As shown in Fig. 5, the esterification conversions for most alcohols exceeded 90% except for methanol and ethanol. Methanol and ethanol exhibited relatively poor activities because of their very low boiling points. As the reaction temperature reaches a certain degree, a mass of methanol or ethanol liquid was converted into vapor. Furthermore, the lengths of the carbon chains in methanol and ethanol are too short; hence, they cannot serve as co-surfactants. On the contrary, 1-butanol and 1-hexanol are common co-surfactants.³¹ In traditional water–oil microemulsions, co-surfactants can change the surface activity and HLB of surfactants, participate in a micelle, and adjust the polarity of water and oil.³² As co-surfactants, 1-butanol and 1-hexanol could easily stay in the interface area, providing more opportunities to contact with oleic acid. Similarly, 1-octanol and lauryl alcohol can serve as co-surfactants, hence, they produced product yields exceeding 90%. Thus, [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane microemulsions are excellent green media for esterification.

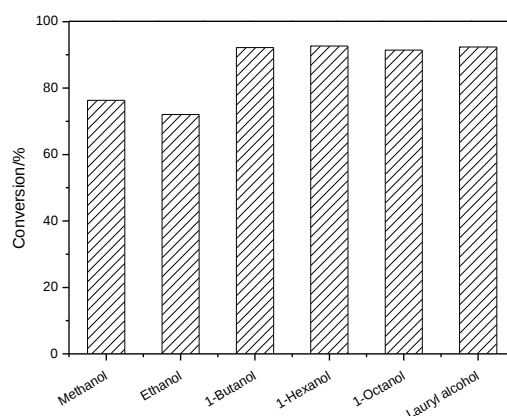


Fig. 5 Esterification of oleic acid with different alcohols, oleic acid: alcohol = 1:5 molar ratio, $T = 373 \pm 1$ K, $t = 6$ h, conversion based on acid value titration

2.5 UV-vis analysis

The micropolarity of ILM was studied through UV-vis absorption spectra measurement. The shift in the absorption maximum of methyl orange (MO) is a sensitive measure of the local environment about ILMs. The absorption spectra of MO in different solvents were studied, and the absorption maximum is red-shifted with increasing polarities of pure solvents.^{33–35} As the water content in microemulsions increases, the visible absorption maximum $\lambda_{\max}$ of MO shifts to long wavelengths (red shift), indicating great polarity.^{33–34} Fig. 6 shows the absorption spectra of MO in ILMs before and after the reaction. The absorption maximum is red-shifted from 395 nm to 425 nm. This red shift in absorption maximum clearly indicates that the resultant water entered the [Bmim]BF₄ microdomain.

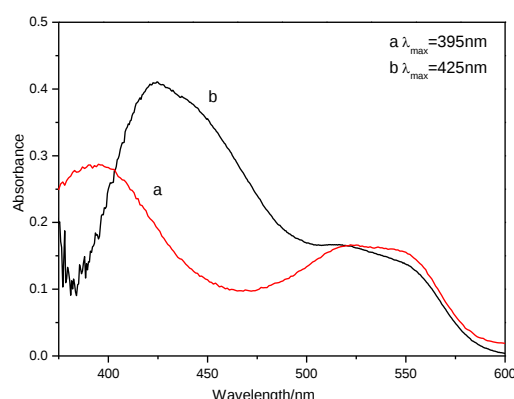
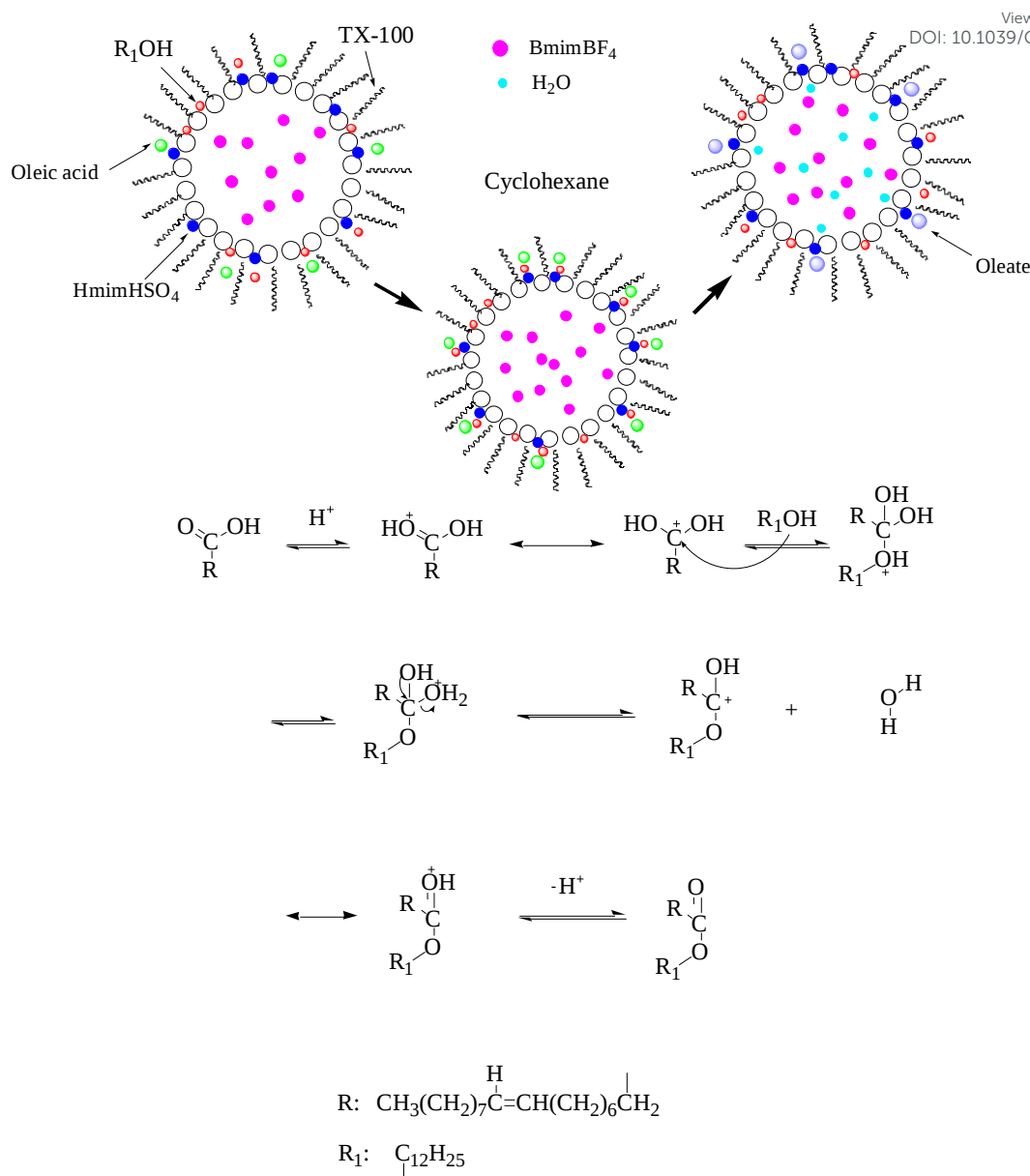


Fig. 6 Absorption spectra of MO in ILM before (a) and after the reaction (b) at 298 ± 1 K, $\text{MO} = 4 \times 10^{-5}$ M

2.6 Mechanism of reaction

Reverse ILM system was a special reaction medium and the proposed reaction mechanism is showed in Scheme 1. Initially, $[\text{Bmim}]\text{BF}_4/\text{TX-100} + [\text{Hmim}]\text{HSO}_4/\text{cyclohexane}$ system provided a high interfacial area of contact to promote the reaction rate. The esterification took place at the interface area in the ILM systems. The $[\text{Bmim}]\text{BF}_4$ microdomain in ILM system entrapped the generated water, which accelerated the formation of ester and promoted the equilibrium process in favor of the products. $[\text{Bmim}]\text{BF}_4$, which is a hydrophilic ionic liquid, contacted with water by hydrogen bonding.³⁵ $[\text{Hmim}]\text{HSO}_4$ could be used as a surfactant-type Brønsted-acid catalyst, and its polar acid heads would congregate because of the formation of ILMs, leading to a relatively high acidity in the interfacial area, and an effective catalytic machinery for esterification.



Scheme 1. Proposed mechanism for esterification in ILMs

3. Experimental

3.1 Materials

[Bmim]BF₄ and [Hmim]HSO₄ were purchased from Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics. All ionic liquids are >99.0 wt % pure. TX-100 (AR), cyclohexane (AR), lauryl alcohol (AR), methanol (AR) and oleic acid (AR) were obtained from Tianjin Kermel Chemical Reagent Science and Technology Co. Ltd. Methyl orange (MO) was supplied by Beijing Chemical Reagent Co. Ltd. Before use, TX-100 and ionic liquids were vacuum-dried at 70 °C for 6 h to

remove excess water. Unless otherwise stated, all experiments were performed in nitrogen atmosphere.

3.2 Construction of pseudo ternary phase diagram

The pseudo ternary phase diagram of the microemulsions were determined at 298 ± 1 K by direct observation. In a typical experiment, mixtures of cyclohexane with surfactant ([Hmim]HSO₄ or mixture of TX-100 and [Hmim]HSO₄ at 4:1 mass ratio) were prepared by changing the mass ratio to 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9. [Bmim]BF₄ was titrated into the mixtures under moderate agitation. The phase boundary was evaluated by observing the phase transition of the solution from clear transparent to turbid. Phase diagrams could be used to characterize the system further and choose the proper reaction system for esterification.

3.3 Preparation of ILM and Esterification in the ILM

Cyclohexane (18.90 mmol) was added into the mixtures of TX-100 (3.40 mmol) and [Hmim]HSO₄, at 4:1 TX-100 to [Hmim]HSO₄ mass ratio, in a round flask at 298 ± 1 K. After achieving thermal equilibrium, the mixtures were titrated with [Bmim]BF₄ (0.88 mmol) under moderate agitation until an optically clear single-phase solution was formed.

Esterification was carried out in the above ILMs under atmospheric pressure after the addition of oleic acid (4.67 mmol) and lauryl alcohol (23.35 mmol). The reaction was allowed to proceed for 4 h to 8 h with vigorous stirring and heating at the desired temperature. After the reaction, the mixture was added into 80 ml methanol and allowed to stand for a few hours. Afterwards, the mixture divided into two phases; the lower phase mainly consisted of the produced lauryl oleate and the upper phase remained clear.

3.4 Characterization

The selectivity means the percentage of yield to conversion. Yield of product was

determined by High Performance Liquid Chromatography (HPLC, Agilent 1100, American Agilent Company) analysis using external standard method. Conversion of oleic acid was determined by acid value titration. The acid value was determined by titration of KOH/ethanol standard solution (0.1 mol/L). The UV–visible absorption spectra were measured by a Shimadzu UV-2450 spectrophotometer. A 4×10^{-5} M MO solution was added to the substance.

4. Conclusions

In conclusion, the [Bmim]BF₄/TX-100+[Hmim]HSO₄/cyclohexane microemulsion was found to be an excellent catalyst system for esterification. The designed microemulsion system had two obvious predominances for esterification. First, a very high yield (> 90%) was obtained after a short reaction time even at mild temperature condition (373 K), which proved that esterification can perform well in the ILM system without the use oxidative and corrosive acid, basic catalyst, or expensive enzyme catalyst. Second, the reaction procedure was simple because removal of generated water by distillation or desiccation is no longer necessary; the generated water entered the [Bmim]BF₄ domain of microemulsion. The superiority of [Hmim]HSO₄ in the ILM system for esterification was due to its two-fold functions; on one hand, it acted as a Brønsted-acid catalyst to catalyze the reaction. On the other hand, it served as a surfactant to enlarge the interface area and entrap the generated water during esterification reaction. Compared with organic reaction using traditional aqueous systems as catalyst and media, the ILM systems showed much more superiority including excellent temperature-independence, high reaction rate, enhanced equilibrium conversion, and controllable reaction region selectivity. We believe that the ILM systems can be a promising alternative for traditional medium in applications for etherification, thioetherification reactions, as well as other organic dehydration reactions.

Acknowledgements

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