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Etherification in cyclohexane/DBSA/water microemulsion system

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Abstract

Etherification reaction of hexanol and *tert*-butyl alcohol in the cyclohexane/dodecylbenzenesulfonic acid (DBSA)/water reverse microemulsion system has been investigated. The effect of several parameters, such as molar ratio of reactants, concentration of DBSA, reaction temperature, w_0 ([H_2O]/[surfactant]) value and various substrates, on the etherification was also studied. The results showed that the optimal reaction conditions for the etherification were as follows: $T = 318$ K, $w_0 = 2$, molar ratio of reactants was 1:1.2 and $c_{DBSA} = 0.05$ M. Furthermore, the comparison reactions in several surfactant systems were also performed and the results showed that the conversion in DBSA system was the highest, which proved the key factor affecting the conversion of the reactants was intrinsic nature of DBSA as a Brønsted acid-surfactant-combined catalyst. Finally, the mechanism of reaction was also put forward. After realizing that DBSA is both acid catalyst and surfactant, we concluded that it was dual functions of acid catalyst and surfactant that played an important role in improving reaction rate and conversion of etherification.

Keywords: Etherification; Microemulsion; DBSA

1. Introduction

Organic ethers are one of the important classes of chemicals which have considerable applications in different areas of chemical industry such as herbicides, disinfectors, pharmaceuticals, plasticizers, solvents and intermediates [1,2]. The Williamson ether synthesis is probably one of the most common methods for preparation of ethers [3], but this kind of method required strongly basic condition to accomplish the conversion of alcohols to halides or tosylates [4,5]. On the other hand, the acid can activate dehydration of alcohols, which provides an alternative important method for preparing ethers [6,7]. However, these acids are corrosive and the excess acid has to be neutralized after the reaction leaving considerable amount of salts to be disposed off into the environment [8,9]. So it is necessary to find an appropriate reaction system to enhance reaction conversion and less corrosive.

Microemulsion is clear, thermodynamically stable fluids of water, oil, and surfactants and is considered as less toxic, less expensive relative to many other solvents [10–12]. It is excellent medium for organic reactions because of its very large interfacial area and its ability of overcoming incompatibility of the reagents [13–17]. To the best of our knowledge, the direct etherification carried out in reverse microemulsion system has not been reported up to date.

Dodecylbenzenesulfonic acid (DBSA) are both Brønsted acid and surfactant, so it can act as an acid catalyst to activate a substrate and as a surfactant to form stable microemulsion with water-insoluble substrates [18]. We called this kind of catalyst as the Brønsted acid-surfactant-combined catalyst (BASC). In the previous work [19], we have studied the esterification in the DBSA microemulsion system in which DBSA acts as surfactant and acid catalyst. The results showed that the remarkable high esterification conversion was obtained in the relatively mild conditions. In the present work, we investigated direct etherification of two different alcohols in the DBSA microemulsion system. The etherification reaction between hexanol and *tert*-butyl alcohol was selected as the model reaction and the effect of reaction parameters such as w_0 ([H_2O]/[surfactant]), molar ratio of reactants, system temperature and the concentration of surfactant on conversion was studied. Furthermore, it was found that the best reaction conditions could be applied to many

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Abbreviations: DBSA, dodecylbenzenesulfonic acid; BASC, Brønsted acid-surfactant-combined catalyst; w_0, [H_2O]/[surfactant]; AOT, sodium 1,4-bis (2-ethylh exyl) sulphosuccinate; TsOH, *P*-toluenesulfonic acid; SDS, sodium dodecyl sulfate; GC, gas chromatograph.

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other etherification reactions and the product conversion was also high.

2. Experimental

2.1. Chemicals

Dodecylbenzenesulfonic acid (DBSA, ≈97% purity) was purchased from Tokyo Kasei Kogyo Co. Ltd. (Japan), sodium 1, 4-bis (2-ethylh exyl) sulphosuccinate (AOT, ≈96% purity) was purchased from ACROS organics. *P*-toluenesulfonic acid (TsOH) and Sodium dodecyl sulfate (SDS) were obtained from Sigma–Aldrich Co. Ltd. (Germany), chemical factory of Beijing and Xizhong chemical factory of Beijing (China), respectively. Ethanol, hexanol, *tert*-butyl alcohol, 1-octanol, 2-tetrahydrofurylmethanol and isoamylol were all from Shanghai chemical reagent factory (China). Cyclohexane was purchased from Tianjin chemical reagent Co. Ltd. (China). All the other chemicals used were analytical grade and were used without further purification.

2.2. Preparation of microemulsion

Microemulsion was prepared by the addition of desired concentration of DBSA into cyclohexane (10 ml). In this mixture, the final w_0 value was adjusted by the addition of the amount of the water. The mixture was briefly shaken until an optically clear single-phase solution was formed.

2.3. Reaction in microemulsion

Synthesis of all the ethers was carried out in the microemulsion mentioned above by introducing 0.003 mol hexanol and 0.0036 mol *tert*-butyl alcohol into the system. The reaction systems were stirred continuously at 318 K for a certain time. After that, samples (100 μl) were withdrawn from the reaction medium, dissolved with ethanol to stop any etherification, and then analyzed subsequently by GC.

2.4. Chromatographic analysis

Samples were monitored on a Varian CP-3380 Gas Chromatograph equipped with a FID detector using an Agilent Technologies HP-5 column (15 m × 0.530 mm × 1.50 μm). The temperature program used begins with 313 K and isothermal hold at 313 K for 2 min, then increased to 373 K at a gradient of 278 K/min, followed by an isothermal hold at 373 K for 2 min, subsequently 373–523 K at a rate of 303 K/min, at which temperature the column was maintained for 20 min; injection port temperature is 473 K; detector temperature is 523 K; carrier gas is nitrogen. Internal standard solution (5 μl) was mixed into above sample, and then 0.5 μl samples were injected in the GC. The conversion percent of hexanol to its *n*-hexylhexaneate was defined as the consumption of hexanol divided the initial amount of hexanol.

3. Results and discussion

3.1. Effect of molar ratio of reactants

The effect of molar ratio of hexanol to *tert*-butyl alcohol on the etherification was studied and the results were shown in Fig. 1. As shown in Fig. 1, the reaction conversion increased obviously with increasing the reaction time and attained equilibrium position in 36 h for all molar ratios. At equilibrium position, very high conversion (73%) can be obtained even if the molar ratio of reactants was 1:1, which proved that DBSA microemulsion system is a very powerful reaction medium for etherification. Because the definitely excessive mole ratio is needed to keep the reaction react completely [20–24]. It is obvious that the conversion of etherification is enhanced when the either of reactant is excessive. From Fig. 1, the conversion of etherification was the highest (86%) when the molar ratio of reactants was 1:1.2 after reaching equilibrium position. However, lower molar ratio of the two alcohols (1:1.5 and 1:2) could not lead to the further increasing of the conversion. So the molar ratio of 1:1.2 was chosen for the following research.

3.2. Effect of reaction temperature

Fig. 2 showed that the effect of temperature on etherification reaction in the temperature region of 303–343 K for 24 h without altering other reaction conditions. It can be seen that the conversion of hexanol to ether increased from 28% to 65% with the increase of the reaction temperature. Before 318 K, the etherification conversion increased distinctly with the temperature, which indicated the characteristics of the acid catalysis. However, the conversion was almost unchanged when the temperature was higher than 318 K. The reason may be that the microemulsion system is unstable at higher temperature though high temperature was favorable for the acid catalysis. Therefore, we selected 318 K as the reaction temperature in the following experiments.

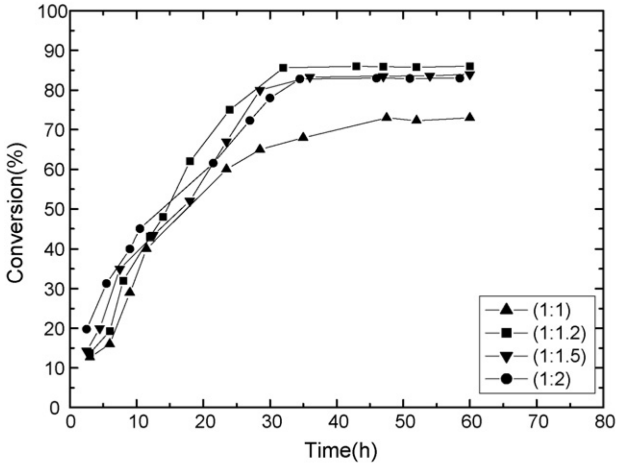


Fig. 1. Effect of molar ratio of hexanol and *tert*- butyl alcohol on conversion, $c_{\mathrm{DBSA}} = 0.05$ M, $T = 318$ K, $w_0 = 2$.

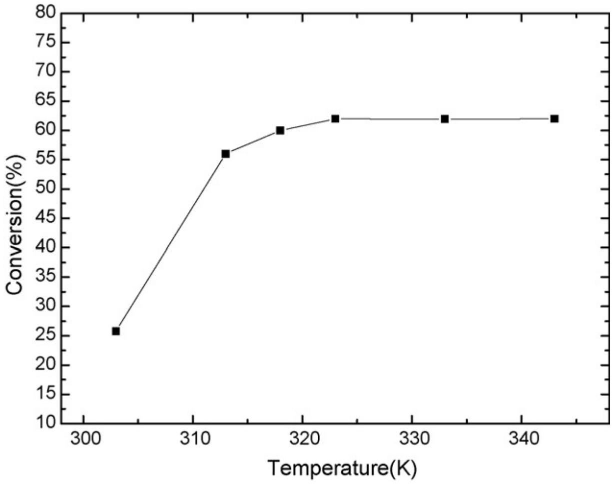


Fig. 2. Effect of reaction temperature on conversion of hexanol, hexanol: *tert*-butyl alcohol = 1:1 (molar ratio), $w_0 = 2$, $c_{\mathrm{DBSA}} = 0.05\,\mathrm{M}$, $t = 24\,\mathrm{h}$.

3.3. Effect of microemulsion w_0 value

The w_0 ($[H_2O]/[\text{surfactant}]$) value was an important factor for the organic reaction in the microemulsion system. We have studied the effect of w_0 on the etherification conversion and the results were presented in Fig. 3. Fig. 3 showed that an increase of w_0 value resulted in a decrease of the equilibrium conversion of hexanol after $w_0 = 2$.

According to the results of calculation, we found that there were 54 μl water produced in the system if 0.003 mol hexanol reacts completely with *tert*-butyl alcohol, which lead to an increase of w_0 value ($w_0 = 8$). When conversion was 90%, the produced water during etherification would be 48 μl (it corresponds to $w_0 = 5$). The produced water can easily enter the water microdomain and enlarge the water droplet.

In general, the organic reactions occurred at interface of the microemulsion. The larger interface area provides the more opportunity of contact each other and the more completely of the reaction. Etherification is a dehydration reaction and the produced little water can easily enter the water microdomain in microemulsion system, which will enlarge the water droplet in microemulsion and also enhance w_0 value. However, the excessive water made the microemulsion transform into emulsifiable or unstable system and the phase interface area decreased. This will lead to the etherification equilibrium towards reverse process, which facilitate ether hydrolysis and reduce the conversion of alcohol.

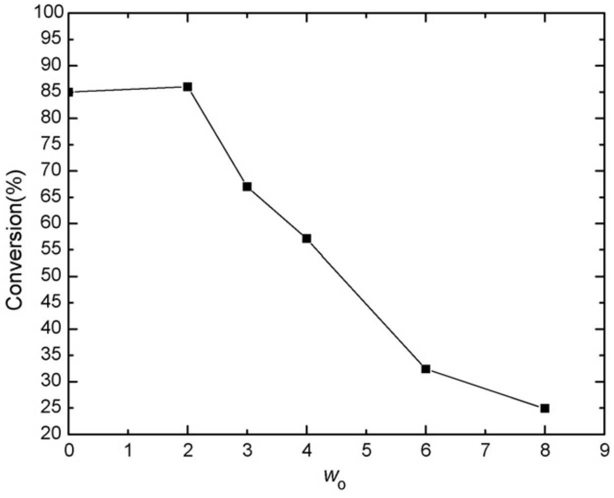


Fig. 3. Effect of w_0 on reaction conversion of hexanol, $c_{\mathrm{DBSA}} = 0.05\,\mathrm{M}$, hexanol with *tert*-butyl alcohol (1:1.2), $T = 318\,\mathrm{K}$, $t = 24\,\mathrm{h}$.

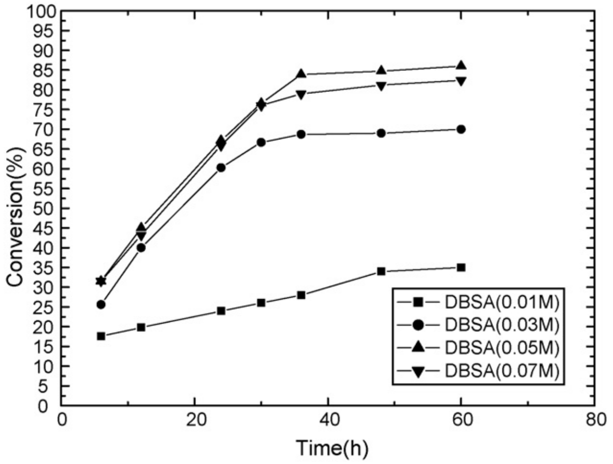


Fig. 4. Effect of DBSA concentration on conversion of hexanol in cyclohexane, hexanol: *tert*-butyl alcohol = 1:1.2, $T = 318\,\mathrm{K}$, $w_0 = 2$.

3.4. Effect of DBSA concentration

We also studied the effect of DBSA concentration on the etherification reaction. Fig. 4 showed that time course of etherification reaction of hexanol and *tert*-butyl alcohol in DBSA system with DBSA concentration varying from 0.01 to 0.07 M.

It is found that the concentration of DBSA remarkably affected the equilibrium position and conversion. The time required to reach the equilibrium positions became shorter as the concentration of DBSA increased (Ca. 50 h for 0.01 M of DBSA, 36 h for 0.03 M and 0.05 M of DBSA, 30 h for 0.07 M of DBSA). With the DBSA concentration increasing from 0.01 to 0.05 M, the equilibrium conversion of hexanol increased from 35% to 86%. On one hand, this was due to the availability of large surface area and acid sites, which favored the dispersion of more active species. On the other hand, the amount of hydrogen ion may increase with increase of DBSA concentration, which made the reaction reach the equilibrium position quickly. The decrease of the conversion at higher DBSA concentration of 0.07 M may be due to more and more single DBSA molecules preventing the formation of carbonium ion from alcohols, which reacts each other to produce ether.

3.5. Etherification of other alcohols

The DBSA system was also applied to etherification with other alcohols as substrate and the results were displayed in Fig. 5. As shown in Fig. 5, when a 1:1 mixture of ethanol with *tert*-butyl alcohol and a 1:1.2 mixture of isoamylol (hexanol, 1-octanol and 2-tetrahydrofurylmethanol) with *tert*-butyl alcohol

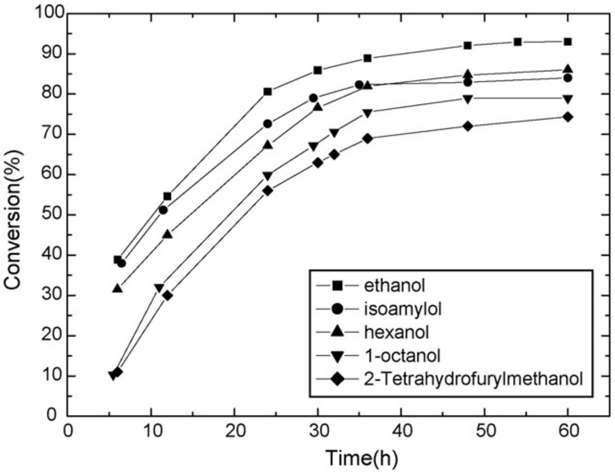


Fig. 5. Reaction condition: ethanol: *tert*-butyl alcohol = 1:1, isoamylol (hexanol, 1-octanol, 2-tetrahydrofurylmethanol): *tert*-butyl alcohol = 1:1.2, $T = 318$ K, $w_0 = 2$.

were etherified in DBSA microemulsion system at 318 K for 313 K, these five etherifications attained the equilibrium position almost simultaneously and the equlibrium conversions were 93%, 84%, 86%, 79%, 74.3%, respectively.

These results indicated that the conversion of substrates decreased at the equilibrium position with the alkyl chain and branch chain increasing. The ethanol reacted with *tert*-butyl alcohol affording ether in a higher conversion than the other alcohols. So the DBSA reverse microemulsion system was preferential to etherification of the short alkyl alcohol.

3.6. Comparison of conversion in several surfactant systems

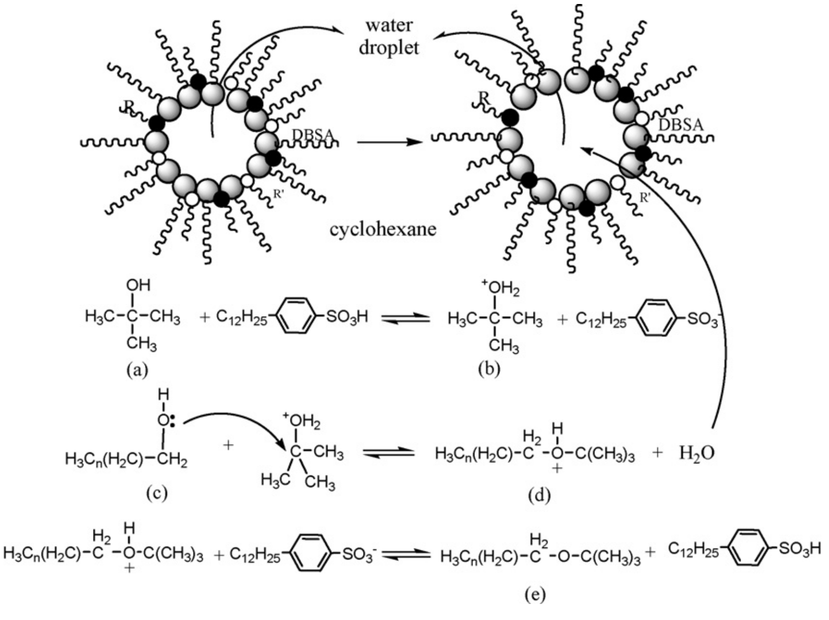
Subsequently, we studied the etherification in the other surfactant microemulsion system and compared them with that in DBSA reverse microemulsion system. The results were listed in Table 1. From Table 1, it is evident that the conversion in DBSA microemulsion system is much higher than that in the other surfactants systems with the same surfactant concentration of 50 mM after reaction proceeding 24 h.

Table 1
Etherification in several reaction systems

Entry	Reaction system	Conversion (%)
1	DBSA	75
2	TsOH	23
3	TsOH + SDS	43
4	SDS	0
5	AOT	0

Reaction condition: hexanol: *tert*-butyl alcohol = 1:1.2, $w_0 = 2$, $t = 24$ h, $T = 318$ K; catalyst concentration: 50 mM.

From Table 1, we can conclude that AOT and SDS as the nonacid surfactants can form the microemulsion but cannot catalyze the etherification reaction. TsOH can catalyze etherification and equlibrium conversion was 23%, this is because TsOH is a kind of organic acid despite it cannot form microemulsion system. A mixture of TsOH and SDS can form the translucent, stable and isotropic microemulsion, therefore, the combination of them not only possesses acid catalysis property, but also the collision opportunities of the reactant increase due to the large phase interface area. As a result, the equlibrium conversion in this system is higher than that in separate system. The DBSA microemulsion system should be the most efficient for the catalysis of etherification reaction and the equlibrium conversion is also the highest (75%, 24 h). The reason is DBSA, as a kind of surfactant, can form stable microemulsion. In addtion, it can catalyze the reaction as a kind of Brønsted acid with the same acidity as H_2SO_4. So it provides the two combined properties of TsOH and SDS, and the acidity of DBSA is stronger



Scheme 1. Proposed mechanism for etherification in microemulsion.

than that of TsOH, so the catalysis effect of DBSA was better than the combination of TsOH and SDS.

Based on the above experiments results, it can be concluded that the Brønsted acid-surfactant combined catalysis system is the most effective system for the etherification conversion under mild conditions.

3.7. Mechanism of reaction

Scheme 1 illustrated the proposed mechanism of etherification in microemulsion system. As shown in Scheme 1, the polar reagents arrange directionally in the interface of the microemulsion by the inducement of DBSA. There are two kinds of alcohol existed, the molecules of alcohol (a) can obtain protons from DBSA molecules and turn to an acidification alcohol (b). The another kind of alcohol (c) uses its lonepair electrons to attack alcohol (b) carbon 180° away from the departing H_2O. This leads to the formation of part intermediate (d) and then the intermediate (d) transforms into production (e) gradually.

The water microdomain in DBSA microemulsion can entrap water produced by etherification, which would accelerate the formation of ether and promote the equilibrium process in favor of the products side.

4. Conclusion

We have described etherification reaction in reverse microemulsion in the presence of DBSA as a Brønsted acid-surfactant-combined catalyst (BASC). This reaction system was found to be applicable to several etherification reactions including long alky chain alcohol (1-octanol and hexanol) and short alky chain alcohol (ethanol and isoamylol). In addition, etherification reactions were carried out under very mild conditions. It is worthy of pointing out that the conversion (75%) of hexanol in DBSA microemulsion system was reached only after 24 h. This high conversion obtained in a short time proved that DBSA microemulsion should be a very promising reaction system for etherification reactions because of its two-fold functions: firstly, it can act as a Brønsted acid to catalyze the reaction; secondly, it can form microemulsion as surfactant to enlarge interface area and entrap water produced during etherification reaction. In this paper, only a little part of alcohols we referred, but it is believed that DBSA microemulsion should also be applicable to synthesis of aryl ether, thioether, heterocyclic ether and naphthyl ether and the relative works is going on presently.

Acknowledgement

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