

A novel quaternary ammonium salt synthesis with dimethyl carbonate as alkylating agent

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Dimethyl carbonate (DMC) could be used as an environmentally friendly alkylating agent to replace the highly toxic dimethyl sulfate for quaternary ammonium salt synthesis. In this work, a novel quaternary ammonium salt was obtained via reaction between DMC and distearyl ester of methyldiethanolamine synthesized from stearic acid and *N*-methyl diethanolamine (MDEA). The optimum synthesis conditions for distearyl ester of methyldiethanolamine were found as mixing the reactants stearic acid and MDEA with molar ratio of 2.10 at about 430 K for 5 h. The quaternization of distearyl ester of methyldiethanolamine with DMC was investigated, and the structure of the quaternary product was measured using IR and MS.

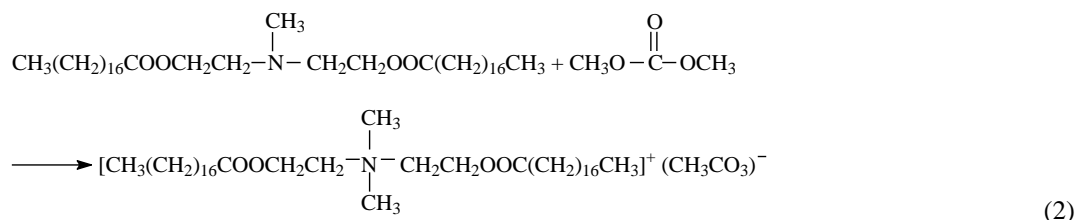
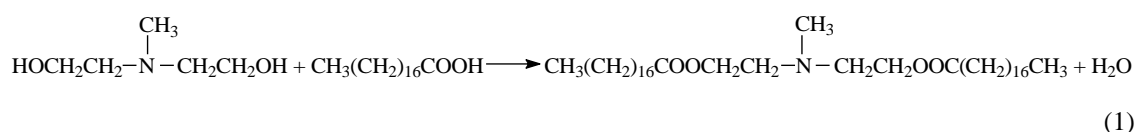
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1. Introduction

There have been an increasing number of researchers who concern the synthesis of quaternary ammonium compounds [1–5], which can be used as fabric softener, antistatic agents, and germicides, to name a few. The quaternization of amines has been the method most generally used for preparing the quaternary ammonium salts. In these quaternization reactions, dimethyl sulfate (or methyl chloride), widely used as alkylating agent to react with tertiary amines, is quite toxic (or a suspected carcinogen). Nowadays, however, chemical syntheses tend to use biodegradable compounds of the lowest toxicity possible, such compounds include dimethyl carbonate

(DMC) [6, 7], which is widely used as an environmentally friendly reactant in the chemical synthesis. Zheng et al [8] synthesized several short carbon chain quaternary ammonium salts from ammonium salts and dialkyl carbonates over an ionic liquid catalyst. In this work, we report a novel long carbon chain quaternary ammonium salt (more excellent performance as a softener) synthesis with DMC as alkylating agent. The optimized reaction conditions for distearyl ester of methyldiethanolamine syntheses (as shown in Eq. 1) were acquired, and the preparation of a novel quaternary ammonium salt from the alkylating agent DMC and distearyl ester of methyldiethanolamine at atmospheric pressure (as shown in Eq. 2) was presented.



2. Experimental

2.1. Synthesis of distearyl ester of methyldiethanolamine

A certain amount of stearic acid was added into a 250 ml glass flask, and heated to dissolve. The catalyst p-

toluenesulfonic acid (PTSA) was dissolved in *N*-methyl diethanolamine (MDEA) solution, and then dropped the above mixture into the flask to react with the excessive stearic acid for a certain time at the specified temperature. The dosage of catalyst PTSA was 1 % by weight based on the weight of the reactants (stearic acid and MDEA). Nitrogen gas was flowed to purge the air and the by-

product water from the reaction system. The reaction products would be analyzed by IR, and IR spectra were obtained as KBr discs on an ABB Bomem FTLA 2000-104 spectrophotometer in the 4000-500 cm^{-1} region.

2.2. Quaternization of distearyl ester of methyldiethanolamine with DMC

The reaction was conducted in a 250 ml glass flask equipped with a thermometer, a distillation apparatus, and a stirrer under refluxing condition. The reaction mixture contained about 0.071 mol distearyl ester of methyldiethanolamine and 0.070 mol DMC. Nitrogen gas was flowed to purge O_2 from the reaction system before reaction. The system was brought to 353 K at atmosphere pressure for 6 h, and the reaction products would be analyzed by IR and MS (Waters Platform ZMD 4000).

3. Results and discussion

The effect of reactants molar ratio $n(\text{Stearic acid})/n(\text{MDEA})$ on the MDEA conversion was investigated, and the results were summarized as shown in Fig. 1. The reaction time was 3 h, and the reaction temperature was 428 K. The MDEA conversion steeply increased at low reactants molar ratio, $n(\text{Stearic acid})/n(\text{MDEA}) < 2.05$, and followed by a gradual leveling off at a $n(\text{Stearic acid})/n(\text{MDEA}) \geq 2.10$. Under the present reaction conditions, the optimum reactants molar ratio $n(\text{Stearic acid})/n(\text{MDEA})$ for distearyl ester of methyldiethanolamine synthesis was about 2.10. It was indicated that a slight excess of stearic acid was beneficial to improving the MDEA conversion.

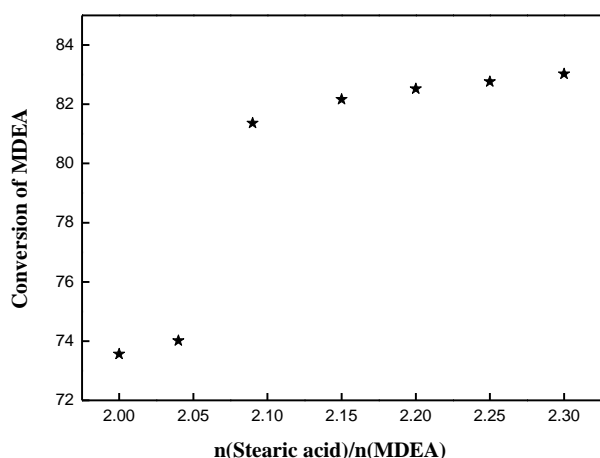


Fig. 1. Effect of $n(\text{Stearic acid})/n(\text{MDEA})$ on the conversion of MDEA.

Fig. 2 showed the effect of reaction temperature in the range of 399–443 K on the conversion of MDEA at atmospheric pressure. The reaction time was 3 h, and the $n(\text{Stearic acid})/n(\text{MDEA})$ was 2.10. As expected, increased temperature affected the synthesis reaction for distearyl ester of methyldiethanolamine very favorably. MDEA conversion was improved greatly with the increase

in reaction temperature, and reached the highest value when the reaction temperature was near 430 K. Hereafter, the conversion of MDEA presented a weak growth trend when keeping on increasing reaction temperature. Conclusively, 430 K could be the optimal reaction temperature for the reaction.

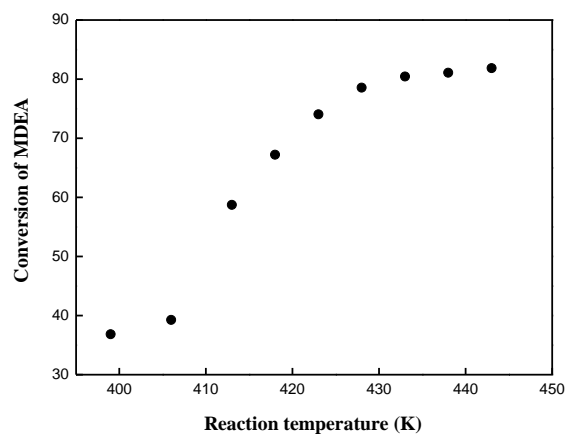


Fig. 2. Effect of reaction temperature on the conversion of MDEA.

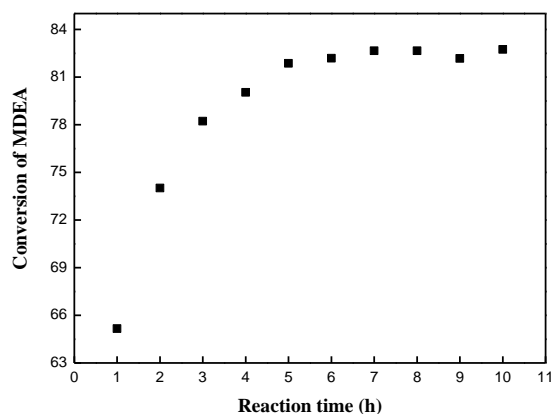


Fig. 3. Effect of reaction time on the conversion of MDEA.

The influence of reaction time on conversion of MDEA was summarized as shown in Fig. 3. The reaction temperature was 428 K, and the $n(\text{Stearic acid})/n(\text{MDEA})$ was 2.10. The conversion of MDEA increased dramatically with increased reaction time from 1 h to 5 h. At 5 h, the MDEA conversion reached a maximum of about 81.9%. When the reaction time was increased from 5 h to 10 h, the MDEA conversion remained almost unchanged. So the optimum reaction time existed for distearyl ester of methyldiethanolamine synthesis, which was about 5 h.

The IR spectrums of MDEA, stearic acid and intermediate product distearyl ester of methyldiethanolamine were shown in Fig. 4. From Fig. 4(C), the prominent peak at 1736 cm^{-1} was due to carbonyl stretching vibration, which confirmed the

formation of the ester. The absence of a peak at 3000–3500 cm^{-1} showed the absence of unreacted alcohol groups, which also indicated the presence of a very small amount of monoester.

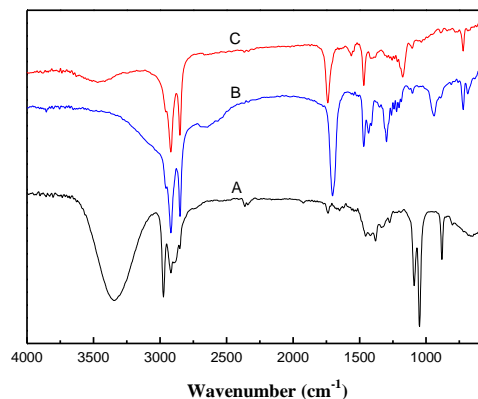


Fig. 4. IR patterns of: (A) MDEA, (B) stearic acid and (C) intermediate product distearyl ester of methyldiethanolamine.

Fig. 5 showed the IR spectrums of quaternary product. CH_2 and CH_3 stretch vibration could be observed at 2918 cm^{-1} and 2849 cm^{-1} . The IR band at 1736 cm^{-1} was due to C=O stretch vibration. The band at 1474 cm^{-1} could be due to the shear vibration of C-H in CH_2 and the weak band at 1412 cm^{-1} was from the in-plane vibration of C-H in $\text{CH}_2\text{-CO}$. The stretch vibration of C-O-C gave the IR band near 1162 cm^{-1} . The band observed at 719 cm^{-1} came from the special absorption of quaternary ammonium salt and the special vibration absorption [9]. In MS spectrum, the peak at m/z 666.6 was associated with the cation fragment of the quaternary ammonium salt, which also proved the presence of the target quaternary product. To sum up, the IR and MS spectra showed that the desired product had formed.

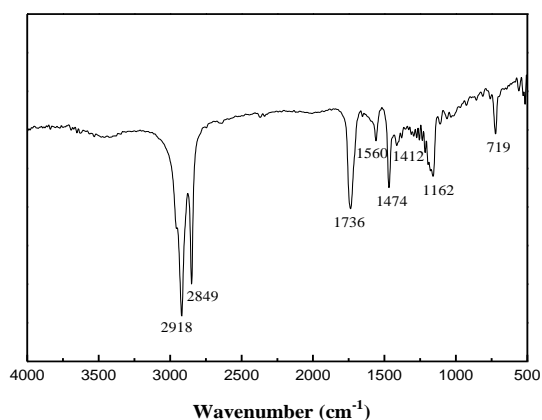


Fig. 5. IR patterns of the synthetic quaternary product.

4. Conclusions

A novel quaternary ammonium salt was successfully synthesized with innocuous DMC as the alkylating agent. For the intermediate product distearyl ester of methyldiethanolamine synthesis, the suitable reactants molar ratio $n(\text{Stearic acid})/n(\text{MDEA})$ was about 2.10, the optimum reaction temperature was about 430 K and the suitable reaction time was 5 h considering the conversion of MDEA. The quaternization of distearyl ester of methyldiethanolamine with DMC was investigated, and the IR and MS results indicated the production of the target quaternary product.

Acknowledgements

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