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A NOVEL BETAINE TYPE ASPHALT EMULSIFIER SYNTHESIZED AND INVESTIGATED BY ONLINE FTIR SPECTROPHOTOMETRIC METHOD

Article Highlights

- A novel betaine type asphalt emulsifier was synthesized
- The optimum reaction condition was obtained
- The chemical structure of the product was characterized by FTIR and ^{1}H-NMR
- Based upon the experimental data, a plausible reaction mechanism was proposed for the reaction. The emulsifier is a rapid-set asphalt emulsifier

Abstract

A novel betaine type asphalt emulsifier 3-(N,N,N-dimethyl acetoxy ammonium chloride)-2-hydroxypropyl laurate was synthesized after three steps by the reaction of lauric acid, epichlorohydrin, dimethylamine and sodium chloroacetate. The optimum reaction conditions were obtained for the synthesis of the first step of 3-chloro-2-hydroxypropyl laurate. The esterification yield reaches 97.1% at the optimum conditions of reaction temperature 80 °C, reaction time 6 h, feedstock mole ratio of epichlorohydrin to lauric acid 1.5, mass ratio of catalyst to lauric acid 2%. The chemical structure of the product was characterized by FTIR and ^{1}H-NMR. The first synthesis step of 3-chloro-2-hydroxypropyl laurate was monitored by online FTIR technique. The by-product was detected by the online FTIR analysis. Based upon the experimental data, a plausible reaction mechanism was proposed for the reaction. The CMC of the objective product has a lower value of 7.4×10^{-4} mol/L. The surface tension at CMC is 30.85 mN/m. The emulsifier is a rapid-set asphalt emulsifier.

Keywords: asphalt, emulsifier, betaine, synthesis, online FTIR.

Emulsions and emulsification processes of asphalt are considered a very important practice in industry nowadays. Compared to hot-mixed asphalt, bituminous emulsions have the advantages of working at ambient temperature, strong adhesive power with mineral aggregate, low energy consumption and little pollution to the environment. They are used extensively in pavement construction and waterproofing industries [1-4].

Bituminous emulsions can be classified into cationic, anionic or nonionic types depending on the charge on the asphalt particle. Anionic emulsifiers, such as long chain sulfonate, alkali metal salt of an alkali lignin and carboxylic acid organic salts, were used widely in the early research stage [5-7]. Cationic emulsifiers have dominated in bitumen emulsion later because of their good emulsifying performance and excellent adhesion to mineral aggregate [8-10]. Most aggregates carry a negative charge, and cationic emulsions can be rapidly attracted and bound to these surfaces. The mainly cationic asphalt emulsifiers are nitrogen-containing organic amine derivatives. Honma *et al.* [11] investigated a cationic slow-set asphalt emulsion composition, which is scarcely affected by temperature and characteristics of the aggregates. Gemini emulsifiers are surfactants with two or more hydrophilic groups and two or more hydrophobic groups in the molecules, and they have more surface--active [12,13]. Rist *et al.* [14] selective synthesis of linear and Gemini quaternary ammonium surfactants by reacting the corresponding alkyl alcohols with

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2-chloro-*N,N*-dimethyl-ethylamine under basic conditions.

Zwitterionic emulsifiers, which can be mainly divided into betaine-type and amino acids, represent an active research area of surfactants as well [15]. The hydrophilic groups in the molecular structure contain both acidic and alkaline groups. Zwitterionic emulsifiers are effective at different pH values. They have excellent emulsifying properties, and good compatibility with anionic, cationic and nonionic surfactants [16,17]. Various researches on betaine emulsifiers have been done [18,19]. Martin and Hemsley [20] studied an asphalt emulsion priming composition using betaine-type emulsifiers. It can be used on road beds to prepare the road bed for paving. Nonionic emulsifiers, such as ethoxylated nonylphenols, can be used as part of an emulsifier or alone in both cationic and anionic slow-setting emulsions. A nonionic emulsifier is obtained by a process comprising the steps of adding ethylene oxide to an alcohol having a long chain, adding propylene oxide to the resulting compound, and again adding ethylene oxide to the resulting compound [21]. It has the desired stability in a stationary state and storability.

In previous papers we have studied different types of asphalt emulsifiers [22,23]. In this study, a new betaine asphalt emulsifier was synthesized. The chemical structures were characterized by FTIR and ^{1}H-NMR. A plausible reaction mechanism was proposed for the reaction according to online FTIR analysis.

EXPERIMENTAL

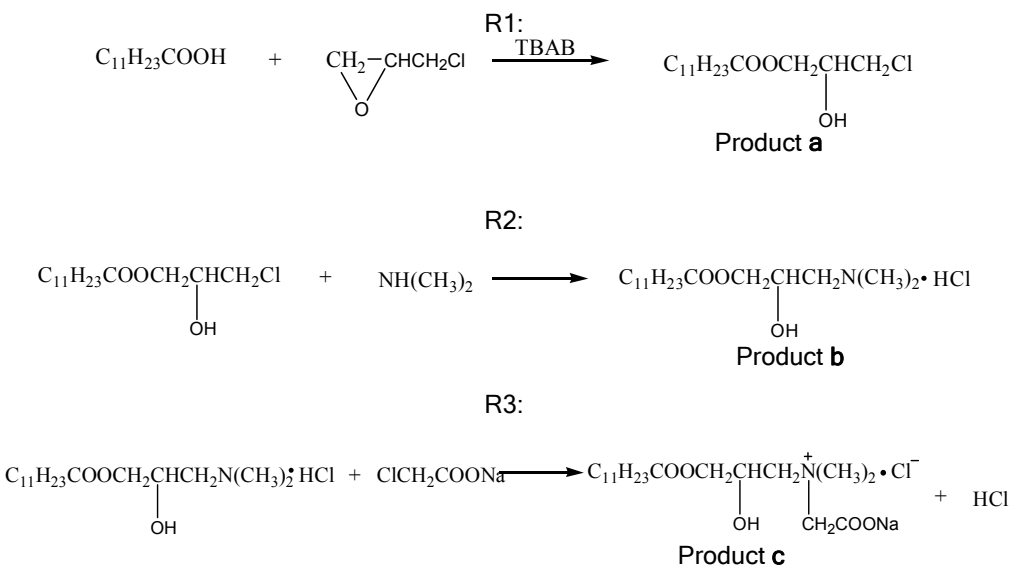
Materials and characterization

Lauric acid was obtained from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Epichlorohydrin was purchased from Xilong Chemical Reagent Co., Ltd, Guangzhou, China. Tetrabutyl ammonium bromide (TBAB) was offered by Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. Dimethylamine (33%) was obtained from Chengdu Kelong Chemical Reagents Factory, Chengdu, China. Chloroacetic acid was purchased from Tianjin DaMao Chemical Reagent Factory, Tianjin, China. All the reagents mentioned above were of analytical grade and used without further purification. Medium-set asphalt emulsifier (a commercial product of TongDa) was provided by Xinxiang TongDa Highway Technology New Material Co. Ltd., Xinxiang, China. Asphalt adopted was AH-90, which was provided by Shengli Refinery of Qilu Petrochemical Company, Zibo, China. The mineral aggregate was the mixture of different size of marble stone.

FTIR spectra were recorded from 400 to 4000 cm^{-1} wavenumber range with averaging 32 scans at a resolution of 4 cm^{-1} on a Bruker Tensor-27 FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer (Bruker, Germany), using $CDCl_3$ as solvent. Chemical shifts (δ) were given in ppm.

Synthesis of betaine type asphalt emulsifier

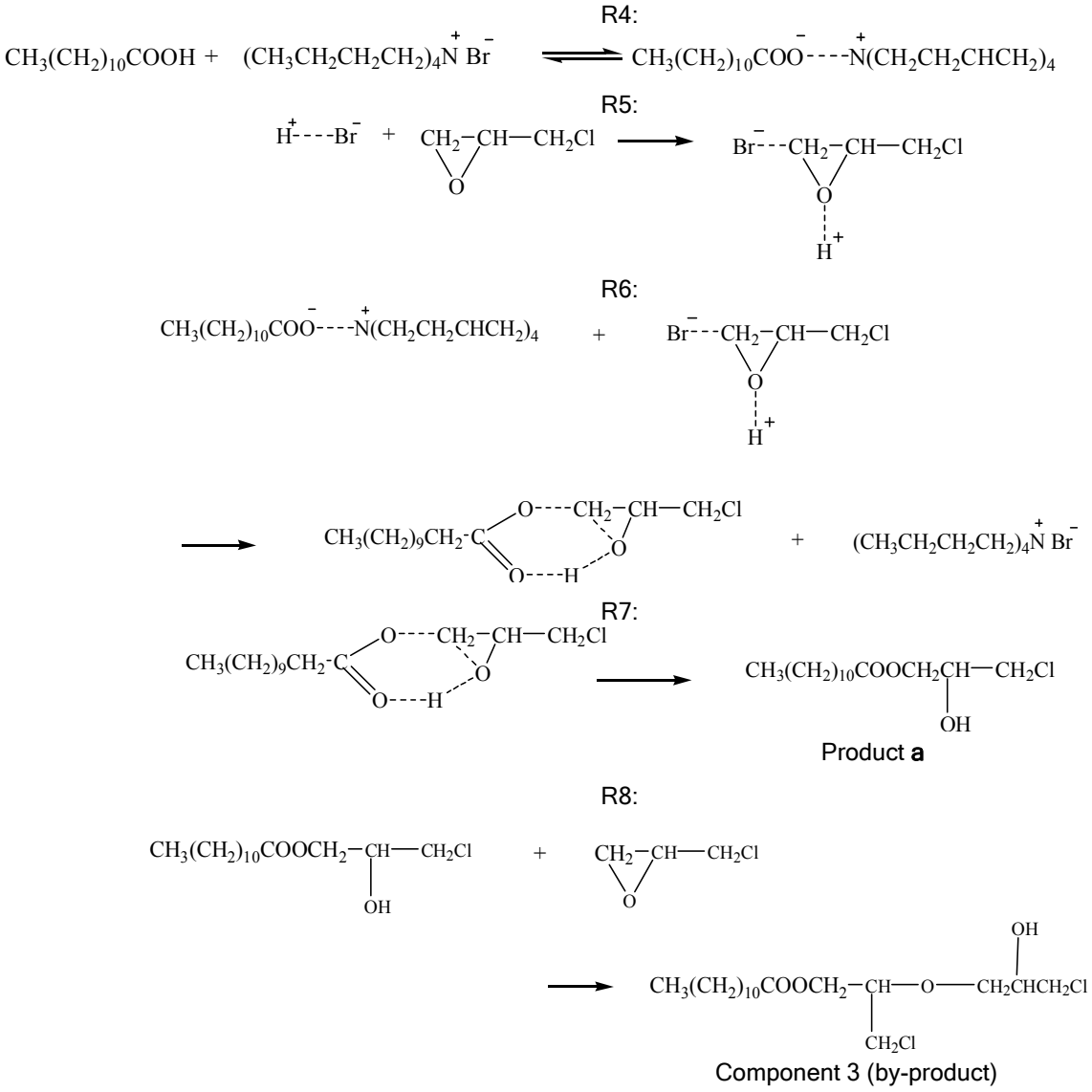
Scheme 1 shows the synthesis routes of asphalt emulsifier.



Scheme 1. Synthetic routes of 3-(N,N,N-dimethyl acetoxy ammonium chloride)-2-hydroxypropyl laurate.

3-chloro-2-hydroxypropyl laurate (a), Step 1. Lauric acid (20.00 g, 0.1000 mol), epichlorohydrin (13.87 g, 0.1500 mol) and 0.40 g tetrabutyl ammonium bromide were added in a three-necked flask. The solution was stirred for 6 h at 80 °C in a water bath. The product **a** was obtained by vacuum distillation (fractions boiling at 126-127 °C under 6.67 kPa were collected). The esterification yield reaches 97.1%. The relative concentration of component 2 (product **a**) is 17.39 at the reaction time 6 h, while the relative concentration of component 3 (the by-product in Scheme 2) is 0.08. Therefore, the yield of product **a** can be calculated as 96.7%, while the yield of the by-product can be calculated as 0.4%. The percent yield of by-product is very low. ^{1}H-NMR (300 MHz, $CDCl_3$), δ / ppm: 0.95 (*t*, 3H, -CH_3), 1.29 (*m*, 16H, -CH_2-), 1.68 (*t*, 2H, -CH_2-C-COO), 2.10(*m*, 1H, -OH), 2.35 (*t*, 2H, -CH_2-COO), 3.70 (*m*, 2H, -CH_2-Cl), 4.12 (*m*, 1H, -CH-), 4.30 (*m*, 2H, -COO-CH_2-).

3-(N,N-dimethylamino hydrochloride salt)-2-hydroxypropyl laurate (b), Step 2. 50 mL anhydrous ethanol, 1.00 g NaOH and 5 mL distilled water were added to 3-chloro-2-hydroxypropyl laurate (**a**), then 33% dimethylamine aqueous solution (16.39 g, 0.1200 mol) was added dropwise and stirred for 4 h at 75 °C in a water bath. The product was processed by vacuum distillation to remove the solvent, then recrystallized with mixed solution of anhydrous ethanol and acetone. The product **b** was dried to a constant weight under vacuum. The combined yield of Steps 1 and 2 obtained by the Mohr method is 86.3%. The relative concentration of component 2 (product **b**) is 2.26 at the reaction time 4 h, while the relative concentration of component 4 (the diquat by-product) is



Scheme 2. The reaction mechanism for synthesis 3-chloro-2-hydroxypropyl laurate.

0.21. Therefore, the yield of product **b** can be calculated as 79.0%, while the yield of the diquat by-product can be calculated as 7.3%. The percent yield of the diquat by-product is low.

3-(*N,N,*N-dimethyl acetoxy ammonium chloride)--2-hydroxypropyl laurate (c), Step 3. Sodium chloroacetate aqueous solution was synthesized by the reaction of 11.34 g (0.1200 mol) chloroacetic acid, 4.80 g (0.1200 mol) NaOH and 30 g distilled water. Then the sodium chloroacetate aqueous solution was added dropwise to 3-(*N,N*-dimethylamino hydrochloride salt)-2-hydroxypropyl laurate (**b**) and stirred for 6 h at 75 °C in a water bath. The product was processed by vacuum distillation to remove the solvent, then recrystallized with mixed solution of anhydrous ethanol and ethyl acetate. The product **c** was dried to a constant weight under vacuum. The combined yield of Steps 1, 2 and 3 obtained by potassium ferricyanide method is 37.9%. The relative concentration of component 3 (product **c**) is 8.19 at the reaction time 6 h, while the relative concentration of component 4 (the diquat by-product) is 0.36. Therefore, the yield of product **c** can be calculated as 36.3%, while the yield of the diquat by-product can be calculated as 1.6%. The percent yield of the diquat by-product is low.

Esterification yield

The yield of product **a** was analyzed by esterification yield. For reaction R1, lauric acid was consumed and acid value decreased. The acid value (*A.V*) of product **a** was measured by the following method: 1.0000 g sample was weighed into a conical flask, then 70 mL 95% ethyl alcohol and 0.5 mL phenolphthalein indicator were added. The solution was titrated with 0.1 mol/L standard KOH solution to the appearance of pink color:

$$A.V = \frac{V_1 C_1 56.1}{m_1} \tag{1}$$

where $A.V$ is the acid value (mg KOH/g), V_1 is the consumed volume of KOH standard solution (mL), C_1 is the concentration of KOH standard solution (mol/L), and m_1 is the mass of the sample to be titrated (g).

The esterification yield (Y_1) of reaction R1 was calculated as:

$$Y_1 = 100 \frac{A.V_0 - A.V}{A.V_0} \tag{2}$$

where Y_1 is the esterification yield of reaction R1 (%) and $A.V_0$ is the initial acid value (mg KOH/g).

*The yield of product **b***

The yield (Y_2) of product **b** was obtained by the Mohr method. For reaction R2, chloride ion was produced. 2.5000 g sample was weighed into a conical flask, then about 50 mL distilled water and 0.1 mL of phenolphthalein indicator was added. The solution was titrated with 0.1 mol/L standard HNO_3 solution to the appearance of colourless. Then, 1 mL of 5% potassium chromate indicator was added. The solution was titrated with 0.1 mol/L standard silver nitrate solution. The endpoint of the titration is identified as the first appearance of a red-brown color of silver chromate. At the same time, a blank titration was performed:

$$Y_2 = 100 \frac{N_2 (V_2 - V_{02}) m}{1000 m_2 n_2} \tag{3}$$

where Y_2 is the yield of product **b**. V_2 is the consumed volume of $AgNO_3$ standard solution (mL), V_{02} is the consumed volume of $AgNO_3$ standard solution in blank test (mL), m is the total mass of sample (g), m_2 is the mass of sample to be titrated (g), N_2 is the concentration of $AgNO_3$ standard solution (mol/L), and n_2 is the mole of lauric acid (mol).

*The yield of product **c***

The yield (Y_3) of product **c** was obtained by potassium ferricyanide method, as the product **c** is a betaine surfactant which acts as a cationic surfactant under the acidic conditions. 3.0000 g sample was weighted and dissolved in 50 mL water, and transferred to a 200.0 mL volumetric flask. Then, 8 mL acetic acid-sodium acetate buffer solution and 50.0 mL potassium ferricyanide aqueous solution (0.05 mol/L) measured by a pipette were added into the 200.0 mL volumetric flask. The resulting solution was diluted to the mark of the 200.0 mL volumetric flask with distilled water, and allowed to stand for 1 h. Then, the mixed solution was filtered with dry filter paper. The initial 20 mL filtrate was abandoned. The following 100.0 mL filtrate was accurately measured with a pipette to a 250 mL iodine flask. 10 mL 20% KI aqueous solution and 10 mL dilute hydrochloric acid (1:1) were added and stored for 1 min. Then 10 mL 10% zinc sulfate solution was added and stored for 5 min. The mixed solution was titrated with 0.05 mol/L standard sodium thiosulfate solution. 3 mL 1% starch indicator was added when the titrated solution became pale yellow. The endpoint of the titration was identified as the blue color disappeared. At the same time, a blank titration was performed:

$$Y_3 = \frac{[(V_{03} - V_3) N_3 3m]}{n m_3 1000} \frac{200}{100} 100 \tag{4}$$

where, Y_3 is the yield of product **c**, V_3 is the consumed volume of sodium thiosulfate standard solution (mL), V_{03} is the consumed volume of sodium thiosulfate standard solution in blank test (mL), N_3 is the concentration of sodium thiosulfate standard solution (mol/L), m is the total mass of sample (g), m_3 is the mass of sample to be titrated (g), and n is the mole of lauric acid (mol).

Online FTIR analysis

The online FTIR analysis was performed on a ReactIR 4000 spectrophotometer (Mettler-Toledo AutoChem, Inc., USA). FTIR spectra were recorded from 650 to 4000 cm^{-1} wavenumber range at a resolution of 4 cm^{-1}. The detector of the online FTIR analysis system was immersed in the solution during the reaction to record the 3D online FTIR spectra. The magnetic stirrer was under operation during the online FTIR measurement.

Surface tension and CMC

In the determination of surface tension and critical micelle concentration (CMC), the sample of emulsifier product **c** was used as purified sample described above by recrystallization. Surface tension of surfactant solutions decreases sharply with the increase of concentration, and nearly does not change when the concentration reaches CMC. Surface tension of surfactant solutions was measured with Krüss Processor tensiometer K12 (Krüss GmbH, Hamburg, Germany). The CMC and the surface tension at CMC were determined by the breaking point of the curve of surface tension to logarithm of concentration.

Performance test of bituminous emulsion

Preparation of bituminous emulsion

In the preparation of bituminous emulsion, the emulsifier of product **c** was used directly after synthesis steps and without purification process. Commercial product of TongDa was also a synthesized mixture in practical usage, which mainly contains quarternary ammonium salt. 12.5 g emulsifier of product **c** or commercial product of TongDa was dissolved in 200 mL water. The pH value of the aqueous solution was adjusted to 2.0 by adding hydrochloric acid, then the solution was heated to 60 °C. 300 g AH-90 asphalt was heated to 120 °C. The bituminous emulsion was prepared by mixing the aqueous solution containing emulsifier and asphalt in a colloid mill for 1 min.

Aggregate mixing experiment

Mineral aggregate (100 g), cement (1 g) and water (7 g) were placed in a 500-mL bowl. Bituminous emulsion (11 g) was then added, and the mixture was stirred at 60 revolutions per minute. The aggregate mixing time was recorded by observation of the mixing performance. The room temperature was 25 °C.

RESULTS AND DISCUSSION

Synthesis optimization of 3-chloro-2-hydroxypropyl laurate

Reaction temperature

The reaction conditions were as follows: reaction time 6 h, feedstock mole ratio of epichlorohydrin to lauric acid 1.5, mass ratio of catalyst to lauric acid 2%. Figure 1 shows that the esterification yield (Y_1) increases with the reaction temperature, and levels off when the temperature is greater than 80 °C.

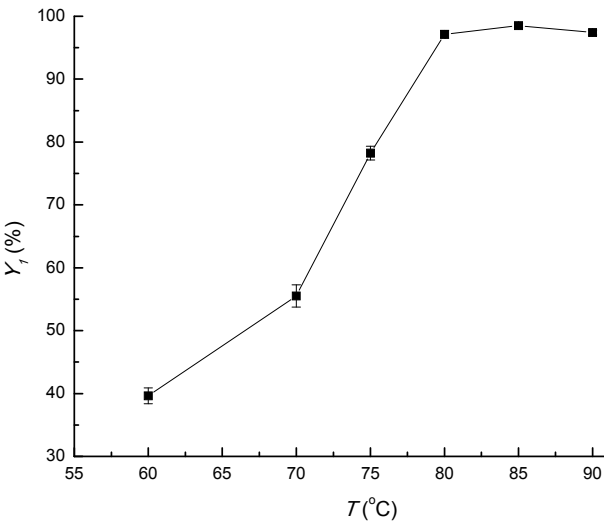


Figure 1. Yield versus reaction temperature.

Reaction time

The reaction conditions were as follows: reaction temperature 80 °C, feedstock mole ratio of epichlorohydrin to lauric acid 1.5, mass ratio of catalyst to lauric acid 2%. Figure 2 shows that the esterification yield increases with the reaction time and levels off after 6 h.

Feedstock mole ratio

The reaction conditions were as follows: reaction temperature 80 °C, reaction time 6 h, mass ratio of catalyst to lauric acid is 2%. Figure 3 represents the esterification yield (Y_1) versus feedstock mole ratio of epichlorohydrin to lauric acid, showing that the esterification yield increases with the feedstock mole ratio in the first stage, then levels off when the feedstock mole ratio is greater than 1.5.

The dosage of catalyst

The reaction conditions were as follows: reaction temperature 80 °C, reaction time 6 h, feedstock mole ratio of epichlorohydrin to lauric acid 1.5. Figure 4 represents the esterification yield (Y_1) *versus* the mass ratio (w) of catalyst to lauric acid. The esterification yield increases with the mass ratio in the first stage, then levels off when the mass ratio is greater than 2.0%.

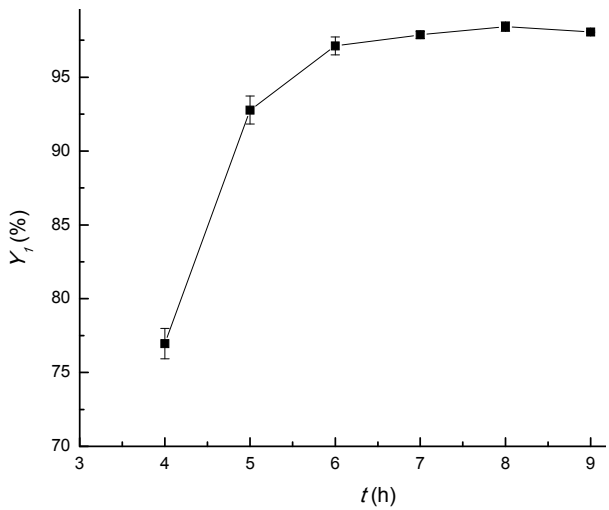


Figure 2. Yield versus reaction time.

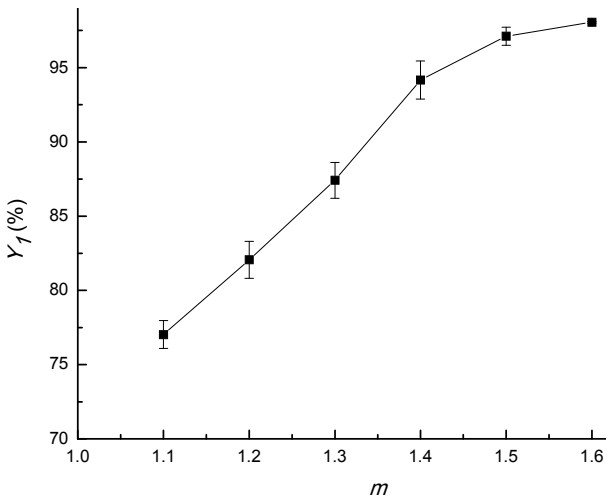


Figure 3. Yield versus feedstock mole ratio.

Overall speaking, the optimum reaction conditions are as below: reaction temperature 80 ºC, reaction time 6 h, feedstock mole ratio of epichlorohydrin to lauric acid 1.5, mass ratio of catalyst to lauric acid 2%. The esterification yield reaches 97.1% at the optimum reaction conditions.

FTIR characterization and online FTIR analysis

FTIR spectra of products **a**, **b** and **c** are available from corresponding author on request. Table 1 gives the peak assignments. The reaction to synthesize 3-chloro-2-hydroxypropyl laurate was monitored by online FTIR technique. In the reaction, the reaction time was up to 7.0 h. The 3D online infrared spectrum throughout the whole reaction process changed a lot (data available from corresponding author on request).

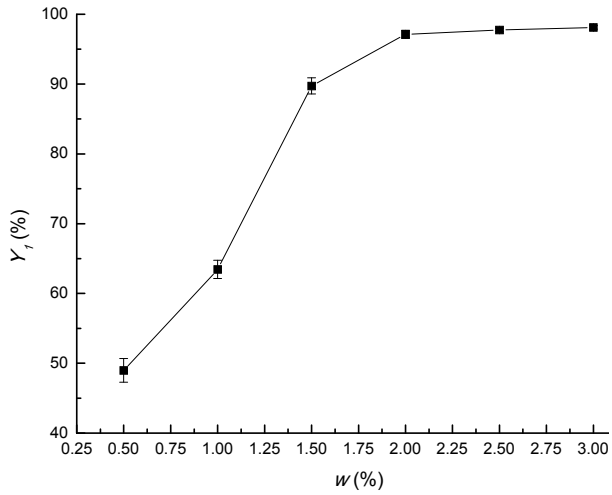


Figure 4. Yield versus mass ratio of catalyst to lauric acid.

Three components were detected by online FTIR analysis. Their FTIR spectra were obtained (data available from corresponding author on request). Table 1 also gives the peak assignments. Therefore, the spectrum of component 1 obtained by online FTIR agrees with the chemical structure of lauric acid. The spectrum of component 2 obtained by online FTIR agrees with the chemical structure of product **a** in Scheme 1. The spectrum of component 3 obtained by online FTIR should be a by-product as shown in Scheme 2.

In the plot of relative concentrations (c) of components 1-3 versus reaction time (data available from corresponding author on request), the relative concentration of component 1 decreases with the reaction time. Therefore, we can ascertain that component 1 should be lauric acid according to the changing trend of concentration and the online FTIR spectrum.

The relative concentration of component 2 increases gradually with reaction time. We can ascertain that component 2 should be the target product **a** to be synthesized according to the changing trend of concentration and the online FTIR spectrum.

The relative concentration of component 3 is small during the reaction. Therefore, we can ascertain that component 3 should be a by-product as shown in Scheme 2 according to the changing trend of concentration and the online FTIR spectrum.

Table 1. Peak assignments in FTIR analysis

Mode	S1(prod a)		S6 (prod a) on-line		S2 (prod b)		S3 (prod c)		S5 (lauric acid)		S7 (by-prod)	
	pk	cm^{-1}	pk	cm^{-1}	pk	cm^{-1}	pk	cm^{-1}	pk	cm^{-1}	pk	cm^{-1}
OH str	1	3358	1	3258	1	3340	1	3378	1	3220	1	3263
CH_3 a str	2	2960	2	2956	2	2956	2	2959	2	2959	2	2958
CH_2 a str	3	2927	3	2925	3	2920	3	2927	3	2931	3	2920
CH_3 s str	4	2874										
CH_2 s str	5	2854	4	2850	4	2861	4	2854	4	2855	4	2850
C=O str	6	1728	5	1738	5	1740	5	1735	5	1708	5	1727
C=O (COO^-) str							6	1610				
CH_2 a bend	7	1465	6	1458	6	1460	7	1465	6	1464	6	1452
CH_3 a bend	8	1428	7	1433	7	1420			7	1430	7	1433
CH_3 s bend	9	1380	8	1378	8	1380	8	1387	8	1385	8	1385
CN str					9	1256	9	1250				
C(=O)-O str	10	1257	9	1253					9	1260	9	1267
COC a str	11	1177	10	1161	10	1171	10	1184				
COH str	12	1074	11	1107	11	1113	11	1086	10	1112	10	1190
COC s str	13	1040	12	1010	12	1045	12	1047				
COC ether str											11	1103
OH out plane	14	945	13	958	13	958	13	955	11	958	12	958
C-Cl str	15	752	14	748							13	760
CH_2 swing	16	718	15	725	14	720	14	670	12	725	14	725

Reaction mechanism of synthesis 3-chloro-2-hydroxypropyl laurate

For reaction R1, we proposed Scheme 2, as shown in reactions R4-R8, based upon the spectra obtained by online FTIR and the concentration changing trends of the three components. Lauric acid and tetrabutyl ammonium bromide forms a transition state firstly (reaction R4), which promotes the reaction of lauric acid with epichlorophydrin to form product **a**. The by-product of component 3 is formed by the reaction of product **a** with epichlorohydrin (reaction R8).

CMC and surface tension

Figure 5 gives the curve of surface tension (σ) *versus* the logarithm of concentration of the product **c** at 298 K. The surface tension showed a shape decrease at first, then remained at a stable level. The CMC of the product **c** has a lower value of 7.4×10^{-4} mol/L, located at the turning point of the curve. The surface tension at CMC is 30.85 mN/m.

Performance evaluation of bituminous emulsion

The aggregate mixing time was 0 s, while the value for the medium-set asphalt emulsifier (commercial product of TongDa) was 35 s. This indicates that the synthesized emulsifier is a rapid-set asphalt emulsifier. Firstly, the synthesized emulsifier is a new asphalt emulsifier. Secondly, it has the advantages of

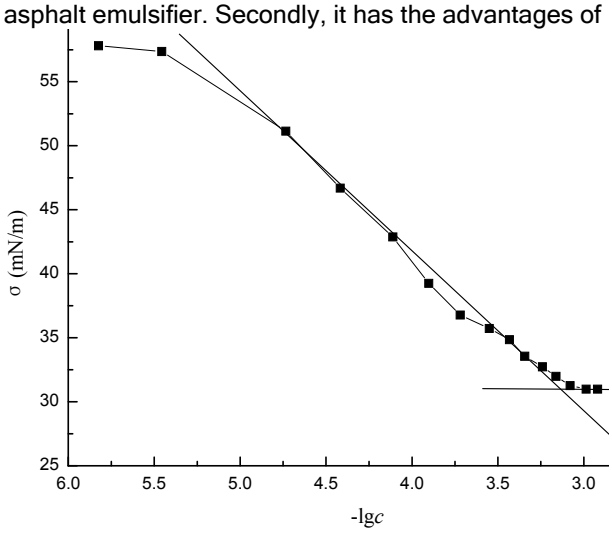


*Figure 5. Surface tension versus the logarithm of product **c** concentration.*

the raw materials of the emulsifier cheap. The raw material cost is 4927 RMB per ton, comparing with 9103 RMB per ton of commercial product of TongDa. Thirdly, the synthesis process is simple, and the technique is mature. Fourthly, the synthesized emulsifier particularly applies to chip seal, where usually the shorter the aggregate mixing time is, the better the effect. Therefore, the synthesized emulsifier can

be designed to perform in a wide variety of applications including chip seal, tack coat, and fog seal in asphalt pavement construction.

CONCLUSIONS

A novel betaine type asphalt emulsifier was synthesized after three steps by the reactions of lauric acid, epichlorohydrin, dimethylamine aqueous solution and sodium chloroacetate. The optimum reaction condition was obtained for the synthesis of the first step of 3-chloro-2-hydroxypropyl laurate. The first synthesis step was monitored by online FTIR technique. The by-product was detected by the online FTIR analysis. Based upon the experimental data, a plausible reaction mechanism was proposed for the reaction. The emulsifier is a rapid-set asphalt emulsifier. It can be designed to perform in a wide variety of applications including chip seal, tack coat, and fog seal in asphalt pavement construction.

Acknowledgments

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NAUČNI RAD

SINTEZA I *ONLINE* FTIR SPEKTROFOTOMETRIJSKO ISPITIVANJE NOVOG EMULGATORA BETAINSKOG TIPA ZA ASFALT

U ovom radu je sintetisan novi emulgator betainskog tipa za asfalt u tri faze reakcijom laurinske kiseline, epihlorohidrina, 3-(N,N,N-dimetil acetoksi amonijum-hlorida)-2-hidroksipropil laurat dimetilamina i natrijum-hloroacetata. Za prvu fazu reakcije gde se sintetiše 3-hloro-2-hidroksipropil laurat nađeni su optimalni reakcioni uslovi. Prinos esterifikacije dostiže 97,1 % pri optimalnim reakcionim uslovima (temperatura 80 °C, vreme reakcije 6 h, molski odnos epihlorhidrin:laurinska kiselina 1:1,5 i maseni udeo katalizatora od 2% u odnosu na laurinsku kiselinu). Hemijska struktura produkta je karakterisana FTIR i ^{1}H-- NMR. Prva faza sinteze 3-hloro-2-hidroksipropil laurata je praćena online FTIR tehnikom. Nuz proizvodi reakcije su detektovani online FTIR analizom. Na osnovu eksperimentalnih podataka pretpostavljen je mehanizam reakcije. Kritična micelarna koncentracija proizvoda ima vrednost nižu od $7{,}4\times10^{-4}$ mol/L. Površinski napon za kritičnu micelarnu koncentraciju je 30,85 mN/m. Dobijeni emulgator je brzi asfalni emulgator.

Ključne reči: asfalt, emulgator, betain, sinteza, online FTIR.

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