The Synthesis and Characterization of a Novel Gemini Cationic Asphalt Emulsifier

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Abstract. A symmetrical Gemini cationic asphalt emulsifier of 1,3-bis(3'-coconut oil amide propyl-dimethyl ammonium chloride)-2-hydroxy propane was synthesized by two steps reaction of coconut oil acyl propyl dimethyl tertiary amine (PKO), epoxy chloropropane and hydrochloric acid. The structure of the product was confirmed by FTIR, ^{1}H NMR and elemental analysis. The optimum reaction condition was obtained by single factor analysis: reaction time 6h, reaction temperature 80℃, feedstock mole ratio of epoxy chloropropane to PKO 0.5. The reaction yield was 54.01% at the optimum reaction conditions. The critical micelle concentration (CMC) of the asphalt emulsifier is 3.65×10^{-2} mol/L. The surface tension at CMC is 27.43mN/m. The emulsifier showed excellent emulsification effect for the asphalt. The prepared bituminous emulsion had higher storage stability. The emulsifier belongs to rapid-set asphalt emulsifier.

Introduction

Emulsified asphalt is a bituminous emulsion, in which the melting asphalt is bended by mechanical force with water containing asphalt emulsifier. It is an oil-in-water emulsion, where the asphalt exists as very tiny particles. Asphalt has many good properties such as excellent adhesion properties, water resistance and aging resistance. It is widely used in waterproofing materials, road repair materials, sealing materials, etc [1-2]. Currently, there are three main forms of asphalt applying: hot asphalt, bituminous emulsion, diluted asphalt [3-4]. Wherein bituminous emulsion is that the asphalt is heated to a molten state, fine asphalt particles are dispersed in emulsifiers and additives in aqueous solution by mechanical force to form oil-in-water emulsion [5-7]. Compared with the other two forms of asphalt applying, bituminous emulsion has many advantages. For example, it can improve construction conditions, reduce costs, save energy, reduce excessive volatilization of asphalt aging and the amount of volatile carcinogens at high temperature [8].

Bituminous emulsion performance depends on the nature of the asphalt emulsifier. According to the different charge properties, asphalt emulsifier is divided into cationic, anionic, nonionic and amphoteric [9]. In recent years, cationic asphalt emulsifier is widely used due to the good performance and high adhesion properties [10]. Negm [11] synthesized a series of cationic surfactants with benzaldehyde, p-aminopyridine, xylene, 1,2-dibromoethane, 1,6-dibromohexane and 1,12-dibromododecane by two-step reaction. Two kinds of Gemini cationic asphalt emulsifier, 1,3-bis(octadecyldimethyl ammonium chloride)-2-propyl alcohol and octadecyl-bis(3-octadecyldimethyl ammonium chloride-2-hydroxypropyl) tertiary amine, were synthesized by the reaction of octadecyl amine, octadecyldimethyl tertiary amine and epichlorohydrin[12]. Li [13] synthesized an asymmetric Gemini cationic surfactants, characterized its structure and discussed the affect factors of stability. Banno [14] synthesized novel cationic surfactants which have biodegradability and chemical recyclability green sustainable. These surfactants were synthesized as following. Firstly, di(iodoalkyl) carbonate 2 was prepared by the carbonate exchange reaction of diphenyl carbonate 1 and iodoalkanol. Then, Gemini-type cationics containing a carbonate linkage were prepared by the reaction of N,N-dimethyl-n-alkylamine and di(iodoalkyl) carbonate 2.

Depending on the breaking speed of asphalt emulsifier, it is divided into slow-set, rapid-set, and medium-set type. Slow-set asphalt emulsifier [15] is the key material for slurry seal. Slurry seal [16] is a solid surface sealing layer which bituminous emulsion, aggregates, water and slag mix by a certain percentage forming a paste and flow of synthetic slurry mixture and then spread evenly on the road. Rapid-set emulsifier [17] is mainly used for chip seal layer and spray patching potholes. When it used as a non-slip layer in road construction, it has the advantages of simple construction process and shortening the time of opening to traffic. Fracturing chippings overlay uses medium-set emulsifier [18].

In previous papers, different kinds of asphalt emulsifiers were synthesized by our research group [12,19,20,21]. A symmetrical Gemini cationic asphalt emulsifier was synthesized by two steps reaction of coconut oil acyl propyl dimethyl tertiary amine (PKO), epoxy chloropropane and hydrochloric acid in this paper. The structure of the emulsifier was confirmed by FTIR, ^{1}H NMR and elemental analysis. The emulsifier has satisfactory emulsification. The emulsifier belongs to rapid-set asphalt emulsifier.

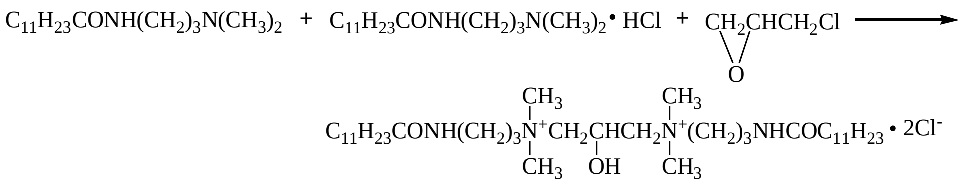
Experimental

Materials and characterization. Coconut oil acyl propyl dimethyl tertiary amine (PKO) was technical grade and obtained from Lianyungang Yihai Chemical Co., Ltd, Lianyungang, China. The other chemical reagents were analytical reagent grade. The asphalt used was AH-90, which was provided by Dongming Petrochemical Company, Dongming, Shandong, China. The mineral aggregate was the mixture of different size particles of marble stone.

The FTIR spectrum was measured at 400 to 4000 cm^{-1} wavenumber range with averaging 16 scans at a resolution of 4 cm^{-1} on a Tensor-27 FTIR spectrophotometer (Bruker, Germany). The ^{1}H NMR spectrum was measured on a Bruker Avance 300M NMR spectrometer (Bruker, Germany), using $CDCl_3$ as solvent and TMS as internal reference. Chemical shifts (δ) were given in ppm. Surface tension of asphalt emulsifier solutions was measured with Krüss Processor Tensiometer K12 (Krüss GmbH, Hamburg, Germany). Elemental analysis was measured by the Elementar vario EL type III element analyzer (Elementar, German).

Synthesis of asphalt emulsifier. Scheme 1 shows the synthesis route of the symmetrical Gemini cationic asphalt emulsifier.

$$C_{11}H_{23}CONH(CH_2)_3N(CH_3)_2 + HCl \longrightarrow C_{11}H_{23}CONH(CH_2)_3N(CH_3)_2 \cdot HCl \quad \text{(R1)}$$



(R2)

Scheme 1 Synthetic route of symmetrical Gemini asphalt emulsifier

Synthesis of coconut oil acyl propyl dimethyl tertiary amine hydrochloride salt: Coconut oil acyl propyl dimethyl tertiary amine (14.23 g, 0.05 mol) was dissolved in 10 mL n-propyl alcohol. At room temperature, concentrated hydrochloric acid (2.5 g, 38%, 0.025mol, 2.12 mL) was dissolved in 6 mL n-propyl alcohol. After being fully dissolved, it was added in n-propyl alcohol solution of PKO. The mixture was stirred for 2 h at room temperature.

1,3-bis(3' -coconut oil amide propyl-dimethyl ammonium chloride)-2-hydroxy propane: The above solution was heated to 80 ℃, then epoxy chloropropane (2.31 g, 0.025 mol) was added in it. The mixture was stirred for 6 h at 80 ℃ in a water bath. The solvent was removed by vacuum distillation. The product was recrystallized by acetone for three times, and vacuum drying for 12h.

The yield measurement. The yield (Y) of the asphalt emulsifier was measured by potassium ferricyanide method. 3.0000 g asphalt emulsifier was weighted and dissolved in 50 mL water, and transferred to a 200 mL volumetric flask. 8 mL acetic acid-sodium acetate buffer solution and 50 mL $K_3[Fe(CN)_6]$ aqueous solution (0.05 mol/L) were added into the volumetric flask. Then, the mixed solution was placed for 1 h. The mixed solution was filtered with dry filter paper. The initial 20 mL filtrate was abandoned. The following 100 mL filtrate was measured accurately to a 250 mL iodine flask. 10 mL 20% potassium iodide aqueous solution and 10 mL dilute HCl (1:1) were added and stored for 1 min. Then, 10 mL 10% $Zn(SO_4)_2$ solution was added and stored for 5 min. The mixed solution was titrated with 0.05 mol/L standard $Na_2S_2O_3$ solution. 3 mL 1% starch indicator was added at the time of the titrated solution being pale yellow. The titration endpoint was at the time of the blue color disappearing. At the same time, a blank titration was also measured.

$$Y = \frac{(V_0 - V) \times C \times 3 \times M}{m \times n \times 2 \times 100/250} \times 100\% \tag{1}$$

Where, Y means the yield of the asphalt emulsifier, %. V means the consumed volume of $Na_2S_2O_3$ standard solution, mL. V_0 means the consumed volume of $Na_2S_2O_3$ standard solution in blank test, mL. C means the concentration of $Na_2S_2O_3$ standard solution, mol/L. M means the total mass of the asphalt emulsifier, gram. m means the mass of asphalt emulsifier to be titrated, gram. n means the mole of PKO, mol.

Surface tension and CMC. Surface tension of the asphalt emulsifier solutions decreases sharply with the increase of concentration, and nearly does not change when the concentration gets CMC. The critical micelle concentration and the surface tension at CMC were at the turning point of the curve of surface tension to logarithm of concentration.

Performance test of bituminous emulsion.

Preparation of bituminous emulsion: 15.0 g asphalt emulsifier was dissolved in 200 g water, then the solution was heated to 65 ℃. The pH value of the asphalt emulsifier aqueous solution was adjusted to 2.0 by adding dilute HCl (1:1). 300 g asphalt (AH-90) was heated to 125 ℃. The bituminous emulsion was obtained by mixing the asphalt emulsifier aqueous solution and the asphalt at a colloid mill for 1 min.

Mixing experiment: 100 g Mineral aggregate, 1 g cement and 8 g water were mixed in a bowl. Then, 11 g bituminous emulsion was added, and the mixture was stirred at a speed of 60 revolutions per minute. The mixing time was measured by observation of the mixing appearance. The room temperature was 32.0 ℃.

Results and discussion

Reaction temperature. The reaction conditions were fixed at: reaction time 6 h, feedstock mole ratio of epichlorohydrin to coconut oil acyl propyl dimethyl tertiary amine 1:2. Fig. 1 gives the yield (Y) versus reaction temperature. As shown in Fig. 1, the yield increases with the reaction temperature and gets maximum value at 80℃, then decreases with the reaction temperature.

Reaction time. The reaction conditions were fixed at: reaction temperature 80 ℃, feedstock mole ratio of epichlorohydrin to coconut oil acyl propyl dimethyl tertiary amine 1:2. Fig. 2 gives the yield (Y) versus reaction time. As shown in Fig. 2, the yield increases with the reaction time and gets maximum value at 6h, then decreases with the reaction time.

Feedstock mole ratio. The reaction conditions were fixed at: reaction temperature 80 ℃, reaction time 6 h. Fig. 3 gives the yield (Y) versus feedstock mole ratio of epichlorohydrin to coconut oil acyl propyl dimethyl tertiary amine (m). As shown in Fig. 3, the yield decreases with the feedstock mole ratio when the feedstock mole ratio greater than 0.5.

Therefore, the optimum reaction conditions can be got: reaction temperature 80 ℃, feedstock mole ratio of epichlorohydrin to coconut oil acyl propyl dimethyl tertiary amine 0.5, reaction time 6 h. The yield is 54.01% at the optimum reaction conditions.

FTIR characterization. Figure 4 is the FTIR spectrum of the asphalt emulsifier. The absorption at 3436 cm^{-1} (peak 1) originates from the O-H stretching. The absorption at 3278 cm^{-1} (peak 2) originates from the N-H stretching in amide. The absorption at 2920 cm^{-1} (peak 3) originates from the methyl asymmetrical stretching. The absorption at 2853 cm^{-1} (peak 4) originates from the methyl symmetrical stretching. The absorption at 1645 cm^{-1} (peak 5) originates from the C=O stretching in amide. The absorption at 1549 cm^{-1} (peak 6) originates from the N-H bending in amide. The absorption at 1472 cm^{-1} (peak 7) originates from the C-N stretching in amide. The absorption at

1263 cm^{-1} (peak 8) originates from the C-O stretching in hydroxyl group. The absorption at 998 cm^{-1} (peak 9) originates from the N-H out-of-plane bending. The absorption at 726 cm^{-1} (peak 10) originates from the methylene in-plane swing vibration.

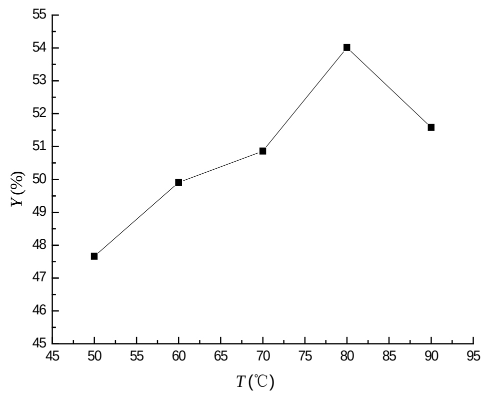


Fig.1. Yield versus reaction temperature

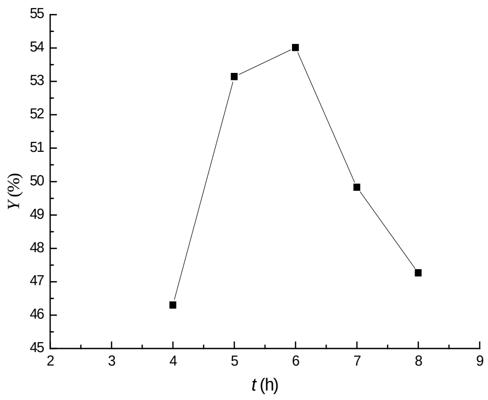


Fig.2. Yield versus reaction time

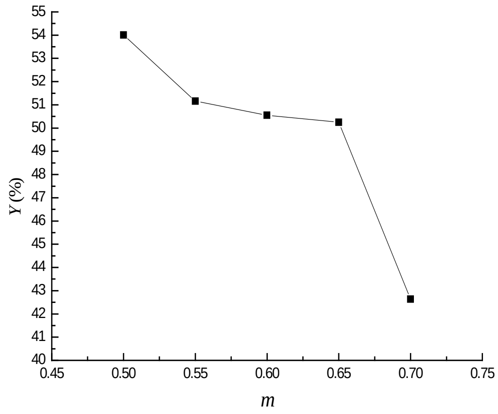


Fig.3. Yield versus feedstock mole ratio

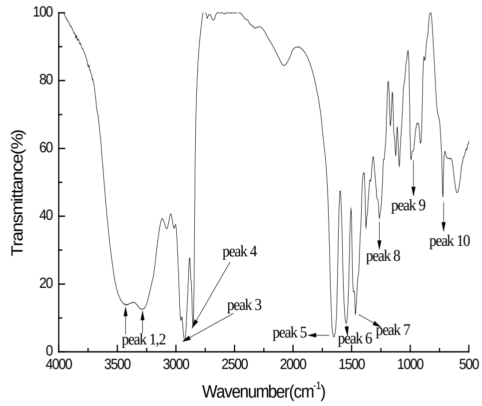


Fig.4. FTIR spectrum of the asphalt emulsifier

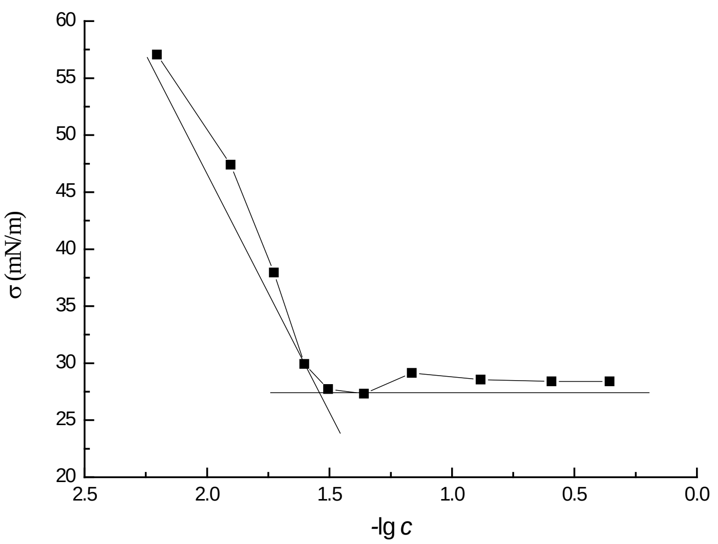


Fig.5. Surface tension vs. the logarithm of concentration

^{1}H NMR analysis. ^{1}H NMR($CDCl_3$, 300Hz) δ: 0.96($-C\underline{H}_3$, t,6H);1.31($CH_3-(C\underline{H}_2)_8-$, m,32H); 1.61 ($C_9H_{19}-C\underline{H}_2-$, s,4H); 2.01($-N^+(CH_3)_2-CH_2-C\underline{H}_2-CH_2-$, d,4H); 2.18($C_{10}H_{21}-C\underline{H}_2-$, t,4H); 3.21-3.70($-N^+(C\underline{H}_3)_2-C\underline{H}_2-CH_2-C\underline{H}_2-$,m,20H);3.73-3.82($-C\underline{H}_2-CH(OH)-C\underline{H}_2-$,m,4H);

3.90-4.10(-CH_2-C$\underline{H}$ (OH)-CH_2-, s, 1H); 6.50-6.85 (-OH, s,1H); 7.70-8.09(-NH-, s,2H) ppm. Therefore, the results of ^{1}H NMR analysis conform to the chemical structure of the asphalt emulsifier.

Elemental analysis. Anal.: Calcd. for C37H78N4O3Cl2: C, 63.70%; H, 11.19 %; N, 8.03 %. Found: C, 57.43 %; H, 11.87 %; N, 7.14 %.

CMC and surface tension. Figure 5 gives the surface tension (σ) versus the logarithm of the asphalt emulsifier concentration (*c*) at 298 K. The surface tension showed a shape decrease firstly, then kept at a constant level. The CMC of the asphalt emulsifier is 3.65×10^{-2} mol/L. The surface tension at CMC is 27.43 mN/m.

Performance test of bituminous emulsion. The symmetrical Gemini cationic asphalt emulsifier has good emulsifying ability for AH-90 asphalt. The bituminous emulsion to be prepared had higher storage stability. There was no separation of aqueous phase and asphalt phase appeared after 5 days. The mixing time was 5 s, which indicated that the emulsifier is a rapid-set asphalt emulsifier. It can be applied to the application of tack coat, fog seal and chip seal in asphalt pavement construction.

Conclusion

A symmetrical Gemini cationic asphalt emulsifier was synthesized by coconut oil acyl propyl dimethyl tertiary amine (PKO), epoxy chloropropane and hydrochloric acid. The optimum reaction condition, the critical micelle concentration (CMC) and the surface tension at CMC of the asphalt emulsifier were obtained. The emulsifier belongs to a rapid-set asphalt emulsifier. It can be applied to the application of tack coat, fog seal and chip seal in asphalt pavement construction.

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