The Synthesis and Characterization of Novel Bis-cationic Asphalt Emulsifier

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Abstract. Three novel bis-cationic asphalt emulsifiers were synthesized by two steps reaction of N-tallow-1,3-diaminopropane, methyl acrylate, sodium hydroxide and chloroacetic acid. The structure of the product was confirmed by FTIR, ¹H NMR and elemental analysis. The emulsifier exhibits satisfactory emulsification. The prepared bituminous emulsion showed higher storage stability. The emulsifier belongs to medium-set and slow-set asphalt emulsifier. It can be designed to perform in a wide variety of applications including tack coat, fog seal, chip seal and slurry seal in asphalt pavement construction.

1 Introduction

Asphalt has many excellent properties such as good adhesion properties, aging resistance and water resistance. It is widely used in road repair, waterproofing materials, sealing materials, etc [1]. Emulsified asphalt performance depends on the nature of the asphalt emulsifier. According to the different charge of asphalt emulsifier, it is divided into cationic, anionic, nonionic, amphoteric [2]. In recent years, it is widely used and studied due to the good performance, high adhesion of cationic asphalt emulsifier [3]. Negm [4] 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. Li [5] synthesized an asymmetric Gemini cationic surfactants, characterized its structure and discussed the affect factors of stability.

Depending on the breaking speed of asphalt emulsifier, it is divided into slow, rapid, and medium set type. Slow set asphalt emulsifier [6] is a key material for slurry seal. Slurry seal [7] is solid surface sealing layer which emulsified asphalt, water, aggregates 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 [8] is mainly used for chip seal layer and spray patching potholes. Fracturing chippings overlay often uses the medium set type emulsifier [9].

In previous papers, we have synthesized different kinds of asphalt emulsifiers [10-14]. Three novel bis-cationic asphalt emulsifiers were synthesized by two steps reaction in this paper. The structure of the emulsifier was confirmed by FTIR, ¹H NMR and elemental analysis.

2 Experimental

2.1 Materials and characterization

N-tallow-1,3-diaminopropane was technical grade and obtained from Zibo HuaRun Chemical Co., Ltd, Zibo, China. All the other reagents were of analytical reagent grade and used without further purification. The asphalt used 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. The 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. The ¹H NMR spectra were recorded on a Bruker Avance 300M NMR spectrometer (Bruker, Germany), using D₂O as solvent and TMS as internal reference. Chemical shifts (δ) were given in ppm. Elemental analyses were performed by the Elementar vario EL type III element analyzer (Elementar, German).

2.2 Synthesis of asphalt emulsifier

Scheme 1 shows the synthesis route of the bis-cationic asphalt emulsifier (A).

Scheme 1. Synthetic route of asphalt emulsifier (A).

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N-tallow-1,3-diaminopropane (326.0 g, 1.00 mol) and 400 g isopropanol were added in a three-necked flask, and heated to 70 °C in a water bath. Methyl acrylate (90.3 g, 1.05 mol) was added dropwise and reacted for 4h. The reaction solution was processed by vacuum distillation to remove the solvent, then recrystallized with anhydrous ethanol for three times to obtained the intermediate.

Sodium chloroacetate aqueous solution was synthesized by the reaction of 196.6 g (2.08 mol) chloroacetic acid, 83.2 g (2.08 mol) NaOH and 560.0 g distilled water. Then the sodium chloroacetate aqueous solution was added dropwise to the reaction solution synthesized above and stirred for 5 h at 65 °C in water bath. Finally, the reaction solution was processed by vacuum distillation to remove the solvent, then recrystallized with anhydrous ethanol for three times to obtained the product.

Scheme 2 shows the synthesis route of the bis-cationic asphalt emulsifier (B).

Scheme 2. Synthetic route of asphalt emulsifier (B).

N-tallow-1,3-diaminopropane (326.0 g, 1.00 mol) and 400 g isopropanol were added in a three-necked flask, and heated to 70 °C in a water bath. Methyl acrylate (175.5 g, 2.04 mol) was added dropwise and reacted for 4h. The reaction solution was processed by vacuum distillation to remove the solvent, then recrystallized with anhydrous ethanol for three times to obtained the intermediate.

Sodium chloroacetate aqueous solution was synthesized by the reaction of 196.6 g (2.08 mol) chloroacetic acid, 83.2 g (2.08 mol) NaOH and 560.0 g distilled water. Then the sodium chloroacetate aqueous solution was added dropwise to the reaction solution synthesized above and stirred for 5 h at 65 °C in water bath. Finally, the reaction solution was processed by vacuum distillation to remove the solvent, then recrystallized with anhydrous ethanol for three times to obtained the product.

Scheme 3 shows the synthesis route of the bis-cationic asphalt emulsifier (C).

Scheme 3. Synthetic route of asphalt emulsifier (C).

N-tallow-1,3-diaminopropane (326.0 g, 1.00 mol) and 400 g isopropanol were added in a three-necked flask, and heated to 70 °C in a water bath. Methyl acrylate (261.6 g, 3.04 mol) was added dropwise and reacted for 4h. The reaction solution was processed by vacuum distillation to remove the solvent, then recrystallized with

anhydrous ethanol for three times to obtained the intermediate.

Sodium chloroacetate aqueous solution was synthesized by the reaction of 196.6 g (2.08 mol) chloroacetic acid, 83.2 g (2.08 mol) NaOH and 560.0 g distilled water. Then the sodium chloroacetate aqueous solution was added dropwise to the reaction solution synthesized above and stirred for 5 h at 65 °C in water bath. Finally, the reaction solution was processed by vacuum distillation to remove the solvent, then recrystallized with anhydrous ethanol for three times to obtained the product.

2.3 Performance test of bituminous emulsion

2.3.1 Preparation of bituminous emulsion

12.5 g emulsifier was dissolved in 200 ml water, then the solution was heated to 60 °C. The pH value of the aqueous solution was adjusted to 2.0 by adding hydrochloric acid. 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.

2.3.2 Demulsification speed test of bituminous emulsion

Demulsification speed of bituminous emulsion was determined according to T0658-1993 standard. B type mineral aggregate (200 g) and water (30 g) were placed in a 500-mL bowl. Bituminous emulsion (50 g) was then added, and the mixture was stirred for 1 min at 60 revolutions per minute. The mixing time and the appearance were recorded by observing the uniform of the aggregate mixing performance.

3 Results and discussion

3.1 Structure characterization of intermediate

Figure 1 gives the FTIR spectrum of the intermediate in Scheme 1. The absorption at 3275 cm⁻¹ (peak 1) is assigned to the N-H stretching. The absorption at 2917 cm⁻¹ (peak 2) is assigned to the methyl asymmetrical stretching. The absorption at 2854 cm⁻¹ (peak 3) is assigned to the methylene symmetrical stretching. The absorption at 1735 cm⁻¹ (peak 4) is assigned to C=O stretching of ester. The absorption at 1569 cm⁻¹ (peak 5) is assigned to N-H bending vibration. The absorptions at 1470 cm⁻¹ (peak 6) and 1376 cm⁻¹ (peak 7) are assigned to the methyl asymmetrical and symmetrical bending vibration, respectively. The absorption at 1207 cm⁻¹ (peak 8) is assigned to C-N stretching. The absorption at 1125 cm⁻¹ (peak 9) is assigned to C-O-C stretching. The absorption at 724 cm⁻¹ (peak 10) is assigned to methylene in-plane swing vibration. Therefore, the FTIR spectrum agrees with the chemical structure of the intermediate to be synthesized.

3.2 Structure characterization of asphalt emulsifier (A)

Figure 2 gives the FTIR spectrum of asphalt emulsifier (A) in Scheme 1. The absorption at 3250-3500 cm^{-1} (peak 1) is assigned to the superimposed peak of O-H and N-H stretching. The absorption at 2918 cm^{-1} (peak 2) is assigned to the methyl asymmetrical stretching. The absorption at 2846 cm^{-1} (peak 3) is assigned to the methylene symmetrical stretching. The absorption at 1737 cm^{-1} (peak 4) is assigned to C=O stretching of carboxylic acid. The absorption at 1634 cm^{-1} (peak 5) is assigned to C=O stretching of carboxylate. The absorptions at 1470 cm^{-1} (peak 6) and 1395 cm^{-1} (peak 7) are assigned to the methyl asymmetrical and symmetrical bending vibration, respectively. The absorption at 1207 cm^{-1} (peak 8) is assigned to C-N stretching. The absorption at 1068 cm^{-1} (peak 9) is assigned to C-OH stretching. The absorption at 926 cm^{-1} (peak 10) is assigned to O-H out-of-plane swing vibration of carboxylic acid. The absorption at 717 cm^{-1} (peak 11) is assigned to methylene in-plane swing vibration. Therefore, the FTIR spectrum agrees with the chemical structure of asphalt emulsifier (A) to be synthesized.

^1H NMR (300 MHz, D_2O), δ : 0.81 (t, 3H, $-\text{CH}_3$), 1.22 (s, 30H, $-\text{CH}_2-$), 1.66 (s, 2H, $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2-$), 2.16 (s, 2H, $-\text{NH}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}^+$), 2.59 (m, 2H, $-\text{NH}^+\text{CH}_2\text{CH}_2\text{COOH}$), 3.12-3.67 (m, 8H, $-\text{CH}_2\text{NH}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}^+\text{CH}_2\text{CH}_2\text{COOH}$), 3.73-4.24 (m, 4H, $-\text{CH}_2\text{COONa}$) ppm.

Anal.: Calcd. for $\text{C}_{28}\text{H}_{54}\text{N}_2\text{O}_6\text{Cl}_2\text{Na}_2$: C, 46.47%; H, 6.92 %; N, 3.87 %. Found: C, 47.02 %; H, 9.43 %; N, 3.98 %.

Figure 1. FTIR of intermediate in Scheme 1.

Figure 2. FTIR spectrum of asphalt emulsifier (A).

3.3 Structure characterization of asphalt emulsifier (B)

Figure 3 gives the FTIR spectrum of asphalt emulsifier (B) in Scheme 2. The absorption at 3250-3500 cm^{-1} (peak 1) is assigned to the superimposed peak of O-H and N-H stretching. The absorption at 2925 cm^{-1} (peak 2) is assigned to the methyl asymmetrical stretching. The absorption at 2850 cm^{-1} (peak 3) is assigned to the methylene symmetrical stretching. The absorption at 1735 cm^{-1} (peak 4) is assigned to C=O stretching of carboxylic acid. The absorption at 1605 cm^{-1} (peak 5) is assigned to C=O stretching of carboxylate. The absorptions at 1470 cm^{-1} (peak 6) and 1395 cm^{-1} (peak 7) are assigned to the methyl asymmetrical and symmetrical bending vibration, respectively. The absorption at 1254 cm^{-1} (peak 8) is assigned to C-N stretching. The absorption at 1068 cm^{-1} (peak 9) is assigned to C-OH stretching. The absorption at 917 cm^{-1} (peak 10) is assigned to O-H out-of-plane swing vibration of carboxylic acid. The absorption at 701 cm^{-1} (peak 11) is assigned to methylene in-plane swing vibration. Therefore, the FTIR spectrum agrees with the chemical structure of asphalt emulsifier (B) to be synthesized.

^1H NMR (300 MHz, D_2O), δ : 0.85 (t, 3H, $-\text{CH}_3$), 1.26 (s, 30H, $-\text{CH}_2-$), 1.70 (s, 2H, $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2-$), 2.24 (s, 2H, $-\text{NH}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}^+$), 2.57-2.64 (m, 4H, $-\text{CH}_2\text{CH}_2\text{COOH}$), 3.01-3.58 (m, 10H, $-\text{CH}_2\text{NH}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_2\text{CH}_2\text{COOH})_2$), 3.83-4.28 (s, 4H, $-\text{CH}_2\text{COONa}$) ppm.

Figure 3. FTIR spectrum of asphalt emulsifier (B).

3.4 Structure characterization of asphalt emulsifier (C)

Figure 4 gives the FTIR spectrum of asphalt emulsifier (C) in Scheme 3. The absorption at 3427 cm^{-1} (peak 1) is assigned to O-H stretching. The absorption at 2925 cm^{-1} (peak 2) is assigned to the methyl asymmetrical stretching. The absorption at 2854 cm^{-1} (peak 3) is assigned to the methylene symmetrical stretching. The absorption at 1733 cm^{-1} (peak 4) is assigned to C=O stretching of carboxylic acid. The absorption at 1606 cm^{-1} (peak 5) is assigned to C=O stretching of carboxylate. The absorptions at 1463 cm^{-1} (peak 6) and 1395 cm^{-1} (peak 7) are assigned to the methyl asymmetrical and symmetrical bending vibration, respectively. The absorptions at 1261 cm^{-1} (peak 8) and 1197 cm^{-1} (peak 9) are assigned to the C-N stretching and C-OH stretching, respectively.

are assigned to C-N stretching. The absorption at 1072 cm^{-1} (peak 10) is assigned to C-OH stretching. The absorption at 930 cm^{-1} (peak 11) is assigned to O-H out-of-plane swing vibration of carboxylic acid. The absorption at 772 cm^{-1} (peak 12) is assigned to methylene in-plane swing vibration. Therefore, the FTIR spectrum agrees with the chemical structure of asphalt emulsifier (C) to be synthesized.

^1H NMR (300 MHz, D_2O), δ : 0.85(t, 3H, $-\text{CH}_3$), 1.25(s, 30H, $-\text{CH}_2-$), 1.70(s, 2H, $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2-$), 2.24(s, 2H, $-\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+-$), 2.63-2.85(m, 6H, $-\text{CH}_2\text{CH}_2\text{COOH}$), 2.93-3.51(m, 12H, $-\text{CH}_2\text{N}^+(\text{CH}_2\text{CH}_2\text{COOH})-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_2\text{CH}_2\text{COOH})_2$), 3.89-4.25(s, 4H, $-\text{CH}_2\text{COONa}$) ppm.

Figure 4. FTIR spectrum of asphalt emulsifier (C).

3.5 Demulsification speed test of bituminous emulsion

The emulsifiers have excellent emulsifying ability to AH-90 asphalt. The prepared bituminous emulsion showed higher storage stability. Table 1 gives the mixing time and the types of the asphalt emulsifiers. It can be designed to perform in a wide variety of applications including tack coat, fog seal, chip seal and slurry seal in asphalt pavement construction.

Table 1. Demulsification speed test of bituminous emulsion.

asphalt emulsifier	mixing time (s)	types of the asphalt emulsifier
A	12	medium-set
B	47	slow-set
C	14	medium-set

4 Summary

Three novel bis-cationic asphalt emulsifiers were synthesized by two steps reaction of N-tallow-1,3-diaminopropane, methyl acrylate, sodium hydroxide and chloroacetic acid. The emulsifier belongs to medium-set and slow-set asphalt emulsifier. It can be designed to

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

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