Synthesis and Properties of Bifunctional Asphalt Emulsifier

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Abstract. Cationic asphalt emulsifier needs to adjust the system to acidity during use, which will bring potential corrosion hazard to emulsified asphalt production equipment. In this paper, a bifunctional asphalt emulsifier with emulsification and corrosion inhibition was synthesized. The results show that the bifunctional cationic asphalt emulsifier has excellent surface activity, the critical micelle concentration is 56.23 μg/g, and the surface tension value is 25.79 mN/m, the prepared emulsified asphalt has good stability, and the stability of 1d and 5d are 0.28 % and 0.97 %, respectively. At the same time, the asphalt emulsifier has good corrosion inhibition performance for different material test pieces and different corrosive environments. The mechanism study shows that the emulsifier forms a dense adsorption protective film on the metal surface, so that the metal surface in the acid environment is protected from corrosion and the corrosion rate is lowered.

1. Introduction
The traditional hot-mix asphalt road construction process has the disadvantages of high energy consumption, high pollution and short construction season [1]. The emulsified asphalt can better solve the above problems and shows good economic and environmental benefits in the road pavement engineering [2]. After nearly a century of research and development, the application of emulsified asphalt as a road material has been greatly developed in its type and application. At present, emulsified asphalt technology has become one of the most important means of road maintenance. Among them, cationic asphalt emulsifier is widely used in road maintenance projects such as micro-surface [3], slurry seal, gravel seal, adhesive layer oil, and penetrating road surface, because the prepared emulsified asphalt has strong adhesion to the aggregate surface and has good anti-flaking performance [4-6].

In the production process, cationic emulsified asphalt generally needs to adjust the pH value of the emulsifier aqueous solution to acidity [7-9]. Therefore, the acidic emulsifier aqueous solution will expose the equipment (such as storage tank, colloid grinding head, transfer pump and pipe) to the acidic corrosive medium. Especially in the preparation of the emulsifier aqueous solution, the pH value of the solution local position is too low and the acid concentration is too high, which brings safety hazard to the emulsified asphalt production unit.

In this paper, a bifunctional asphalt emulsifier with emulsification and corrosion inhibition was synthesized to reduce the corrosion hazard in the preparation of emulsified asphalt. The surface activity and emulsifying properties of asphalt were studied. The static corrosion evaluation method was used to test the corrosion inhibition effect of the emulsifier in different corrosion environment, and the corrosion inhibition mechanism was discussed.
2. Experimental part

2.1. Experimental reagents and instruments

Reagents: potassium hydroxide; hydrochloric acid; stearic acid; petroleum ether (Boiling range 90~120 °C); hydrochloric acid; triethylenetetramine; formaldehyde; acetophenone; phenolphthalein; bromophenol blue, all chemically pure, Sinopharm Group Chemical Reagents Ltd.

Instruments: PHSJ-3F Potentiometric Titrator; Analytical Balance ME204T/02; Colloid Mill (HerberPink); Surface Tension Meter (Germany dataphysics DCAT21); JSM-5410LN Scanning Electron Microscope; 98-1-B type Electronic Thermostat Electric Sleeve; ZXZ rotary vane type vacuum pump.

2.2. Experimental methods

2.2.1. Emulsifier synthesis method. The emulsifier was synthesized by amidation and imidazoline cyclization reactions using organic acids and polyamines as raw materials.

First, a certain molar ratio of stearic acid and triethylenetetramine were added into a 500 ml three-necked flask, and petroleum ether was added as a water-carrying agent. The amount of petroleum ether was about 10 wt% of the total mass of the reaction system. The reaction was carried out at 140-180 °C for 3.0 to 4.0 hours, and the water formed by the reaction and the acid value of the reaction product were measured. Then, the reaction product was subjected to a vacuum distillation operation at 0.065 MPa (vacuum degree) and 120 °C to remove the water-carrying agent. The amide product after distillation under reduced pressure was reacted at 0.092 MPa (vacuum degree) at 250~260 °C for 3.5 to 4.0 hours to form an imidazoline. Then, at a temperature lower than 100 °C, formaldehyde and acetophenone were slowly added to the imidazoline at a molar ratio of 1:1:1, and the reaction was stirred for 2 hours to obtain a Mannich base type imidazoline emulsifier.

2.2.2. Preparation of emulsified asphalt. A certain amount of asphalt emulsifier was added to 400 g of water for dissolution, and the aqueous solution was adjusted to a certain pH with hydrochloric acid, and the aqueous solution was heated to 50 °C. 600 g of asphalt was weighed and heated to 135 °C. The above aqueous emulsifier solution was added to a colloid mill, and then a colloid mill was started, followed by slowly adding hot bitumen under stirring and emulsification in a colloid mill for 1 min. The emulsified asphalt was taken out and quickly cooled to room temperature.

2.2.3. Determination of emulsifier and emulsified asphalt properties. The surface tension of the emulsifier was measured by a sheet method. The target product solutions of different concentrations were prepared separately, and the surface tension σ at 25 °C was measured. Then, the measured surface tension σ was plotted against lgC to obtain the critical micelle concentration (CMC) value of the target product and the surface tension value at CMC.

The stability of the emulsified asphalt was measured according to T0655-1993 (Emulsified Asphalt Storage Stability Test), and the storage stability was measured for 1 day and 5 days, respectively.

2.2.4. Corrosion assessment test method. Corrosion inhibition performance of the emulsifier was evaluated by using static corrosion weight loss method. The corrosive medium was a certain concentration of emulsifier hydrochloric acid aqueous solution, the treated corrosion test piece was placed in a corrosive medium under atmospheric pressure, and soaked for 4 hours at a certain test temperature. Then, the test piece was taken out, washed, and dried. Weighing, calculating the weight loss, taking the results of three sets of parallel tests to calculate the average corrosion rate, according to the corresponding blank test to obtain the corrosion inhibition rate.
2.2.5. **Research methods of corrosion mechanism.** The surface morphology of the test piece was studied using a scanning electron microscope. The corrosion test piece to be tested was dried with filter paper and naturally dried at room temperature, and the surface of the representative test piece was selected as the analysis surface. Finally, the acceleration voltage of the scanning electron microscope was selected to be 30 kV.

3. **Results and discussion**

3.1. **Emulsifying properties of bifunctional asphalt emulsifier**

The different mass fractions were prepared as aqueous emulsifier solutions, and the surface tension and CMC value of the bifunctional asphalt emulsifier were measured. Taking $\lg C$ as the abscissa, the surface tension $\sigma$ is plotted on the ordinate, as shown in Figure 1.

![Figure 1. Plot of the $\lg C$ VS $\sigma$](image)

It can be seen from Fig. 1 that the turning point of the curve is $\lg C = -4.25$, so that the critical micelle concentration value of the product is $56.23 \mu g / g$ (mass fraction). The surface tension value at the critical micelle concentration was $25.79 mN/m$. This product has a lower critical micelle concentration and a $\sigma$ CMC value compared to other emulsifier products.

The synthetic product was used as an emulsifier to emulsify Karamay AH-90 asphalt. The emulsification effect of the emulsifier on the asphalt was evaluated mainly by the storage stability of the emulsified asphalt. The specific emulsification conditions and stability are shown in Table 1.

| Table 1. Asphalt emulsification process conditions |
|-----------------------------------------------|
| **Asphalt** | Karamay AH-90 |
| Asphalt dosage | 60 wt% |
| Emulsifier dosage | 2.4 wt% |
| Asphalt temperature | 135°C |
| Aqueous emulsifier solution temperature | 50°C |
| Storage stability | 1d, % | 0.28 |
| | 5d, % | 0.97 |
It can be seen from Table 1 that the emulsified asphalt has good storage stability when the amount of emulsifier is 2.4 wt%, and the synthetic bifunctional asphalt emulsifier has good emulsifying properties for Karamay AH-90 asphalt.

3.2. Corrosion inhibition performance of Bifunctional asphalt emulsifier

3.2.1. Corrosion assessment under different pH conditions. Using N80 as the corrosion test piece, the corrosion inhibition performance of the asphalt emulsifier prepared at pH 1-5 was investigated. Other corrosion conditions were: corrosion temperature 90 °C, corrosion time 4 h. The experimental results are shown in Table 2.

| pH | emulsifier dosage /wt% | corrosion rate /g.m\(^{-2}\).h\(^{-1}\) | corrosion inhibition rate / % |
|----|-----------------------|-----------------------------------|-----------------------------|
| 1  | 0                     | 63.45                             | 97.92                       |
|    | 2                     | 1.32                              |
| 2  | 0                     | 17.93                             | 96.88                       |
|    | 2                     | 0.56                              |
| 3  | 0                     | 2.87                              | 85.71                       |
|    | 2                     | 0.41                              |
| 4  | 0                     | 0.68                              | 48.53                       |
|    | 2                     | 0.35                              |
| 5  | 0                     | 0.54                              | 44.44                       |
|    | 2                     | 0.30                              |

It can be seen from Table 2 that in the blank test without asphalt emulsifier, when the pH value is lower than 3, the corrosion rate of the corrosion medium to the N80 test piece is very large. If there is no protective measure, it will cause serious corrosion. As the acid concentration decreases, the corrosion rate decreases. After adding 2 wt% of the bifunctional asphalt emulsifier into the aqueous solution, even at pH 1, the corrosion rate will fall below 1 g.m\(^{-2}\).h\(^{-1}\), and the corrosion inhibition rate will reach 97.92 %. It indicates that the bifunctional emulsifiers has good corrosion inhibition performance on N80. When the pH value is greater than 4, since the corrosion rate of the blank test itself is already very low, the corrosion inhibition rate is not obvious after the addition of the asphalt emulsifier.

3.3. Discussion on Corrosion Inhibition Mechanism of Bifunctional Asphalt Emulsifier

In order to further investigate the mechanism of the corrosion inhibition of the bifunctional emulsifier, the surface of the test piece of the original test piece, the blank test piece and the test piece in the bifunctional emulsifier hydrochloric acid aqueous solution were observed by SEM. It was found through the photo that the surface of the original test piece (Fig. 2-a) has a small number of regular parallel scratches, although it is affected by the processing such as polishing and polishing, but the surface is generally flat and smooth. In the blank test, after the test piece was immersed in a corrosive medium of pH 1 for 4 hours, it was found that there were many corrosion pits and severe local corrosion (Fig. 2-b). In the 2 wt% bifunctional emulsifier aqueous hydrochloric acid system, although the pH value is also adjusted to 1, it can be seen from Fig. 2-c that a relatively uniform and dense protective film was formed on the surface of the test piece, which was under the protection of this film. The surface of the test piece was protected from the strong erosion by the corroded medium, and the corrosion rate was significantly reduced compared with the blank test.
Figure 2. SEM images of the surface of the test piece (a: the original test piece; b: the test piece in the corrosive medium of pH 1 for 4 hours; c: the test piece in the bifunctional emulsifier aqueous hydrochloric acid solution)

4. Conclusion
In this paper, a bifunctional asphalt emulsifier with emulsification and corrosion inhibition was synthesized. The surface activity and emulsifying properties were studied. The corrosion inhibition performance of the bifunctional asphalt emulsifier was tested. The following conclusions were obtained:

(1) The prepared bifunctional cationic asphalt emulsifier has good surface activity, the CMC value is low, and the surface tension value at CMC is 25.79 mN/m, and the prepared emulsified asphalt has good storage stability.

(2) Under the acidic conditions of emulsified asphalt production, the prepared bifunctional asphalt emulsifier has good corrosion inhibition performance for different corrosive environments;

(3) SEM showed that a dense adsorption protective film was formed on the metal surface after adding the prepared asphalt emulsifier. Under the protection of the protective film, the metal surface under the acid environment was protected from corrosion and reduced.

Acknowledgments
This work was sponsored by the Weifang University Doctoral Research Fund (2018BS08) and Weifang Science & Development Plan (2018GX019).

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