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A New Type Surfactant for Enhanced Oil Recovery

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A new surfactant namely 2-*p*-alkylbenzoyl-1-carboxyethane sulfonates (ABCES) has been synthesized by Friedel-Crafts acetylation and sulfonation reaction using surfural extracted petroleum fraction. The presence of sulfo and carboxyl groups in the synthesized compound was identified by IR analysis. The critical micellar concentration (CMC) and minimum surface tension of ABCES at 20 ºC is 1.76 mg/L and 36.18 mN/m, respectively. The surfactant was superior to petroleum sulfonate (PS) which is prepared with petroleum fraction. Ultralow interfacial tension were obtained by 0.3 % ABCES solution in a 0.6-1.2 % Na_2CO_3 solution and were maintained at 0.3 % ABCES + 1.2 % Na_2CO_3 solution with Ca^{2+} + Mg^{2+} concentration ≤ 600 mg/L while for PS Ca^{2+} + Mg^{2+} concentration ≤ 300 mg/L. ABCES was acted as a low cost, highly tolerant to Ca^{2+} + Mg^{2+} surfactant for enhanced oil recovery.

Key Words: Friedel-Crafts acetylation, Sulfonation, Surfactant.

INTRODUCTION

Surfactants are widely used in the enhanced oil recovery (EOR)[1,2]. Nowadays, the work is concentrated on two aspects. First, the price of surfactant is the main reason that the surfactant can not spread widely for EOR. The second aspect is the surfactant should have the pronounced tolerant to the Ca^{2+} + Mg^{2+}. It is known that Ca^{2+} + Mg^{2+} ions can complex with surfactant, resulting in the deterioration of the interfacial active for surfactant[3-5]. In order to resolve this problem, a new surfactant referred as 2-*p*-alkylbenzoyl-1-carboxyethane sulfonates (ABCES) has been synthesized by Friedel-Crafts acetylation and sulfonation reaction using surfural extracted petroleum fraction. The interfacial tension is compared with petroleum sulfonate (PS) which is prepared with petroleum fraction. The current work may be building block for the further study.

EXPERIMENTAL

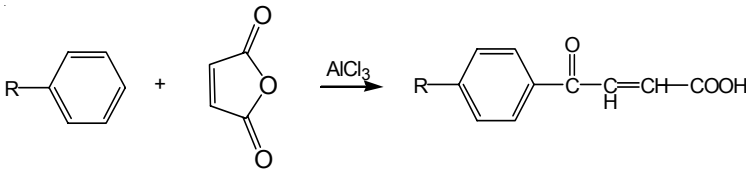
cis-Butenedioic anhydride, $AlCl_3$, H_2SO_4, dichloroethane, *iso*propyl alcohol and hexane were analytical reagents.

Crude oil: Surfural extracted petroleum fraction (The content of aromatic was about 52 % and the molecular weight was about 432) and petroleum fraction (the content of aromatic was about 20 % and the molecule weight was about 382).

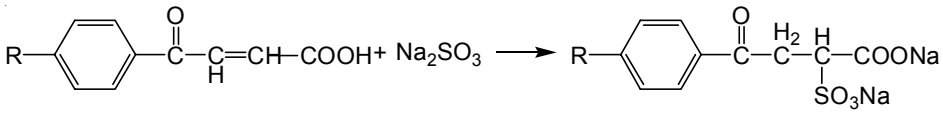
The molecule structure of synthesized surfactant was characterized by a FT/IR-430 analyzer.

Synthesis of 2-*p*-alkylbenzoyl-1-carboxyethane sulfonates (ABCES)

Friedel-Crafts acetylation reaction: The intermediate compound of ABCES was synthesized by Friedel-Crafts acetylation reaction in the presence of catalytic amounts of $AlCl_3$ at room temperature. Then the $AlCl_3$ was removed by adding H_2SO_4 (66 %) and isopropyl alcohol. The reaction process is shown as:



Sulfonation reaction: Sulfonation reaction of the intermediate was carried out by Na_2SO_3 at room temperature, then the 2-*p*-alkylbenzoyl-1-carboxyethane sulfonates was obtained.



The synthesized product is orange-yellow in colour and the purity of ABCES is 91 %. The interfacial active of ABCES has been compared with PS.

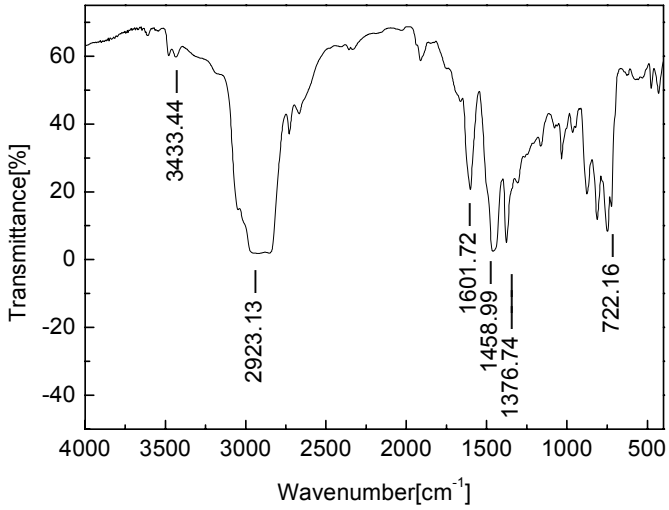
Performance test: The superficial tension of ABCES was measured using a Kruss-K12 analyzer at 20 ºC and the interfacial tension of ABCES was analyzed by a Texas-500 analyzer at 45 ºC. The interfacial tension value referred as a stabilized value unless other especial mention.

RESULTS AND DISCUSSION

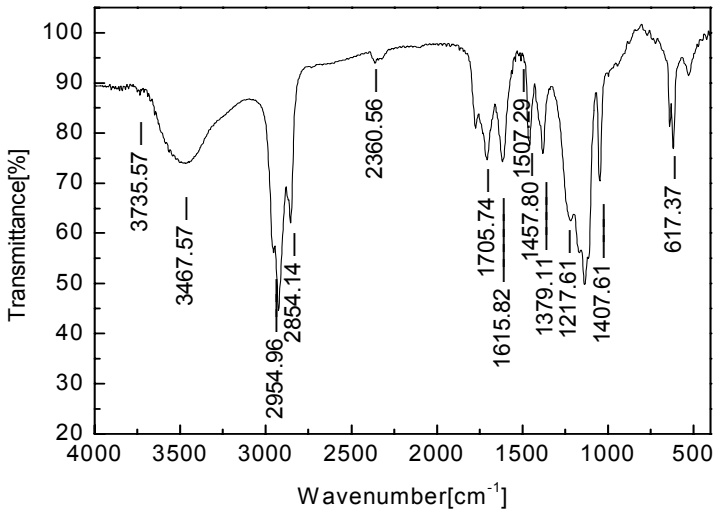
Compared with Fig. 1(a), the peaks at 1047 and 1217 cm^{-1} in Fig. 1(b) were assigned to S-O symmetric and asymmetric variation stretch, revealing the presence of sulfonic in ABCES. The peaks at 1457 and 1615 cm^{-1} were attributed to the stretch of C-O bond, suggesting the existence of carboxyl group. The analysis of IR showed that the final product ABCES has been obtained by Friedel-Crafts acetylation and sulfonation reaction.

The technique of API-ES is suitable for the analysis of polar and non-polar compound which the molecule weight is lower than 1600. Generally, a lot of ion peaks and quasi-ion peaks has been appeared in the diagram. Therefore the technique of API-ES can be used to analyze the distribution of molecular weight of unknown compound.

Fig. 2 showed the MS diagram of ABCES. The m/z value of synthesized compound was distributed in 350 and 650. It can be found that the stronger ion response domain was attributed in 450 and 600, suggesting that the distribution of relative molecule weight of ABCES compound. The relative molecule weight was calculated in the following equation:



(a)



(b)

Fig. 1. IR analysis of PS (a) and ABCES (b)

$$\overline{M_i} = \sum_{i=a}^{b} M_i \frac{P_i}{\sum_{i=a}^{b} P_i}$$

where M_i is the m/z value of a certain molecule, P_i is corresponding to the relative abundance. According to the above equation, the relative molecule weight of ABCES after ionization is found to be 530, whereas the relative molecular weight of its sodium is 576.

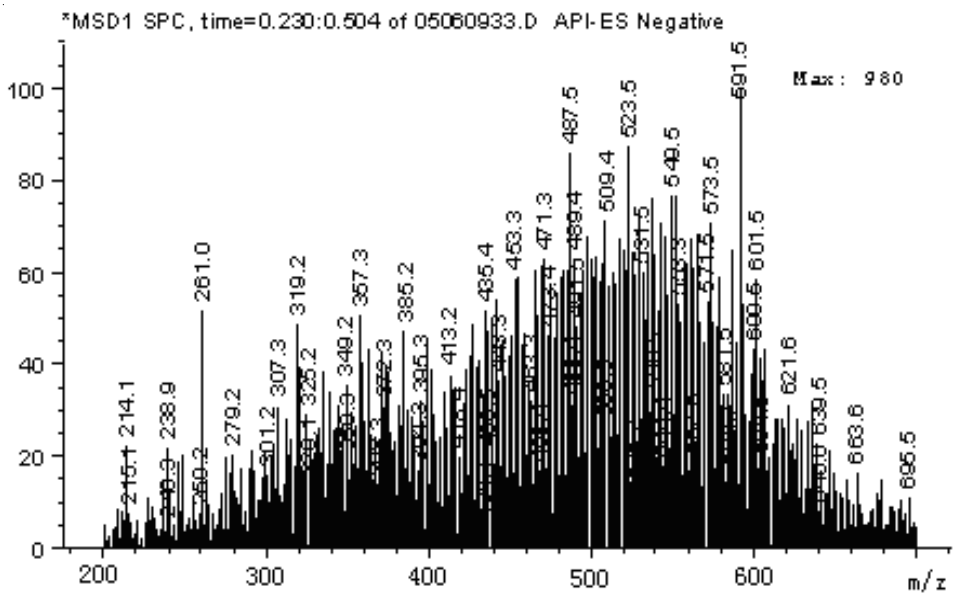


Fig. 2. MS diagram of ABCES

Performance test

Superficial performance test: As ABCES is a new surfactant, the interfacial performance of ABCES is necessary for present studies. The superficial tension of ABCES at 20 ºC is shown in Fig. 3. It can be seen that the critical micellar concentration (CMC) and minimum surface tension are obtained at 1.76×10^{-3} g/L and 36.18 mN/m, respectively.

Fig. 4 showed the superficial tension of ABCES and PS. It is evident that the superficial tension, CMC value and minimum surface tension of ABCES is lower than that of PS, indicating that ABCES has a higher superficial active.

Interfacial performance test: The transient interfacial tension test of ABCES is shown in Fig. 5. It is found that the transient interfacial tension of ABCES at a certain concentration decreased with the increase of Na_2CO_3 concentration. This is attributed to the change of double capacitance layer which is leading to distribution of the ABCES molecule becoming more compact. On the other hand, the increase of Na_2CO_3 concentration also leaded to the decrease of interfacial tension. The interfacial tension is 10^{-2} mN/m when the quality fraction is 0.05 %. While the quality fraction increased 0.15 and 0.3 %, the interfacial tension maintained around 10^{-3} mN/m.

It is known that the mineralizing water under stratum contained much Ca^{2+} + Mg^{2+} which decreased the superficial active of surfactant. So the tolerant to Ca^{2+} + Mg^{2+} surfactant become an important index. In the present work, the tolerant to Ca^{2+} + Mg^{2+} surfactant is investigated by addition surfactant and Na_2CO_3 when the quality fraction is at 0.3 and 1.2 %, respectively. The Ca^{2+} and Mg^{2+} are obtained

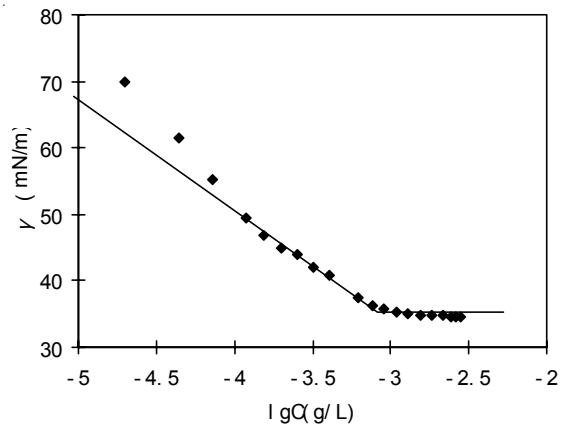


Fig. 3. Superficial tension of ABCES at 20 ºC

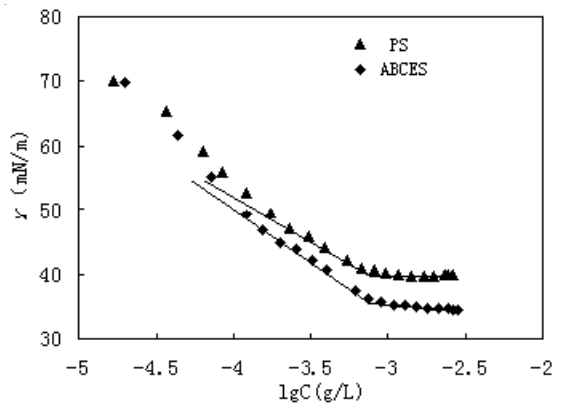


Fig. 4. Superficial tension of ABCES and PS at 20 ºC

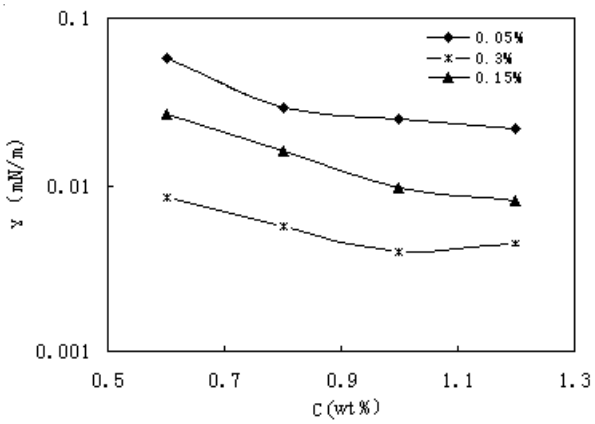


Fig. 5. Transient interfacial tension of ABCES at 20 ºC

by addition equal mass of $CaCl_2$ and $MgCl_2$. Fig. 6 showed the interfacial tension of ABCES and PS with the concentration of Ca^{2+} and Mg^{2+}. It is found that the ultralow interfacial tension (10^{-3} mN/m) of ABCES and PS is obtained when the Ca^{2+} and Mg^{2+} concentration below 600 and 300 mg/L, respectively, revealing that the tolerant to Ca^{2+} + Mg^{2+} of ABCES for enhanced oil recovery (EOR) is superior to PS. This can be explained by the structure of ABCES in which the sulfonic and carboxylate group can complex with much Ca^{2+} + Mg^{2+}.

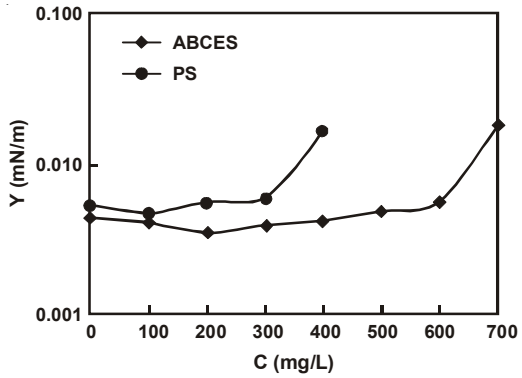


Fig. 6. Relation between the interfacial tension of surfactant and the concentration of Ca^{2+} and Mg^{2+}

Conclusion

(i) A new surfactant compound referred as 2-*p*-alkylbenzoyl-1-carboxyethane sulfonates (ABCES) has been synthesized by Friedel-Crafts acetylation and sulfonation reaction. The synthesized compound has been characterized by IR analysis. (ii) The critical micellar concentration (CMC) and minimum surface tension of ABCES are lower than that of petroleum sulfonate (PS), revealing that the surfactant properties of ABCES is superior to PS. (iii) The ultralow interfacial tension and highly tolerant to Ca^{2+} + Mg^{2+} of ABCES suggested that ABCES can act as an effective surfactant for enhanced oil recovery (EOR).

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