Preparation of Sulfosuccinate Amphoteric Fatliquoring Agent

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Abstract: A novel amphoteric fatliquoring agent was obtained through three steps. The first step is esterification of fatty acid with niethanolamine. Then, the result product reacted with maleic anhydride, finally followed by sulfonation. The choice of the catalyst in the esterification reaction was investigated and the effects of the raw material ratios, the reaction temperature and the reaction time were studied. The optimum conditions for each step were determined.

Key words: amphoteric; sulfosuccinate; fatliquoring agent

1 Introduction

Amphoteric fatliquor is developed later than other fatliquor agents, however it has many good performances, such as low toxicity, good biodegradability, excellent resistance to hard water and high concentrations of electrolytes, outstanding softness, flatness and antistatic property, a certain degree of sterilization, good emulsification and dispersion as well as compatibility with other fatliquor agents.[1] It is more popular in recent years because of all the advanced properties, especially its perfect fatliquoring effect and ecological effect. Its species and amounts also increase. At the present time, it is necessary to develop amphoteric fatliquor of fine quality. A new type of sulfonate surfactants has been developed by bringing cation into the structure of sulfosuccinate. The compound not only retains good wetting, penetration and emulsification power of original sulfosuccinate anion, but also has cationic surfactant function. So, it is the composition of amphoteric fatliquor with excellent performance and multi function.

2 Experimental

2.1 Materials

Higher fatty acid, diethanolamine, maleic anhydride, toluene-p-sulfonic acid and sodium sulfite were of analytical reagent grade.

2.2 Synthetic experiment

2.2.1 Synthetic of diethanolamine fatty acid ester

Fatty acid was first put into four-neck bottle with agitator, water segregator and condenser, and then heated to melting. A certain amount of diethanolamine, catalyst and an amount of methylbenzene (solvent and carrying water agent) was added with recirculation water being injected and warmed-up to reacting temperature to react for a certain time in reflux condition. During the reaction, acid value was measured to follow the reaction process. After the reaction, the methylbenzene was eliminated by reduced pressure distillation and the diethanolamine fatty acid ester was obtained

2.2.2 Maleic anhydride esterification reaction

The synthetic product in the first step was added into four-neck bottle and warmed-up to 65℃, an amount of maleic anhydride was added in several times. At the same time, the temperature was raised to a certain level. The reaction was maintained at this temperature for a certain time.

2.2.3 Sulfitation reaction

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Sodium sulfite aqueous solution was added into the reaction bottle to react a certain time under thermal insulation condition. The residual the sodium sulfite was determined to show the end point of the reaction.

2.3 Analysis and detection

2.3.1 Determination of acid value[2]

Conversion rate of fatty acid is calculated by measuring acid value.

2.3.2 *Determination of sodium sulfite content in product*

The content of sodium sulfite was calculated as the literature. [3]

3 Results and discussion

3.1 The synthesis of diethanolamine aliphatic ester

3.1.1 Effect of catalyst

A suitable catalyst in esterification favors smooth progress of reaction and can raise the conversion rate. Conventional inorganic acid catalyst is sulfuric acid and hydrochloric acid; however, they are strong corrosive. Using phosphorous acid as a catalyst in esterification, not only conversion ratio is high, but also it has smaller causticity. In addition, organic acid like toluene-p-sulfonic acid can be used as a catalyst. In this reaction, acid catalysis is used for the generation of ester. The effects of phosphorous acid and toluene-p-sulfonic acid on the conversion rate and color were examined with mole ratio as 1: 1, temperature as 140℃. The results are showed in Tab. 1.

Tab. 1 Effects of the catalyst on the conversion rate

Catalyst	Conversion rate O%					color
	1h	2h	3h	4h	5h	
None	77.4	80.6	85.3	89.4	91.8	light
sulphurous acid	80.2	88.4	93.6	96.7	96.5	dark
toluene-p-sulfonic acid	79.3	85.6	91.4	95.6	94.8	dark

As shown in Tab. 1, the conversion rate can reach 90% more in 5h without the catalyst, but with the catalyst the time can be reduced to 3h. The conversion rate was a little higher using phosphorous acid as catalyst than toluene-p-sulfonic acid. However, toluene-p-sulfonic acid can maintain relatively high conversion rate; the color of production was light and causticity is low too. Because of the advantages, toluene-p-sulfonic acid was chosen as the catalyst.

3.1.2 Effect of the time and temperature on conversion rate

The effect of time and temperature on conversion ratio was researched with mole ratio as 1: 1, the quantity of toluene-p-sulfonic acid 0.5%. The results are showed in Fig. 1. The conversion rate increased rapidly at the beginning of the esterification, especially in the initial 3h in the reaction. But the growth of conversion rate tended to slow gradually after 3hr, then the curve of conversion ratio over time was tending to gentle gradually after 4h. This phenomenon shows that esterification approached to the terminal point soon. Therefore, the reaction time was set as 4h. Figure 1 also shows that the convert ratio rose with the increase of the temperature, however, the trend become unobvious with temperature above 140℃. So the temperature is determined as 140℃.

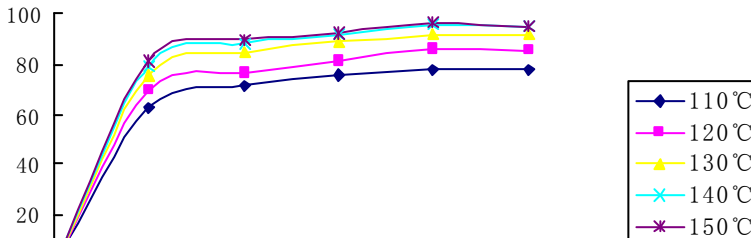

Fig.1 Effect of time and temperature on the conversion ratio

3.2 Esterification of maleic anhydride

The reaction of diethanolamine fatty acid ester and maleic anhydride belongs to esterification reaction of the alcohol and acid, so it can not be carried out in medium with water, or else, maleic anhydride will open loop to become inactivate, and the auto polymerization will easily occur. [4] Since the maleic anhydride is easy to sublimate, the whole experimental installation should be kept warm to avoid the sublimation product of maleic anhydride to crystallize on the side of the bottle. The alkalinity of RCOO- is weak and easy to leave in nucleophilic reaction, so catalyst needn't to be added on synthesizing monoester. [5] In the reaction, the diester will be easy to produce with the excessive diethanolamine fatty acid ester. This will lower the water solubility and stability of the product. If too much maleic anhydride is added, it will be difficult to eliminate in the product, and this will lead to the waste of the raw materials. Therefore, the desirable mole ratio of the maleic anhydride to diethanolamine fatty acid ester is 1.1-1.2:1. Diester is easy to form with the side reaction if the temperature is too high. Similarly, the reaction will not be carried out completely, if the temperature is too low. Thus, temperature as 100-110℃ is suitable. Conversion ratio is calculated with the change of acid value and it is used to express the degrees of the reaction. As shown in Fig. 2, the conversion rate of the maleic anhydride increased with the rise of the reaction time. The increase was the highest in the initial 3h and became slow gradually after 3h. The conversion ratio kept similar after 4h, so the reaction time is set as 4h.

Fig.1 Reaction time's effect on the convert ration

3.3 Sulfitation reaction

The monoester molecule has one double bond; it will be oxidized by oxygen in the air. Thus, sulfonation reaction should be carried out immediately after the esterification. Otherwise, the color of the product will become dark. Neutralization and sulfitation for the maleic acid monoester is a special system.

The reaction between double bond and sulphite will be carried out quickly in the mild condition. The quantitative property of reaction is good and technology practicability is better, which is due to the special property of maleic acid ester. Sodium sulfite is chosen as a sulfonating agent and the extent of sulfonation reaction can be controlled with the conversion ratio of sodium sulphite. Reaction temperature ranges from 70 to 75℃, the amount of the sulfonating agent should be a little excessive to make the product have good solubility. Normally, the mole ratio of the maleic anhydride and sulfonation agent is 1:1.05-1.1, the time is 2h.

4 Conclusions

The technology of synthesizing the Sulfosuccinate amphoteric fatliquor agent was confirmed in this work. The technology is as follows:

(1)Diethanolamin fatty acid ester was produced with fatty acid and diethanolamine, with material inorganic acid PTSA as catalyst at 140℃ for 3hr.

(2)The conditions in the second step are as follows: mole ratio of maleic anhydride and diethanolamine fatty acid ester as 1.1-1.2; temperature as 100-110℃; time as 3h; without catalyst.

(3)The third step is the sulfitation reaction with sodium sulfite as sulfonating agent. The temperature is 70-75℃, the mole ratio of monoester and sulfonating agent is 1:1.05-1.1, the time is 2h.

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