Preparation of Polyamide Surfactant with Collagen Hydrolysate from Tannery Solid Wastes

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Abstract

Amphoteric surface active agent behaves the properties of cationic, anion, and nonionic in acidic, alkaline, and neutral solution. It is soluble in water, acid, alkali, and even in inorganic salt solution. It is good in hard water resistance, sterilization, compatibility, and antistatic property.

Amphoteric surfactant with amino acid is low in toxicity, irritation, biodegradability, and affinity to human body, while it is good in antibacterial and antistatic. So it widely used in cosmetics, detergents, and other related industrial fields. In the recent years, natural amino acids and their derivatives have found an active research and development in such fields as cosmetics, medicine, food, and pesticide.

In the present paper, polyamide surfactant was prepared with collagen hydrolysate from tannery solid wastes. Such reaction condition that may affect the properties of the resultant products as raw materials ratio, pH, temperature, and dosage of acetone was discussed. The surface activity of the product was studied as well. The optimum synthetic conditions were obtained as follows: The ratio among lauroyl chloride, collagen hydrolysate, and acetone of 1:2:2(v/v/v), the pH of 9~10, and the temperature of 20~25℃.

Key Words： Collagen hydrolysate; N-lauroyl amino acid; surfactant; acylation

1. Introduction

Amphoteric surfactant with amino acid, a kind of amphoteric surface active agent, behaving properties of both cationic and anion, is low in toxicity, irritation, biodegradability, and affinity to human body, while it is good in antibacterial and antistatic. So it widely used in cosmetics, detergents, and other related industrial fields (Yangyi, S.C. 1988; Xingyilang, Z.C. 1989). Recent years, natural amino acids and their derivatives have found an active research and development in various fields such as cosmetics, medicine, food, and pesticide. And this surfactant is envisioned a bright prospect.

In China, solid wastes from tanneries annually are more than 140 tons, mainly including waste hair, dander, shaved leather scraps, trimming materials, cutting chip, etc., with

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high-quality natural collagen protein (Changdao, M. et al. 1997). The focus is still on studies of collagen extraction. But preparation of polyamide surfactant with collagen hydrolysate from tannery solid wastes has been studied in detail. In the present paper, polyamide surfactant was prepared with collagen hydrolysate from tannery solid wastes. By the study, a novel surfactant is prepared, and the pollution of solid wastes from tannery may be reduced.

2. Materials and method

2.1 Preparation of collagen hydrolysate

The collagen powder（6g） was dissolved in a sodium hydroxide solution (120ml, 1 mol/L) , and the solution was hydrolyzing for 4 hours. The solution obtained was decolored by activated carbon and then filtered (Yanan, W. et al. 1996).

2.2 Preparation of polyamide surfactant

In a three-necked round-bottomed flask, the mixture containing collagen hydrolysate and acetone was stirred thoroughly, and lauroyl chloride was slowly added. 20% NaOH solution was added into it, and the reaction was kept for 3 hours to yield the polyamide surfactant.

2.3 Test of the reaction extent

Hydrogen chloride was generated during the reaction, in the form of hydrochloric acid in aqueous solution. Because of the reaction between hydrogen chloride and silver nitrate, the silver chloride was precipitated in the solution .In this paper, this precipitation was filtered, dried and weighed. The extent of acylation reaction was then calculated indirectly. The reaction conditions could be determined as well.

2.4 Foaming property

The sample(1%, 20ml) was added into the 100mL cylinder with a tap, agitated 20 times in 10 seconds. After being still for 30 seconds, the volume of the solution V and the volume of foam V1 were tested (Peicheng, Z. et al 1992) (foaming property= solution volume V / foam volume V1).

3. Results and discussion

3.1 Effects of the ratio of lauroyl chloride to collagen hydrolysate

3.1.1 Optimum proportion of lauroyl chloride and collagen hydrolysate to the reaction

By controlling pH 10, the temperature 20 oC, the effects of the ratio of lauroyl chloride to collagen hydrolysate on reaction was studied.

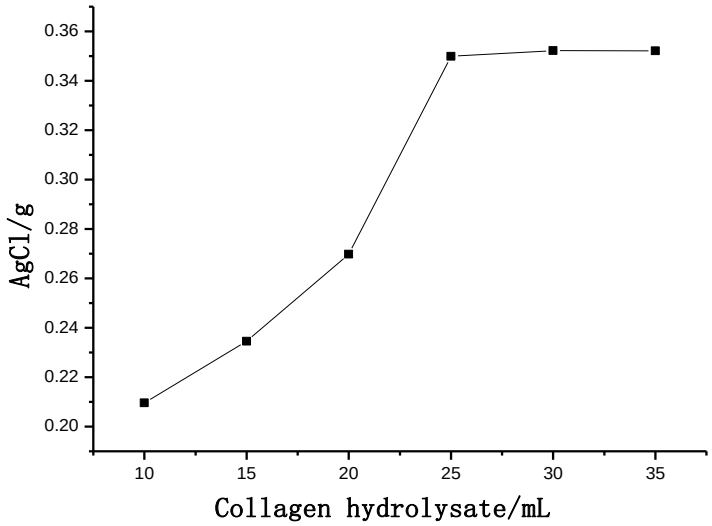

Fig. 1 Effects of the ratio of lauroyl chloride to collagen hydrolysate on reaction

Fig. 1 shows that with the increasing amount of increasing, the silver chloride produced increases. At a certain amount of lauroyl chloride, when the collagen hydrolysate is insufficient, further increasing the amount of collagen hydrolysate will accelerate the condensation reaction. At the over-dose collagen hydrolysate, the product remains unchanged. It can be concluded that the optimum ratio of lauroyl chloride to collagen hydrolysate is 1:2(v/v).

3.1.2 Effects of the ratio of lauroyl chloride to collagen hydrolysate on foaming property

Fig. 2 suggests a peak value in foaming property with increasing the mixedamino acid. At a low amount of collagen hydrolysate, the foaming of polyamide surfactant increases with increasing the collagen hydrolysate amount in a certain extent, and the change is small. This result is related to the amount of surfactant. At a high content of surfactant, the foaming is obvious and stable. At an excessive amount of collagen hydrolysate, a poor foaming was found, which may be related to the action of hydrophilc agent.

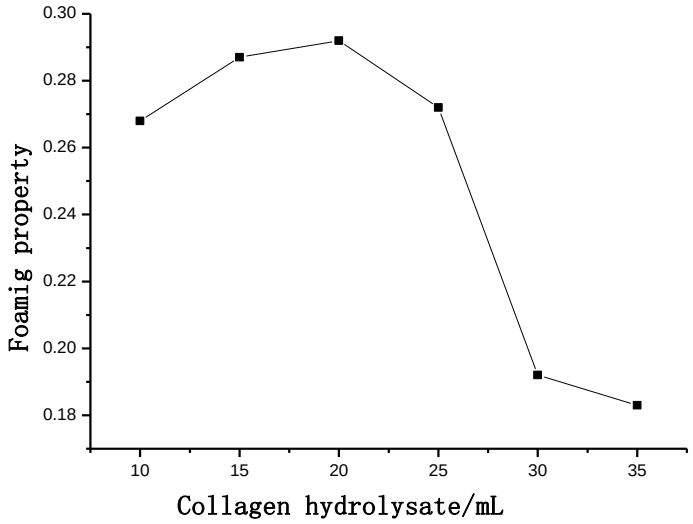

Fig. 2 Effects of the ratio of lauroyl chloride and collagen hydrolysate on foaming property

3.2 Effects of pH on the reaction extent and properties of surfactant

3.2.1 Effects of pH on the reaction extent

At the temperature 20 oC, the ratio among lauroyl chloride, collagen hydrolysate, and acetone of 1:2:2(v/v/v), the effects of pH on the acylation reaction were studied.

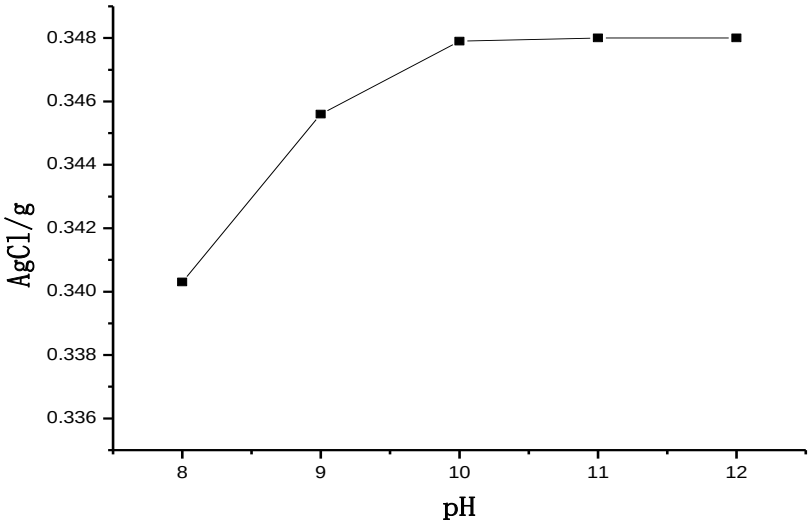

Fig. 3 Effects of pH on the reaction

With pH 10, the reaction extent reaches the peak, indicating the most silver chloride was obtained. In acidic conditions, amino in the collagen hydrolysate will exist in the protonated state to reduce nucleophilic ability of the amino group. So the acylation reaction can not be conducted as usual. At an alkaline condition, however, the OH- concentration is enough for the hydrolysis reaction of acyl chloride, which does not good for the production of the intended product. Therefore, it is reasonable to control the reaction in a weak alkaline

condition for the acylation reaction, and the pH of 10 is most suitable for the acylation reaction.

3.2.2 Effects of pH on foaming, emulsifying property

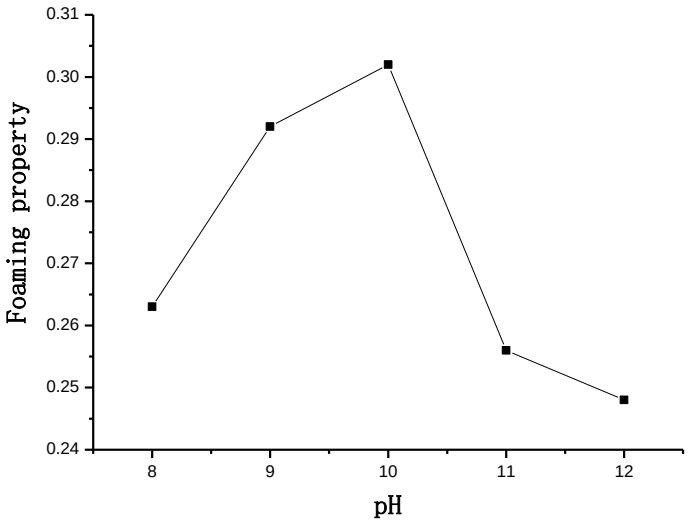

Fig. 4 Effects of pH on foaming property

Polyamide surfactant and its foaming property are the optimum with pH 10 (Fig. 4). In Fig. 3, with pH 10, the reaction extent reaches the highest. The explanation is that foaming property increases with the increasing pH (pH＜10) .However, with pH＞10, foaming property decreases with increasing pH. Because of side effect, lack of polyamide surfactant leads to this opposite trend.

3.3 Effects of temperature on the reaction extent and properties of surfactant
3.3.1 Effects of temperature on the reaction extent

By controlling the temperature 20℃, the ratio among lauroyl chloride, collagen hydrolysate, and acetone of 1:2:2(v/v/v), effects of temperature on the acylation reaction was studied.

As seen in Fig. 5, the increase of silver chloride reveales that the temperature has an influnce on the reaction.With the temperature increasing, the acylation reaction will be promoted. It is also found that acylation reaction stops changing above 25℃.The temperature can not only speed up acylation reaction, it also accelerates the yield of polyamide surfactant and the hydrolysis of acyl chloride. Therefore, room temperature is optimum.

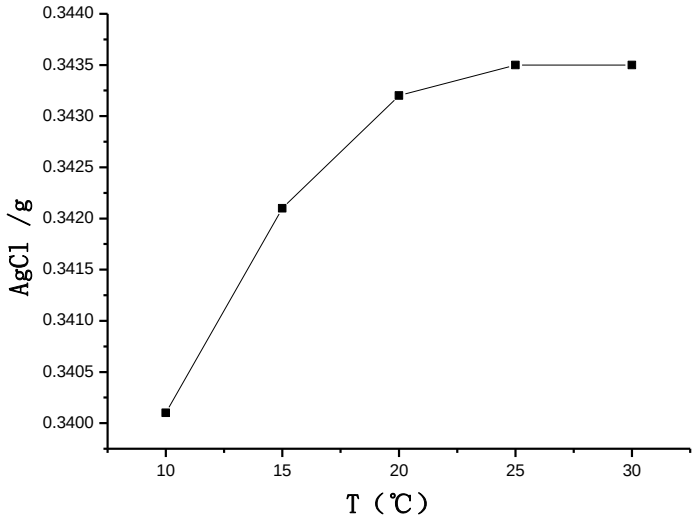

Fig. 5 Effects of temperature on the reaction extent

3.4 Effects of dose of acetone on the reaction extent

By controlling pH 10, the temperature 20℃, the ratio of lauroyl chloride to collagen hydrolysate 1：2(v/v), effects of dose of acetone on reaction was studied.

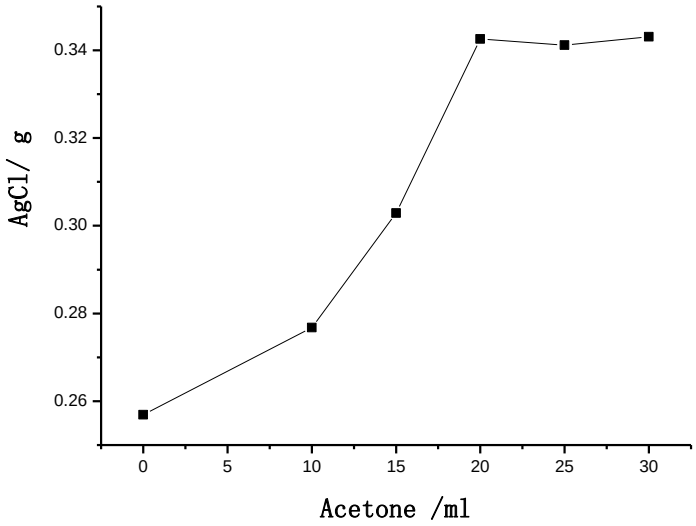

Fig. 6 Effects of dose of acetone on the reaction extent

In Fig. 6, with less than 20ml acetone, silver chloride transformed from chloride ion in reaction increases with the increasing volume of acetone. When the amount of acetone is more than 20ml,the polycondensation reaction balance is achieved. This is because collagen hydrolysate is a complex mixedamino acid, lauroyl chloride is a oil-soluble material.And they can not be soluble well. Mixing with lauroyl chloride and collagen hydrolysate, acetone is conducive to the effective collision between lauroyl chloride and collagen hydrolysate, promoting acylation reaction.

4. Conclusions

The optimum synthetic conditions of polyamide surfactant are :

• The ratio among lauroyl, collagen hydrolysate, and acetone= 1:2:2(v/v/v)

• The pH= 9~10

• The temperature= 20~25℃

And, it is denoted that the foaming characteristics of polyamide surfactant depended closely on the proportion of lauroyl and collagen hydrolysate.

5. Acknowledgements

The financial supports from the National Natural Science Foundation of China (Grant No. 50973097, 21076199) and the Department of Science and Technology of Henan Province (No. 124300510030) are greatly appreciated.The authors are grateful to all the staffs in the Laboratory of Leather Chemistry and Engineering of Zhengzhou University.

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