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SYNTHESIS OF ZINC STEARATE FROM ZINC OXIDE AND STEARIC ACID USING A COMBINATION OF SODIUM DODECYL SULFATE AS ANIONIC AND POLYVINYL ALCOHOL AS NONIONIC SURFACTANT

Assoc. Prof. Stanislav Bayryamov, PhD
Department of Repairing, Reliability, Mechanisms,
Machines, Logistic and Chemical Technologies,
Agrarian and Industrial Faculty,
"Angel Kanchev" Univesity of Ruse
E-mail: sbayryamov@uni-ruse.bg

Abstract: *Zinc stearate known also as zinc soap has a variety of applications in cosmetics, pharmacy, automotive industry, agricultural machinery, polymer industry, food industry, fat industry, powder metallurgy, etc. The wide application of this product determines the search for different methods and protocols for its more economical obtaining. The present study combined the use of sodium dodecyl sulfate as an anionic surfactant and polyvinyl alcohol as a nonionic surfactant in the synthesis of zinc stearate from zinc oxide and stearic acid. The process was carried out at a temperature of 70°C. As the data showed, the yield of zinc stearate was almost quantitative (99,6%) and the dispersion of the product in water was found to contain 39.6% by weight of zinc stearate with viscosity of 330 centipoises at 25°C. The data would help to optimize the procedure for obtaining zinc salts of higher fatty acids needed for industry.*

Keywords: *Stearic acid, zinc oxide, synthesis, polyvinyl alcohol (PVA), sodium dodecyl sulfate (SDS).*

INTRODUCTION

Higher fatty acids and their derivatives, such as salts, esters, aminoesters and amides, represent an attractive area of scientific interest and practical application (Kopchev, V., Pavlikianova, A., Kopchev, P., 2005) (Kopchev, V., Pavlikianova, A., Kopchev, P., 2007) (Kopchev V., Kopchev P., 2009) (Kopchev V., 2012) (Kopchev V., 2012) (Kopchev, V. P., 2023) (Kopchev, V. P., 2023) (Kopchev, V., 2024).

Zinc stearate, as well as other metal carboxylates, is widely applied in many areas of industry. By exploiting its "non-stick" properties, it is used in the production of polyesters and polyurethanes, in the rubber industry and powder metallurgy (Anneken, D. J., Both, S., Christoph, R., Fieg, G., Steinberner, U., Westfechtel, A., 2006). It is used as a catalyst, especially as an "activator" to accelerate the reaction of forming covalent bonds between sulfur atoms in the rubber vulcanization. This increase in the rate of the process is due to the fact that zinc has a favorable effect on the interaction of the polyolefin with sulfur, and its salt with stearic acid provides it with good solubility in the hydrophobic environment created by the polyolefins. Due to its amphiphilicity (hydrophilicity and lipophilicity), it finds application as a phase transfer catalyst used in fat saponification processes (Anneken, D. J., Both, S., Christoph, R., Fieg, G., Steinberner, U., Westfechtel, A., 2006). Besides, stearate salts are widely used as emulsion stabilizers and also as viscosity-enhancing and opacity-enhancing agents. Zinc stearate is also used as a component of paints, giving them gloss, and as a preservative for oil paintings in order to preserve them. In addition zinc stearate is used as a biodegradable environmentally friendly lubricant, as well as an additive to lubricating oils to increase tribological properties.

Also, except as stated above, zinc stearate is widely used in pharmacy and cosmetics. For example, zinc stearate improves the final appearance of the product and its texture ("Zinc Stearate Cosmetics Info", 2013). Moreover, in cosmetics, this metallic soap is used as a lubricant and thickening agent as well as to hold the liquid and oil elements together. In cosmetics and formulation chemistry, zinc stearate used in make-up formulations such as face powders, foundation creams, facemasks, lipsticks, eyeliner, eye shadows etc.

There are various methods supported by corresponding protocols for the synthesis of zinc stearate and other higher fatty acids metallic salts described in US Patents: US 6,162,836; US

6,689,894 B1; US 8,404,743 B2; US 4,307,027; US 4,060,535; US 3,803,188; and US 3,476,786; as well as Russian patent RU 2,516,663,C1.

From all that has been said so far, it is clear that thanks to its unique properties, zinc stearate finds an extremely diverse application in various fields of industry, which in turn increases the demand for new approaches, methods and protocols for its preparation. This aims, on the one hand, to raise the efficiency of the synthesis process and increase the yields of the final product, and on the other hand, to reduce its cost price.

The purpose of the present work is based on the combination of SDS as an anionic surfactant and PVA as a nonionic surfactant for the synthesis of zinc stearate as a dispersion in water with the aim of optimizing the process of obtaining the final product with a higher yield and lower cost.

EXPOSITION

Zinc stearate, among other zinc salts of fatty acids, occupy an important place in agricultural and automotive technology due to the fact that, along with their main role as additives to oils, they are biodegradable and environmentally friendly. In this regard, studies on its synthesis are aimed at finding convenient approaches to solve the issue related to its large-scale production. Some protocols use high temperature to carry out the process. Such are described in patents RU 2,516,663,C1 and US 3,803,188. Russian patent RU 2,516,663,C1 also uses hydrochloric acid as a catalyst to speed up the process. Other methods apply different surfactants (US 6,162,836 and US 6,689,894 B1), and still others apply a high stirring speed of the order of 3600 rpm (US 4,060,535) or use a roller mill (US 3,476,786).

In the patent US 6,162,836 zinc stearate was prepared as an aqueous dispersion. The process involved adding the molten stearic acid to the aqueous dispersion of zinc oxide. The interaction of stearic acid with ZnO was under moderate stirring and in the presence of surfactant or polyvinyl alcohol. In the patent, maintaining the aqueous dispersion was to be at a temperature higher than the melting point of stearic acid. In the mentioned method and protocols, zinc stearate was produced by a direct wet precipitation process, in the form of an aqueous dispersion with a small final product particle size, low viscosity and high yields.

In this work, the synthesis of zinc stearate was carried out using the modified methodology of Kato, Y., described in the patent US 6,162,836. In the patent, a cationic surfactant was used, and the reaction temperature was 60°C. Therefore, good yields and a final product with acceptable characteristics were achieved.

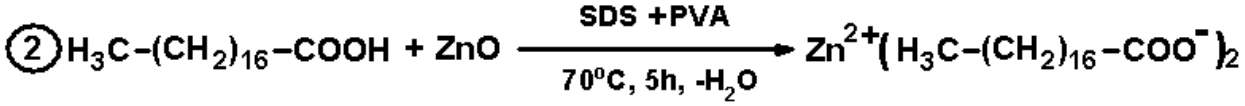

Fig. 1 Reaction scheme for synthesis of zinc stearate from ZnO and stearic acid

EXPERIMENTAL PROCEDURE

Synthesis of zinc stearate using a combination of SDS and PVA

In a 1000 mL three necked round bottom flask fitted with a thermometer, reflux condenser and electromagnetic stirrer, 8.50 g (Mm = 81.408 g.mol^{-1}; 0.104 mol) of zinc oxide were placed. After that, 130 mL of distilled water were added to it and shaked to obtain dispersion. To the prepared reaction mixture 1.43 g (Mm = 288.37 g.mol^{-1}; 4.96 mmol) of SDS and 1.43 g of PVA were added and dissolved therein. After, 50 g (Mm = 284.48 g.mol^{-1}; 0.176 mol) of stearic acid (m.p. 69.3°C) was added to 500 mL Erlenmeyer flask, heated with vigorous stirring to about 70°C and gradually added to the aqueous mixture in the flask. The three-neck round-bottomed flask filled with the obtained dispersion, equipped with a thermometer, a reflux condenser and an electromagnetic stirrer, was placed on a hot plate and the reaction mixture was stirred for 5 hours at a temperature of 70°C. After ending of the reaction, the mixture was allowed to stand at room temperature, thus obtaining an aqueous dispersion of zinc stearate. The yield of zinc stearate was 99.6% and the dispersion of the final product in water was found to contain 39.6% by weight of zinc stearate with viscosity of 330 centipoises at 25°C. The average particle diameter was between 2.0-3.0 μm.

Synthesis of zinc stearate without the use of surfactant

The final product was prepared by the same manner as in the previous protocol except that the surfactant was not used. The yield of zinc stearate was 22.9% with the viscosity of 210 centipoises at 25°C, and the average particle size in the range between 5.0-10.0 μm. The dispersion of the final product in water was found to contain 21.2% by weight of zinc stearate.

^{1}H NMR and ^{13}C NMR spectroscopy analysis

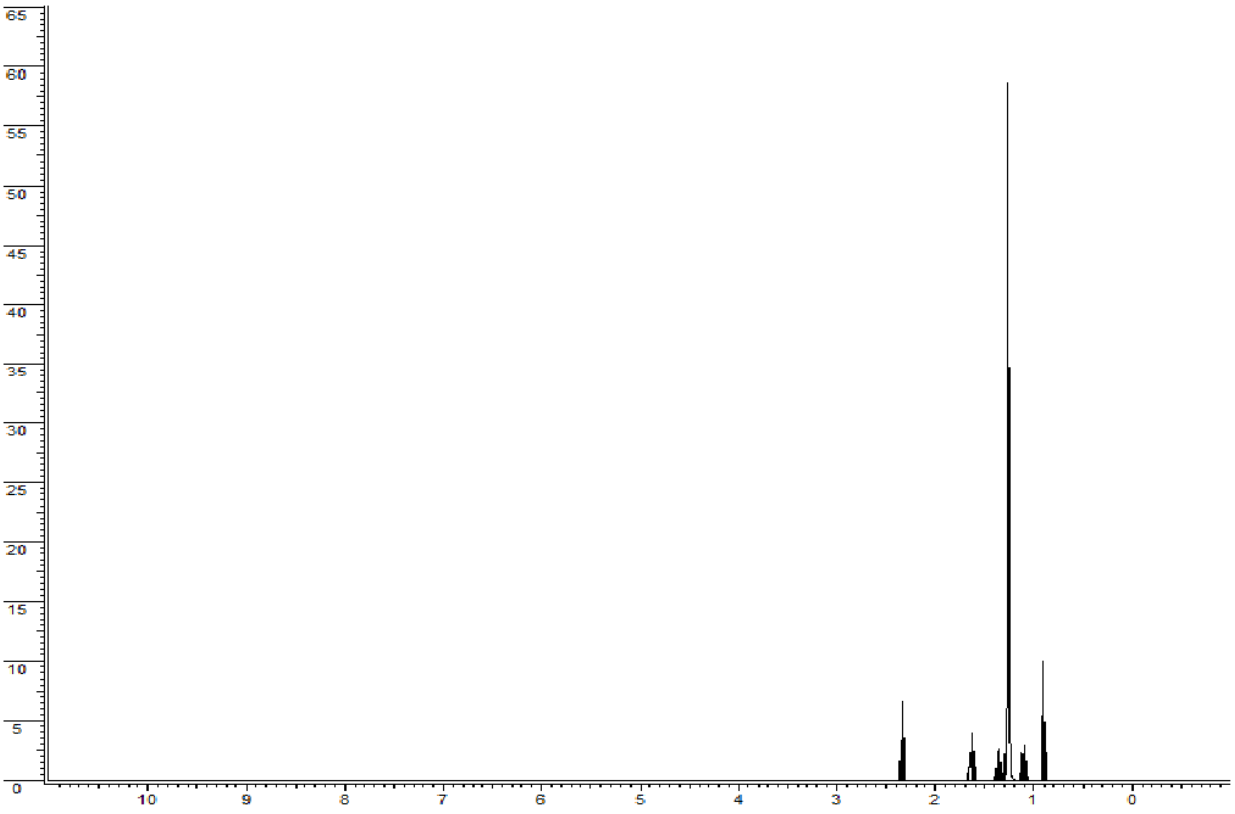

Fig. 2 ^{1}H NMR spectrum of Zn stearate

^{1}H NMR: δ = 0.94(t, 6H, 18-CH_3, 18'-CH_3), 1.08-1.16(m, 4H, 16-CH_2, 16'-CH_2), 1.22-1.36(m, 48H, 4-CH_2, 4'-CH_2, 5-CH_2, 5'-CH_2, 6-CH_2, 6'-CH_2, 7-CH_2, 7'-CH_2, 8-CH_2, 8'-CH_2, 9-CH_2, 9'-CH_2, 10-CH_2, 10'-CH_2, 11-CH_2, 11'-CH_2, 12-CH_2, 12'-CH_2, 13-CH_2, 13'-CH_2, 14-CH_2, 14'-CH_2, 15-CH_2, 15'-CH_2), 1.38-1.44(m, 4H, 17-CH_2, 17'-CH_2), 1.64-1.72(m, 4H, 3-CH_2, 3'-CH_2), 2.38(t, 4H, 2-CH_2, 2'-CH_2).

^{13}C NMR: δ = 15.79(18-CH_3, 18'-CH_3), 21.33(17-CH_2, 17'-CH_2), 25.11(3-CH_2, 3'-CH_2), 29.79(4-CH_2, 4'-CH_2), 29.93(5-CH_2, 5'-CH_2), 30.08(6-CH_2, 6'-CH_2), 30.25(15-CH_2, 15'-CH_2), 30.44(7-CH_2, 7'-CH_2, 8-CH_2, 8'-CH_2, 9-CH_2, 9'-CH_2, 10-CH_2, 10'-CH_2, 11-CH_2, 11'-CH_2, 13-CH_2, 13'-CH_2), 30.84(14-CH_2, 14'-CH_2), 33.84(16-CH_2, 16'-CH_2), 37.57(2-CH_2, 2'-CH_2), 163.44(2C=O, 1-COO^-, 1'-COO^-).

FT - IR spectral analysis

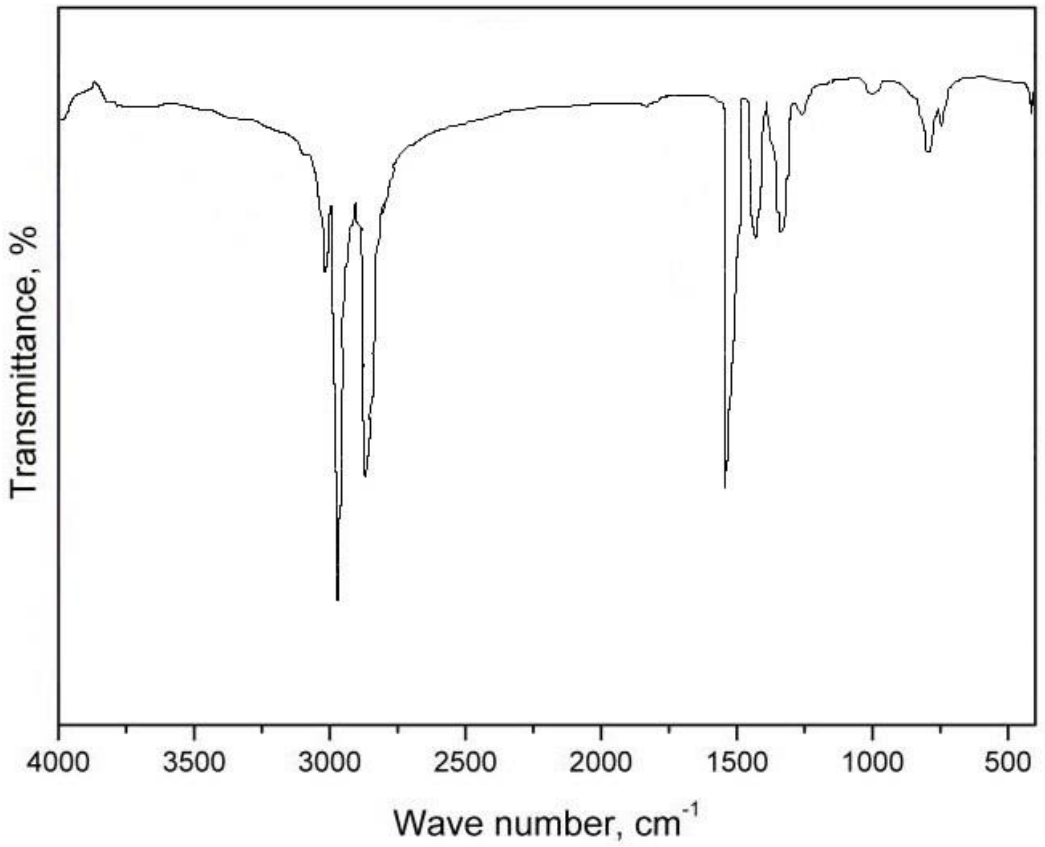

Fig. 3 FT - IR spectrum of Zn stearate

The spectrum of the prepared Zn stearate was obtained after its freeze drying, using KBr pellets. The infrared spectra of Zn stearate with the characteristic absorption bands are at 3020 cm^{-1}, 2950 cm^{-1} and 2830 cm^{-1} corresponding to characteristic CH_2 stretching vibrations, 1570 cm^{-1}, 1420 cm^{-1} corresponding to the zinc carboxylate, 1370 cm^{-1}, 1250 cm^{-1}, 970 cm^{-1}, 800 cm^{-1} and 750 cm^{-1} corresponding to CH_2 groups.

Particle size analysis

The particle size as well as the size distribution of zinc stearate particles were determined using a laser diffraction apparatus brand MICROTRACK MRB model SYNC, with a working range of 0.01μm - 4mm.

RESULTS AND DISCUSSION

Unlike the patent US 6,162,836, which used both cationic surfactants, SDS and PVA, but each of them separately, to obtain the final product suspension, the present work used the combination of SDS as an anionic and PVA as a nonionic agent. For comparison, in the development of the patent, when using a cationic surfactant, for example pentaethylenehexamine, the yield of zinc stearate was 95.7%, and its content in the aqueous dispersion was 41.2% with a viscosity at 25ºC: 150 centipoises. In another example, using a condensate of stearic acid and aminoethylethanolamine named Ahcovel A-type, as a cationic surfactant, the yield of zinc stearate was 96.1% and its content in the aqueous dispersion was 39.4% with a viscosity at 25°C: 130 centipoises. In a third example, using dodecyltrimethylammonium chloride as a cationic surfactant, the zinc stearate yield was 99.1% and its content in the aqueous dispersion was 40.2% with a viscosity at 25ºC of 110 centipoises. When using SDS as an anionic emulsifier, the zinc stearate yield was 97.3% and its content in the aqueous dispersion was 40.9% with a viscosity at 25°C of 410 centipoises. In the case of using PVA as a nonionic surfactant, the yield of zinc stearate was 99.3%, and its content in the aqueous dispersion was 38.7% with a viscosity at 25°C - 290

centipoises. From what has been said so far, it can be concluded that the highest yield is obtained when using PVA as a nonionic surfactant, but alone. Therefore, the author has resorted to using the combination of SDS and PVA with the aim of increasing the yield and improving other characteristics of the final product.

As can be seen from the data in Table 1, when carrying out the reaction without the participation of emulsifier, the yield of zinc stearate was much lower (22.9 %) compared to carrying out the reaction using the combination of SDS as an anionic surfactant and PVA as nonionic surfactant (yield: 99.6 %). Furthermore, when comparing the other characteristics, the values are in favor of carrying out the reaction using the combination of SDS and PVA: average particle diameter 5.0-10.0 μm (without surfactant) and 2.0-3.0 μm (SDS + PVA).

Table 1 Characteristics of Zn stearate, derived from ZnO and stearic acid, without surfactant or using a combination of SDS + PVA

№	Characteristics	Without surfactant	SDS + PVA, 1:1
1	Yield, %	22.9	99.6
2	Viscosity at 25ºC, cps	210	330
3	Average diameter, μm	5.0-10.0	2.0-3.0
4	Weight percentage in dispersion, %	21.2	39.6

CONCLUSION

Zinc stearate was synthesized in two different ways. In the first way, the synthesis was realized without the participation of an emulsifier. In the second method, zinc stearate was obtained using a combination of sodium dodecyl sulfate as anionic and polyvinyl alcohol as nonionic surfactant. When comparing the two methods, the data show that when the combination of the two emulsifiers is used, the reaction proceeds much better with higher yields of the final product. The author hopes that the work will contribute to increasing the efficiency of the process for obtaining this product so important to the industry.

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