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SYNTHESIS OF QUATERNARY AMMONIUM COMPOUNDS FROM NATURAL MATERIALS

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ABSTRACT

Quaternary ammonium compounds were derived from tallow and coconut oil. Amides were prepared by reacting the coconut oil and tallow with amines (triethylamine and trimethylamine). Then by reaction of amide with alkyl halide (1-bromo butane, 1-chlorobutane and iodoethane) compounds were prepared. The purity of these compounds was checked by chemical analysis and IR spectrometry. The activities of these compounds were checked on cane juice for its clarification.

Key words: Quaternary ammonium compounds, Fat, Oil, FTIR.

INTRODUCTION

From the past seven decades synthetic quaternary ammonium compounds (QACs) from tertiary amines has been recognized in which quaternary ammonium nitrogen attached to four variable branches impart the major features of the classes of QACs[1]. On the lists of both the U.S. Environmental Protection Agency and the Organization for Economic Co-operation and Development QACs are among the High Production Volume Chemicals. Nucleophilic substitution reaction of alpha-olefins or fatty acid originated tertiary amines with alkyl halide or benzyl halide also produced the QACs. These compounds have extensive industrial applications as emulsifier and surfactants are getting special attention[2-4]. QACs have two different groups; hydrophobic alkyl groups and a hydrophilic, positively charged central nitrogen atom, which retains its cationic character at all pH values. These two groups affect their physical and chemical properties. The aqueous solubility of QACs increases as alkyl chain length of the molecule decrease and vice versa. QACs rapidly and strongly adsorbed on the inorganic and organic surfaces like clays, minerals, biomass and sediments, with the increase of alkyl chain length sorption on biomass and sediments

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increase on contrary ionic interaction in minerals and clays become dominant and decreased alkyl chain length favors the sorption[5-7]. In this work, three QACs were synthesized from tallow and coconut oil and check their activity for clarification of cane juice.

EXPERIMENTAL

Materials and methods

Collection of tallow and coconut oil

Raw tallow of goat was collected from the butchery, melted at low temperature and removed the proteinous mass by hot filtration. Filtrate was stored in freezer in order to check the formation of oxidative products. To avoid the adulteration of oil, it was extracted with hexane. Hexane was recovered by distillation and pur oil stored in freezer.

Acid value of fat and oil

Ten grams each of fat and oil was taken in 250 mL volumetric flask added 50 mL of ethanol and ether (1:1) and neutralized with 0.1 M potassium hydroxide separately using phenolphthalein as indicator.

Saponification value

Two grams each of fat and oil was taken in 200 mL flask added 25 mL of ethanolic solution of potassium hydroxide and boiled under reflux condenser for 1 hr with continuous stirring separately. Titrate excess alkali with 0.5 M hydrochloric acid using phenolphthalein as indicator.

Ester value

Ester value was calculated by subtracting the acid value from saponification value.

Iodine value

0.5 g each of fat and oil was taken in 250 mL glass stopper flask added 10 mL of chloroform and 25 mL of wijs reagent in each flask shake vigorously and allowed to stand in dark for half an hour. 50 mL of water and 15 mL of 10% potassium iodide was added in each flask. Titrated with sodium thiosulphate using starch solutions as indicator till blue color disappear.

Thin layer chromatography of tallow and coconut oil

1% solution of each fat and oil in chloroform as well 2% solution of palmitic acid, oleic acid, stearic acid, myristic acid and lauric acid as standard was run on silica gel plate

using hexane, diethyl ether and acetic acid (80:19:1) solvent system. Iodine chamber was used as locating agent.

Fatty acid from tallow and coconut oil

Ten grams each of fat and oil was taken in 250 mL Erlenmeyer flask, added 2.3 g potassium hydroxide and 20 mL triethylene glycol and maintained at 160^0C for five min to ensure complete hydrolysis of fatty material. Cooled the thick syrupy solution at room temperature added 50 mL of water and acidified with 10 mL of concentrated hydrochloric acid. Solution was extracted with ether, washed the ether layer with saturated sodium chloride solution and dried the mixture over anhydrous sodium sulphate. Evaporated the solution on water bath and mixture of fatty acid was obtained.

Preparation of amide from fatty acid

5.0 g of fatty acid mixture and 5.0 mL trimethyl amine in round bottom flask refluxed for 12 h at 115^0C and product obtained was washed with ether and characterized by IR spectra. Similarly amide from fatty acid was prepared using trimethyl amine.

Synthesis of QACs

Thirty grams each of fatty amide and 1-bromo butane was refluxed in round bottom flask for 16 h at 115 ^{0}C then continued heating to evaporate any unreacted amide. QACs were also prepared from fatty amide using same procedure with 1-chlorobutane and iodoethane.

Recrystallization and purification

The crude product was dissolved in 50.0 mL of hot water and washed with ether to remove unreacted halide. The resulting aqueous solution was washed carbon tetrachloride, water layer was collected and allowed to evaporate at room temperature.

TLC and IR spectra of QACs

Fifteen mg of each QAC was dissolved in 5 mL of ethanol and spotted on TLC plate. The eluting solvent was petroleum ether, ether and acetic acid (90: 10:1). The spots were located by spraying the 0.1% acid fuchsin and brilliant green in ethanol (96%) as locating agent. IR spectra of each QAC were taken for confirmation.

Clarification activity of QACs

100 mL of cane juice was taken into 250 mL flask after adjusting the pH at 7.0 with

lime added 0.5 % QAC (in ethanol) and heated at 80 ^{0}C for 2 min. Stopped heating and allowed to stand for 30 min.

RESULTS AND DISCUSSION

The fatty acids were prepared from the tallow and coconut oil by solvent extraction method using n-hexane. Different tests were performed to find out the purity of these materials like acid value, saponification value, ester value, iodine value presented in Table 1 and thin layer chromatography.

Table 1: Characteristics of tallow and coconut oil

Compounds	Acid value	Saponification value	Ester value	Iodine value
Tallow	0.50	186.00	185.50	38.07
Coconut oil	28.00	241.23	213.23	10.00

The obtained results were considerably good when compare with actual value given in the literature. Three alkyl halides; 1-chloro butane, 1-bromobutane and iodoethane were used for synthesis of QACs from amide. The chloro and bromo butane gave better yield than iodoethane. The purified bromo, chloro and iodo QAC by reaction of ethyl fatty amide washed with carbon tetrachloride was evaporated to dryness. The IR spectra elaborate the synthesized compounds as Bromo QAC: yield: 83.68%; IR (cm^{-1}) 1468, 1394 (Quaternary N^+), Chloro QAC: yield: 81.63%; IR (cm^{-1}) 1464, 1374 (Quaternary N^+), Iodo QAC: yield: 53.68%; IR (cm^{-1}) 1461, 1398 (Quaternary N^+). While the purified bromo, chloro and iodo QAC by reaction of methyl fatty amide washed with carbon tetrachloride was evaporated to dryness. The IR spectra elaborate the synthesized compounds as Bromo QAC: yield: 81.18%; IR (cm^{-1}) 1462, 1394 (Quaternary N^+), Chloro QAC: yield: 80.23%; IR (cm^{-1}) 1462, 1375 (Quaternary N^+), Iodo QAC: yield: 51.76%; IR (cm^{-1}) 1465, 1392 (Quaternary N^+). The ethanolic solution of each QAC was mixed with cane juice purchased from juice seller from local market of Lahore-Pakistan, and checked its function as clarifier. Chloro QAC was found be satisfactorily as compared to bromo and iodo QAC.

CONCLUSION

QACs were synthesized from locally available tallow and coconut oil as raw material which worked as surface active reagent for the clarification of sugar cane juice. As these compounds are being used in tons per year in production of different products in industry especially in sugar industry. Thus a big amount of foreign reserved can be saved by synthesis of such cheaper compounds.

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