SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF QUATERNARY HYDROXYALKYLAMMONIUM SALTS

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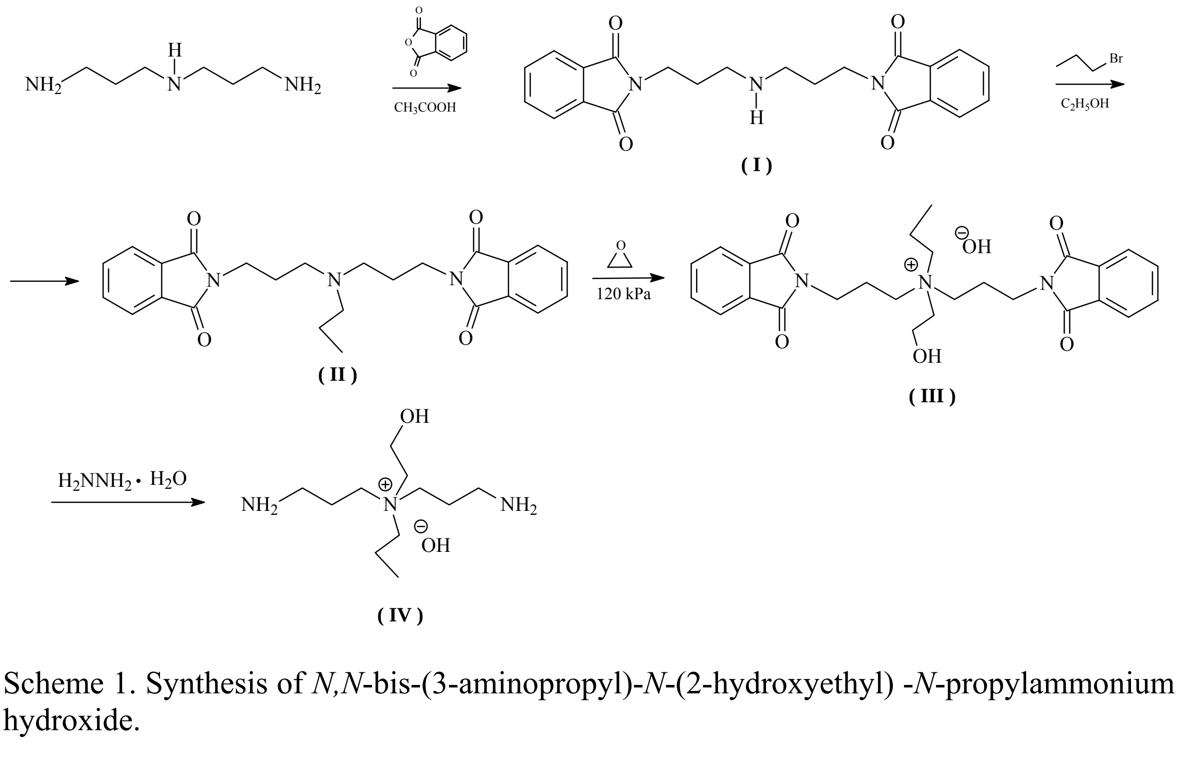
Introduction

Quaternary ammonium compounds having two alkyl chains and two hydrophilic groups in a molecule have been reported to show unexpected physicochemical properties in comparison with quaternary ammonium compounds having one alkyl chain and one hydrophilic group [1]. They show a good water solubility, much lower critical micelle concentration values (cmc), lower surface tension of aqueous solutions, very good foaming properties and high viscosity of their aqueous solutions.

In our studies of antimicrobial agents, we have designed and prepared so far new quaternary ammonium salts with two hydrophobic alkyl chains and two hydrophilic groups [2]. In this paper we present an efficient method of synthesis of novel quaternary ammonium compounds in which a hydroxyl group is connected to alkyl chain (Scheme 1). The spectroscopic properties (FTIR, ESI-MS, ^{1}H NMR, ^{13}C NMR) of these compounds have been investigated and compared to spectra of quaternary ammonium salts previously obtained.



Scheme 1. Synthesis of *N,N*-bis-(3-aminopropyl)-*N*-(2-hydroxyethyl) -*N*-propylammonium hydroxide.

Experimental section

The reagents and solvents were used of commercially available reagent quality. Preparation of *N,N*-bis-(3-phthalimidopropyl)amine (I) and *N,N*-bis-(3-phtalimidopropyl)-*N*-propylamine (II) were described in the last papers [2,3]. *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium hydroxide (III) were obtained by a reaction of *N,N*-bis-(3-phtalimidopropyl)-*N*-propylamine (II) with ethylene oxide in water-methanol mixture. The epoxidation reactions were performed in a steel reactor at 70^0C under pressure 100-120 kPa. The ethylene oxide consumption was precisely measured and recorded by a computer. After evaporation of the solvents, the highly viscous liquid was obtained (III). The crude product was used for the synthesis of compound (IV) with monohydrate hydrazine in ethanol at room temperature for 24 h. After this time, the precipitate, 2,3-dihydrophtalazine-1,4-dione, was filtered out and the residue was evaporated under vacuum to give yellow, highly viscosous oil. The TLC analysis have shown that quaternary ammonium salt (IV) was obtained almost quantitatively. To get the crystals of (III), the *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate (V) was prepared by a reaction of *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium hydroxide (III) with 2,4,6-trinitrophenol in water at room temperature for 48 h. Crude *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate was purified by a crystallization from acetonitryle (m.p.144^0C).

The structures of the prepared compounds were confirmed by molecular spectroscopy. The NMR spectra were measured with a Varian Gemini 300VT spectrometer, operating at 300,07 Hz and 75,46 Hz for ^{1}H and ^{13}C, respectively. Infrared spectra were recorded using a FTIR Bruker IFS 113v and IFS 66v/S spectrometers, in nujol and fluorolube. The ESI (electrospray) mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. The sample solutions were prepared in methanol at a concentration of approximately 10^{-5}M. The standard ESI mass spectra were recorded at the cone voltage 30V (50V, 80V).

Results and discussion

Quaternary ammonium salts having one or three nitrogen atoms and one hydroxyl group in alkyl chains were prepared by reactions shown in Scheme 1. Compounds (I) and (II) were obtained with very high yields due to the high reactivity of the primary and secondary alkylamine towards phthalic anhydride and alkyl halide, respectively. The ethylene oxide has been found to be an effective agent for preparing quaternary ammonium salts. The yield of the reaction with ethylene oxide under chosen conditions was over 70%.

The structures of synthesized compounds have been confirmed by FTIR, ESI-MS, ^{1}H and ^{13}C NMR spectroscopy.

FTIR spectra of *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate is shown in Fig. 1.

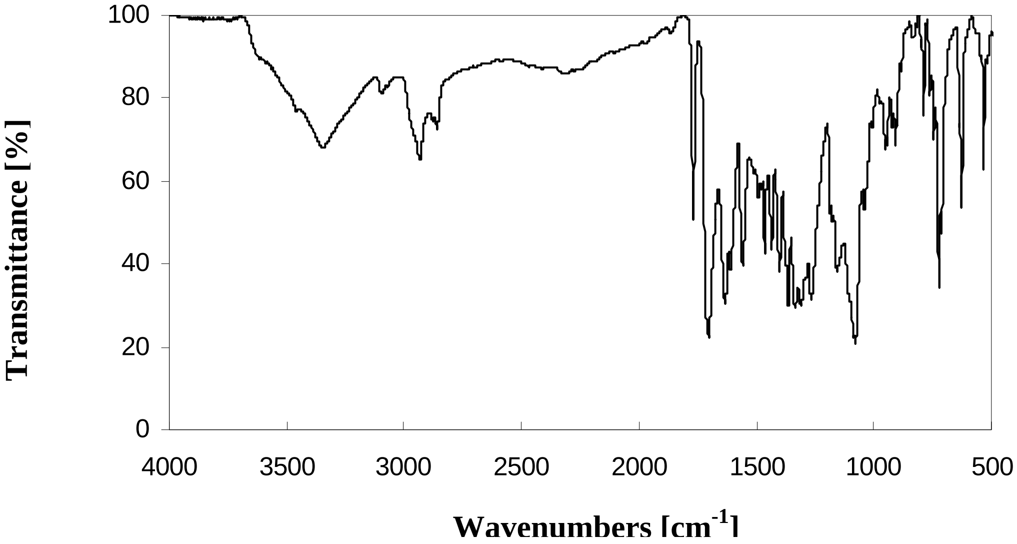


Fig. 1. FTIR spectra of *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate.

The FTIR spectrum shows a characteristic band in the region 1768-1702 cm^{-1} which is due to stretching, asymmetric and symmetric, vibrations of carbonyl group, ν(C=O), in a phthalimide moiety. No split of the carbonyl bands was observed what confirms the equivalence of the all carbonyl groups in the molecule. The broad band with a center about 3450 cm^{-1} corresponds to the stretching vibrations of OH group.

In the ^1H NMR spectra of *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate the protons of methylene groups are observed as triplets and multiplets in the range 1,8 – 3.7 ppm [1.87 (2H, m), 2.31 (4H,m), 3.53 (2H, m), 3.79 (6H, m)], methyl group at 1.92 ppm (3H, t) and ArH at 7.83 (8H, m).

In the ^{13}C NMR spectra of *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate the signals of carbon atoms of methylene groups are observed in the range 16.0 – 61.6 ppm and the peak of methyl group lies at 10.7 ppm. Aromatic carbon atoms resonate in the range 123.6 – 134.8 ppm. The signal of carbonyl group is observed at 168.5 ppm.

In the ESI spectrum of the *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate the most characteristic signal is at m/z 478. With increasing cone voltage the intensity of peak at m/z 478 decreases and the intensity of the signals at m/z 188 and m/z 160 increases. The most likely fragmentation pathway of these fragments of ammonium salt is shown in Figure 2. The ESI-MS spectra of *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium hydroxide show peaks corresponding to the fragmentation pieces including $C_{27}H_{32}N_3O_5$ (m/z 478), $C_{27}H_{32}N_3O_5 \cdot H_2O$ (m/z 496) and $C_{27}H_{32}N_3O_5 \cdot 2H_2O$ (m/z 514). The obtained results indicate that the physicochemical properties of ammonium salts depend on the counter anion.

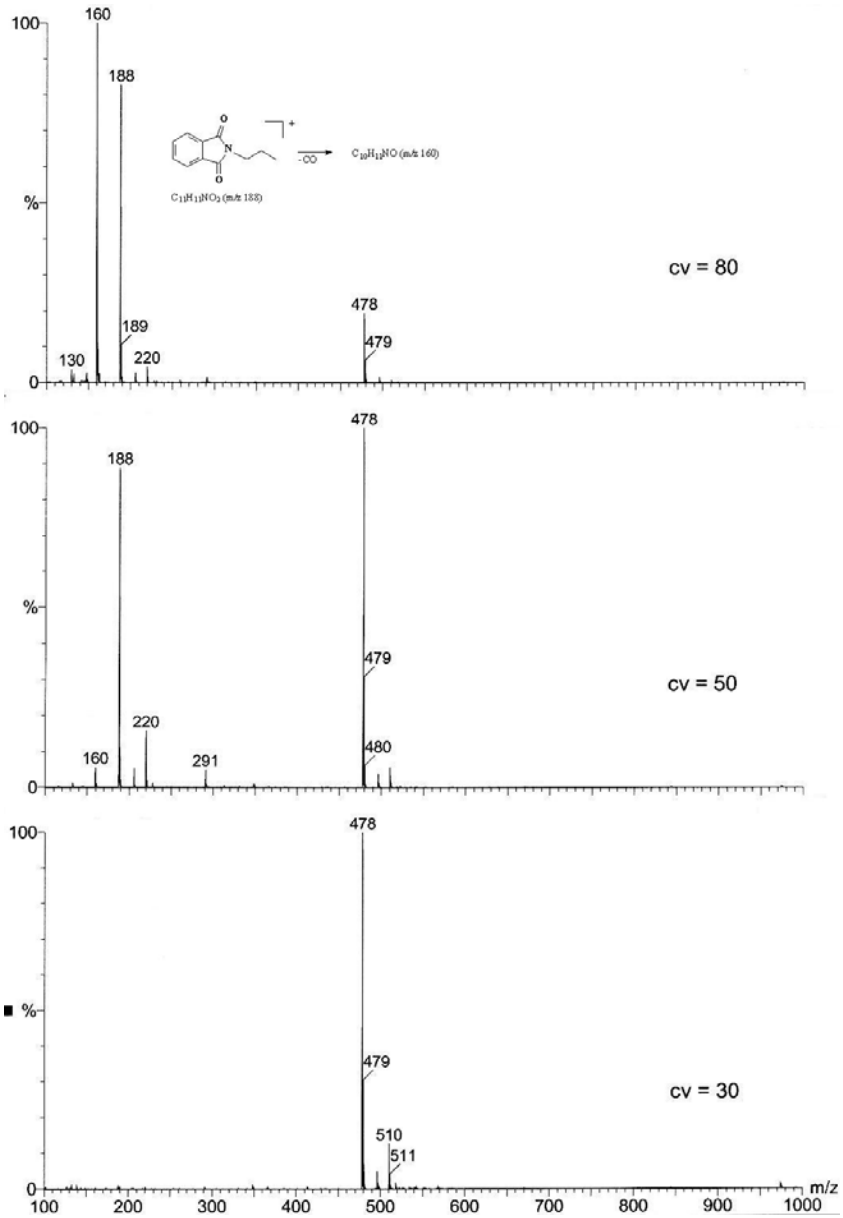


Fig. 2. The ESI-MS spectra of *N,N*-bis-(3-phthalimidopropyl)-*N*-(2-hydroxyethyl)-*N*-propylammonium picrate.

References

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