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ORIGINAL ARTICLE

Synthesis, Characterization and Properties of New Lauryl Amidopropyl Trimethyl Ammoniums

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Abstract A new lauryl amidopropyl trimethyl ammonium methyl carbonate with the formula $CH_3(CH_2)_{10}CONH(CH_2)_3N^+(CH_3)_3CH_3CO_3^-$ was synthesized via a high pressure process with tertiary amines and dimethyl carbonate, and its chemical structure was confirmed using ^{1}H-NMR spectra, mass spectral fragmentation, and FTIR spectroscopic analysis. In addition, several quaternary ammonium salts with new counterions X^- (X^-=HCO_3^-, $HCOO^-$, CH_3COO^-, $CH_3CH(OH)COO^-$) were also synthesized by the ion exchange reaction of methyl carbonate quaternary ammoniums with corresponding acids. The surface activities of these compounds were measured, including surface tension (γ), critical micelle concentration and minimum surface area (A_{min}) at 25 °C. Adsorption and micellization free energies of these quaternary ammonium salts in their solutions showed a good tendency towards adsorption at interfaces. The antimicrobial activities are reported for the first time against representative bacteria and fungi for lauryl amidopropyl trimethyl ammoniums. It was found that the antimicrobial potency was Gram-positive bacteria > fungi > Gram-negative bacteria.

Keywords Lauryl amidopropyl trimethyl ammonium · Dimethyl carbonate · Surface properties · Antimicrobial activity

Introduction

Quaternary ammonium salt cationic surfactants have attracted considerable attention due to their wide range of application, rapid development, and good prospects of valuable research [1–4]. A conventional quaternary ammonium salt cationic surfactant is always the long-chain alkyl quaternary ammonium salt and has some toxicity and poor biodegradability. In addition, the methylating agents of the synthesis of these compounds are commonly methyl chloride, methyl bromide, and dimethyl sulfate. They inevitably contaminate the environment.

In order to obtain cationic surfactants with better properties, while resolving toxicity and biodegradability, scientists have done a lot of research [5–7]. Numerous studies have confirmed that the water-soluble and biodegradability could be improved by adding new polar groups such as an ether, ester, amide, polyoxyethylene chain imidazoline ring and so on into the molecular structure of a typical quaternary ammonium cationic surfactant [8–12].

In this paper, a new series of quaternary ammonium salts containing amide groups were synthesized by use of non-toxic green chemical material, i.e., dimethyl carbonate. The surface activity and antimicrobial activity of these quaternary ammonium salt compounds were studied.

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Experimental Procedures

Synthesis of Lauryl Amidopropyl Trimethyl (Abridged as LAPTM) Ammonium Methyl Carbonate ($LAPTMA\text{-}CH_3CO_3$)

Dimethyl carbonate (0.2 mol), lauryl amidopropyl dimethyl amine (0.1 mol) and methanol solvent (0.5 mol) were introduced into a 100-ml stainless steel autoclave reactor and heated with stirring. At 1.4 MPa, the reaction mixture was stirred for 10 h at 150 °C. After the reaction, excess dimethyl carbonate and methanol solvent were vacuum-stripped in a rotary evaporator. Then the products were extracted in the water layer through a two-phase extraction with water and ethyl acetate. Water was removed by vacuum distillation and the remaining viscous brown liquid was purified by silica gel column, using methanol as the eluent. The final mixture was collected and recrystallized from acetone to give the compound with a yield of 90 %. The structure of the compound was confirmed by IR, ^{1}H NMR and MS.

Synthesis of LAPTM Ammonium with New Counterions

LAPTM ammonium methyl carbonate (0.01 mol), 0.01 mol of water or organic acids (formic acid, acetic acid and lactic acid) and methanol solvent (5 ml) were introduced into a 50-ml round-bottomed flask and heated with stirring. The reaction conditions were as follows: temperature 35 °C, reaction time 4 h. After the reaction, the mixture was condensed under reduced pressure and the crude products were recrystallized from acetone to give the lauryl trimethyl quaternary ammonium salts (94 % yields). The structure of the compound was confirmed by IR and MS.

Analytical Methods

Infrared (IR) spectra were recorded on a Nicolet islo FT-IR spectrometer. ^{1}H-NMR spectra were acquired on a Bruker AV-300 NMR spectrometer using $CDCl_3$ as solvent. Chemical shifts were reported in ppm related to internal tetramethylsilane. Mass spectra (MS) were performed on the AB SCIEX API3200LC/MS/MS spectrometer.

The surface tension of aqueous solutions was measured at 25 °C using a Dataphysics tensiometer DCAT11 by the Wilhelmy plate method.

The antimicrobial activity of the new compounds was tested against reference strains of Gram-positive (*Staphylococcus aureus* ATCC 6538) and Gram-negative (*Escherichia coli* ATCC 11105, *Pseudomonas aeruginosa* ATCC9027) and fungi (*Candida albicans* ATCC 10231). The antimicrobial activity was assessed by using the filter paper disk diffusion method. Initial screening for antibacterial and antifungal activity was performed by impregnating 6-mm sterile filter paper disks with 10 mg/ml of each substance and dried at 37 °C. Disks were distributed on the surface of dried agar plates inoculated with the microorganisms at approximately 10^6 cfu ml^{-1}. Plates were incubated at 37 °C for 24 h. Benzalkonium chloride was used as a reference because it is a common antiseptic agent. The presence of an absolute inhibition zone around the disk was used as the diameter of inhibition zones. Results are summarized in Table 2.

Results and Discussion

Preparation and Spectroscopic Characterization of the Lauryl Amidopropyl Trimethyl Ammoniums

The general formula and process of the lauryl amidopropyl trimethyl ammoniums are shown in Scheme 1.

These compounds were structurally characterized by their IR, ^{1}H-NMR and MS spectra. The details of these spectral characterizations were as follows. In all cases, the spectra acquired were consistent with the assigned structures of the compounds.

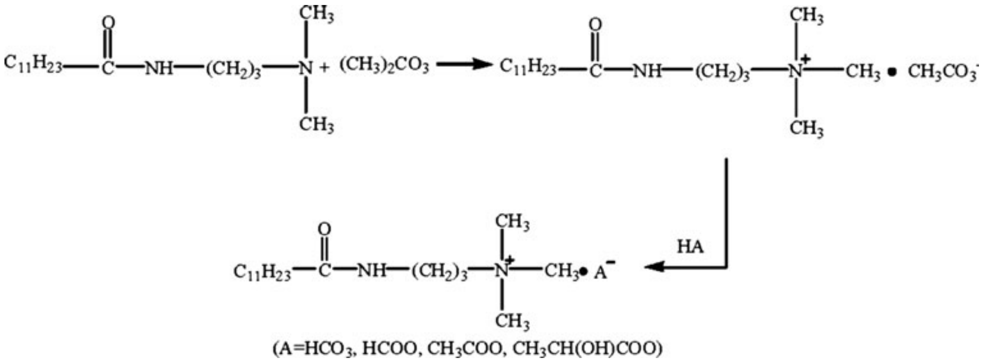
$LAPTMA\text{-}CH_3CO_3$: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 0.84–0.89 (t, 3H, CH_3), 1.24 (s, 16H, $(CH_2)_8$), 1.60–1.65 (m, 2H, CH_2), 2.10–3.37 (m, 2H, CH_2-CO), 2.10–3.37 (m, 2H, N-CH_2-CH_2), 3.28–3.42 (m, 2H, NH-CH_2), 3.28–3.42 (t, 2H, N-CH_2), 3.46 (s, 9H, N-CH_3), 3.65 (s, 3H, N-CH_2), 6.95 (s, H, N–H); Mass Spectra: Cationic scanning *m/e*: 299.7, 240.6. 240.6 is the fragment ion of 299.7, its appearance indicated that the DP voltage is too high to make the parent ion crack in the ion source; Anion scanning *m/e*: 74.9; FTIR Spectra: The broad band at 3,416 cm^{-1} characterized the NH groups. The stretching band at 2,851 cm^{-1}, 2,920 cm^{-1} characterized the CH_3 and CH_2 groups, respectively. The stretching band at 1,654 cm^{-1}, 1,630 cm^{-1} characterized the C=O groups. The stretching band at 1,105 cm^{-1} characterized the $COOCH_3$ groups.

LAPTM ammonium formate (LAPTMA-HCOO): Mass Spectra, Cationic scanning *m/e*: 299.5; Anion scanning *m/e*: 44.9. FTIR Spectra, 1,731 cm^{-1} characterized the C=O groups.

LAPTM ammonium acetate ($LAPTMA\text{-}CH_3COO$): Mass Spectra, Cationic scanning *m/e*: 299.5; Anion scanning *m/e*: 58.9. FTIR Spectra, 1,647 cm^{-1} characterized the C=O groups.

LAPTM ammonium lactate ($LAPTMAMA\text{-}CH_3CHOH\text{-}COO$): Mass Spectra, Cationic scanning *m/e*: 299.5; Anion scanning *m/e*: 88.6. FTIR Spectra, 3,385 cm^{-1} characterized the OH groups. 1,648 cm^{-1} characterized the C=O groups.

Scheme 1 Synthesis of the lauryl amidopropyl trimethyl ammoniums



(A=HCO$_3$, HCOO, CH$_3$COO, CH$_3$CH(OH)COO)

Surface Activity

The minimum surface tension (γ_{CMC}) values were acquired by analyzing the plateau region of the plots. A summary of the data is compiled in Table 1, which shows that the new lauryl amidopropyl trimethyl ammoniums surfactants significantly reduce the surface tension of the solution at low concentrations, indicating that these molecules adsorb strongly at the air/water surface and they are highly effective aqueous surfactants. From Table 1, we can see that these synthesized lauryl amidopropyl trimethyl ammoniums reduced the surface tension of water to a minimum value of approximately 28 mN m^{-1} at a concentration of 2.34×10^{-2} mol L^{-1}.

The critical micelle concentration (CMC) values were determined using a series of aqueous solutions at various concentration and estimated from the break point of each surface tension versus concentration (on log scale) curves. The relation between the surface tension and the concentration (log c) of the synthesized surfactants at 25 °C is represented in Fig. 1. The concentration ranges were chosen to cover a large range (from 0.05 to 0.0001 mol/L) to describe all the expected changes in the behaviors of the surface tension of the surfactant solutions. As is seen in Fig. 1, the surface tension-concentration relations are characterized by two distinguishable regions, one at the lower concentration range at which the surface tension values decrease rapidly, the other at higher concentrations at which the surface tension values remain almost constant. The dramatic change in slope of the surface tension versus log surfactant concentration curves suggests that these lauryl amidopropyl trimethyl ammoniums surfactants are forming micelles. In addition, it is clear that, as the hydrophilicity of the counterion is decreased, lower concentrations of the surfactants are needed to get equivalent surface tension values (Fig. 1). Furthermore, the results also showed that the CMC value decreases with decreasing the hydrophilicity of the counterion (Table 1). This trend suggests that an increase in the hydrophilicity of the compounds decreases the efficiency of the surfactant.

The maximum surface excess of the surfactant solution ($\Gamma_{\max}$), is defined as the concentration of the surfactant molecules at the interface near the critical micelle concentration. The maximum surface excess of the synthesized lauryl amidopropyl trimethyl ammoniums was calculated using the approximate form of the Gibbs adsorption isotherm equations:

$$\Gamma_{\max} = -\frac{1}{2.303nRT}\left(\frac{\partial \gamma}{\partial \log C}\right)_T \tag{1}$$

The minimum surface area ($A_{\min}$) or the area occupied by each surfactant molecule at the air/water interface is calculated according to the formula:

$$A_{\min} = \frac{1}{N_{\mathrm{A}}\Gamma_{\max}} \tag{2}$$

where $R = 8.3144$ J mol^{-1} K^{-1}, N_{A} = Avogadro's number, $\Gamma_{\max}$ is the maximum surface excess at a constant temperature. In our solution, we can set $n = 2$.

The minimum surface area ($A_{\min}$) appears to be determined by the area occupied by the hydrated hydrophilic groups, rather than by the hydrophilic group, because the

Table 1 Surface tension (γ_{CMC}), critical micelle concentration (CMC), minimum surface area ($A_{\min}$), free energy changes of adsorption (ΔG_{ads}) and micellization (ΔG_{mic}) of the synthesized lauryl amidopropyl trimethyl ammoniums at 25 °C

Compound	γ_{CMC} (mN m^{-1})	CMC (mol l^{-1})	$A_{\min}$ (A_2)	ΔG_{mic} (KJ mol^{-1})	ΔG_{ads} (KJ mol^{-1})
LAPTMA-CH$_3$CO$_3$	29.04	2.24×10^{-2}	35.12	−19.37	−28.49
LAPTMA-HCOO	28.15	2.34×10^{-2}	28.74	−19.26	−26.88
LAPTMA-CH$_3$COO	30.19	2.40×10^{-2}	30.59	−19.20	−26.94
LAPTMA-CH$_3$CHOHCOO	33.69	2.57×10^{-2}	33.29	−19.03	−26.75

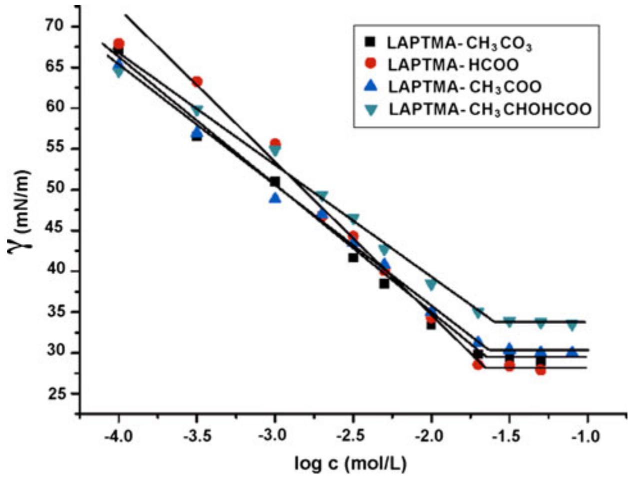


Fig. 1 Surface tension versus the logarithm of the aqueous molar concentration (log *c*) of synthesized lauryl amidopropyl trimethyl ammoniums at 25 °C

chains in typical ionic or nonionic surfactants with hydrophilic groups at one end of the molecule do not lie flat on an interface but rather are somewhat tilted with respect to it. It is confirmed by the $A_{\min}$ values in Table 1, that the area occupied by each surfactant molecule of the ammonium formate, ammonium acetate and ammonium lactate surfactants at the interface increases as the hydrophilicity of the counterion increases.

The free energies of adsorption (ΔG_{ads}) and micellization (ΔG_{mic}) were calculated according to Rosen's methodology:

$$\Delta G_{\mathrm{mic}} = RT \ln\left(\frac{\mathrm{CMC}}{55.5}\right) \tag{3}$$

$$\Delta G_{\mathrm{ads}} = \Delta G_{\mathrm{mic}} - 6.022(\gamma_0 - \gamma\mathrm{CMC})A_{\min} \tag{4}$$

where $R = 8.3144$ J mol^{-1} K^{-1}, γ_0 is the surface tension of the bidistilled water, γ_{CMC} is the surface tension at the CMC. $A_{\min}$ is the area occupied by each surfactant molecule at the air/water interface.

The negative values of ΔG_{ads} and ΔG_{mic} in Table 1 indicates that both adsorption and micellization are spontaneous at 25 °C. The free energy of micellization (ΔG_{mic}) of the lauryl amidopropyl trimethyl ammonium surfactants increases as the hydrophilicity of the counterion increases, indicating that the processes are not thermodynamically favored.

Thus far, most of the traditional surfactants counterion have been inorganic ions and there have been many reports about the study of the changes of surface tension with the hydrophobic chain length. However, the influence of surfactant counterions on the surface tension has been rarely reported in the literature. The data in Table 1 indicates that organic counterions have a significant influence on surface tension. The surface tension variation trend of ammonium formate, ammonium acetate, and ammonium lactate is gradually increasing. As the hydrophilicity of the counteranion increases, the surface tension value increases. The same results appeared in our previous studies [13]. We have also confirmed that the quaternary ammonium salts with these organic counterions all showed better properties than the quaternary ammonium salt with Cl^- as a counterion [13]. From the above comparison and contrast, one can safely conclude that the interaction between the counterion and the cationic charged group has a significant influence on surface tension.

Antimicrobial Activity

The results of the disc-diffusion assay (Table 2) show that all of the synthesized compounds displayed bactericidal activity slightly less or greater to that of the control on all four strains tested. On *Staphylococcus aureus*, all strains show excellent bactericidal activity to that of the control. However, on the other strains tested, there were structural differences in efficacy, with some structures of acetic and lactic ammoniums showing high efficacy.

Sterilization is due to the adsorption and penetration of surfactant molecules at the microbial surface. The adsorption and penetration depends on the hydrophobic chain length, surface activities, and the dosage of these cationics. With the same hydrophobic chain length and dosage, compounds which were easily absorbed and permeated into the bacterial cell membrane exhibited better bactericidal properties. The data in Table 1 describe the

Table 2 Antibacterial and antifungal in vitro activity of synthesized surfactants using the disc-diffusion method at 10 mg/ml

Compound	Microorganism-inhibition zone diameter (mm)			
	Staphylococcus aureus	*Escherichia coli*	*Pseudomonas aeruginosa*	*Candida albicans*
LAPTMA-CH_3CO_3	28.6	11.0	13.2	11.2
LAPTMA-HCOO	35.4	17.9	10.9	31.3
LAPTMA-CH_3COO	34.7	23.0	18.9	33.7
LAPTMA-$CH_3CHOHCOO$	38.1	23.3	19.7	33.9
Benzalkonium chloride	21.9	20.4	18.5	20.3

adsorption potential of the synthesized compounds at the interfaces. Formate, acetic, and lactic ammoniums showed a similar free energy change of adsorption at the interfaces. However, acetic and lactic ammoniums showed higher bactericidal activities while formate ammoniums did not. It is more likely that the penetration of formate ammoniums is weaker than acetic and lactic ammoniums in some bacteria.

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