ORIGINAL ARTICLE

Properties of the Quaternary Ammonium Salts with Novel Counterions

Hui-cheng Yan · Qiu-xiao Li · Tao Geng · Ya-jie Jiang

Abstract The Krafft temperatures, surface tensions and bacteriostatic efficacies of a series of dodecyl/tetradecyltrimethylammonium salts with new type counterions based on the general formula $RN^+(CH_3)_3 \ A^-$ were measured. The results revealed that the Krafft temperatures of the studied products were below 0 °C and the surface tensions of water were decreased to 22–42 mN m^{-1} when applying these surfactants at a concentration range from 10^{-2} to 10^{-4} mol L^{-1}. Moreover, the physicochemical parameters such as the saturation adsorption value, the minimum area per surfactant molecule and the standard thermodynamic parameters of adsorption and micellization varied with different counterions for these prepared quaternary ammonium salts. In addition, the bacteriostatic tests showed that the counterions with shorter carbon chain lengths were associated with greater efficacy for the novel quaternary ammonium salts studied here.

Keywords Novel counterion · Krafft temperature · Surface activity · Thermodynamic property · Bacteriostatic efficacy

Introduction

It is well known that the quaternary ammonium salts (QAS) are used for wood preservation, phase transfer catalysts, fabric softeners, electrostatic providers, biocides, germicides, dispersants, hair conditioners, and so on [1, 2].

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Because of this widespread use, the synthesis research of QAS is always of great interest, and a lot studies are concerned with the cationic part of QAS [1–4]. However, the modification of counterions is rarely reported.

Commonly, QAS are prepared by alkyl agents such as alkyl halides or dimethyl sulfate, which inevitably contaminate the environment and bring toxicity to the target products [2]. Moreover, the counterions of QAS are confined to Cl^-, Br^- and $CH_3OSO_3^-$, thus restricting the development of QAS. In order to break this bottleneck, researchers have began to focus on a green quaternization agent—dimethyl carbonate (DMC) [5]. Meanwhile, a useful compound derived from quaternary ammonium salts methyl carbonates (QASMC), has been synthesized from DMC and a tertiary amine [6, 7]. Compared to the conventional QAS, this kind of QASMC can easily react with different acids to prepare the QAS with novel counterions due to the weak acidity of counterions arising from monomethyl carbonates groups. In this way, many kinds of QAS were able to be prepared and these novel QAS possess special characteristics [6]. It is obvious that the relationships between the structures of the counterions and their properties should be given more attention.

There are a lot of studies about the effect of counterions on the properties of anionic surfactants [8–14], indicating that the different types of counterions play an important role in the improvement of solution properties such as the surface activities and phase behavior. However, similar works for cationic surfactants are much less common. Therefore, it was deemed necessary to investigate the effect of different counterions on the properties of QAS.

In the present work, a series of dodecyl/tetradecyltrimethylammonium salts were developed. The Krafft temperatures of the synthesized surfactants were measured, and their surface activities and thermodynamic properties

were studied. Moreover, the bactericidal efficacy of the novel surfactants against *Escherichia coli* and *Staphylococcus aureus* were also evaluated.

Experimental

Chemical Reagents

Dodecyl/tetradecyldimethylamine (the molar ratio of dodecyldimethylamine and tetradecyldimethylamine is 0.4:0.6) and dimethyl carbonate were obtained from Shanghai Jinshan Jingwei Chemical Co. Ltd. and Shandong Shida Shenghua Chemical Co. Ltd. in China, respectively. Formic acid, acetic acid, propionic acid, ethacetic acid, hexanoic acid, octanoic acid, decanoic acid and ethyl acetate were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. in China.

Preparation of the Dodecyl/ Tetradecyltrimethylammonium Salts

The intermediate product, dodecyl/tetradecyltrimethylammonium mono-methyl carbonate (D/TTAMC), was prepared from dimethyl carbonate (DMC) and dodecyl/tetradecyldimethylamine [7]. Then, the QAS (D/TTAMC obtained) was reacted with one of the organic acids (formic, acetic, propionic, butanoic, hexanoic, octanoic and decanoic) to synthesize the corresponding quaternary ammonium salts. When the reaction was complete, the excess solvent was removed in a rotary evaporator and the target products were collected. All of the prepared crude products were purified five times by recrystallization in ethyl acetate to obtain the pure QAS with novel counterions. The synthesis route of targeted products is shown in Scheme 1.

Characterization of the Structures

The structures of the novel QAS were characterized by IR (Model 273-30, Hitachi, Japan) and ^{1}H NMR (Model DRX300, Bruker, Germany).

The Krafft Temperature Measurement

The Krafft temperature was measured by gradually heating 1 wt% turbid liquid (0.10 g sample was added into 10.0 mL deionized water) in a thermostatic bath until a transparent solution was formed, according to visual observation. The heating steps were 0.5 °C with 10 min equilibration time at each temperature. The test was repeated several times (usually five times) until a constant temperature was achieved [15].

Surface Tension Measurement

A series of sample solutions were prepared in deionized water with the concentrations ranging from 10^{-5} to 10^{-2} mol L^{-1}. The solutions were kept for 2 h in a thermostatically refrigerated shaker at a temperature of 25 ± 0.2 °C before the surface tension measurement was carried out. The aqueous solution equilibrium surface tension was measured with a K-12 tensiometer (Krüss, Germany) with a platinum ring and the test was repeated three times for each concentration. Prior to measurement, the surface tension of deionized water was confirmed in the range of 72.3 ± 0.3 mN m^{-1}.

Evaluation of the Bacteriostatic Efficacy of the Novel QAS

The method was following procedure QB/T 2738-2005 [16]. First of all, 90 mg L^{-1} of sample solution, 0.03 mol L^{-1} of

Scheme 1 Synthetic route of the dodecyl/tetradecyltrimethylammonium salts with novel counterions
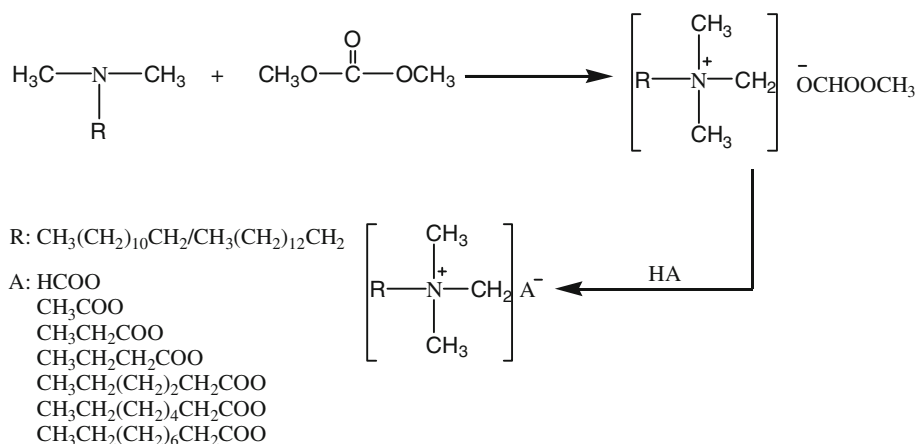
phosphate buffered brine (PBS) and nutrient agar plates were prepared. Here, it must be stressed that the PBS and nutrient agar plates, whose pH values were adjusted to 7.2–7.4, were sterilized under pressure (121 °C) for 20 min. Then, 0.10 mL of a bacterial solution (the bacteria were either *E. coli* or *S. aureus*, and the bacterial concentration was $1–9 \times 10^4$ CFU mL^{-1}) was added to a 5.0-mL sample solution and mixed for 2 min. After that, 0.10 mL of the mixed solution was dropped into a test tube with 5.0 mL of sterile PBS solution, and the test tube was shaken vigorously several times and allowed to stand for 10 min. Finally, 1.0 mL dilute solution was withdrawn and laid over the nutrient agar plate using sterile glass spreader. The plates were incubated for 48 h at 37 °C and the viable cell count was noted by the colony count method. A control test, which contains no quaternary ammonium salts, was also included in the experiment. The experiment was repeated three times for each sample.

Results and Discussion

IR and ^{1}H NMR of the QAS with Novel Counterions

The structures of the QAS with novel counterions were characterized by IR and ^{1}H NMR. The results are as follows. Dodecyl/Tetradecyltrimethylammonium formate (D/TTAF): IR (KBr, v, cm^{-1}): 2,924–2,854 (C–H), 1,586 (C=O), 1,467 (C–N); ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 0.816–0.837 (t, 3H, CH$_3$), 1.213–1.286 (m, (CH$_2$)$_9$/(CH$_2$)$_{11}$), 3.237 (s, 9H, N–CH$_3$), 3.325–3.352 (t, 2H, N–CH$_2$), 8.699 (s, 1H, HCOO).

Dodecyl/Tetradecyltrimethylammonium acetate (D/TTAA): IR (KBr, v, cm^{-1}): 2,929–2,850 (C–H), 1,576 (C=O); ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 0.871–0.901 (t, 3H, CH$_3$), 1.263–1.352 (m, (CH$_2$)$_9$/(CH$_2$)$_{11}$), 1.738 (s, 2H, CH$_2$), 1.942 (s, 3H, CH$_3$COO), 3.317 (s, 9H, N–CH$_3$), 3.361–3.379 (t, 2H, N–CH$_2$).

Dodecyl/Tetradecyltrimethylammonium propionate (D/TTAP): IR (KBr, v, cm^{-1}): 2,971–2,867 (C–H), 1,602 (C=O), 1,463 (C–N); ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 0.884–0.927 (t, 3H, CH$_3$), 1.089–1.1140 (t, 3H, CH$_3$CH$_2$COO), 1.281–1.360 (m, (CH$_2$)$_9$/(CH$_2$)$_{11}$), 1.756 (s, 2H, CH$_2$), 2.188–2.264 (t, 2H, CH$_3$CH$_2$COO), 3.321 (s, 9H, N–CH$_3$), 3.331–3.404 (t, 2H, N–CH$_2$).

Dodecyl/Tetradecyltrimethylammonium ethacetate (D/TTAE): IR (KBr, v, cm^{-1}): 2,960–2,859 (C–H), 1,586 (C=O), 1,475 (C–N); ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 0.874–0.896 (t, 3H, CH$_3$), 1.273–1.348 (m, (CH$_2$) and (CH$_2$)$_9$/(CH$_2$)$_{11}$), 1.72 (s, 2H, CH$_2$), 2.029–2.143 (t, 2H, CH$_2$), 3.321 (s, 9H, N–CH$_3$), 3.331–3.404 (t, 2H, N–CH$_2$).

Dodecyl/Tetradecyltrimethylammonium hexanoate (D/TTAH): IR (KBr, v, cm^{-1}): 2,975–2,854 (C–H), 1,593 (C=O), 1,473 (C–N); ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm):

0.863–0.878 (t, 6H, 2CH$_3$), 1.240–1.257 (m, (CH$_2$)$_3$ and (CH$_2$)$_9$/(CH$_2$)$_{11}$), 1.740 (s, 2H, CH$_2$), 2.137–2.161 (t, 2H, CH$_2$), 3.360 (s, 9H, N–CH$_3$), 3.361–3.374 (t, 2H, N–CH$_2$).

Dodecyl/Tetradecyltrimethylammonium octanoate (D/TTAO): IR (KBr, v, cm^{-1}): 2,975–2,857 (C–H), 1,576 (C=O), 1,469 (C–N); ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 0.794–0.810 (t, 6H, 2CH$_3$), 1.186–1.35 (m, 32H, (CH$_2$)$_5$ and (CH$_2$)$_9$/(CH$_2$)$_{11}$), 1.618 (s, 2H, CH$_2$), 2.087–2.131 (t, 2H, CH$_2$), 3.243 (s, 9H, N–CH$_3$), 3.268–3.299 (t, 2H, N–CH$_2$).

Dodecyl/Tetradecyltrimethylammonium decanoate (D/TTAD): IR (KBr, v, cm^{-1}): 2,960–2,854 (C–H), 1,602 (C=O), 1,468 (C–N); ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 0.865–0.876 (t, 6H, 2CH$_3$), 1.250–1.263 (m, 36H, (CH$_2$)$_7$ and (CH$_2$)$_9$/(CH$_2$)$_{11}$), 1.718 (s, 2H, CH$_2$), 2.153–2.162 (t, 2H, CH$_2$), 3.360 (s, 9H, N–CH$_3$), 3.363–3.372 (t, 2H, N–CH$_2$).

Krafft Temperature

The Krafft temperature, T_K, is an important parameter for the ionic surfactants. Generally, T_K is defined as the temperature above which ionic surfactant rapidly starts to solubilize in water to form micelle [1, 15]. Obviously, when the operating temperature exceeds the T_K, the surfactant solution may form micelle at certain concentration, and thus, the solution can show good surface activity. Here, the T_K of the novel QAS were measured and the results were shown in Table 1.

In Table 1, it was clearly seen that the T_K values of these surfactants were lower than 0 °C. This indicates that the novel QAS has a wide temperature range, which is known to extend the surfactant applications.

The Minimum Surface Tension and Critical Micelle Concentration

In order to investigate the surface activities of these novel QAS, the equilibrium surface tensions of deionized water solution were measured and their isotherms were plotted as in Fig. 1. As a result, the surface tension curves varied with different carbon chain length of counterions and all the novel surfactants could significantly reduce the surface tension of water at low concentration. The specific parameters based on the curves were shown in the Table 1. It is noteworthy that the absence of a minimum in the surface tension curves around the CMC corroborates the high purity of the surfactants.

It was observed from Table 1 that the surface tension of water was reduced considerably by the novel surfactants, and most of the novel QAS had much lower γ_{CMC} values than that of conventional QAS with chloride anions. This result indicated that the surface activities of the QAS with

Table 1 Surface properties of the quaternary ammonium salts

	D/TTAC	D/TTAF	D/TTAA	D/TTAP	D/TTAE	D/TTAH	D/TTAO	D/TTAD
T_K (°C)	<0	<0	<0	<0	<0	<0	<0	<0
CMC (mol/L)	0.0070	0.0037	0.0039	0.0089	0.0069	0.0018	0.0010	0.00030
γ_{CMC} (mN/m)	38.69	33.53	35.42	42.71	40.31	34.10	26.96	22.80
π_{CMC} (mN/m)	33.61	38.77	36.88	29.59	31.99	38.20	45.34	49.50
PC_{20}	2.70	3.10	3.05	2.30	2.57	3.30	3.82	4.52
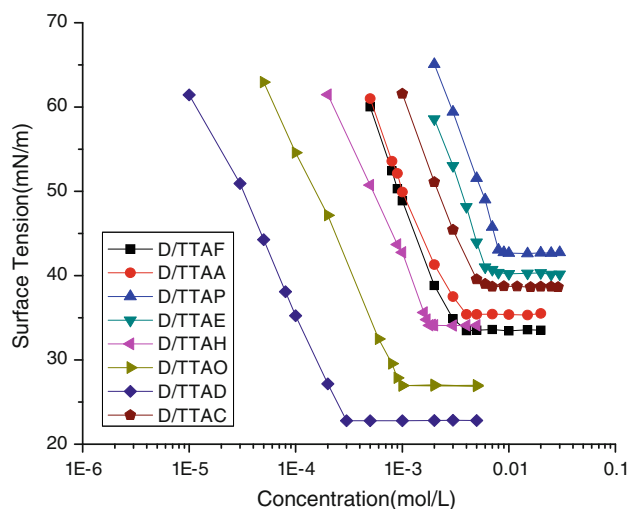
Fig. 1 Surface tensions of aqueous solutions of the novel QAS at 25 °C

novel counterions were enhanced compared to the common one.

It was also observed from Table 1 that the γ_{CMC} values of the novel QAS increased until the counterions contain three carbons, and then the γ_{CMC} values decreased continually on increasing the chain length of the counterions. The trend can be explained in the following way: the propionate and butanoate ionics can partly intrude into the adsorption layer, probably resulting in diminished accumulation of the cationic segment at the air/water interface and hence the γ_{CMC} values are higher than the others. However, the hexanoate, octanoate and decanoate ionics are surface active ionics and they can easily insert themselves into the adsorption layer; the effective adsorption of these surfactants increased because the influence of electrostatic attraction between the cationic part and counterions. Therefore, their minimum surface tensions are greatly decreased at the air/water interface.

The CMC values of the novel QAS (except D/TTAP), as presented in Table 1, are smaller than that of dodecyl/tetradecyltrimethylammonium chloride (D/TTAC), indicating that these compounds aggregate more easily in the solution.

Their micellization processes took place at concentration levels of approximately 10^{-3} mol/L^{-1} or much lower. In Table 1, we can also see that the CMC values were decreased significantly when the carbon chain length of the counterions exceeded six carbons. This decrease can be attributed to the fact that the electrostatic repulsion of the cationic head group can be efficiently shielded with increasing chain length of the counterions and the process is helpful for micelle formation. In addition, these counterions can aggregate to form micelles by themselves due to their own surface activities. It is thus apparent that the three kinds of QAS can significantly reduce the concentrations of micelle formation.

The Effectiveness and Efficiency of Surface Tension Reduction

The effectiveness and efficiency of surface tension reduction can be estimated by Eqs. 1 and 2, respectively.

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \tag{1}$$

$$PC_{20} = -\log_{10} c_{(\pi=20)} \tag{2}$$

in which γ_0 is the surface tension of pure water, γ_{CMC} is the surface tension of the solution at the CMC, and $c_{(\pi=20)}$ is the concentration of surfactant that reduces the surface tension by 20 mN m^{-1} at the air/water interface.

For the known conventional QAS as the D/TTAC π_{CMC} it is less than 35 mN m^{-1}, whereas for the ones studied presently, most of the π_{CMC} values are much larger than 35 mN m^{-1} (especially the D/TTAO and D/TTAD), as shown in Table 1. The fact suggests that most of the novel QAS may be regarded as cationic surfactants of high effectiveness as far as the surface tension reduction is concerned. The PC_{20} values were shown by the similar results as compared to D/TTAC, indicating that most of QAS with novel counterions have better efficiency of adsorption at the air/water interface. In a word, most of the novel QAS have much higher surface activities than that of conventional QAS with chloride.

More importantly, we can see from Table 1 that the π_{CMC} and PC_{20} values have the same change trends. It is evident that the effects of these counterions on QAS have

the consistency between the effectiveness and efficiency of surface tension reduction.

Adsorption at the Air/Water Interface

The maximum surface excess concentrations (Γ_{max}) at the air/water interface are obtained from the Gibbs adsorption isotherm equations (Eq. 3) [1, 13, 19].

$$\Gamma = -\frac{1}{2.303 \times nRT}\left(\frac{\partial\gamma}{\partial\log c}\right)_T \qquad (3)$$

where $R = 8.314$ J (mol K)$^{-1}$, $T = 298.15$ K, $(\partial\gamma/\partial\log c)$ is the slope of the linear portion in the range of concentrations immediately before the CMC. In our solutions, due to the electrolyte activity, we can set $n = 2$ in Eq. (3) for D/TTAF, D/TTAA, D/TTAP and D/TTAE. However, for D/TTAH, D/TTAO and D/TTAD, we consider $n = 1$ and $\Gamma_+ = \Gamma_- = 1/2\Gamma_{total}$ because these extended carbon chains of counterions can easily insert themselves into the adsorption layer, and the opposite charges of cationic part and anionic one in adsorption layer could be counteracted by themselves, so the diffused electric doublet layer disappears at the air/water interface [17–19]. The Γ_{max} values are used to calculate the minimum area per surfactant molecule (A_m) using Eq. 4 [1, 13, 19].

$$A_m = \frac{10^{16}}{N\Gamma_{max}} \qquad (4)$$

where Γ_{max} is in mol cm^{-2} (for the QAS with long carbon chains of counterions, $\Gamma_{max} = \Gamma_{total}$), N is Avogadro's number and A_m is in Å^2/molecule.

The calculated results presented in Table 2 confirm that the carbon chain length of counterions plays an important role in determining the maximum surface excess concentration (Γ_{max}) and the minimum area per surfactant molecule (A_m) at the air/water interface. In Table 2, it is worth noting that the Γ_{max} values of the cationic part decreases with increasing the carbon chain length of the counterions. However, for more than six carbons, the Γ_{max} values of the cationic segment tends to increase.

In addition, another fact is also seen in Table 2. When the carbon chain length of counterions exceeds six carbons, the minimum area per surfactant molecule (A_m) of the novel surfactants is decreased significantly in comparison with the counterions containing one or two carbons. Their A_m values were close to 30 Å^2, which were lower than the others (>50 Å^2). This fact reveals that the molecules of cationic surfactants with long-chain counterions (six or more carbon atoms) are arranged closer than the cationic surfactants with short-chain counterions at the air/water interface.

Thermodynamic Properties

The standard Gibb's free energy of micellization (ΔG_{mic}) values for these novel QAS can be calculated from Eq. 5 [1, 19].

$$\Delta G_{mic}^{\theta} = 2RT\ln_{CMC} \qquad (5)$$

where, R is 8.314 J (mol K)$^{-1}$ and T is 298.15 K.

The standard Gibb's free energy of adsorption (ΔG_{ad}) values for these investigated surfactants are obtained using Eq. 6 [20, 21].

$$\Delta G_{ad}^{\theta} = \Delta G_{mic}^{\theta} - 0.602\pi_{CMC} A_{CMC} \qquad (6)$$

here, A_{CMC} is in Å^2/molecule, and π_{CMC} is the surface pressure at CMC in the air/water interface (mN m^{-1}).

The standard Gibb's free energy of micellization and adsorption values are presented in Table 3. It may be easily concluded that the micellization and adsorption processes are spontaneous because all the data are negative. Moreover, it was also found that the standard Gibb's free energy of adsorption is more negative than that of the standard

Table 2 The surface adsorption parameters of the novel surfactants

	D/TTAC	D/TTAF	D/TTAA	D/TTAP	D/TTAE	D/TTAH	D/TTAO	D/TTAD
$\Gamma_{max} \times 10^{10}$ (mol/cm^2)	3.05	3.26	3.20	2.99	2.93	2.34[a]	2.47[a]	2.64[a]
A_m (Å^2)	54.46	50.95	51.91	55.56	56.69	35.49	33.76	31.46

[a] The Γ_{max} values are the maximum surface excess concentrations of the cationic part

Table 3 Thermodynamic parameters of micellization and adsorption for the novel surfactants

	D/TTAC	D/TTAF	D/TTAA	D/TTAP	D/TTAE	D/TTAH	D/TTAO	D/TTAD
ΔG_{mic} (kJ/mol)	−24.58	−27.74	−27.48	−23.40	−24.66	−31.32	−34.24	−40.20
ΔG_{ad} (kJ/mol)	−25.68	−28.94	−28.64	−24.39	−25.75	−32.14	−35.16	−41.14

Table 4 The rate of bacteriostasis of the novel QAS

The rate of bacteriostasis (%)	Sample						
	D/TTAF	D/TTAA	D/TTAP	D/TTAE	D/TTAH	D/TTAO	D/TTAD
E. coli	97	96	95	93	90	96	93
S. aureus	98	87	72	69	58	61	40

Gibb's free energy of micellization for the same surfactant. This result showed that the process of adsorption of surfactant molecules at the air/water interface precedes the micellization in the bulk.

It should be denoted that the change in ΔG_{mic} values of the entire novel QAS in Table 3 agreed with the trend shown by the critical micelle concentration values listed in Table 1. Especially, the ΔG_{mic} values of D/TTAH, D/TTAO and D/TTAD are found to become more negative compared to the other novel QAS. The result indicated that the micellization of these surfactants are more easily than the others. This may be ascribed to the strong "shielding effect" with the counterions on the surface of the micelle [1, 19]. On the other hand, the free energy of adsorption showed the same change trend as the ΔG_{mic} values with increasing the carbon chain length of counterions.

Bacteriostatic Efficacy of the Novel QAS

The bacteriostatic property is one of the main characteristic applications of the quaternary ammonium salts [22–24]. In this work, the effect of the novel QAS on antimicrobial properties against *E. coli* and *S. aureus* at a concentration level of 90 mg L^{-1} were measured. The rate of bacteriostasis is calculated by the relationship:

$$\text{The rate of bacteriostasis}\,(\%) = \frac{A - B}{A} \times 100\% \qquad (7)$$

here, A is the average CFU of control sample, and B is the average CFU of test sample.

The rate of bacteriostasis of the novel QAS against *E. coli* and *S. aureus* are shown in Table 4. It is clearly seen that all the novel QAS have high bacteriostatic efficacy for E. coli at a concentration level of 90 mg L^{-1} because the rates of bacteriostasis were much higher than 90%. However, for *S. aureus*, the bacteriostatic activities are greatly affected by the chain length of the counterions. The results from Table 4 show that the bacteriostatic efficacy of the tested QAS gradually decreases with increasing the carbon chain length of counterions, especially if it exceeds six carbons with the rate of bacteriostasis being lower than 60%. The results for these novel QAS indicated that the chain length of the counterions was shorter, and the bacteriostatic efficacy of the QAS against *S. aureus* was better.

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