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ORIGINAL ARTICLE

Micellar Properties for Propoxylated Surfactants in Water/Alcohol Solvent Mixtures and Their Antibacterial and Polyester Fabric Antistatic Performances

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Abstract Two propoxylated quaternary amine surfactants characterized by two and six average PO adduct numbers (PO-2 and PO-6 QA surfactants) were synthesized to investigate the micellar properties of propoxylated cationic surfactants in water/alcohol mixtures. The effect of PPO groups on micelle formation was explored using conductivity, UV–vis spectroscopy, dynamic light scattering techniques. Regular or reverse micellization occur with water or alcohol rich solvent mixtures, respectively. For intermediate composition no micellization occurs. Also the performances in antibacterial and antistatic fabrics were studied. PO-2 QA surfactant has excellent antibacterial activities against both the Gram-negative bacterium *Escherichia coli* and the Gram-positive bacterium *Staphylococcus aureus* while both surfactants have good antistatic activity over polyester fabric.

Keywords Micellar properties · Cationic propoxylate surfactant · Water/alcohol mixtures · Antibacterium · Polyester fabric antistatic property

Introduction

Ethoxylate or propoxy ethoxylate surfactants with hydrophilic PEO groups in aqueous solutions have been investigated both experimentally and theoretically [1, 2]. But the micellization behavior in water for a propoxylated surfactant with hydrophobic PPO groups which have an affinity for short alkyl chain alcohol has been not widely studied [3]. Water as an important solvent of high polarity is generally used in the research of surfactant molecule self-assembly, such as stearate-g-dextran micelles made in aqueous solution for the delivery of antitumor drug [4]. However surfactant micelles formed in water/organic solvent mixtures are useful as enzyme catalysis microreactors, encapsulated proteins and nanoreactors for the synthesis of silver and copper nanoparticles and to extract oil and proteins from vegetable meals [5–7]. Short alkyl chain alcohols as the most studied nonaqueous polar solvents, for example ethanol and isopropanol, are miscible with water [8]. It is interesting to investigate propoxylated surfactant micellar properties in water/alcohol mixtures to address (a) how the composition of those solvent mixtures affects surfactant micellization behavior, (b) the contributions of PPO groups to micellar performances, (c) whether micelles are formed in all solvent mixtures.

In this paper, two propoxylated cationic surfactants, each made up of hydrophobic segments alkyl (C12) and PPO chains (2 or 6 PPO/C12 molar ratio) and a polar head group (Quaternary Ammonium), were synthesized. The micellization behaviors of the two surfactants were investigated using water/ethanol and water/isopropanol mixtures (the values of dielectric constant of the two water/alcohol mixtures are between 80.1 and 18.2).

The critical micelle concentration (CMC) of the two surfactants in solvent mixtures and pure water were measured using the conductivity method [9, 10]. Dynamic light scattering (DLS) was used as an auxiliary method to determine the presence or absence of surfactant micelles and their particle size distributions in water/alcohol mixtures, as opposed to SAXS which measures the micellar

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structure [11–13]. The surfactant micellar properties were probed by measuring the characteristic adsorption spectra of methyl orange (MO) probe molecules solubilized in the micelle using UV–vis spectroscopy [14]. As known quaternary ammonium surfactants have attracted considerable attention due to their antibacterial and fabric antistatic properties [15–17]. We also explored their application prospects as antimicrobial and polyester fabric antistatic agents.

Experimental

Materials

Both dodecylamine and propylene oxide were purchased from Kermel Ltd (Tianjin, China). Absolute ethyl alcohol, isopropanol, petroleum ether, sodium hydroxide, dimethyl sulfate, diethyl ether and methyl orange (MO) were all purchased from Aldrich. All chemicals of analytical grade were used as received. Double distilled water was used in analytical experiments.

Synthesis of PO-*n* (*n* = 2, 6) Dodecylmethylpropoxylammoniummethyl Sulfate Samples

The synthesis of dodecylmethylpropoxylammoniummethyl sulfate was performed in two steps as shown in Scheme 1.

First, the propoxylation of dodecylamine was carried out in an autoclave at 185 °C using a base catalyst by controlling the mole ratio of propylene oxide to dodecylamine to produce the dodecylpropoxylamine samples with specific average PO adduct numbers (2 = PO 2-AQ; 6 = PO 6-AQ). The catalyst was not neutralized at the end of the reaction because neutralization caused the product to gel. The experimental average PO adduct numbers determined by elemental analysis using a PerkinElmer 2400 C H N analyzer are shown in Table 1 and approximately agreed with the theoretical values.

Secondly, the two dodecylpropoxylamine samples were quaternized with dimethyl sulfate in a 500-ml four-necked flask, stirred for 3 h at 82 °C. The yields determined by cationic-active matter titrimetric method, were for PO 2-AQ 87.4 % and for PO 6-AQ 83.6 %. The sticky products were extracted with double distilled water to remove unreacted dodecylpropoxylamine and the aqueous phases were distilled under reduced pressure at 85 °C to give sticky products which were further purified by column chromatography using petroleum ether/ethyl acetate/acetone: 0.04/1/3. After the purification of two products as above the purities of PO 2-AQ and PO 6-AQ are 97.5 and 95.3 %, respectively.

The molecular structures were characterized using Fourier transform infrared spectroscopy (FTIR) with a Hitachi 270-30 spectrometer and nuclear magnetic resonance with a Varian Inova-400 MHz spectrometer.

FT-IR and ^{1}H-NMR peak assignments for PO-*n* (*n* = 2, 6) QA as follows:

n = the total average adduct number of PO   x = 0, 1, 2, ... n
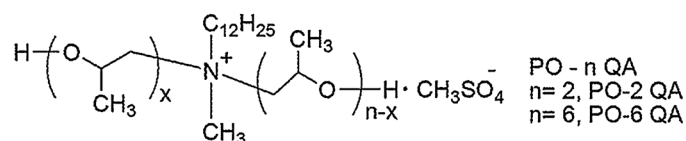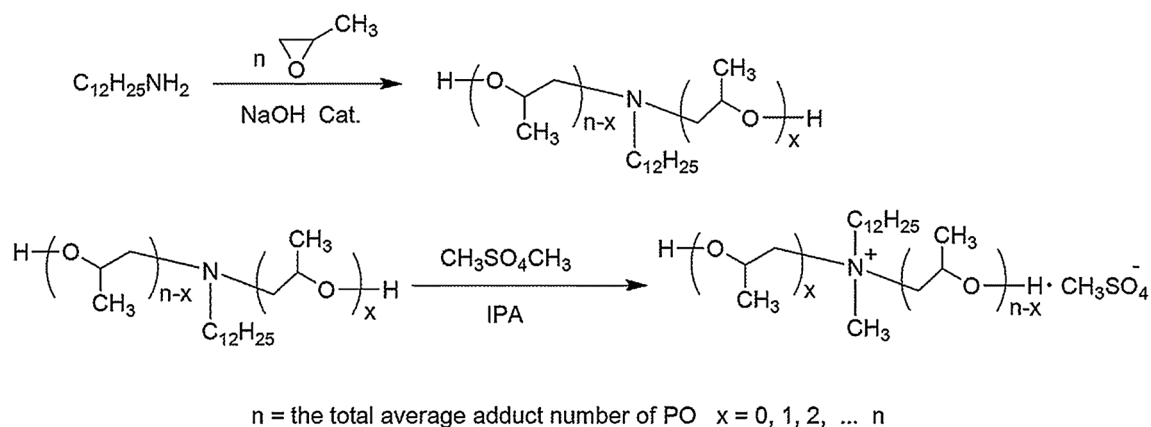
Scheme 1 Synthetic routes and acronyms for PO-*n* (*n* = 2, 6) QA

Table 1 The average PO adduct numbers of dodecylpropoxylamine samples by elemental analysis

Theoretical average PO adduct number	Elemental carbon (%)		Found average PO adduct number	Elemental hydrogen (%)		Found average PO adduct number	Elemental nitrogen (%)		Found average PO adduct number
	Calc.	Real		Calc.	Real		Calc.	Real	
2	71.703	71.702	2	13.037	13.033	2	4.644	4.653	1.99
6	67.497	67.668	5.72	11.895	11.936	5.73	2.623	2.705	5.72

(a) PO-2 QA (yield: 87.4 %): mp 163–166.2 °C. IR (KBr): O–H stretching (3415 cm^{-1}); C–H symmetric and asymmetric stretching (2925 cm^{-1}); C–H bending (1460 cm^{-1}); C–O–C stretching (1068, 944 cm^{-1}); C–O stretching (1134 cm^{-1}). ^{1}H-NMR (CDCl$_3$, ppm): δ: 0.89 (t, 3H, **CH$_3$** (CH$_2$)$_{11}$), 1.1–1.5 (m, 26H, (OCHC**H$_3$**CH$_2$)$_2$ and CH$_3$(**CH$_2$**)$_{10}$CH$_2$N$^+$), 1.85 (t, 2H, CH$_3$(CH$_2$)$_{10}$**CH$_2$** N$^+$), 3.12 (s, 3H, **CH$_3$**N$^+$), 3.2–3.65 (m, 6H, (OC**H**C**H$_3$CH$_2$**)$_2$), 3.73 (s, 3H, **CH$_3$**SO$_4$$^-$).

(b) PO-6 QA (yield: 83.6 %): mp 163–166.2 °C. IR (KBr): O–H stretching (3479 cm^{-1}); C–H symmetric and asymmetric stretching (2920 cm^{-1}); C–H bending (1460 cm^{-1}); C–O–C stretching (1095, 952 cm^{-1}); C–O stretching (1255 cm^{-1}). ^{1}H-NMR (CDCl$_3$, ppm): δ: 0.86 (t, 3H, **CH$_3$** (CH$_2$)$_{11}$), 1.05–1.41 (m, 38H, (OCHC**H$_3$**CH$_2$)$_6$ and CH$_3$(**CH$_2$**)$_{10}$CH$_2$N$^+$), 1.75 (m, 2H, CH$_3$(CH$_2$)$_{10}$ **CH$_2$**N$^+$), 3.24 (s, 3H, **CH$_3$**N$^+$), 3.26–3.75 (m, 18H, (OC**H**C**H$_3$CH$_2$**)$_6$), 3.91 (s, 3H, **CH$_3$**SO$_4$$^-$).

Micellar Properties of QA Surfactants in Water/Alcohol Mixtures

The determination of CMC was done with the conductivity method [10, 22] using a DDS-307A conductivity meter (INESA Scientific Instrument Ltd, shanghai, China.).

PO-n (n = 2, 6) QA micelles in solvent mixtures were detected using a Zetaplus particle size analysis (Brookhaven Instruments Corporation, USA) equipped with a He–Ne laser beam at a scattering angle of 90° The micelle hydrodynamic diameter in water/alcohol mixtures was calculated from the Stokes–Einstein equation using the estimated diffusion coefficients which were obtained by fitting the autocorrelation functions using a non-negatively constrained least-squares algorithm. Whatman filter membranes were used to filter samples and the quartz cell was rinsed with filtered water and dried in a vacuum oven before each measurement.

The Micellar properties in the solvent mixtures of PO-n (2, 6) AQ were studied by using UV–vis computer controlled spectrometer (UV-6100, Beijing Instrument CO.) The light beam transmission length of a quartz cell was at 1 cm. Methyl orange (MO) as the probe was mixed at appropriate concentrations with the surfactant solutions prepared in advance.

Antimicrobial and Polyester Fabric Anti-static Properties

Antimicrobial Treatment

Antimicrobial activity measurements against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) for two cationic surfactants were performed. *E. coli* and *S. aureus* were collected using two wire transfer loops and incubated separately in 10 mL of shaken tris-buffered saline (TBS) at 37 °C. When the cultures became turbid they were streaked on tryptic soy agar (TSA) plates for 24 h at 37 °C. After another generation of cultures for *E. coli* and *S. aureus*, the strains (5 × 10^5 CFU) can be used for the antimicrobial tests of two surfactants. Their antimicrobial activities were determined by the bacteria inhibitive rates.

Polyester Fabric Antistatic Treatment

Polyester cloth patches were immersed in the solutions of PO-n (n = 2, 6) surfactants at 2 mmol/L for 1 min and hung up to dry at 25 °C. Polyester cloth patches treated and untreated with the surfactants were stored at 25 °C and relative humidity 50 ± 2 % for 48 h. The fabric static effect depends on both electrostatic and static charge dissipation capacities on its surface or on electrostatic charge attenuation velocity which could be indicative of the change of resistance on fabric surface. We used an Adventest R8340A resistance gauge to test the resistance values on surfaces of those Polyester fabrics and confirmed fabric antistatic properties of two surfactants dependent on the fabric surface resistivity.

Results and Discussion

QA Surfactants Micellization Behaviors in Water/Alcohol Mixtures

The measured CMC values determined by the conductivity method, as a function of solvent mixture composition, for

Table 2 PO-2 QA CMC and dielectric constants for water/alcohol mixtures

Ethanol mole fraction (%)	Dielectric constant	CMC (mmol/L)	Isopropanol mole fraction (%)	Dielectric constant	CMC (mmol/L)
100	24.3	6.617	100	18.2	1.148
86	28.7	7.833	82.5	23.5	1.192
75.5	32.5	7.95	70	28.3	1.613
50.7	43.7	0	54	35.9	0
38.2	50.7	0	44	49.8	0
13.3	68.3	0	32	39	0
8.5	72.3	15.082	4.5	74.9	0
3	77.2	11.528	2.3	77.4	9.423
0	80.1	10.803	1.2	78.6	9.166

Table 3 PO-6 QA CMC and dielectric constants for water/alcohol mixtures

Ethanol mole fraction (%)	Dielectric constant	CMC (mmol/L)	Isopropanol mole fraction (%)	Dielectric constant	CMC (mmol/L)
100	24.3	4.091	100	18.2	0.606
86	28.7	5.527	82.5	23.5	0.681
75.5	32.5	5.591	70	28.3	0.797
50.7	43.7	0	54	35.9	0
38.2	50.7	0	44	49.8	0
13.3	68.3	0	32	39	0
8.5	72.3	7.47	4.5	74.9	0
3	77.2	6.985	2.3	77.4	5.879
0	80.1	6.909	1.2	78.6	5.364

the PO-2 AQ and PO-6 AQ are reported in Tables 2 and 3, respectively. The dielectric constants of the solvent mixture calculated using the Lichtenecker's equation [18] are also reported.

In pure water, regular micellization behavior of the two surfactants was observed. With increasing alcohol mole fraction, the formation of micelles in alcohol diluted aqueous solutions was gradually suppressed until the maximal CMC of PO-2 and PO-6 QA was reached for 15.082 mmol/L at an ethanol mole fraction of 8.5 % and 5.879 mmol/L at an isopropanol mole fraction of 2.3 %, respectively. No micellization behavior occurred in the intermediate water/alcohol mixtures with further addition of alcohol to the solvent mixtures.

In surfactant aqueous solutions, water molecules through intermolecular hydrogen bonds creates a structure around the hydrophobic part of each surfactant molecule [19]. In short alkyl chain alcohol diluted aqueous solutions, the tetrahedral arrangement of water molecules around the alcohol hydroxyl is different than the structure created by water molecules in the bulk around the short alkyl chain of alcohol. In other words, water molecules form intermolecular hydrogen bonds with alcohol hydroxyls rather than alcohol short alkyl chains [20]. The hydrogen bond network around the surfactant hydrophobic chain constructed by water molecules influenced by alcohol hydroxyls alters the entropic driving force of surfactant micellization. With increasing alcohol molecules per PO-2 or PO-6 QA surfactant molecule, water molecules of ordered structure around the hydrophobic chains were progressively substituted with alcohol molecules so that the entropic driving force for micellization dropped off.

Aramaki [21] found that the surfactant aggregates disassembled into surfactant monomers with the addition of alcohol to the solvent mixture, which resulted from the penetration of alcohol molecules into the paliform outer sphere of surfactant aggregates. However, the regular micellization behaviors of PO-n ($n = 2, 6$) QA in water rich alcohol/water mixtures restrained by the increase in alcohol molecules are probably due to the decline of the entropic driving force and the effect of alcohol molecule penetration into the micelle shells. With the weak entropic driving force and enhanced penetration effect, regular micelles collapsed in the intermediate binary systems.

In water diluted alcohol solutions, PO-n ($n = 2, 6$) QA surfactant micelle formation recovered and their maximal

CMC reached 7.95 mmol/L PO-2 QA at an ethanol mole fraction of 75.5 % and 0.797 mmol/L PO-6 QA at 70 mol% for isopropanol. Further increase of alcohol composition in the solvent mixtures also favored micelle formation. Michor [22] found that dioctyl sodium sulfosuccinate (AOT) did not form micelles in intermediate water alcohol binary systems but its micellization behavior recovered in alcohol rich water/alcohol mixtures. With the increase of alcohol molecules in the solvent mixture, the CMC of AOT surfactant decreased to the value in pure alcohol. The decline of the CMC with the polarity of water diluted alcohol solutions is due to the enthalpy property of AOT reverse micellization behavior [22].

In pure alcohol, the dipole–dipole interactions of surfactant head groups plays a leading role in the formation of inverse micelles rather than the entropic driving force. With the increase of water content, compared to increasing polarity of water diluted alcohol binary system, the strength of surfactant headgroup–headgroup interactions declined to the point that the maximal CMC was reached or that no reverse micellization behavior occurred. PO-2 or PO-6 QA cationic molecules with more charge in the water diluted alcohol solutions of more water composition would result in repulsive force among their polar headgroups so that their reverse micelles formed were restrained corresponding to the CMC of PO-2 QA in the 75.5 mol% ethanol of 7.95 mmol/L and in the 86 mol% ethanol mixture of 7.833 mmol/L. The continuous decrease of PO-2 or PO-6 QA CMC with alcohol content in alcohol rich solvent mixtures is also related to the occurrence of reverse micelle formation.

The influence of the composition of water/alcohol mixtures on the micellization behaviors of the two cationic surfactants is strictly linked with dielectric constants of water/alcohol binary systems. The two surfactants have regular micellization behavior at dielectric constants varied from 77.4 to 80.1. The dielectric constant ranges of water/alcohol mixtures in which no micellization behavior occurred are between 43.7 and 68.3 in ethanol water mixtures and from 35.9 to 74.9 in isopropanol water solutions. There is an overlap dielectric constant range from 43.7 to 68.3 for two surfactants in water/ethanol mixtures and water/isopropanol mixtures. The reverse micelles of the two surfactants were formed in solvent mixtures at dielectric constants varied from 28.3 to 18.2 and their continuously decreased CMC in that dielectric constant range are due to the stronger strength of surfactant molecules head group-head group interactions in the less polar solvent mixtures. The not perfectly equal correspondence in CMC value at the same dielectric constant for the two mixture is due to the other parameters that affect the CMC (the solvent molecular structure, the Snyder polarity and Hildebrand solubility [23]).

The difference of micellization behaviors between the two surfactants (for example, the CMC of PO-6 QA is

Table 4 Parameters for PO-n ($n = 2, 6$) QA micellizations in water/alcohol mixtures

Alcohol mole fraction (%)	ΔG^0_{agg} (kJ/mol)		$\Delta\Delta G^0_{agg}$ (kJ/mol)
	PO-2	PO-6	
Ethanol mole fraction (%)			
3	−11.218	−12.298	−1.080
0	−11.057	−12.325	−1.268
Isopropanol mole fraction (%)			
82.5	−16.679	−18.066	−1.387
70	−15.929	−17.676	−1.747

always lower than that of PO-2 QA) triggered us to investigate the role and kind of contributions of PPO groups in propoxylated cationic surfactant micellization behaviors in water/alcohol mixtures. Table 4 shows the standard free energy for surfactant aggregation in solvent mixtures calculated by a standard Gibbs free energy equation [24]. Higher absolute value of aggregation standard free energy for PO-6 surfactant in the same solvent mixtures indicated that the contributions of PPO groups to surfactant micellization behaviors exist. By comparing these differences of standard free energy for aggregation between two surfactants in the same solvent mixtures we could determine how PPO groups affect surfactant micellization behavior in those mixtures [25]. The structure of solute hydrophobic segment in water is substantially affected by the hydrophobic effect [19]. The absolute values of aggregation standard free energy difference between PO-2 and PO-6 surfactants in the ethanol diluted aqueous solutions decreased with water content and the contribution of PPO groups is also weak, which indicates that the role of PPO groups in the formation of propoxylated surfactant micelles in water rich solvent mixtures is related to the hydrophobic contribution. The decreased absolute value for aggregation standard free energy difference between the two surfactants in the water diluted isopropanol solutions with dielectric constants of those solvents decreased and thus the weak contribution of PPO groups manifested that the efficiently screening electrostatic contribution of PPO groups would effect for propoxylated cationic surfactant micelles formed in isopropanol rich solvent mixtures. The contributions of PPO groups are related to the hydrophobic and electrostatic contributions to regular and reverse micelle formation in water/alcohol mixtures, respectively.

Dynamic Light Scattering (DLS)

The results of DLS analysis for different concentrations of PO-n (2,6) AQ and different water/alcohol mixtures are shown in Figs. 1, 2, 3, 4. DLS measurements did not detect
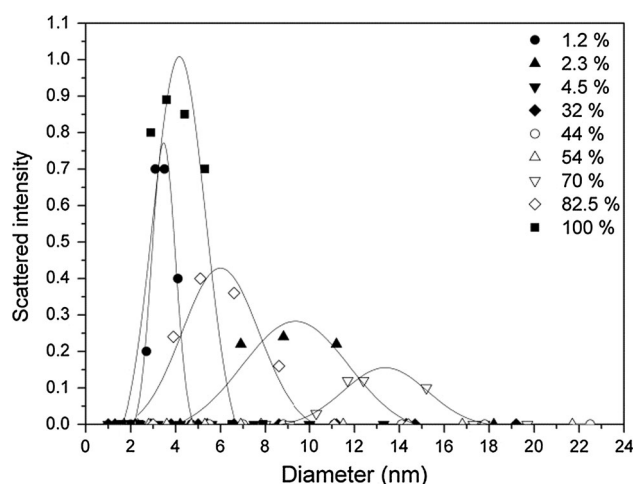
Fig. 1 The intensity-weighted particle size distributions for PO-2 QA surfactant at 10 mmol/L in water/isopropanol mixtures at different isopropanol mole fractions
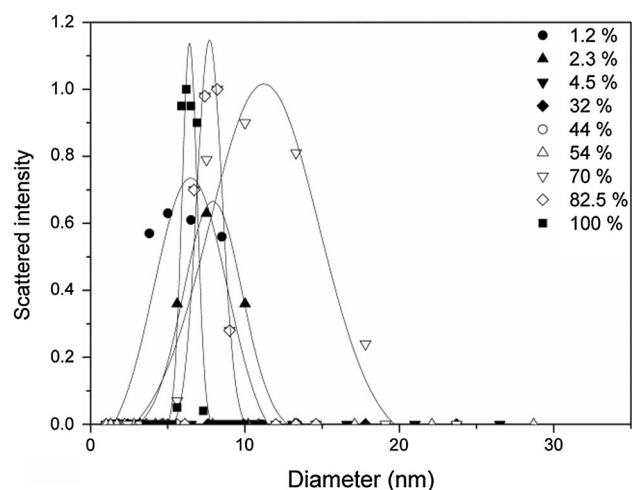

Fig. 2 The intensity-weighted particle size distributions for PO-6 QA surfactant at 7 mmol/L in water/isopropanol mixtures at different isopropanol mole fractions
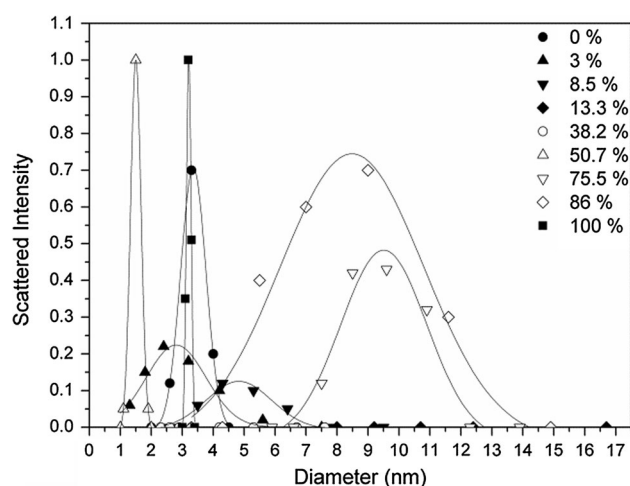

Fig. 3 The intensity-weighted particle size distributions for PO-2 QA surfactant at 16 mmol/L in water/ethanol mixtures at different ethanol mole fractions

any particle size distribution for the no micellization behavior in water/alcohol mixtures which were investigated by the conductivity technique. The scattered intensities for PO-n ($n = 2$, 6) QA surfactants in regular or inverse micellization behavior solvent mixtures show average diameters from 3.2 to 13.5 nm. The average diameters between 3 and 5 nm for surfactant nanoparticles in water/alcohol mixtures are typical of spherical micelles [26]. These small nanoparticles at the average radius lower than 1 nm for PO-2 QA in the solvent mixture at 50.7 mol% of ethanol are indicative of submicelles rather than micelles [22], which is consistent with the conductivity result of no PO-2 QA micellization behavior in that solvent mixture.

The size of reverse micelles formed in water/organic solvent mixture is related to the mole ratio of water to surfactant, which results in relatively large reverse micelles formed in the reverse micellization behavior water/alcohol mixtures with more water content [27]. In some reverse micellization solvent mixtures PO-2 or PO-6 QA molecules can aggregate into relatively large nanoparticles with average diameters from 10 to 13.5 nm and the average diameter of surfactant micelles progressively increases with the alcohol content decreasing corresponding to the average diameters for PO-2 QA micelles in 70 mol% isopropanol solvent mixture at 13.5 nm and in pure isopropanol at 3.9 nm.

UV–Vis Spectroscopy

We selected methyl orange (MO) as a probe to investigate the microenvironment of propoxylated quaternized surfactant micelles in water/ethanol mixtures and found that two propoxylated surfactants with two and six average PO adduct numbers had a similar effect on the absorption spectra of MO. The PO-6 QA/water/ethanol system was chosen as a representative for the probe experiments. Any peak of UV–vis adsorption spectra of MO molecules in the surfactant/water/isopropanol systems was not detected. So MO molecules applied in the surfactant/water/isopropanol systems were unsuitable to probe the microenviroment of micelles.

To determine whether MO molecules preferential locate in the bulk of water/ethanol mixtures or around the PO-6 QA micelles, we first determined the preferable partition of MO probe molecules in water, ethanol and surfactant using PO-6 QA/water and PO-6 QA/ethanol solutions. The
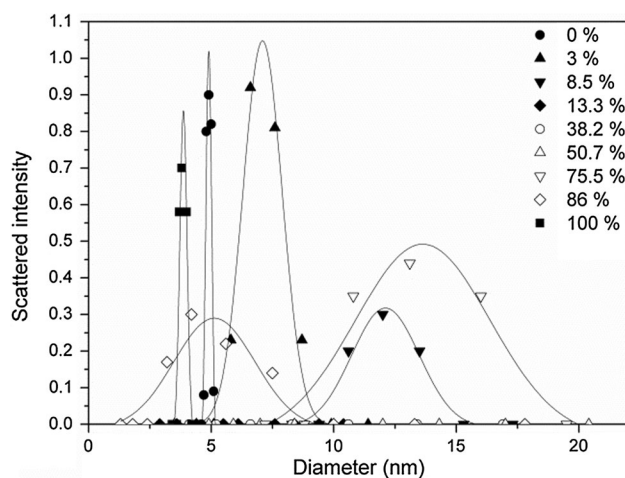
Fig. 4 The intensity-weighted particle size distributions for PO-2 QA surfactant at 9 mmol/L in water/ethanol mixtures at different ethanol mole fractions

absorption spectra of MO in water and in ethanol at different PO-6 POQA surfactant concentrations are shown in Fig. 5.

The maximum absorbance wave lengths (λ_{max}) of MO in pure water and pure ethanol are 466 and 417 nm, respectively. The shift in wave length illustrates the MO probe's response to changes in the microenvironment. The λ_{max} of MO in PO-6 QA/ethanol solutions at a surfactant concentration of 0.1 mmol/L is 418 nm, which is about the same as that in 10 mmol/L surfactant in ethanol solution and similar to that probed in pure ethanol at 417 nm, indicating the probe molecules are not affected by the formation of inverse micelles in ethanol and have a more preferable partition in bulk ethanol than reverse micelles. The λ_{max} of MO molecules dissolved in 10 mmol/L surfactant in water is 427 nm which is much lower than that in pure water (466 nm). This indicates that the probe molecules are not in the bulk water but in the cores of regular micelles which are hollow or filled with a few water molecules so that MO molecules prefer to interact with the PPO groups in the regular micelles. Therefore, it can be deduced that the probe molecules in the PO-6 QA/water/ethanol ternary systems prefer to locate in ethanol over water or in the vicinity of PPO groups.

Figure 6 shows the absorption spectra of MO in ethanol rich water/ethanol solutions, the intermediate water ethanol binary systems and ethanol diluted water solutions at a surfactant concentration of 10 mmol/L. The PO-6 QA molecules in ethanol diluted aqueous solutions are aggregated into regular micelles as determined from CMC measurements. The λ_{max} of MO in 0.9 mol% ethanol solution of PO-6 QA is 419 nm which is more than that shown in surfactant ethanol solution (418 nm) but lower than in aqueous surfactant solution at 427 nm. If MO
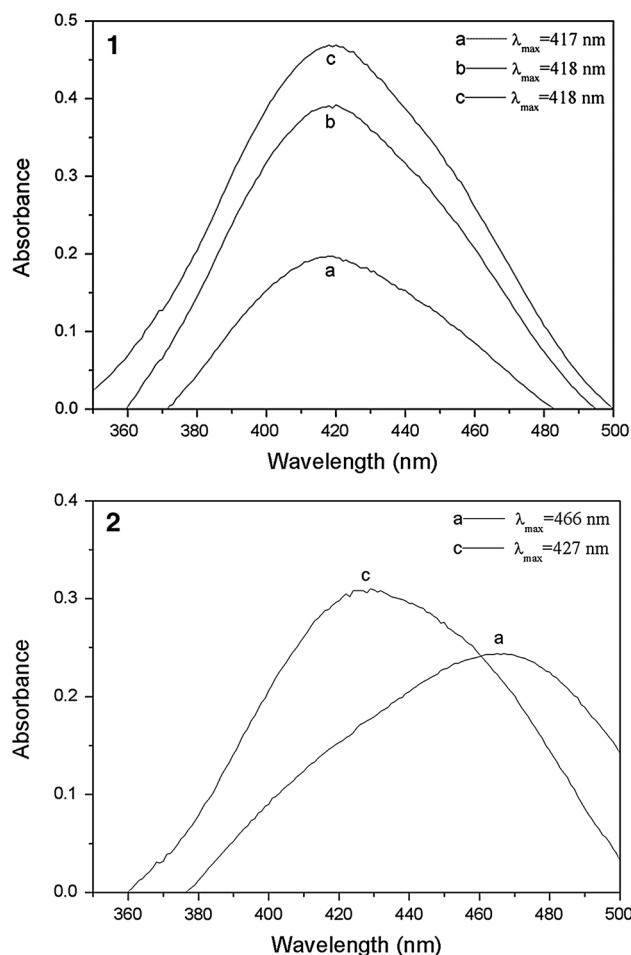

Fig. 5 Absorption spectra of MO in the PO-6 QA surfactant/ethanol solutions (1) and PO-6 QA aqueous solutions (2) as a function of the surfactant concentration: a 0 mmol/L, b 0.1 mmol/L, c 10 mmol/L

molecules are located in the ethanol free cores of regular micelles, the λ_{max} should be equal to 427 nm. If the MO molecules are located in nano-pools comprised of ethanol molecules or probe molecules only, λ_{max} should be much higher than 419 nm. If the nano-pools consisted of both ethanol and MO molecules, λ_{max} should be at 418, indicating MO probe, water and ethanol molecules were encapsulated in regular micelles with probe molecules dissolved in the nano-pools consisting of ethanol rich water/ethanol nanoscale mixture. The slow increase in λ_{max} of MO in the water rich ethanol/water solutions of PO-6 QA surfactant with increasing ethanol mole fraction show that the microenvironment polarity of MO molecules also increases and thus the aqueous content of nano-pools in regular micelles increases with the decrease of water content in the bulk solvent but is still insignificant compared with ethanol composition.

The λ_{max} of MO in water diluted ethanol solutions of the surfactant with a 10 mmol/L slow decrease when the
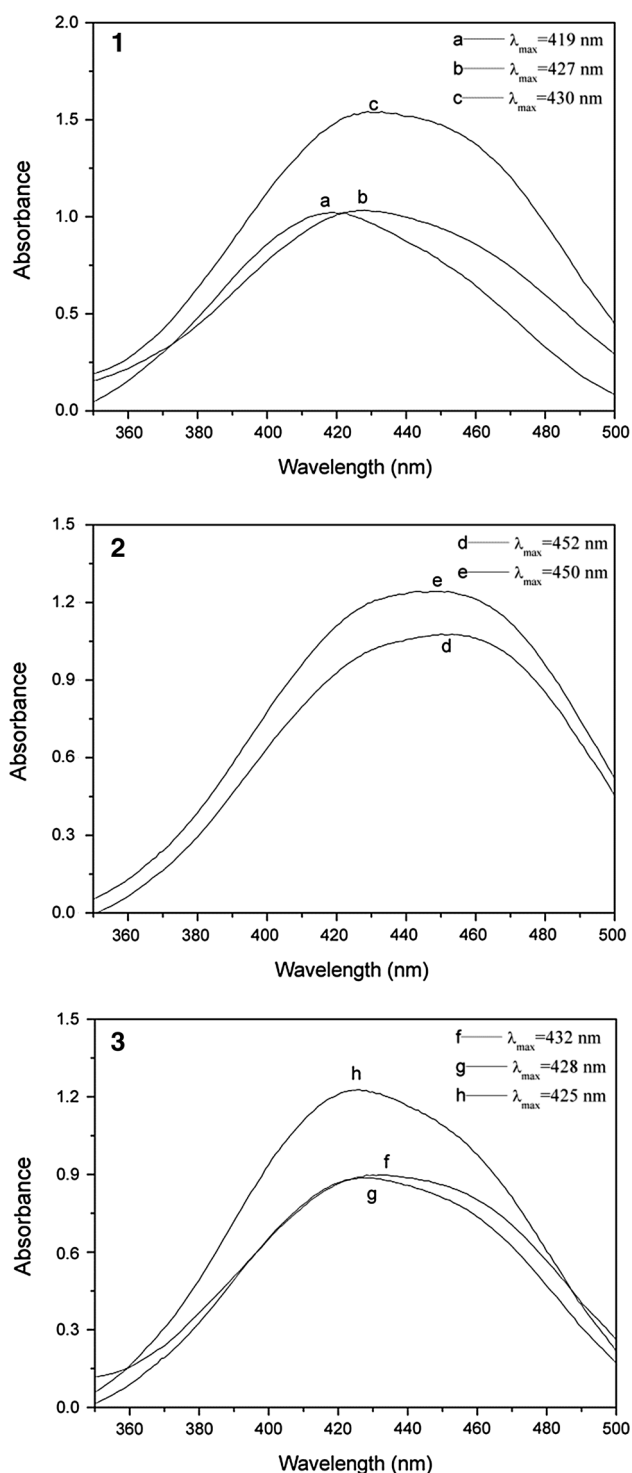
Fig. 6 Absorption spectra of MO in the PO-6 QA/water/ethanol ternary systems at the surfactant concentration of 10 mmol/L as a function of ethanol mole fraction: *h* 97.4 %, *g* 86 %, *f* 75.5 %, *e* 20.7 %, *d* 13.3 %, *c* 8.5 %, *b* 3 %, *a* 0.9 %

increase in the ethanol mole fraction is lower than that in the intermediate mixtures. MO molecules in those solutions dissolved in the bulk solvent mixtures rich in ethanol and

their λ_{max} values were substantially affected by the bulk solvent polarities.

When MO probe molecules are immersed in 13.3 mol% ethanol solution (also known as the no micellization behavior mixture determined by CMC and DLS measurements), λ_{max} suddenly increases to 452 nm which is far higher than in water rich mixtures. In the intermediate water/alcohol binary systems, no micelles are formed and MO molecules dispersed in those solvent mixtures experience far higher water content compared with the aqueous composition in nano-pools of regular micelles.

Antibacterial and Fabric Antistatic Properties of PO-*n* (*n* = 2, 6) Surfactants

The antibacterial activity of the two propoxylated surfactants against the Gram-negative bacterium *Escherichia coli* and the Gram-positive bacterium *Staphylococcus aureus* are shown in Fig. 7a. Interestingly, the inhibition rates against two bacterium strains by PO-2 QA are excellent (98 % for both microorganisms). PO-6 QA surfactant shows a very low antibacterial activity (17.6 % for *Escherichia coli* and 21.7 % for *Staphylococcus aureus*, respectively). The cationic surfactant head groups are likely adsorbed onto anionic sites of the bacterium cell wall by electrostatic interactions and changes the permeability of the cell wall and membrane. This causes the introduction of toxic substances into the bacterium cell cytoplasm and thus cell death [15, 16]. The strength of electrostatic interactions of propoxylated cationic surfactants with anionic sites of the bacteria cytoderm is impaired by large PPO groups, which results in higher antibacterial activity of the PO-2 QA surfactant than that of the PO-6 QA surfactant.

Fabric surface specific resistance (ρ_s), is derived by the surface resistance (R_s), the inner diameter of the circular shield electrode (D), the diameter of potential electrode (d) and the constant π, by Eq. 1 [17, 28]

$$\rho_s = R_s \times \frac{2\pi}{\ln \frac{D}{d}} \qquad (1)$$

The difference log value ($\Delta \lg \rho_s$) of fabric surface specific resistances between treated and untreated fabric surfaces with surfactant is calculated using Eq. 2 [17, 28]

$$\Delta \lg \rho_s = \lg \rho_{untreat} - \lg \rho_{treat}. \qquad (2)$$

PO-*n* (*nn* = 2, 6) QA surfactants have a good antistatic effect as shown in Fig. 7b. The propoxylated cationic surfactants solvated in water covered the polyester fabric surfaces very well. The PPO groups in the propoxylated cationic surfactant limited the adsorption of water from the air to fabric surface and thus impeded the surface charge outflow.
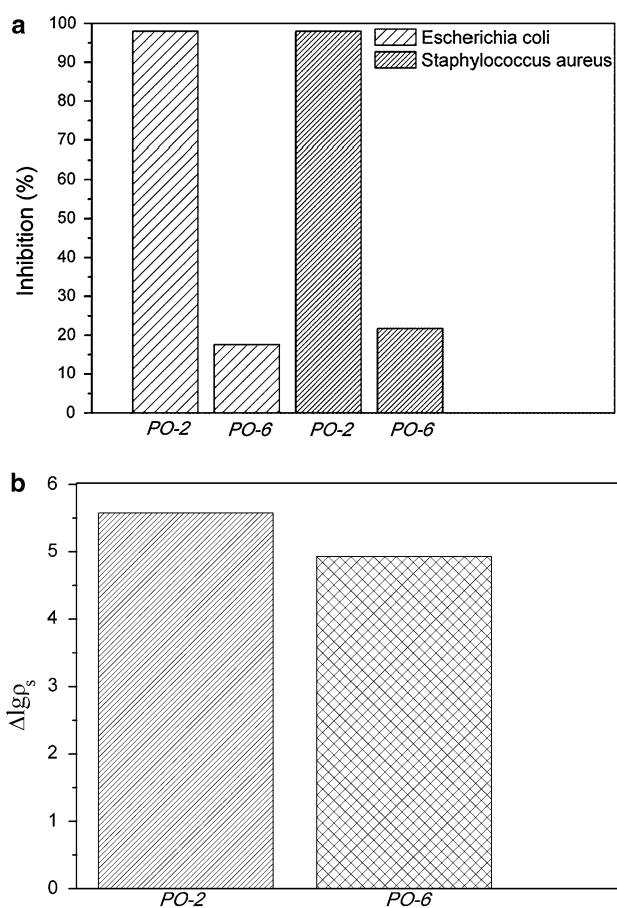
Fig. 7 Antibacterial and polyester fabric antistatic performances of PO-*n* (*n* = 2, 6) surfactants: **a** the inhibition of *E. coli* and *S. aureus* by two surfactants; **b** the log value reduction of specific resistance on the surface of polyester fabrics treated with two surfactants

Conclusions

Two propoxylated cationic surfactants with two and six average PO adduct numbers were successfully synthesized and characterized by elemental analysis, FT-IR and ^{1}H NMR spectroscopy. The micellization behaviors of two surfactants, PO-*n* (*n* = 2, 6) QA, in water/alcohol mixtures have been investigated using the conductivity method and further confirmed by DLS and UV–vis spectroscopy techniques. To create a wide spectrum of dielectric constants of solvent mixtures we used ethanol and isopropanol to separately mix with water and the effect of solvent mixtures composition and PPO groups on PO-*n* (*n* = 2, 6) micellization behaviors was studied. The regular, inverse and no micellization behaviors varied with the composition of water/alcohol mixtures. Hydrophobic and electrostatic contributions of PPO groups to the surfactant micellar properties occurred in the regular and reverse micellization behaviors solvent mixtures, respectively. DLS could detect nanoparticles size distributions of two surfactants micelles

in the micellization behavior solvent mixtures rather than these mixtures in which no micelles were formed. Also the UV–vis spectroscopy of MO molecular probe inside regular micelles formed in water/ethanol mixtures was confirmed and aqueous composition for the nano-pool of regular micelles filled with ethanol rich solvent mixtures increased with ethanol content.

PO-2 QA surfactant of excellent antibacterial activities against both the Gram-negative bacterium *Escherichia coli* and the Gram-positive bacterium *Staphylococcus aureus* and an ability to substantially decrease the resistance on polyester fabric surface has potential as antibacterial and polyester fabric antistatic agents.

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