J Surfact Deterg (2015) 18:487–493
DOI 10.1007/s11743-014-1650-x

ORIGINAL ARTICLE

# Effect of Polyoxyethylene Chain Length on the Physicochemical Properties of *N*,*N*-Dimethyl-*N*-dodecyl Polyoxyethylene Amine Oxide Hybrid Surfactants ($C_{12}EO_nAO$, with $n = 1–4$)

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Received: 7 August 2014 / Accepted: 18 November 2014 / Published online: 3 February 2015


**Abstract** In order to determine the structure-performance relationship of nonionic-zwitterionic hybrid surfactants, *N*,*N*-dimethyl-*N*-dodecyl polyoxyethylene (*n*) amine oxides ($C_{12}EO_nAO$) with different polyoxyethylene lengths ($EO_n$, $n = 1–4$) were synthesized. For homologous $C_{12}EO_nAO$, it was observed that the critical micelle concentration (CMC), the maximum surface excess ($\Gamma_m$), CMC/$C_{20}$, and the critical micelle aggregation number ($N_{m,c}$) decreased on going from 1 to 4 in $EO_n$. However, there were concomitant increases in surface tension at the CMC ($\gamma_{CMC}$), minimum molecular cross-sectional area ($A_{min}$), adsorption efficiency (p$C_{20}$), and the polarity ($[I_1/I_3]_m$) based on the locus of solubilization for pyrene. The values of log CMC and $N_{m,c}$ decreased linearly with $EO_n$ lengthening from 1 to 4, although the impact of each EO unit on the CMC of $C_{12}EO_nAO$ ($n = 1–4$) was much smaller than that typically seen for methylene units in the hydrophobic main chains of traditional surfactants. Compared to the structurally related conventional surfactant *N*,*N*-dimethyl-*N*-dodecyl amine oxide ($C_{12}AO$), $C_{12}EO_nAO$ ($n = 1–4$) have smaller CMC, $A_{min}$, and CMC/$C_{20}$, but larger p$C_{20}$, $\Gamma_m$, and $N_{m,c}$ with a higher $[I_1/I_3]_m$. This may be attributed to the moderately amphiphilic $EO_n$ ($n = 1–4$) between the hydrophobic $C_{12}$ tail and the hydrophilic AO head group.

**Keywords** Hybrid surfactant · *N*,*N*-dimethyl-*N*-dodecyl polyoxyethylene (*n*) amine oxide · Structure-performance relationship

**Electronic supplementary material** The online version of this article (doi:10.1007/s11743-014-1650-x) contains supplementary material, which is available to authorized users.

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## Introduction

Nonionic-ionic hybrid surfactants, especially those having a polyoxyethylene chain segment between the hydrophilic head group and hydrophobic tail, always display dual properties of both nonionic and ionic surfactants [1, 2]. For example, they show better electrolyte properties and water hardness tolerance. The traditional representatives are alcohol ether sulfates (AES) [3], alcohol ether carboxylates (AEC) [4], and sodium alkyl-benzyl polyoxyethylenated propanesulfonates (ABEPS) [2]. However, the synthesis and surface activity of nonionic-zwitterionic hybrid surfactants have seldom been reported to date.

One US patent [5] reveals the synthesis of *N*,*N*-dimethyl-*N*-alkyl polyoxyethylene amine and the corresponding amine oxides from commercially available AES. One Japanese patent [6] reports the synthesis of *N*,*N*-dimethyl-*N*-alkyl polyoxyethylene amine-based betaines from commercially available fatty alcohols. Due to the length distribution of the alkyl tails and polyoxyethylene segments in commercially available AES and polyethoxylated fatty alcohols ($AEO_n$), the corresponding amine oxides and betaines are mixtures of different molecules. Thus, it is hard to determine the structure-performance relationships of these hybrid surfactants when they are synthesized using commercially available AES or $AEO_n$ as starting materials.

Here, *N*,*N*-dimethyl-*N*-dodecyl polyoxyethylene (*n*) amine oxides ($C_{12}EO_nAO$) with different polyoxyethylene lengths ($EO_n$, $n = 1$–4) were synthesized (see Fig. 1). Many important physicochemical parameters of these hybrid surfactants, such as the critical micelle concentration (CMC), the surface tension at the CMC ($\gamma_{CMC}$), the adsorption efficiency ($pC_{20}$), the maximum surface excess ($\Gamma_m$), the minimum molecular cross-sectional area ($A_{min}$), the value of $CMC/C_{20}$, and the mean micelle aggregation number ($N_m$), were determined using surface tension and fluorescence probe methods. The dependences of CMC, $A_{min}$, and the critical aggregation number $N_{m,c}$ on polyoxyethylene length ($EO_n$) were deduced.

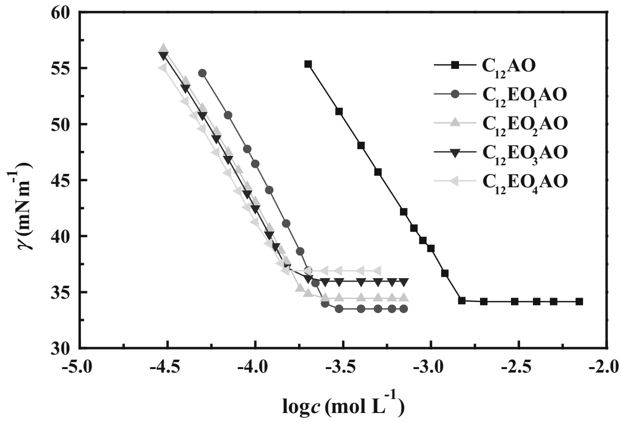


**Fig. 2** The plots of the surface tension ($\gamma$, mN $m^{-1}$) *versus* log *c* (concentration of surfactant, mol $L^{-1}$) for $C_{12}EO_nAO$ ($n = 0$–4) at 25 °C

## Experimental Section

### Materials

1-Bromododecane ($Br–C_{12}$), polyethylene glycol ($EO_n$, $n = 1$–4), sodium hydride (NaH), dimethylamine (DMA), and $H_2O_2$ (30 wt%) were used as received without further purification. $C_{12}EO_nAO$ ($n = 1$–4) were synthesized according to the previously reported method [7], and their molecular structures were confirmed by means of electrospray ionization mass spectrometry (ESI–MS) and $^1H$ nuclear magnetic resonance ($^1H$ NMR). The results of ESI–MS and $^1H$ NMR, and the corresponding interpretation using $C_{12}EO_3AO$ as a representative example, can be seen in the Electronic Supplementary Material (ESM) Fig. 1S and Fig. 2S as complementary data. Deionized water was obtained from a Millipore Milli-Q water purification system (Millipore, USA).

### Analytical Methods

Surface tension ($\gamma$, mN $m^{-1}$) measurements were conducted on a drop volume tensiometer at 25 ± 0.1 °C. The outer radius of the glass capillary was 0.58 mm. In the procedure for $\gamma$ measurements, a sufficient aging time is necessary for the pendant drop surface to reach an equilibrium state. The aging time of the drop surface was determined from a plot of $\gamma$ versus the drop detachment time *t* (min) (ESM Fig. 3S). Finally, the drop volume was corrected by the Harkins–Brown method [8]. The surface activity parameters, specifically CMC, $\gamma_{CMC}$, $pC_{20}$, $\Gamma_m$, and $A_{min}$, were obtained or calculated [9] from $\gamma$-log *c* (the concentration of surfactant) curves (Fig. 2). The calculation of $\Gamma_m$ and the related regression coefficients are listed in ESM Table 1S as supplementary data. The CMC values were confirmed by the pyrene $I_1/I_3$ method [10].

The micellar aggregation ($N_m$) was measured by the time-resolved fluorescence method [11–13]. Time-resolved fluorescence measurements were performed using an FLS920 lifetime measurement spectrometer. An excitation pulse width of 1.5 ns was provided by a nanosecond flash lamp containing hydrogen gas as the medium at a pressure of 0.40 ± 0.02 bar. The pulse repetition rate was 40 kHz. The fluorescence was excited at 335 nm and detected at 393 nm with a fast photomultiplier tube. The fluorescence photon counts were accumulated using the technique of time-correlated single-photon counting (ESM Fig. 4S). The slit width and the excitation level were maintained at values such that the count rate did not exceed 2,000 cps in order to prevent pulse pile-up.

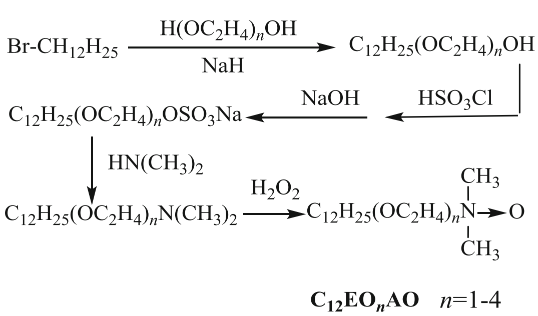


**Fig. 1** The synthesis route of $C_{12}EO_nAO$ ($n = 1$–4)

## Results and Discussion

### Surface Activity Parameters of $C_{12}EO_nAO$ ($n = 1$–4)

Plots of $\gamma$ versus log *c* for $C_{12}EO_nAO$ ($n = 1$–4) used in this work and for the corresponding structurally related traditional counterpart $C_{12}AO$ are shown in Fig. 2. It can be seen that $\gamma$ gradually decreases to a plateau region with increasing surfactant concentration. This decrease in surface tension indicates that the surfactant molecules are adsorbed at the air/solution interface, and the discontinuity seen in the $\gamma$-log $c$ curves suggests the formation of micelles in aqueous solution. Here, it is worth mentioning that no evidence of any surface tension minima was found in the $\gamma$-log $c$ curves [14]. The surface activity parameters, such as CMC, $\gamma_{CMC}$, p$C_{20}$, $\Gamma_m$, and $A_{min}$, were obtained and/or calculated [9] from the $\gamma$-log $c$ curves and are listed in Table 1.

As can be seen in Table 1, the CMC value for $C_{12}AO$ determined in this work is in good agreement with the value of $1.18 \times 10^{-3}$ mol $L^{-1}$ (ring method) reported in the literature [15], despite the difference in $\gamma$ determination methods. All of the CMC values of the hybrid surfactants studied in this work are of the order of $10^{-4}$ mol $L^{-1}$ and are smaller than that of $C_{12}AO$. A similar relationship holds for sodium dodecylpolyoxyethylene sulfates ($C_{12}$-$EO_nS$, $n = 2$–4) and the corresponding sodium dodecyl sulfate ($C_{12}S$) [2]. This may be attributed to the hydrophilicity of the hybrid surfactants in this work incrementally increasing from hydrophobic ($C_{12}$) to moderately amphiphilic $EO_n$ ($n = 1$–4) to a hydrophilic AO group. As regards the change in hydrophilicity at the water/air interface, one can argue that it changes from hydrophobic (air), through a moderately amphiphilic interfacial zone ($EO_n$, $n = 1$–4), to hydrophilic (water) [1], whereas the hydrophilicity of the structure-related counterpart, $C_{12}AO$, changes discontinuously from hydrophobic ($C_{12}$) to hydrophilic (AO) without an intermediate moderately amphiphilic transition zone ($EO_n$, $n = 1$–4). This accounts for the higher surface activity of the hybrid surfactants used in this work.

Furthermore, the CMC values of $C_{12}EO_nAO$ decreased with the length of the $EO_n$ segment ($n$) increasing from 1 to 4. A linear correlation between log CMC and $n$ was observed, as shown in Fig. 3. Generally, for a homologous series of traditional surfactants, the CMC follows the empirical Stauff–Klevens rule, which indicates a logarithmic relationship between CMC and the number of carbon atoms in the alkyl main chain, as shown in the following Eq. (1):

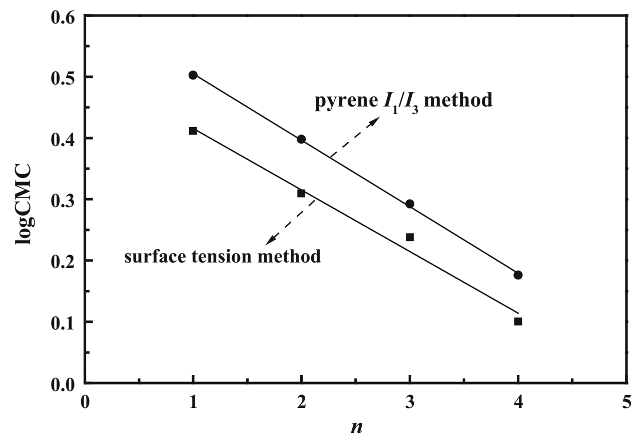


**Fig. 3** The linear correlation between log CMC and $n$ for $C_{12}EO_nAO$ ($n = 1$–4)

$$\log \text{CMC} = A - Bn_C \quad (1)$$

where $A$ and $B$ are constants for a particular homologous series and temperature, and $n_C$ is the number of carbon atoms in the hydrocarbon main chain. The constant $A$ varies with the nature and number of hydrophilic groups, while $B$ is a constant that reflects the effect of each additional methylene group on the CMC. Based on the Stauff–Klevens rule, the relationship between $EO_n$ length ($n$) and log CMC (in $10^{-4}$ mol $L^{-1}$) for $C_{12}EO_nAO$ ($n = 1$–4) was determined as Eq. (2):

$$\log \text{CMC} = 0.61 - 0.11n (R^2 = 0.9990). \quad (2)$$

For traditional zwitterionic and nonionic surfactants, the constant $B$ is approximately 0.5, which means that the CMC decreases by a factor of about 10 for each two methylene groups added to the hydrophobic main chain [16]. Here, the constant $B$ for $C_{12}EO_nAO$ ($n = 1$–4) is obviously smaller than that for traditional zwitterionic and/or nonionic surfactants. This indicates that the impact of each EO unit on the CMC of hybrid surfactants $C_{12}EO_nAO$ ($n = 1$–4) is much smaller than that of a methylene group

**Table 1** The surface active parameters of $C_{12}EO_nAO$ ($n = 1$–4) at 25 °C

| Surfactants | CMC ($10^{-4}$ mol $L^{-1}$) | | $\gamma_{CMC}$ (mN $m^{-1}$) | $\Gamma_m$ ($10^{-6}$ mol $m^{-2}$) | $A_{min}$ ($\times10^{-19}$ $m^2$) | p$C_{20}$ | CMC/$C_{20}$ |
|---|---|---|---|---|---|---|---|
| | Surface tension | Fluorescence | | | | | |
| $C_{12}AO$ | 15.30 | 15.40 | 34.15 | 4.71 | 3.53 | 3.55 | 5.44 |
| $C_{12}EO_1AO$ | 2.58 | 3.18 | 33.50 | 6.40 | 2.59 | 4.20 | 4.09 |
| $C_{12}EO_2AO$ | 2.04 | 2.50 | 34.45 | 6.01 | 2.76 | 4.33 | 4.36 |
| $C_{12}EO_3AO$ | 1.73 | 1.96 | 35.97 | 5.93 | 2.80 | 4.35 | 3.87 |
| $C_{12}EO_4AO$ | 1.26 | 1.50 | 36.90 | 5.52 | 3.01 | 4.39 | 3.10 |

in the hydrophobic main chain, and is more akin to that of a methylene group in a side chain [17]. This could provide further evidence in support of the above hypothesis that the chain segment of $EO_n$ serves as a moderately amphiphilic zone between the hydrophilic head group and the hydrophobic tail [1].

The value of $pC_{20}$ reflects the efficiency of surfactant adsorption at the air/water interface. The larger the value of $pC_{20}$ is, the higher is the adsorption efficiency of the surfactant. As shown in Table 1, the value of $pC_{20}$ increased significantly from 3.55 to 4.20 when $n$ was increased from 0 to 1, indicating that the efficiency of $C_{12}EO_1AO$ adsorption at the air/water interface was larger than that of $C_{12}AO$; a similar tendency has been observed for $C_{12}S$ and $C_{12}EO_nS$ ($n = 2$–4) [2]. However, $pC_{20}$ for $C_{12}EO_nAO$ showed a slight increase with increasing length of $EO_n$ from 1 to 4, which could be attributed to the moderately amphiphilic $EO_n$ segment between the hydrophilic head group (AO) and the hydrophobic tail ($C_{12}$).

The CMC/$C_{20}$ ratios of the hybrid surfactants in this work are smaller than that of $C_{12}AO$. The CMC/$C_{20}$ ratio is correlated with structural factors in the micellization and adsorption processes. A surfactant with a larger CMC/$C_{20}$ ratio has a greater tendency to adsorb at interfaces than to form micelles. Thus, the CMC/$C_{20}$ data in Table 1 indicate that $C_{12}EO_nAO$ surfactants have a lower tendency to adsorb at interfaces than to form micelles. Additionally, the CMC/$C_{20}$ ratio of $C_{12}EO_nAO$ shows a slight decrease with increasing length of $EO_n$ from 1 to 4, which is opposite to the trend for traditional polyoxyethylenated (POE) nonionic surfactants [17]. For POE nonionic surfactants, the CMC/$C_{20}$ ratio increases with increasing the number of EO units at a constant hydrophobic chain length. Thus, the $EO_n$ chain in $C_{12}EO_nAO$ hybrid surfactants cannot be considered as a purely hydrophilic group as in POE nonionics.

The minimum molecular cross-sectional areas ($A_{min}$) of $C_{12}EO_nAO$ ($n = 1$–4) surfactants are smaller than that of $C_{12}AO$, and hence their maximum surface excesses ($\Gamma_m$) are accordingly larger. However, the values of $A_{min}$ for $C_{12}EO_nAO$ increase with increasing length of $EO_n$ from 1 to 4, which may be attributed to coiling of the longer $EO_n$ chain [2, 19]. On the other hand, the $EO_n$ chain in the hybrid surfactant of $C_{12}EO_nAO$ is probably suitably predisposed to form intermolecular hydrogen bonds with $H_2O$ at the air/water interface, as a result of which the $\gamma_{CMC}$ increases slightly with increasing $EO_n$ chain length from 1 to 4. Similar trends have been observed for the surfactants $C_{12}EO_nS$ ($n = 2$–4) [2] and POE nonionics [18]. The difference in $\gamma_{CMC}$ between $C_{12}AO$ and $C_{12}EO_1AO$ may be ascribed to their different molecular structures.

Polarity of the Micellar Microenvironment

The emission spectrum of pyrene features five vibrational bands, of which the first ($I_1$, around 373 nm) is enhanced in a polar microenvironment, whereas the third ($I_3$, around 384 nm) is not sensitive to the surrounding environment. It is known that pyrene preferentially dissolves in hydrophobic regions. Thus, the ratio $I_1/I_3$ can be exploited to probe the formation of micelles and the micropolarity of surfactant aggregates [20]. It can be seen in Fig. 4 that when the surfactant concentration reaches the CMC, the value of $I_1/I_3$ decreases rapidly. Thus, the correlation of $I_1/I_3$ and $c$ may be employed to determine the CMC of surfactants (ESM Fig. 5S) [10]. The CMC values for $C_{12}AO$ and $C_{12}EO_nAO$ in this work are listed in Table 1; the corresponding log CMC-$n$ relationship was obtained according to Eq. (3) and is presented graphically in Fig. 3.

$$\log \mathrm{CMC} = 0.52 - 0.10n (R^2 = 0.9771) \quad (3)$$

As can be seen from Table 1, Eqs. (2) and (4), the results of CMC (and the correlation of log CMC vs. $n$) for $C_{12}AO$ and $C_{12}EO_nAO$ determined by the surface tension method are in good agreement with those determined by the pyrene $I_1/I_3$ ratio method.

For aqueous micelle solutions of $C_{12}AO$ and $C_{12}EO_n$-AO, the values of $I_1/I_3$ (defined as $[I_1/I_3]_m$) are 0.93 ($C_{12}AO$), 0.94 ($C_{12}EO_1AO$), 0.95 ($C_{12}EO_2AO$), 1.01 ($C_{12}EO_3AO$), and 1.02 ($C_{12}EO_4AO$), respectively. Pyrene is a strongly hydrophobic probe and its solubility in water is very low (2–3 μM). In the presence of micelles, it is preferentially solubilized in the interior hydrophobic regions of these aggregates. The inner cores of typical micelles can be considered as hydrocarbon-like. However, considering that pyrene $I_1/I_3$ in water is around 1.56 and in pure hydrocarbon is around 0.61 [21], it seems that the

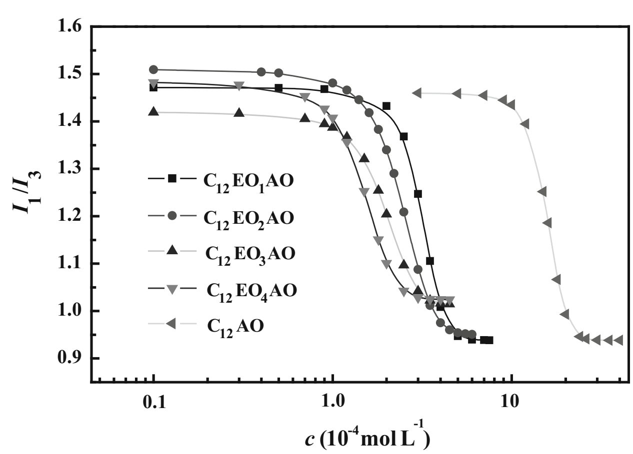


**Fig. 4** The plots of $I_1/I_3$ *versus* $c$ for $C_{12}EO_nAO$ ($n = 0$–4) at 25 °C

locus of solubilization of pyrene can be neither the inner hydrocarbon-like cores nor the surfaces of micelles in the cases of $C_{12}AO$ and $C_{12}EO_nAO$. Furthermore, considering the rigid planar structure of pyrene, it seems that its locus of solubilization is probably the palisade layer, i.e. the hydrophobic-hydrophilic transition zone in these micelles [22, 23]. In the case of $C_{12}AO$ micelles, the palisade layer may consist of methylene groups near the end of the hydrophilic AO group, while for $C_{12}EO_nAO$ ($n$ = 1–4) this layer is probably made up of part of the EO units due to its moderately amphiphilic character. Hence, the polarity of the palisade layer in the $C_{12}AO$ micelles is likely to be somewhat lower than that in $C_{12}EO_nAO$ ($n$ = 1–4) and accordingly the $[I_1/I_3]_m$ values of $C_{12}EO_nAO$ ($n$ = 1–4) are slightly larger than that of $C_{12}AO$. Moreover, the $[I_1/I_3]_m$ of $C_{12}EO_nAO$ shows a slight increase with increasing $n$ from 1 to 4 (see Fig. 4).

## Micellar Aggregation Number $N_m$

Plots of $N_m$ *versus* $c$ for the hybrid surfactants $C_{12}EO_nAO$ ($n$ = 1–4) used in this work and the corresponding traditional surfactant $C_{12}AO$ are shown in Fig. 5. It can be seen that $N_m$ increases with increasing surfactant concentration. A quite good empirical linear correlation between $N_m$ and $c$ was observed within a certain surfactant concentration range from 3 × CMC to 10 × CMC. Similar correlations have been observed for imidazolium-based cationic and zwitterionic surfactants [9, 17]. The corresponding mathematical equations for $N_m$ and $c$ are listed in Table 2 (the coefficient constants are given in parentheses). Therefore, the critical micellar aggregation number ($N_{m,c}$) can be obtained by extrapolating the linear equations for $N_m$ and $c$ back to the CMC values, and are listed in Table 2. Here, the parameter $N_{m,c}$ describes the number of surfactant monomers for the first micelle corresponding to the defined

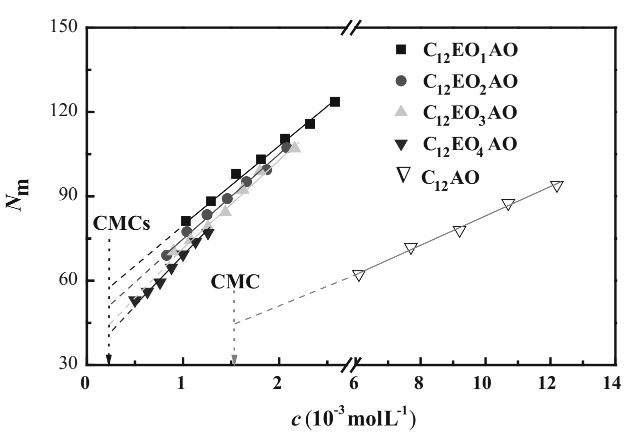


**Fig. 5** The linear correlation between $N_m$ and $c$ for $C_{12}EO_nAO$ ($n$ = 0–4) at 25 °C

**Table 2** The linear equations of $N_m$–$c$ and the corresponding $N_{m,c}$ for $C_{12}EO_nAO$ ($n$ = 0–4) at 25 °C

| Surfactant | $N_m$–$c$ equation | $N_{m,c}$ |
|---|---|---|
| $C_{12}AO$ | $N_m = 5.20c + 30.97$ ($R^2 = 0.994$) | 39 |
| $C_{12}EO_1AO$ | $N_m = 26.94c + 54.25$ ($R^2 = 0.994$) | 63 |
| $C_{12}EO_2AO$ | $N_m = 29.33c + 46.01$ ($R^2 = 0.994$) | 53 |
| $C_{12}EO_3AO$ | $N_m = 30.65c + 41.72$ ($R^2 = 0.988$) | 48 |
| $C_{12}EO_4AO$ | $N_m = 33.36c + 35.39$ ($R^2 = 0.991$) | 40 |

CMC at a certain temperature, which is difficult to obtain by other routine methods.

As shown in Table 2, the $N_{m,c}$ of $C_{12}AO$ and $C_{12}EO_4AO$ are approximately equal, which indicates that both surfactants should have almost the same degree of compactness in the micelles. It has been thought that water can enter the micelles and extend up to four carbons from the head group [21]. In micelles with compact head groups, the $I_1/I_3$ ratios are lower, indicating lower water penetration compared to that in micelles with larger head groups [21]. However, the data in Table 1 demonstrate that the $A_m$ values of $C_{12}EO_nAO$ ($n$ = 1–3) are smaller than that of $C_{12}AO$, while the $N_{m,c}$ of $C_{12}EO_nAO$ ($n$ = 1–3) are larger than that of $C_{12}AO$ (see Table 2). All of these results indicate that the $C_{12}EO_nAO$ ($n$ = 1–3) micelles are more compact, allowing less water penetration, compared to the $C_{12}AO$ micelles. On this basis, the $[I_1/I_3]_m$ of $C_{12}EO_nAO$ ($n$ = 1–3) might be expected to be smaller than that of $C_{12}AO$, but the data in Fig. 4 demonstrate the opposite trend. As discussed in the above section on the polarity of the micellar microenvironment, the locus of solubilization for pyrene is likely to be the palisade layer of $C_{12}EO_nAO$ ($n$ = 1–4) and $C_{12}AO$ micelles, and the polarity of this layer of $C_{12}EO_nAO$ ($n$ = 1–4) micelles is higher than that of $C_{12}AO$ micelles due to the higher polarity of the $EO_n$ chain compared to methylene groups. Therefore, as shown in Fig. 4, the $[I_1/I_3]_m$ values of $C_{12}EO_nAO$ ($n$ = 1–4) are larger than that of $C_{12}AO$, despite almost equal $N_{m,c}$ values for $C_{12}AO$ and $C_{12}EO_4AO$ systems.

For the homologous hybrid surfactants $C_{12}EO_nAO$ ($n$ = 1–4), with increasing $n$ from 1 to 4, $A_m$ increases (see Table 1) while $N_{m,c}$ gradually decreases (Fig. 6). An approximately linear empirical correlation of $N_{m,c}$ and $n$ can be described by Eq. (4):

$$N_{m,c} = 69.5 - 7.4n(R^2 = 0.9773, n = 1 - 4). \quad (4)$$

## Conclusions

Nonionic-zwitterionic hybrid surfactants $C_{12}EO_nAO$ with different polyoxyethylene chain lengths ($n$ = 1–4) have

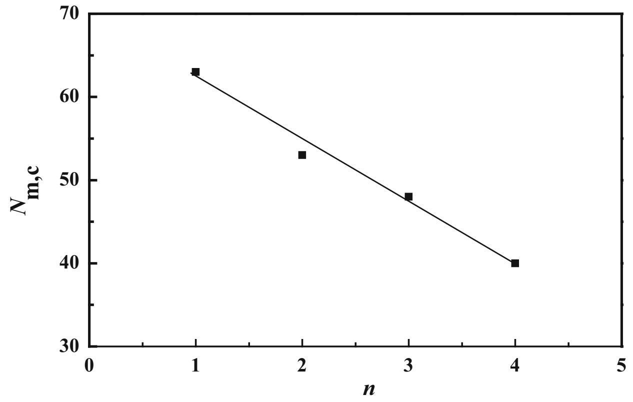


**Fig. 6** The linear correlation between $N_{m,c}$ and $n$ for $C_{12}EO_nAO$ ($n$ = 1–4) at 25 °C

been synthesized. For homologous $C_{12}EO_nAO$, the values of CMC, $\Gamma_m$, CMC/$C_{20}$, and $N_{m,c}$ decrease with increasing $n$ in $EO_n$ from 1 to 4. Concomitantly, the parameters of $\gamma_{CMC}$, $A_{min}$, p$C_{20}$, and $[I_1/I_3]_m$ of the locus of solubilization for pyrene increase. The log CMC and $N_{m,c}$ decrease linearly with $EO_n$ lengthening from 1 to 4, although the impact of each EO unit on the CMC of $C_{12}EO_nAO$ ($n$ = 1–4) is much smaller than that of a methylene unit in the hydrophobic main chains of traditional surfactants. Compared to the structurally related conventional surfactant $C_{12}AO$, $C_{12}EO_nAO$ ($n$ = 1–4) have smaller CMC, $A_{min}$, and CMC/$C_{20}$, but larger p$C_{20}$, $\Gamma_m$, and $N_{m,c}$, with a higher $[I_1/I_3]_m$. This may be attributed to the moderately amphiphilic $EO_n$ ($n$ = 1–4) between the hydrophobic $C_{12}$ tail and the hydrophilic AO head group.

**Acknowledgments** This work was jointly supported by the National Natural Science Foundation of China under Grant No. 21071065, the Scientific Research Foundation for the Returned Overseas Chinese Scholars (2011), State Education Ministry, Qinlan Project of Jiangsu Province, and Zhejiang Zanyu Technology Co. Ltd. of Zhejiang Province.

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