



Surface properties, aggregation behavior and micellization thermodynamics of a class of gemini surfactants with ethyl ammonium headgroups

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ARTICLE INFO

Article history:

Received 22 November 2011

Accepted 14 March 2012

Available online 23 March 2012

Keywords:

Gemini surfactants

Ethyl ammonium headgroups

Enhanced aggregation capability

Full understanding

ABSTRACT

Cationic gemini surfactant homologues alkanediyl- α,ω -bis(dodecyldiethylammonium bromide), $[C_{12}H_{25}(CH_3CH_2)_2N(CH_2)_S N(CH_2CH_3)_2C_{12}H_{25}]Br_2$ (where $S = 2, 4, 6, 8, 10, 12, 16, 20$), referred to as $C_{12}C_S C_{12}(Et)$ were synthesized systematically. This paper focused on various properties of the above gemini surfactants in order to give a full understanding of this series of surfactants. The following points are covered: (1) surface properties, which include (i) effect of the spacer carbon number on the general properties and (ii) the effect of added NaBr on the general surface properties; (2) aggregation behavior in bulk solution, including (i) morphologies of above gemini surfactants classed as having short spacers, middle-length spacers and long spacers and (ii) superior vesicle stability against high NaBr concentration for the long spacer gemini surfactants; (3) thermodynamic properties during micellization and the effect of spacer carbon number on them; and (4) perspectives for the further use and application of these compounds.

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1. Introduction

As a novel class of surfactants, gemini (dimeric) surfactants consisting of two single-chain ionic surfactants linked by a spacer group at or near the headgroups have aroused much interest since the early 1990s of the last century because of their unique physical and aggregation properties [1–5]. Various reports on the synthesis, structural characteristics, surface and aggregation properties of gemini surfactants have recently appeared, which revealed that gemini surfactants possess superior physicochemical properties compared with those of corresponding monomer surfactants, such as lower critical micelle concentration (*cmc*), high dependence on spacer structure, better solubilizing ability and unusual aggregation morphologies [6–10]. Owing to these unique properties, gemini surfactants have been widely used in industrial detergency, gelation of organic solvents, template synthesis of various materials, etc. [11–14]. Therefore, nowadays, investigation on gemini surfactants is still an attractive subject for advanced international research.

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Considerable efforts have been made to design and synthesize new forms of gemini surfactants, and most of them have been focused on the effect of spacer length or its flexibility and hydrophobicity [2]. The most widely studied gemini surfactants are the homologous series of bis(quaternaryalkylammonium bromide) surfactants, abbreviated as $C_M C_S C_M(Me)$ where M and S stand for the carbon atom number in the side alkyl chain and the methylene spacer, respectively [15,16], here the headgroup (Me) is added in order to distinguish from our compounds. Compared with the numerous studies on the spacer groups, although there are some works on the structural variation of gemini surfactant's polar headgroup, such as changing the cationic quaternary ammonium to anionic sulfonate, carboxylate and phosphate [5,7,17–20], the research on the microstructure transformation with the variation of hydrocarbon part of the headgroup is still rare, saying nothing of comprehensive properties in details.

In our previous work [10], we have reported that the hydrocarbon part of the headgroup plays an important role in regulating the aggregate microstructure in the gemini surfactant systems. When a series of gemini surfactants alkanediyl- α,ω -bis(dodecyldiethylammonium bromide), $[C_{12}H_{25}(CH_3CH_2)_2N(CH_2)_S N(CH_2CH_3)_2C_{12}H_{25}]Br_2$, designated as $C_{12}C_S C_{12}(Et)$ (where $S = 4, 6, 8, 10, 12$) were designed and synthesized, they showed enhanced aggregation capability than those of the corresponding $C_{12}C_S C_{12}(Me)$, namely spherical vesicles were formed in the aqueous solutions of the

former gemini while only micelles for latter. Therefore, further investigation is deserved on the various properties of $C_{12}C_5C_{12}(Et)$ series gemini surfactants. In this paper, besides the gemini surfactants $C_{12}C_5C_{12}(Et)$ with middle-length spacer ($S = 4, 6, 8, 10, 12$), one short and two long spacer gemini surfactants ($C_{12}C_2C_{12}(Et)$, $C_{12}C_{16}C_{12}(Et)$ and $C_{12}C_{20}C_{12}(Et)$) have also been involved in order to give a full understand on this gemini surfactants series, including surface, aggregation and thermodynamics properties. We hope our studies will supply a systematic comprehension of (1) effect of increasing hydrocarbon parts of the polar headgroup on the surface and aggregation behavior; (2) variation of obvious extent of the above effect against the changing space length; (3) the difference induced by salt addition among two gemini surfactant systems with methyl and ethyl headgroups, respectively; (4) giant vesicles formation and the surfactant molecular arrangement in gemini systems with long spacer.

2. Experimental section

2.1. Materials

Gemini surfactants $C_{12}C_2C_{12}(Et)$ and $C_{12}C_5C_{12}(Et)$ ($S = 4, 6, 8, 10, 12, 16, 20$) used in this study as illustrated in Fig. 1 were synthesized by our group [10,21] consulting the corresponding papers [15,22,23].

2.2. Krafft point determination

The Krafft temperatures all were determined using surfactant solutions of concentration close to 1 wt.% (i.e. well above the *cmc* of the investigated surfactants) using visual observation method.

2.3. Surface tension measurement

Surface tension measurements were carried out using the drop volume method according to the literatures [24,25]. Critical micelle concentration (*cmc*) was determined by the cross-point of the two lines before and after *cmc* on the γ -lgC curve. The measurement temperature was controlled at 25.0 ± 0.1 °C.

2.4. Fluorescence probe experiment

An ethanol solution of pyrene was introduced into the gemini surfactant solutions. The final pyrene concentration was 5×10^{-7} mol/L, and the ethanol volume was less than 1% of the total solution volume (usually the effect of ethanol at this concentration on the surfactant aggregates is insignificant [26]). The fluorescence spectra of pyrene solubilized in the investigated solutions were recorded using a Hitachi F4500 spectrofluorometer in the range of

350–450 nm at an excitation wavelength of 335 nm. I_1/I_3 corresponds to the ratio of the fluorescence intensities of the first ($\lambda = 374$ nm) and third ($\lambda = 384$ nm) vibronic peaks and was used to monitor the formation of hydrophobic microdomains. The critical micelle concentration (*cmc*) value can be taken as the concentration that corresponds to the intercept between the linear extrapolations of the rapidly varying portion of the curve and of the almost-horizontal portion at high concentration.

2.5. Transmission electron microscopy (TEM)

Micrographs were obtained with a JEM-100CX II transmission electron microscope by the negative-staining method and freeze-fracture technique. (1) Negative-stained method: uranyl acetate solution (1%) was used as the staining agent. One drop of the solution was placed onto a carbon Formvar-coated copper grid (230 mesh). Filter paper was employed to suck away the excess liquid. (2) Freeze-fracture technique: fracturing and replication were carried out in an EE-FED.B freeze-fracture device equipped with a JEE-4X vacuum evaporator.

2.6. Electrical conductivity measurement

Electrical conductivity was used to determine the *cmc* and the micelle ionization degree (κ) values of different gemini surfactant solutions. The conductivity of the surfactant solution was measured as a function of concentration, using Orion 162A conductivity meter. Measurements were performed in a temperature-controlled, double-walled glass container with a circulation of water. Sufficient time was allowed between successive additions to allow the system to equilibrate. During the measurement, the temperature of the solution was maintained at 25.0 ± 0.1 °C.

2.7. Micelle aggregation number measurement

Micelle aggregation number was determined by steady-state fluorescence quenching (SSFQ) method Using a probe (pyrene) concentration of 2.5×10^{-6} mol/L which is much smaller than the micelle concentration, [micelle], and increasing the quencher ($C_{12}PyCl$) concentration such that the ratio $[Q]/[micelle]$ varies between, for example, 0 and 2, the variation of the fluorescence emission intensity is given by the following equation:

$$I_0/I_Q = \exp([Q]/[micelles]) \quad (1)$$

The plot of $\ln(I_0/I_Q)$ against $[Q]$ at constant surfactant concentration permits the determination of the micelle aggregation number, N , from

$$N = (C - cmc)/[micelles] \quad (2)$$

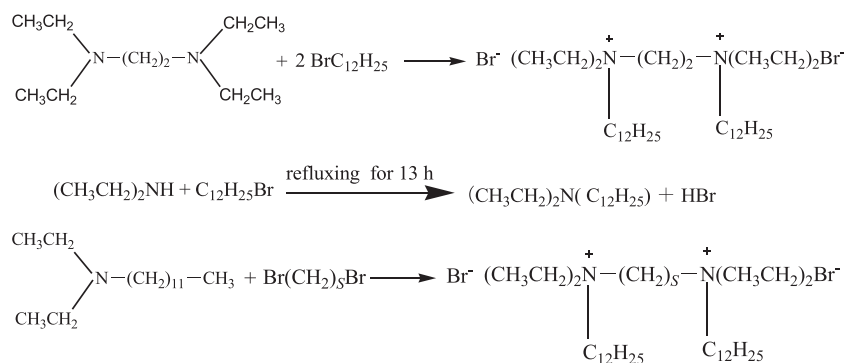


Fig. 1. Schemes of reaction routes for the synthesis of investigated gemini surfactants $C_{12}C_2C_{12}(Et)$ and $C_{12}C_5C_{12}(Et)$ ($S = 4, 6, 8, 10, 12, 16, 20$).

2.8. Isothermal titration microcalorimetry (ITC)

The calorimetric measurements were performed with the commercial microcalorimetric-measuring channel of the 2277 TAM (Thermometric AB, Jarfalla, Sweden). Raw data curves were integrated using Digital 4.1 software. The heat flow for the titration was measured as programmed. The observed enthalpies (ΔH_{obs}) were obtained by integrating the areas of the peaks in the plot of thermal power against time. All experiments were performed at 25.0 ± 0.1 °C.

3. Results and discussion

3.1. Adsorption at air/water interface and micellization

Before the surface tension measurement, Krafft points of $C_{12}C_5C_{12}(\text{Et})$ series ($S = 4, 6, 8, 10, 12$) were measured to insure the absolute dissolution for the above surfactants in water at the experimental temperature. It can be seen from Table 1 that this $C_{12}C_5C_{12}(\text{Et})$ series ($S = 4, 6, 8, 10, 12$), namely with middle-length spacer, had low Krafft points, indicating good solubility in water.

The surface tension curves as a function of the surfactant concentrations of $C_{12}C_5C_{12}(\text{Et})$ series ($S = 4, 6, 8, 10, 12$) at 25.0 °C are shown in Fig. 2. The values of the critical micelle concentration (cmc) and surface tension at cmc (γ_{cmc}) are listed in Table 1 in Supplementary material. Because the cmc values for our cationic gemini surfactants are low enough and our surfactants are highly purified, so the activity coefficients can be approximated to 1, the concentration of surfactant can be used to replace the activity of surfactant in the usual form of Gibbs equation which has been proved by Zana et al. [27–29]. The possibility of a partial binding of a counterion by a dimeric surfactant ion at concentrations $C < cmc$ arose in the analysis of the plots of the surface tension γ vs. C for dimeric surfactant solutions [30]. From the γ -lgC curves just below the cmc , maximum surface excess concentration (Γ_{max}) is calculated by the following Gibbs equation,

$$\Gamma_{\text{max}} = -\frac{1}{2.303nRT} \left(\frac{d\gamma}{d \lg C} \right)_T \quad (3)$$

where C is the concentration of surfactant aqueous solution, $R = 8.314$ J/mol/K, $T = 298.15$ K, γ is expressed in mN/m, n is a constant and depends on the number of species constituting the surfactant adsorbed at the interface [29]. The minimum area occupied per surfactant molecule (A_{min}) at air/water interface is related to the surface excess Γ_{max} as follows:

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} \quad (4)$$

where N_A is the Avogadro constant. The values of Γ_{max} and A_{min} for $C_{12}C_5C_{12}(\text{Et})$ series surfactants are also summarized in Table 1 in Supplementary material. However, it has been argued that for gemini surfactants, even the value $n = 3$ or $n = 2$ should be used in calculating Γ_{max} [31–34]. Nevertheless, if the value used for n affects the calculated values of Γ_{max} and A_{min} , it has no bearing on the way Γ_{max} and A_{min} vary with the spacer carbon number S . Here, $n = 3$ was mainly adopted to calculate and discuss the surface property parameters of $C_{12}C_5C_{12}(\text{Et})$ series referring to those of $C_{12}C_5C_{12}(\text{Me})$ series reported by Zana et al. [29]. On the other hand, compared with the result of monomer surfactant DTEAB (dodecyl triethylam-

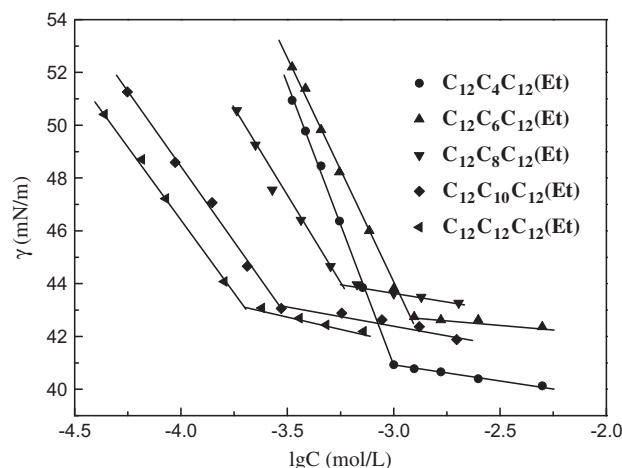


Fig. 2. Variation of the surface tension with the concentration of the $C_{12}C_5C_{12}(\text{Et})$ series at 25.0 °C, where $S = 4, 6, 8, 10, 12$.

monium bromide, $A_{\text{min}} = 0.71$ nm²), it seems that $n = 3$ is more reasonable.

As shown in Fig. 2: (I) The cmc values of $C_{12}C_5C_{12}(\text{Et})$ ($S = 4, 6, 8, 10, 12$) were almost equal to those of their methyl homologous compounds, while they were much lower than their monomer DTEAB ($cmc = 1.3 \times 10^{-2}$ mol/L), presenting the most outstanding characteristic of gemini surfactants in comparison with the conventional single-chain surfactants. The cmc values of the above gemini surfactants showed a volcano change with the variation of spacer carbon number S of 4–12, and the maximum was gotten at $S = 6$. When $S \geq 8$, the cmc values decreased, which can be attributed to that the spacer becomes more hydrophobic with the increase in spacer length, resulting in the enhancement of aggregation ability. (II) With the variation of spacer length, the γ_{cmc} of Me and Et series showed similar changing trend, as firstly increased until $S = 8$ then decreased at $S \geq 10$. The γ_{cmc} of Et series were slightly bigger than those of Me series, loose arrangement of molecules at air/water interface induced by bigger headgroup should account for this phenomenon. (III) A_{min} increased with the increasing S and tended to gentle at $S = 8$ –10. Generally speaking, in the range of $S < 10$, A_{min} increases rapidly with S ; at $S \geq 10$ –12, the spacer becomes too hydrophobic to remain in contact with water and moves to the air side of the interface, adopting a folded conformation [35]. As a result, the headgroups are closer to each other and A_{min} decreases upon increasing S . However, it should be mentioned that for gemini surfactants with middle-length spacer, the decrease in A_{min} brought by the bending of spacer cannot sufficiently counteract the increase in A_{min} brought by the prolongation of spacer, because of the inadequate flexibility and weak bending effect. Consequently, the net effect exhibits that with the increase in spacer length, A_{min} gradually increases and this increasing trend gradually becomes gentle and constant. We are well-founded to presume that the above-mentioned bending effect will be predominant and show a decrease in A_{min} when the spacer length is longer enough.

To avoid the problem of the coefficient n , we prepared surfactant solutions containing a swamping concentration of electrolyte at least 100 times higher than the maximum concentration used for surface tension measurements in the premicellar region. In this case [36,37], $n = 1$ is taken, because the swamping electrolyte concentration provides a constant ionic strength of the solution. Fig. 3 shows the surface tension curves of $C_{12}C_5C_{12}(\text{Et})$ series ($S = 4, 6, 8, 10, 12$) with the addition of 0.02 mol/L NaBr, and the corresponding cmc values and surface property parameters are listed in Table 2 in Supplementary material. Also, the variations of γ_{cmc} and A_{min} of

Table 1
Krafft points of $C_{12}C_5C_{12}(\text{Et})$ systems ($S = 4, 6, 8, 10, 12$).

S	4	6	8	10	12
Krafft point (°C)	<5	<0	<5	<5	<5

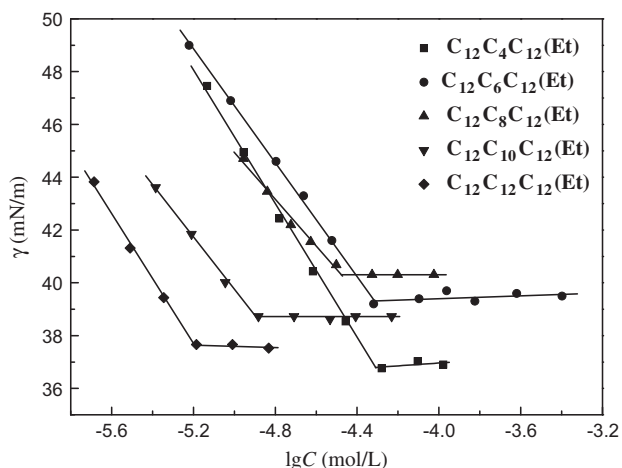


Fig. 3. Variation of the surface tension with the concentration of the $C_{12}C_5C_{12}(Et)$ series at 25.0 °C with 0.02 mol/L NaBr, where $S = 4, 6, 8, 10, 12$.

$C_{12}C_5C_{12}(Et)$ series with middle-length spacer with and without 0.02 mol/L NaBr addition are compared with each other, as shown in Fig. 4.

First, compared with the surface tension curves without NaBr, the addition of NaBr into $C_{12}C_5C_{12}(Et)$ systems ($S = 4, 6, 8, 10, 12$) regressed the curves shape to usual one, of which the surface tension nearly kept linear and constant upon increasing C at $C > cmc$. Second, it can be clearly seen from the table that with the addition of NaBr, the cmc values dramatically decreased and this decreasing trend looked more obvious with the increase in spacer length. Third, γ_{cmc} and A_{min} also exhibited decreasing trend with 0.02 mol/L NaBr addition, which is consistent with the traditional single-chain surfactants just the extent of decrease made clear. It can be attributed to that the addition of NaBr can compress the double layer around the polar headgroups and screen the electrostatic repulsion among the surfactant molecules, resulting in the nearness of headgroups which makes the surfactant molecules a compact arrangement. Because each gemini surfactant molecule possesses two polar headgroups, this compressing effect seems more obvious than that of traditional surfactant.

Moreover, the differences of both γ_{cmc} and A_{min} between the systems with and without NaBr addition were more apparent when $S \geq 8$. The reason is that with the increase in spacer, the flexibility of spacer increased, and the electrostatic repulsion between the gemini dications was reduced by NaBr addition, thus making the compression between the polar headgroups in one molecule

to a great extent. While for $S < 8$, the spacer was relatively rigid which made the compressing extent of the headgroups unobvious with the change of S , consequently the decreasing trend of γ_{cmc} and A_{min} induced by NaBr addition hardly changed with the variation of S . Generally speaking, the addition of NaBr not only screens the electrostatic repulsion among the surfactant molecules, but also makes the bending of the spacer to a great extent consequently induces a remarkable decrease in γ_{cmc} and A_{min} , especially for gemini surfactants with longer spacer.

3.2. Aggregation and microstructure in aqueous solution

In order to give a full understanding of the aggregation behavior of gemini surfactants with ethyl ammonium headgroup, we summarized the morphologies observed by TEM for the $C_{12}C_5C_{12}(Et)$ series ($S = 2, 4, 6, 8, 10, 12, 16, 20$) in Fig. 5.

Our previous work have proved that for the $C_{12}C_5C_{12}(Et)$ series with middle-length spacer, that is, $S = 4, 6, 8, 10, 12$, spherical vesicles can be formed in their aqueous solutions besides small micelles [10]. While for short spacer surfactant, that is, $S = 2$, elongated cylindrical micelles coexisted with the spherical micelles, and the spherical micelles were dominant compared with the little elongated ones based on the results of TEM, DLS and rheology measurements [38]. The aggregation behavior of the above two kinds of $C_{12}C_5C_{12}(Et)$ surfactants was quite different from the corresponding $C_{12}C_5C_{12}(Me)$ one, indicating that the polar headgroups of gemini surfactants play an important role in aggregation and microstructure in aqueous solution. Compared with $C_{12}C_5C_{12}(Me)$ series ($S = 4, 6, 8, 10, 12$), of which TEM micrographs showed only densely packed spherical micelles and no vesicles could be observed [16], it can be attributed to that the increase in the hydrocarbon parts of the polar headgroup from methyl to ethyl is beneficial to enhance the aggregation capability of the surfactants with multi-headgroups. However, for $C_{12}C_2C_{12}(Me)$, with the increase in the hydrocarbon parts of the polar headgroup from methyl to ethyl, that is, $C_{12}C_2C_{12}(Et)$, its aggregation capability was weakened, behaving that more elongated micelles and shear thickening phenomenon in rheological experiment for $C_{12}C_2C_{12}(Me)$ aqueous solution [39,40] were substituted for little elongated ones and Newtonian response [38]. All of these results demonstrate that when the spacer is shorter enough, the enhanced hydrophobic effect induced by the increase in headgroup from methyl to ethyl cannot counteract the impeditive space effect, resulting in the decrease in aggregation capability.

Furthermore, it is interesting to find that giant vesicles with diameter up to thousands of nanometers can be observed in the

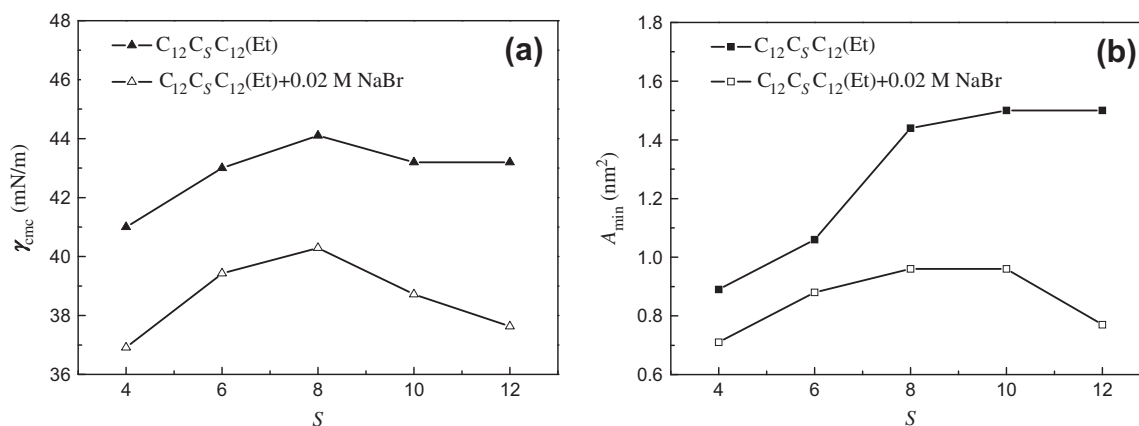


Fig. 4. Variations of (a) γ_{cmc} and (b) A_{min} of the $C_{12}C_5C_{12}(Et)$ serials before and after 0.02 mol/L NaBr addition, where $S = 4, 6, 8, 10, 12$.

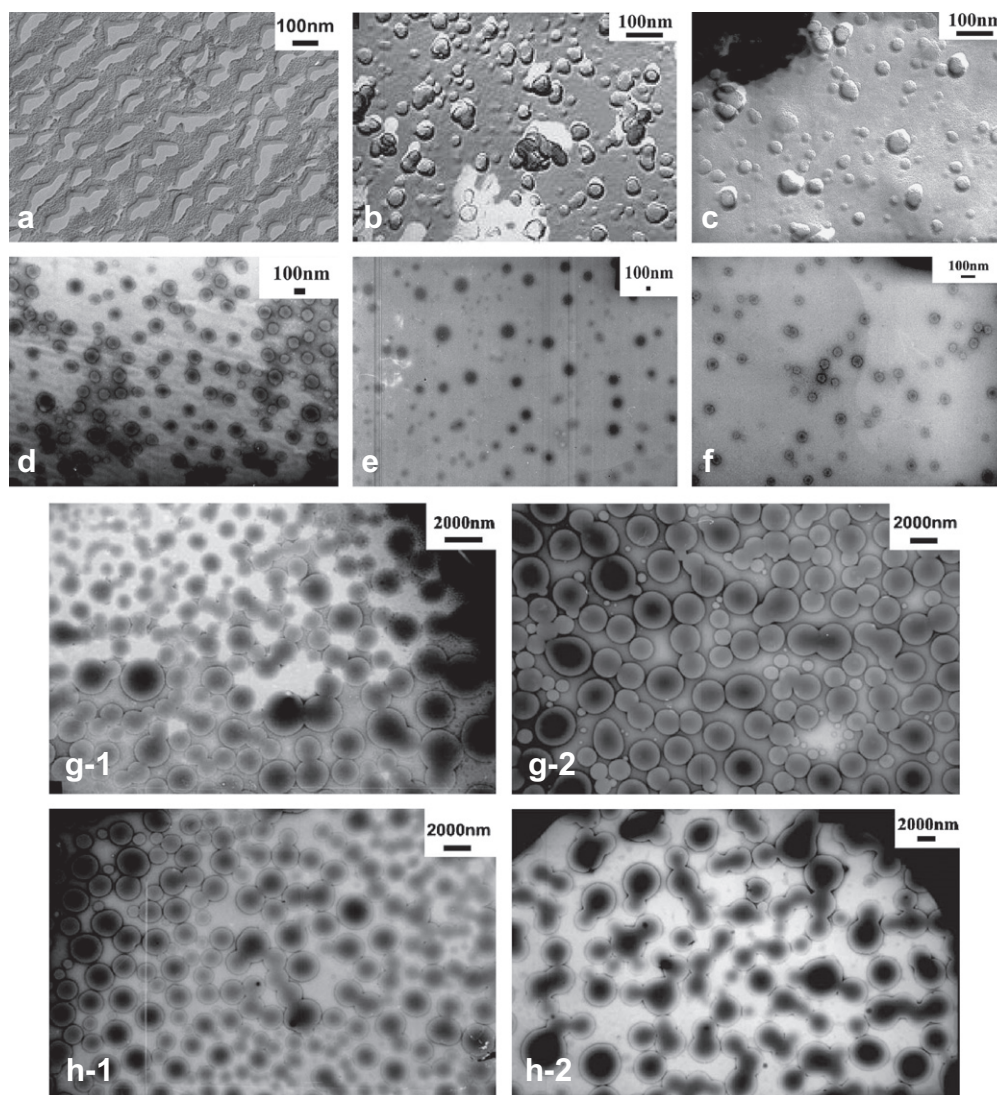


Fig. 5. TEM micrographs of the aqueous solutions of $C_{12}C_5C_{12}(Et)$ series by negative-staining or freeze-fracture method: (a) 20 mmol/L $C_{12}C_2C_{12}(Et)$; (b–f) 10 mmol/L $C_{12}C_5C_{12}(Et)$, $S = 4, 6, 8, 10, 12$; (g-1) 1 mmol/L $C_{12}C_{16}C_{12}(Et)$; (g-2) 10 mmol/L $C_{12}C_{16}C_{12}(Et)$; (h-1) 1 mmol/L $C_{12}C_{20}C_{12}(Et)$; (h-2) 5 mmol/L $C_{12}C_{20}C_{12}(Et)$.

aqueous solutions of $C_{12}C_{16}C_{12}(Et)$ and $C_{12}C_{20}C_{12}(Et)$ (Fig. 5g and h), going with obvious phenomena of vesicle aggregation and fusion. It is indicated that with the spacer further increased, the aggregation ability of gemini surfactants is greatly enhanced, exhibiting the ability of forming giant aggregates. Next, salt effect on the aggregation behavior of $C_{12}C_{16}C_{12}(Et)$ system was further performed. As shown in Fig. 6a, spherical vesicles could still be observed after the addition of 20 mmol/L NaBr into the aqueous solution of $C_{12}C_{16}C_{12}(Et)$, even NaBr concentration up to 100 mmol/L. Compared with the situation without NaBr, NaBr addition not only decreased the vesicle size, but also made the vesicles show good dispersion. Similar results were obtained in $C_{12}C_{20}C_{12}(Et)$ systems. According to our previous report [10], only 20 mmol/L NaBr addition can destroy the vesicles formed in $C_{12}C_5C_{12}(Et)$ systems with middle-length spacer, that is, $S = 4, 6, 8, 10, 12$, it is indicated that vesicles formed in gemini surfactants with long spacer ($C_{12}C_{16}C_{12}(Et)$ and $C_{12}C_{20}C_{12}(Et)$) possess good stability in resisting inorganic salt destruction. Based on the results of Engberts et al. [7], when the spacer group in gemini surfactant is long enough, the molecules prefer to membrane spanning arrangement in aggregates, here, it is more appropriate to be called bolaamphiphiles with branched chain. Owing to the presence of membrane

spanning bolas, the aggregates formed in bolaamphiphile systems usually keep superior stability; therefore, they can sustain harsh environments, such as high salt concentrations, extreme temperatures, or very acidic environments [41–44]. This is the reason why the vesicles formed in the systems of gemini surfactants $C_{12}C_{16}C_{12}(Et)$ and $C_{12}C_{20}C_{12}(Et)$ are stable in the presence of high concentration NaBr.

3.3. Fluorescence probing studies of micelle micropolarity

In this work, the micelle micropolarities of the $C_{12}C_5C_{12}(Et)$ series (where $S = 4, 6, 8, 10, 12$) micelles were characterized by the values of I_1/I_3 in the fluorescence emission spectra of micelle-solubilized pyrene. This ratio is very sensitive to the polarity of the pyrene immediate environment [45]. The steady-state fluorescence profiles and the corresponding results are shown in Fig. 7 and Table 2. As seen in Table 2, the I_1/I_3 data for the investigated surfactant micelles had a broad maximum stretching from $S = 4$ to 6 and then decreased at larger values of S , indicating that the immediate environment of pyrene located turns more hydrophobic when $S \geq 8$. The value of the micelle micropolarity is dependent mostly on the micelle composition at the solubilization site of pyrene, that

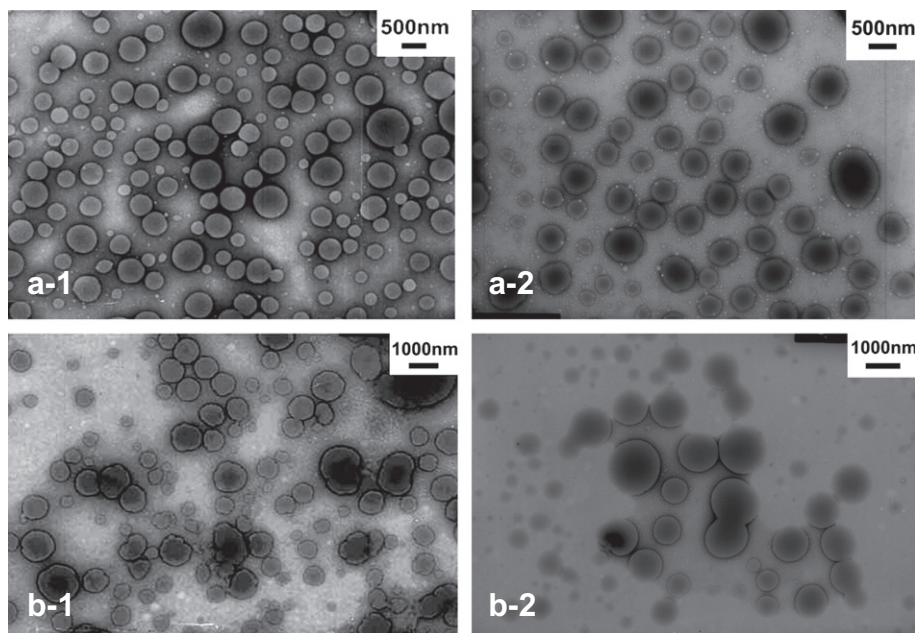


Fig. 6. TEM micrographs of the aqueous solution of 10 mmol/L $C_{12}C_{16}C_{12}(Et)$ (a) and 1 mmol/L $C_{12}C_{20}C_{12}(Et)$ (b) with the addition of NaBr at different concentrations: (1) 20 mmol/L and (2) 100 mmol/L.

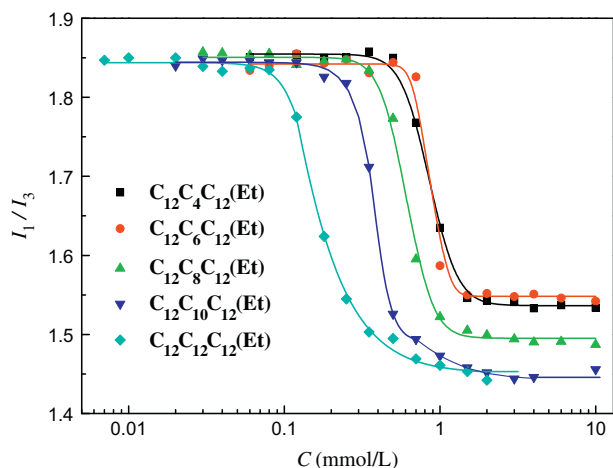


Fig. 7. Variation of I_1/I_3 ratio as a function of surfactant concentration for the $C_{12}C_5C_{12}(Et)$ series at 25.0 °C, where $S = 4, 6, 8, 10, 12$.

Table 2

Values of cmc , pyrene I_1/I_3 ratio and aggregation number (N) for the $C_{12}C_5C_{12}(Et)$ series based on steady-state fluorescence probing studies at 25.0 °C, where $S = 4, 6, 8, 10, 12$.

S	4	6	8	10	12
cmc (mmol/L)	1.16	1.22	0.85	0.50	0.32
I_1/I_3 (after cmc)	1.54	1.55	1.50	1.44	1.45
N	13	12	12	–	10

is, the palisade layer [46]. Thus, the decrease in I_1/I_3 with the increasing S is mainly due to the replacement of water molecules present in the palisade layer by the methylene groups of the increasingly longer spacers. This conclusion is consistent with that of the surface property studies. Recalling the cmc of the $C_{12}C_5C_{12}(Et)$ surfactants had a maximum at $S = 4–6$, this variation was interpreted as indicating that the spacer group of the

$C_{12}C_5C_{12}(Et)$ surfactants go from an aqueous environment to the micelle core when $S \geq 8$. Also, the cmc data obtained from fluorescence profiles are shown in Table 2, which has a same variation against S , and they are in agreement with those from surface tension measurements.

As mentioned above, the vesicles formed in $C_{12}C_5C_{12}(Et)$ series (where $S = 4, 6, 8, 10, 12$) were sensitive to NaBr, and even small amount of NaBr addition would destroy the vesicles, which make the assemblies in this kind of systems changing from the coexistence of vesicles and micelles to sole micelles. Here, the micelle aggregation number (N) of the $C_{12}C_5C_{12}(Et)$ ($S = 4, 6, 8, 12$) micelles with 0.1 mol/L NaBr addition was determined by steady-state fluorescence quenching method. Compared with time-resolved fluorescence quenching technique, steady-state fluorescence quenching is a more simple method to estimate the aggregation number in spite of lower accuracy with underestimation [47]. Nevertheless, if the steady-state fluorescence quenching method affects the accurate values of aggregation number, it has no bearing on the way of aggregation number (N) varies with the spacer carbon number S . As shown in Fig. 8, N values of $C_{12}C_5C_{12}(Et)$ ($S = 4, 6, 8, 12$) were 13, 12, 12, 10 with good linear fitting, respectively, indicating that values of N are only slightly dependent on the spacer carbon number S . This smaller micelle aggregation number also indicates that the micelles formed in $C_{12}C_5C_{12}(Et)$ systems were small and must be nearly spherical at the concentration investigated.

3.4. Thermodynamics of aggregates formation

Based on the studies of surface and aggregation properties, the thermodynamics during the aggregates formation in the aqueous solution of $C_{12}C_5C_{12}(Et)$ ($S = 4, 6, 8, 10, 12$) was also performed by microcalorimetry study. Fig. 9 illustrates the variation of observed enthalpies (ΔH_{obs}) with surfactant dilution into water at 25.0 °C. According to these results, the enthalpy of micellization (ΔH_M^\ominus) can be obtained directly, and based on the Eqs. (3) and (4) [48], the free energy of micellization (ΔG_M^\ominus) and the entropy of micellization (ΔS_M^\ominus) can be calculated:

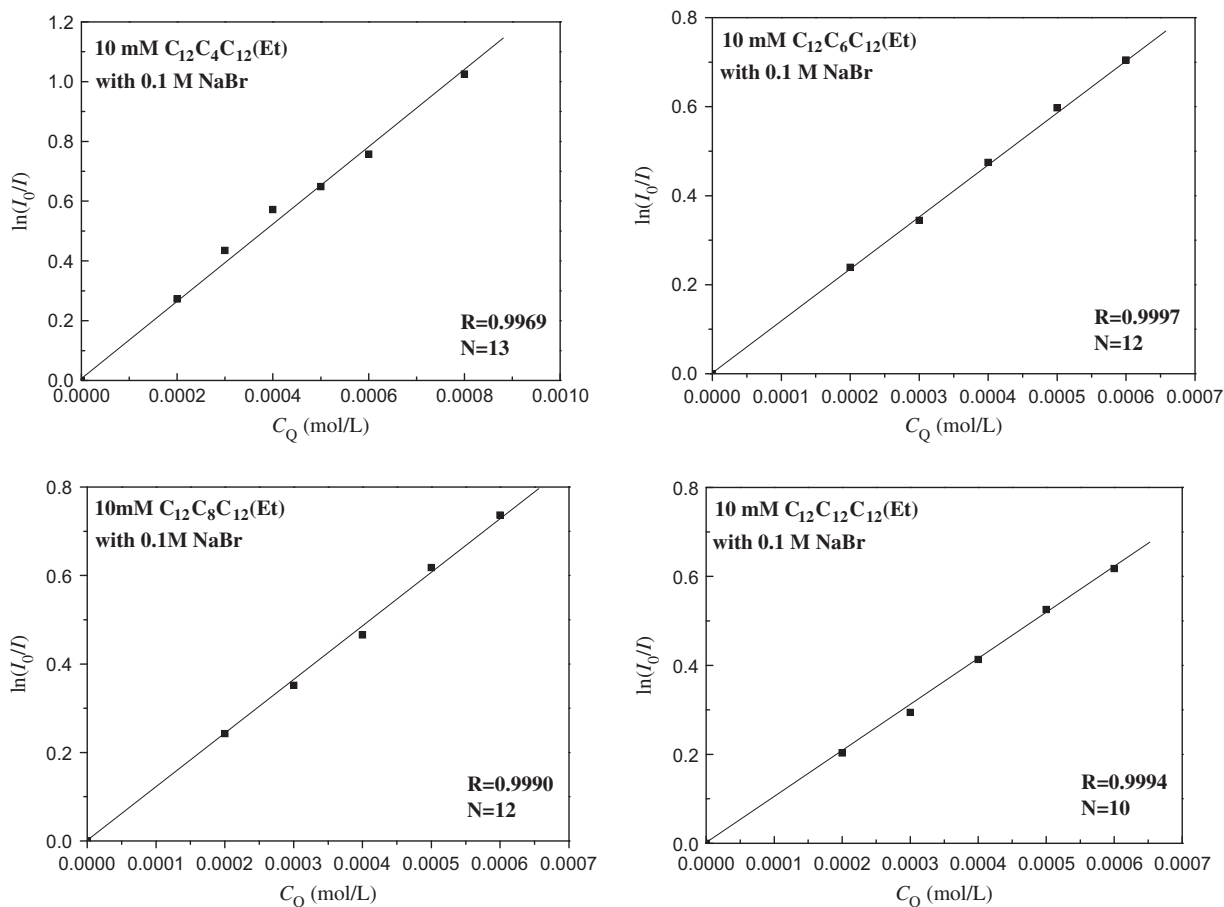


Fig. 8. Micelle aggregation number of 10 mmol/L $C_{12}C_S C_{12}(Et)$ ($S = 4, 6, 8, 12$) aqueous solution with 0.1 mol/L NaBr addition.

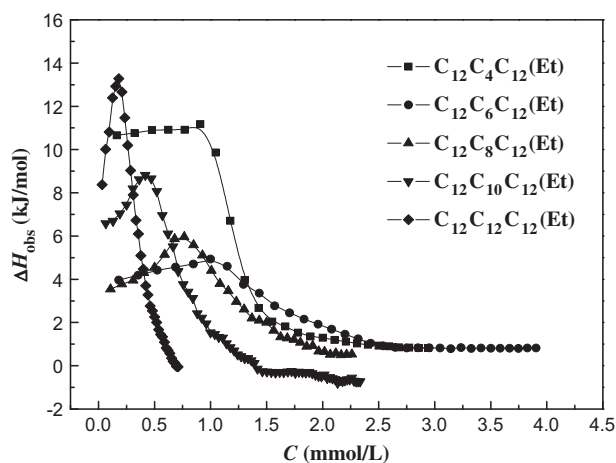


Fig. 9. Variations of observed enthalpies (ΔH_{obs}) of dilution into water with final surfactant concentration (C) of the $C_{12}C_S C_{12}(Et)$ series at 25.0 °C, where $S = 4, 6, 8, 10, 12$.

$$\Delta G_M^\ominus = (3 - 2\alpha)RT \ln(2cmc) - RT \ln 2 \quad (5)$$

$$\Delta S_M^\ominus = (\Delta H_M^\ominus - \Delta G_M^\ominus) / T \quad (6)$$

where α is micelle ionization degree, given by the ratio of slopes after and before cmc in the plot of conductivity vs. surfactant concentration [15]. It should be mentioned that there are micelles

and vesicles coexisting in the aqueous solution of 10 mmol/L $C_{12}C_S C_{12}(Et)$ ($S = 4, 6, 8, 10, 12$), thereby the observed enthalpy value includes the enthalpies of both micellization and vesicle formation. The obtained thermodynamics parameters are listed in Table 3, and also the enthalpy of micellization with 0.02 mol/L NaBr addition is given in order to find the effect of vesicle formation on the enthalpy. Table 3 shows that the cmc values obtained from microcalorimetry were in good agreement with those from surface tension plots, and the micelle ionization degree (α) was found to increase with S .

The plots of thermodynamics parameters during aggregates formation against S are visually given in Fig. 10, from which it is seen that:

- All ΔH_M^\ominus values were negative, indicating that micelle formation is an exothermic process for the investigated surfactants. Also, the effect of spacer carbon number (S) was seen to be very important. First, ΔH_M^\ominus increased as increasing S from 4 to 8 and showed a maximum at $S = 8$. Then, ΔH_M^\ominus decreased as $S > 8$. Moreover, NaBr addition induced a considerable decrease in ΔH_M^\ominus when $S \geq 8$ while a slight change for $S = 4$ and 6, illustrating that NaBr addition is beneficial to the aggregation formation, especially for gemini surfactants with relatively longer spacer.
- When $S = 4-8$, $-T\Delta S_M^\ominus$ values looked constant, but the absolute values of ΔH_M^\ominus decreased, resulting in $T\Delta S_M^\ominus > -\Delta H_M^\ominus$, indicating that $T\Delta S_M^\ominus$ makes a major contribution to ΔG_M^\ominus and the micellization of our surfactants is entropy-driven. When $S > 8$, $-T\Delta S_M^\ominus$ increased with the increasing S , illustrating that the extent of entropy-driven micellization becomes weak with the increase in S .

Table 3

Thermodynamics parameters of micellization for $C_{12}C_5C_{12}(Et)$ series at 25.0 °C, where $S = 4, 6, 8, 10, 12$.

S	cmc (mmol/L)	α	ΔH_M^\ominus (kJ/mol)	ΔG_M^\ominus (kJ/mol)	$-T\Delta S_M^\ominus$ (kJ/mol)	ΔS_M^\ominus (J/mol)	ΔH_M^\ominus (0.02 mol/L NaBr added) (kJ/mol)
4	1.00	0.30	-10.4	-33.4	-22.9	77.1	-8.9
6	1.12	0.39	-8.1	-30.6	-22.5	77.5	-7.4
8	0.54	0.52	-5.5	-28.9	-23.4	78.5	-13.8
10	0.33	0.64	-8.6	-26.5	-17.9	60.0	-16.6
12	0.19	0.74	-14.1	-24.6	-10.5	35.2	-22.6

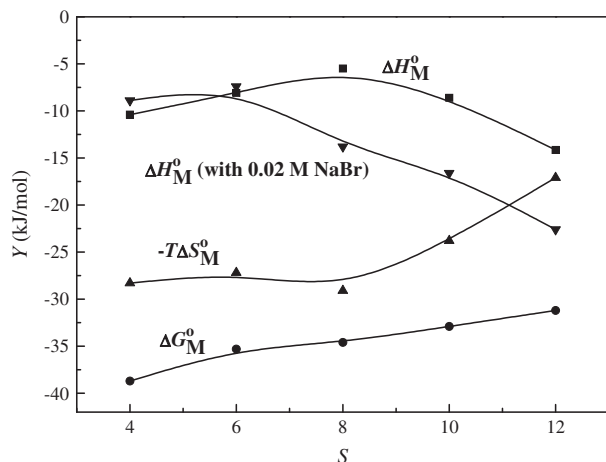


Fig. 10. Effect of the spacer carbon number S on the thermodynamics parameters during aggregates formation for $C_{12}C_5C_{12}(Et)$ series ($S = 4, 6, 8, 10, 12$) at 25.0 °C.

- (iii) All ΔG_M^\ominus values were negative, indicating that micelle formation is a spontaneous process for the investigated surfactants. Based on Eq. (5), ΔG_M^\ominus values are affected by both critical micelle concentration (cmc) and micelle ionization degree (α). It is clearly shown in Fig. 10 that the changing trend of ΔG_M^\ominus vs. S was in accordance with that of α , that is, with the increase in spacer length, both α and ΔG_M^\ominus increased.

4. Perspective and conclusions

This work focuses on the physicochemical properties of a novel class of gemini surfactants with two ethyl ammonium moieties as the polar headgroup. Several interesting properties have been shown in comparison with similar gemini surfactants with methyl ammonium as headgroup. In terms of surface, aggregation and thermodynamic properties, the most interesting property is the ability to form vesicles, which is brought about by the hydrophobic effect owing to increasing the hydrophobic chain content of the polar headgroup, especially for the surfactant having multi-polar headgroups.

In addition, compared with the tremendous amount of conventional surfactant mixed systems, the oppositely charged mixed systems of this gemin/conventional surfactant are still less to be explored. However, the special structure of gemini surfactants provides a convenient way to tailor the molecular arrangement and the interaction between molecules, so as to affect the aggregate structures and phase behavior [7,16,49]. Our studies have demonstrated that as the headgroup size is changed from Me to Et, the mixed system of $C_{12}C_6C_{12}(Et)/SL$ (sodium laurate) is in favor of ASTP (surfactant aqueous two-phase system) formation than

$C_{12}C_6C_{12}(Me)/SL$ mixture [38], which open a broad vista in the world of gemini surfactant mixed with the oppositely charged gemini/conventional surfactants.

In summary, the headgroup plays an important role in regulating the aggregate microstructure in the surfactant systems, especially for the surfactant having multi-polar headgroups, such as gemini surfactants, for which the influence on the molecular properties by the variation of headgroups may be greater than that in conventional single-chain surfactant system. The increase in the hydrophobic effect induced by the hydrocarbon parts of the polar headgroup will be beneficial to the aggregation of the molecules. These studies will attract attention to the headgroup effects for gemini surfactant systems in colloid and interface science, including surface, aggregation and thermodynamic properties. We expect to see more interesting work appearing in this field in the near future.

Acknowledgments

We are grateful for financial support from the National Natural Science Foundation of China (Grants Nos. 21003124 and 21073006) and Urumqi Science and Technology project (No. H101133001).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2012.03.044>.

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