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Aggregates of alginates binding with surfactants of single and twin alkyl chains in aqueous solutions: Fluorescence and dynamic light scattering studies

Biye Ren *, Yiming Gao, Lu Lu, Xinxing Liu, Zhen Tong *

Research Institute of Materials Science, South China University of Technology, Guangzhou 510640, China

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Abstract

The natural polyelectrolytes, especially polysaccharides, are intensively used in foods, cosmetics, and pharmaceuticals with many amphiphiles. Alginate chain contains three types of dyad sequential blocks as MM, GG, and MG, and these residue sequences endow the alginate chains with different stiffness. It is therefore interesting to illustrate the effect of chemical composition and sequence of alginate on the aggregation with positively charged surfactants. The single-tail cationic surfactant dodecyltrimethyl ammonium bromide (DTAB) and twin-tail (Gemini) surfactant ethanediyl-1,2-bis (dodecyldimethylammonium bromide) (12-2-12) were allowed to bind on the natural polyanion of sodium alginate with different M/G ratios (0.6 and 1.85, respectively). The interaction and aggregation were investigated using fluorescence emission of pyrene probes and dynamic light scattering to reveal effects of the polyelectrolyte composition and surfactant structure. The results indicated that the cooperative aggregation was much stronger for the Gemini surfactant 12-2-12 than that for the single-tail DTAB with the same tail length and the binding strength of alginate to the both 12-2-12 and DTAB with the same tail length was almost identical. Also, the *cac* was almost independent of the alginate composition and M and G sequence. Dynamic light scattering illustrated that the hydrodynamic radius R_h for a surfactant-bound alginate chain was always smaller than that without binding. Particularly, the R_h exhibits two very different change trends with the surfactant concentration. Binding with 12-2-12 produced a deep minimum R_h at quite a lower surfactant concentration than its *cac*, while R_h monotonically decreased with increasing DTAB concentration. The appearance of the minimum R_h could be attributed to the hairpin-like conformation of the alginate chain formed due to binding with 12-2-12.

Keywords: Sodium alginate; Cationic surfactant; Gemini surfactant; Polyelectrolyte–surfactant interaction; Fluorescence probe; Dynamic light scattering

1. Introduction

In the last two decades, the interaction and aggregation of polyelectrolytes with oppositely charged surfactants in aqueous solutions have received substantial attention (Goddard & Ananthapadmanabhan, 1993). The mixture of polyelectrolytes and surfactants has found wide industrial applications, such as enhanced oil recovery operation (Chiu & Kuo, 1999), home and personal care industries, etc. (Goddard & Ananthapadmanabhan, 1998). Several techniques are available to examine polyelectrolyte–surfactant interaction, such as fluorescence (Chandar, Somasundaran, & Turro, 1988; Kogej & Škerjanc, 1999; Winnik & Regismond, 1998), viscometry (Anthony & Zana, 1996), dynamic and static light scattering (Fundin & Brown, 1994; Li, Wetting, & Verrall, 2005; Villetti, Borsali, Crespo, & Soldi, 2004), small-angle neutron scattering (Claesson et al., 2000), turbidity (Kayitmazer, Seyred, Dubin, & Staggemeier, 2003), etc. The driving force of this aggregation is predominantly governed by the electrostatic interaction between polyelectrolytes and surfactants as well as the hydrophobic interaction between surfactants

* Corresponding authors. Tel./fax: +86 20 8711 2886.
E-mail addresses: mcbyren@scut.edu.cn (B. Ren), mcztong@scut.edu.cn (Z. Tong).

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(Goddard, 1986). The binding process can occur in a cooperative manner, where the surfactant molecule bound on the polyelectrolyte can promote other surfactant molecules to bind onto the nearest neighboring sites through hydrophobic association. The polymer hydrophobicity, charge density, chain flexibility, ionic strength, and the nature of the surfactant are all decisive factors governing the binding and aggregation (Anthony & Zana, 1996; Chu & Tomas, 1986; Kayitmazer, Shaw, & Dubin, 2005; Magny, Illiapoulos, Zana, & Audebert, 1994). Although numerous experiments on polyelectrolyte–surfactant systems have been reported, little concerns the natural polyelectrolytes binding with surfactants, especially for polysaccharides, which are intensively used in foods, cosmetics, and pharmaceuticals with many amphiphiles.

Alginate is a binary linear natural polyelectrolyte containing 1,4-linked α-L-guluronate (G) and β-D-mannuronate (M) arranged in a non-regular blockwise pattern (Fig. 1), which is widely used as a gelling agent in food and pharmaceutical applications (Moe, Dragel, Skjåk-Bræk, & Smidsrød, 1995; Haug, Larsen, & Smidsrød, 1997). Another important application of alginate is to form gels in the presence of divalent cations (Lu, Liu, Dai, & Tong, 2005). There are three types of dyad sequential blocks as MM, GG, and MG. These residue sequences endow the alginate chains with different stiffness. Consequently, the mean square end-to-end distance per uronate residue for the G component is 2.2 times larger than that for the M component (Matsumoto, Kawai, & Masuda, 1992). The chemical composition and sequence of the M and G residues depend on the biological source, growth, and seasonal conditions. It is therefore interesting to investigate the effect of chemical composition and sequence of alginate on the aggregation with positively charged surfactants.

On the other hand, Gemini surfactants, which have two hydrocarbon tails connected to two ionic or polar head groups separated by a spacer, have some unique properties, such as better solubilizing, wetting and foaming, remarkably low *cmc* (critical micelle concentration) values, lower Krafft temperatures, and much more efficient for decreasing water surface tension compared with conventional single-tail surfactants (Menger & Kerper, 2000; Zana, 2002). However, little has been known for the binding of Gemini surfactants on polyelectrolytes (Yoshimura, Nagata, & Esumi, 2004; Wetting & Verrall, 2001), especially a comparative study on the single-tail surfactant with the same tail length. It is interesting whether the binding efficiency for the Gemini surfactant is just a double of the single-tail one. Also we wonder whether the aggregate structure is the same for the surfactant–polyelectrolyte complexes with single or twin alkyl tails.

Therefore, we chose in the present study two alginate samples with different M/G ratios to bind with either a Gemini surfactant or a single-tail surfactant with the same tail length of 12 carbons for comparison. Classical probe fluorescence emission and dynamic light scattering were applied to determine the critical aggregation concentration (*cac*) and hydrodynamic radius systematically.

2. Experimental section

2.1. Materials

Pyrene (99%) was purchased from Aldrich and recrystallized from ethanol. Dodecyltrimethyl ammonium bromide (DTAB) was purchased from Beijing Chemical Reagents Co. Cationic Gemini surfactant ethanediyl-1,2-bis-(dodecyl-dimethyl-ammonium bromide) with the structure of $[C_{12}H_{25}(CH_3)_2N(CH_2)_2N(CH_3)_2C_{12}H_{25}]$-$Br_2$, referred to as 12-2-12 (Fig. 2), was synthesized from *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and dodecyl bromide according to the method of Zana, Benrraou, and Rueff (1991) and purified by manifold crystallization from a mixture of acetone and ethyl acetate. Milli-Q purified water was used throughout. The structure of 12-2-12 was confirmed by ^{1}H NMR spectroscopy (Bruker Avance 300) and purity was verified by elemental analysis (Elementar vario EL). ^{1}H NMR($CDCl_3$): $\delta = 0.87$ (t, 6H, CH_3C), 1.24–1.37 (m, 36H, $C(CH_2)_9C$), 1.82 (m, 4H, CCH_2CN^+), 3.51 (s, 12H,

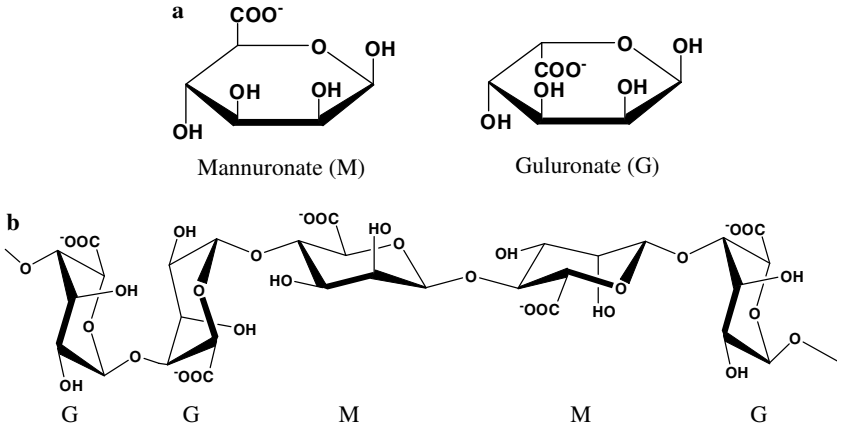

Fig. 1. Monomer units of alginate: (a) mannuronate (M) and guluronate (G). (b) The alginate chain with different G and M sequences.

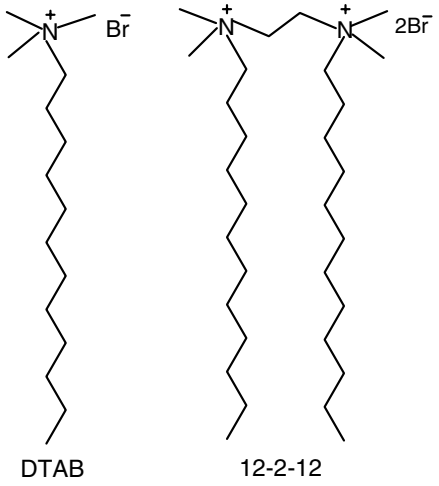

Fig. 2. The chemical structure of surfactants DTAB and 12-2-12.

Table 1
Characterization of alginate samples

Sample	$M_W \times 10^{-4}$	M_W/M_n	M/G	F_G	F_M	F_{GG}	F_{MM}	F_{GM}
MLGH-2	41	6	0.60	0.63	0.38	0.45	0.20	0.18
MLGL-4	122	24	1.85	0.35	0.65	0.17	0.47	0.18

(CH_3)$_2N^+$), 3.70 (t, 4H, $CCCH_2N^+$), 4.77 (t, 4H, $N^+CH_2CH_2N^+$). Elemental analysis: 12-2-12: Calcd. for $C_{30}H_{66}N_2Br_2$: C, 58.62; H, 10.82; N, 4.56. Found: C, 57.82; H, 11.18; N, 4.43.

Two sodium alginate samples provided by Kimitsu Chemical Industries Co., Japan, were purified according to our previous method (Liu, Qian, Shu, & Tong, 2003). Briefly, the alginate aqueous solution about 5 wt% was dialyzed in distilled water using cellulose tubular membranes (cut-off molecular weight is 14,000) until the conductivity of water outside became constant before and after refreshing. Then, the solution was filtered and freeze-dried to produce purified dry sample. Molecular weight (M_W) and its distribution of alginates were determined by GPC with a Waters apparatus using the elution of 0.1 M Na_2SO_4 aqueous solution and the standards of narrowly distributed PEO. The molar ratio of mannuronate (M) to guluronate (G) residues (M/G) and the molar fraction of GG, MM, and GM (MG) diad sequences F_{GG}, F_{MM}, and F_{GM} were determined by ^{1}H NMR according to Grasdalen, Larsen, and Smidsrød (1979) and Grasdalen (1983) in D_2O of 14 mg/mL at 70 °C. The characterization results are summarized in Table 1.

2.2. Measurements

Fluorescence emission of pyrene probes was measured using a Hitachi F-4500 spectrophotometer at 25.0 ± 0.1 °C. The excited wavelength is 335 nm and both the excitation and emission slits were 2.5 nm. Dynamic light scattering was carried out at scattering angle of 90° and 25 °C with a ALV apparatus (Germany) using a helium–neon laser (633 nm, 35 mW) and the data were analyzed with the ALV-5000/E software supplied by the maker. The solution was filtered through a 0.45 μm Millipore membrane into a 10 mm diameter cylindrical glass cell thoroughly cleaned.

The solution for fluorescence measurement was prepared as follows: 2 μL of acetone stock solution of pyrene (1.0 mmol/L) was added to a 10 mL volumetric flask. After the solvent was evaporated by blowing nitrogen, the alginate solution was added. Afterwards, the surfactant was added to the flask and diluted to 10 mL with water. The final pyrene concentration was 2.0×10^{-4} mmol/L. The aqueous alginate solution of constant concentration of 0.1 g/L (corresponding to 0.463 mmol repeat unit/L) was used in all experiments. The solution was continuously stirred overnight at room temperature prior to measurements.

3. Results and discussion

3.1. Fluorescence

Fluorescence probe technique is efficient in examining the polyelectrolyte–surfactant interaction and aggregation. The monomer pyrene exhibits five fine emission bands between 370 and 400 nm and the emission intensity ratio of the first to the third bands, I_1/I_3, is usually considered as a polarity measure of the microenvironment around the pyrene moiety (Winnik, 1993). For example, the I_1/I_3 value is 0.58 in hexane and 1.87 in water (Dong & Winnik, 1982). Hence, the I_1/I_3 value can be used to probe the micelle and aggregate formation.

Neumann, Schmitt, and Iamazaki (2003) reported that when the concentration of alginate is increased a larger number of polymeric hydrophobic microdomains will be present, the I_1/I_3 ratio of pyrene in 3.0 g/L alginate is 1.60 which is smaller than pyrene in water (1.87), so 0.1 g/L alginate concentration was used in the present study to avoid the hydrophobic microdomains in higher alignate concentration. The I_1/I_3 ratio of pyrene probes as a function of the surfactant concentration is shown in Fig. 3 for the two sodium alginate samples binding with two surfactants. All the curves show a sigmoidal decrease as the surfactant concentration increases. In the low surfactant concentration range, the I_1/I_3 ratio is approximately a constant of about 1.7, indicating that pyrene is localized in a polar environment. Then, the I_1/I_3 undergoes a sharp decrease, indicative of the appearance of surfactant aggregates (*cac*) because pyrene is gradually solubilized in the hydrophobic micelle phase. Eventually above the *cac*, the I_1/I_3 remains approximately a constant of a value between 1.2 and 1.3 because pyrene is thoroughly surrounded in the micelle environment. The *cac* value is determined from the intersecting point of linear extensions of the rapidly decreasing part and the horizontal part of the curve (see Fig. 3) (Regev & Zana, 1999). The *cac* values of these two surfactants bound on the sodium alginate samples in Table 2 with their corresponding *cmc* values and *cac*/*cmc* ratios.

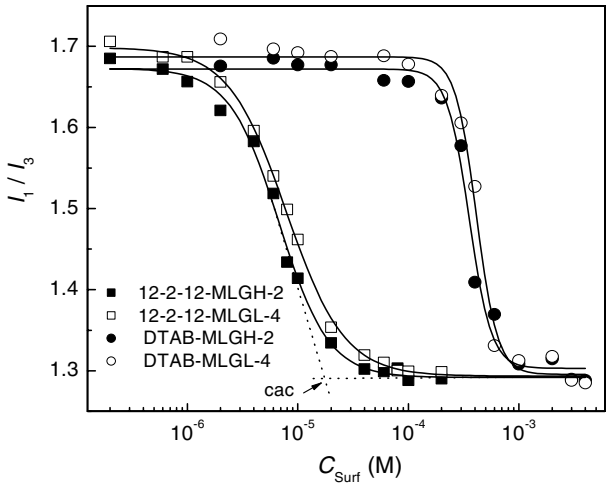

Fig. 3. The I_1/I_3 ratio of pyrene probe as a function of surfactant concentration in alginate solutions (0.1 g/L).

Table 2
cmc of surfactants and *cac* in alginate solutions

Surfactant	*cmc* (mM)	*cac* (mM) *cac*/*cmc*			
		(with MLGH-2)		(with MLGL-4)	
DTAB	20	0.57	0.029	0.66	0.033
12-2-12	1	0.019	0.019	0.025	0.025

The *cmc* of DTAB and 12-2-12 determined by the same fluorescence probe technique is 20 and 1 mM, respectively. For the DTAB–alginate binding complex, the *cac* is 0.57 mM (MLGH-2) and 0.66 mM (MLGL-4) and for the 12-2-12–alginate binding complex, the *cac* is 0.019 mM (MLGH-2) and 0.025 mM (MLGL-4). Therefore, the *cac* is about two orders of magnitude lower than the *cmc* for all of these surfactant–alginate binding complexes. In other words, at the *cac* the molar ratio of DTAB to the uronate unit of alginate is 1.2 and 1.4 for MLGH-2 and MLGL-4, respectively. This means that every charged group on the alginate chain can be occupied and there still are DTAB molecules un-neutralized in either the solution or complex at the *cac*. This aggregation is due to both the electrostatic interaction between positively charged surfactant molecules and negatively charged polymer chains and the hydrophobic interaction between the alkyl chains of the surfactants and hydrophobic moieties of the polymer chains. In contrast, at the *cac* the molar ratio of 12-2-12 to the uronate unit of alginate is only 0.041 and 0.054 for MLGH-2 and MLGL-4, respectively, corresponding to about 95 mol% of carboxyl groups unbound in the alginate at the *cac*. These values are much lower than a half of the corresponding ones at the DTAB *cac*. This fact indicates that the effect of a twin (or a Gemini) surfactant on the cooperative binding is much higher than the double of the single-tail surfactant with the same tail length.

It is noteworthy that the *cac* values for the same surfactant binding on two alginate samples have only a slight difference, almost independent of the alginate composition expressed by the M/G ratio. At low alginate concentrations, both DTAB and 12-2-12 bind on the negatively charged carboxyl groups of alginate chains in a cooperative manner within segment level and the difference in main chain stiffness due to the guluronate (G) content has little effect on this cooperative aggregation. Consequently, both the MLGH-2 and MLGL-4 alginate samples produce an almost similar *cac* value for a given surfactant.

As for comparison of the Gemini surfactant 12-2-12 with single-tail surfactant DTAB, the *cac* of 12-2-12–alginate is much lower than that of DTAB–alginate. We use the *cac*/*cmc* ratio as a measure to describe the interaction strength of the surfactant binding on alginate to eliminate the inherent difference in the *cmc* (Kogej & Škerjanc, 1999). The lower *cac*/*cmc* value suggests the stronger enhancement of polyelectrolyte to the binding interaction, leading to the cooperative aggregation at lower surfactant concentration. As shown in Table 2, the *cac*/*cmc* ratio for the 12-2-12–alginate is close to that for the DTAB–alginate, indicating that the binding strength of alginate to both Gemini and single-tail surfactants with the same tail chain length is almost identical. Thus, the apparent difference in the *cac* values for these surfactants comes from the difference in the aggregation capability of these surfactants themselves. Because the 12-2-12 has two hydrocarbon tails connected to two polar head groups separated by two ethylene groups, which make it easy to cause the cooperative aggregation, in spite of existence of oppositely charged polyelectrolytes.

3.2. Dynamic light scattering

A well-known experimental tool in the study of polyelectrolyte–surfactant systems is dynamic light scattering (DLS) that allows determination of aggregate size and size distributions (Fundin & Brown, 1994; Villetti et al., 2004). In the present research, the DLS technique was carried out to determine the aggregate size for the surfactant-bound alginates. The measured time–intensity correlation function was analyzed with CONTIN (Provencher, 1979) to obtain distribution function of the hydrodynamic radius R_h. For dilute solution with a monodisperse decay, the electric field autocorrelation function $g^1(t)$ relates to time t as follows:

$$g^1(t) = e^{-\Gamma t}, \quad (1)$$

where Γ is the decay rate, which is related to the diffusion coefficient D by $D = (\Gamma/q^2)_{q\to 0}$ and q is the scattering wave vector. The hydrodynamic radius R_h is calculated from the diffusion coefficient D using the Stokes–Einstein relation:

$$R_h = \frac{k_B T}{6\pi\eta D_0}, \quad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the medium viscosity. The measured R_h of alginate samples MLGH-2 and MLGL-4 at a concentration of 0.1 g/L in aqueous solution is 127 ± 2 and 140 ± 3 nm, respectively. Fig. 4 shows the correlation

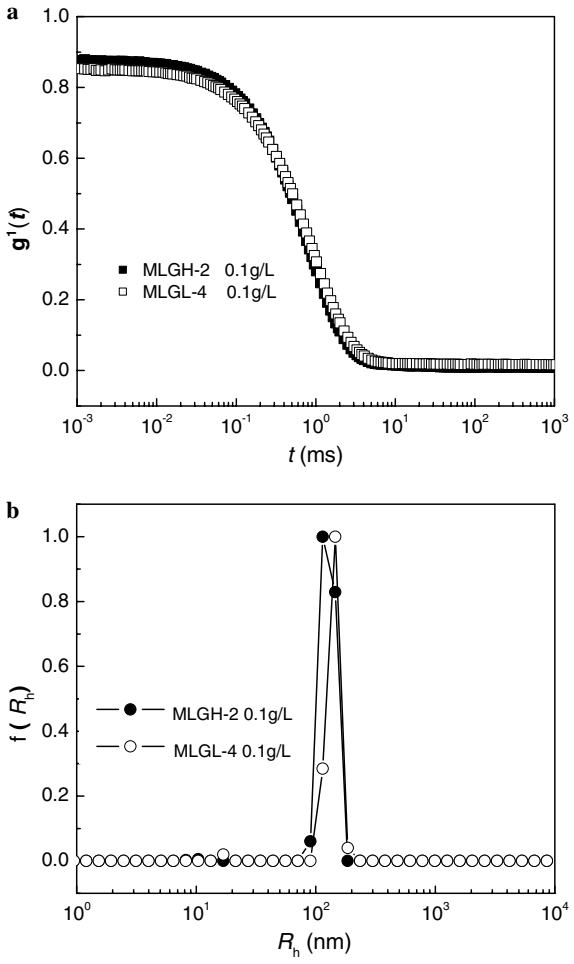

Fig. 4. (a) Correlation function for MLGH-2 and MLGL-4 of $C_{Alg} = 0.1$ g/L and (b) intensity weighted distribution of the hydrodynamic radius.

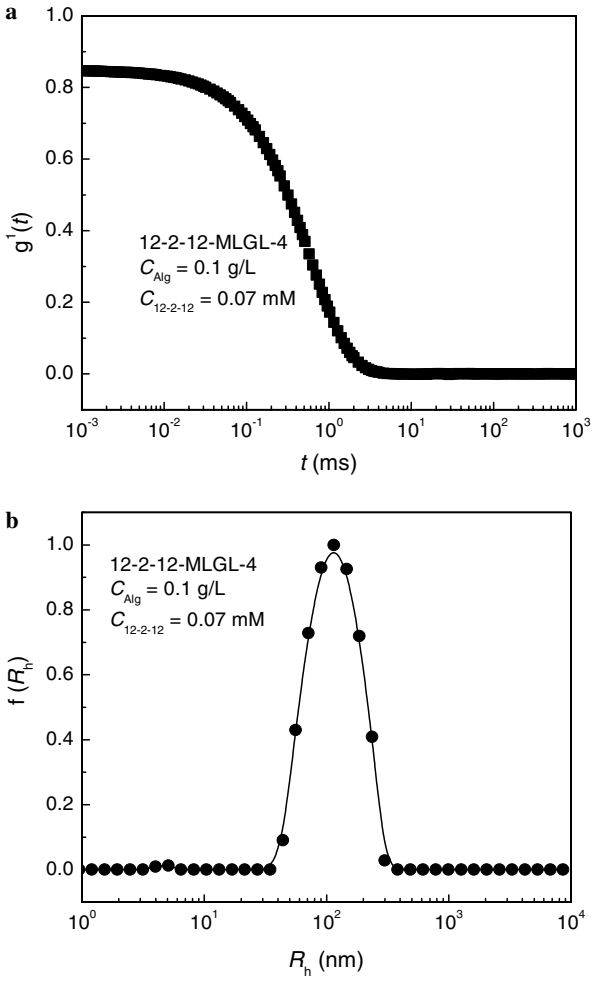

Fig. 5. (a) Correlation function for 12-2-12-MLGL-4 complex of $C_{Alg} = 0.1$ g/L and $C_{12\text{-}2\text{-}12} = 0.07$ mM and (b) intensity weighted distribution of the hydrodynamic radius.

function and the corresponding hydrodynamic radius R_h distribution $f(R_h)$ for the MLGH-2 and MLGL-4 in salt-free aqueous solution.

The surfactant concentration in the solution for light scattering measurement was controlled around the *cac* to avoid precipitation, which is much lower than their *cmc*. Fig. 4 shows the $g^1(t)$ correlation function for the 12-2-12–alginate (MLGL-4) solution and the corresponding hydrodynamic radius R_h distribution $f(R_h)$. There is only a single narrow peak for this surfactant–alginate complex at this concentration, indicating that the aggregate formed in dilute solutions has a similar size. Fig. 5 depicts the distribution of the hydrodynamic radius for 0.1 g/L of MLGH-2 alginate in the solution absent (the bottom curve) and present of 12-2-12. The alginate MLGH-2 as well as all the 12-2-12–MLGH-2 complexes with different surfactant concentrations in aqueous solution exhibited only one peak in the R_h distribution.

Surfactant concentration dependence of the hydrodynamic radius R_h is depicted in Figs. 6 and 7 for the aggregates with two kinds of surfactants, the data for the DTAB complexes were taken from the main peak. For the same surfactant bound on the two alginate samples with different M/G ratios, no obvious alginate sample dependence can be observed in R_h with increasing surfactant concentration. This further confirms that difference in the alginate composition and M and G sequence does not change the surfactant–alginate complex size. The size of the aggregates is always smaller than that of the alginate chain alone due to the hydrophobic interaction between bound alkyl chains of the surfactants, the cooperative binding effect, and the elimination of alginate charges. For the DTAB–alginate aggregates in Fig. 6, R_h drops rapidly to about 75 nm with increasing DTAB concentration to its *cac* and then gradually decreases to 55 nm at a high surfactant concentration of 2.0 mM (corresponding to 4.32 DTAB molecules/carboxyl group). This means that the alginate chain is monotonically contracted to a more compact globule after binding with DTAB molecules. This contraction can be attributed to the hydrophobic aggregation between the DTAB alkyl tails bound on the same alginate chain and the screen to the electrostatic repulsion by the excess DTAB molecules in the solution.

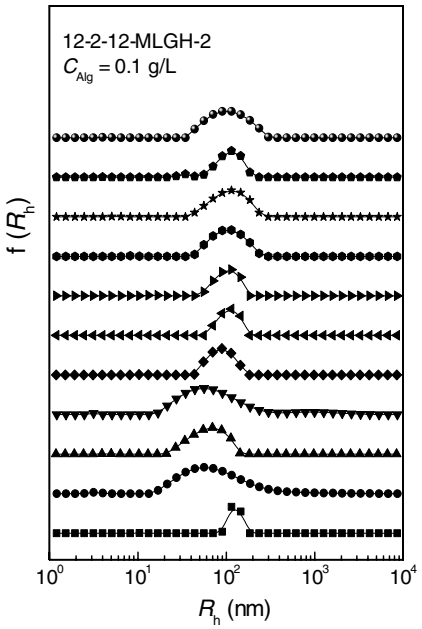

Fig. 6. Distribution of the hydrodynamic radius R_h for the alginate MLGH-2 of 0.1 g/L in the absence (the bottom curve) and presence of 12-2-12. The 12-2-12 concentration from the bottom is 0, 0.005, 0.008, 0.01, 0.015, 0.02, 0.03, 0.05, 0.07, 0.10, and 0.125 mM.

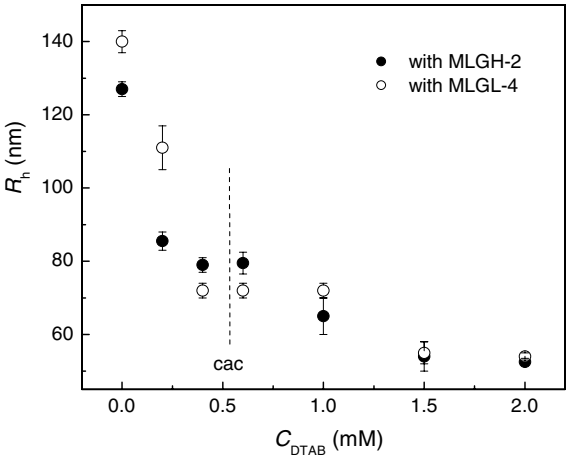

Fig. 7. Hydrodynamic radius of DTAB–alginate complexes as a function of DTAB concentration.

While for the Gemini surfactant 12-2-12–alginate aggregates in Fig. 7, once a small amount of Gemini surfactant was added there appeared a minimum R_h value of ~55 nm at about 0.008 mM of 12-2-12 for the two alginate samples, and then R_h increased again to about 100 nm as the 12-2-12 concentration approached to its *cac*. The R_h change in Fig. 8 manifests two characteristics for the Gemini surfactant 12-2-12 binding on polysaccharide alginate as schematically illustrated in Fig. 9. Because there are two positive charges at one head of 12-2-12 separated only by two CH_2 groups, they must attract two uronate units closer when bound on an alginate chain. This means that the distance between two uronate rings is reduced within about

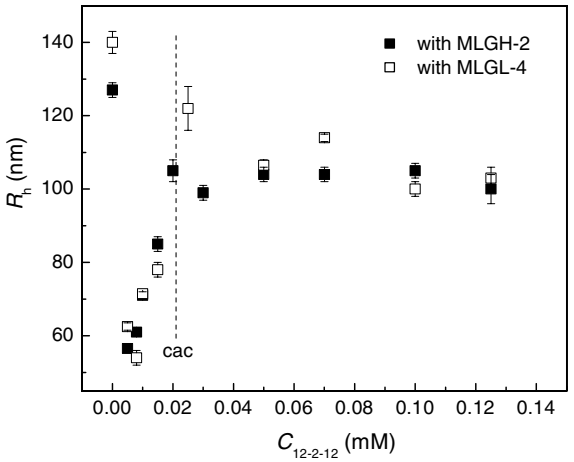

Fig. 8. Hydrodynamic radius of 12-2-12–alginate complexes as a function of 12-2-12 concentration.

0.38 nm after bound by one 12-2-12 surfactant molecule to form a hairpin-like conformation (Fig. 9a), resulting in appearance of the minimum R_h at the 12-2-12 to carboxyl group being 1% in mole. Uhríková et al. also reported a minimum in the R_h values at the surfactant concentration of ~0.09 mmol/L for the 12-4-12 binding DNA but their R_h values for the aggregates were always lower than that without surfactant (Uhríková, Zajac, Dubničková, & Pisárčik, 2005). The other characteristic is that the R_h for the 12-2-12-bound alginate reaches a level about 100 nm as the surfactant concentration above *cac*, much higher than 55 nm for the DTAB-bound alginate even if the 12-2-12 concentration is one order of magnitude lower than that of DTAB. This may be due to that the twin tails in one 12-2-12 molecule would take a volume much larger than the double of that taken by the single tail in DTAB (Fig. 9b). These results also demonstrate by dynamic light scattering that the effect of a twin (or a Gemini) tail chains on the binding complex is not simply doubling the single-tail effect with the same chain length. Zana et al. reported that the 12-*s*-12 form thread-like micelle when the spacer is short ($s = 2, 3$, where s is the number of CH_2 groups linking two charged heads) (Danino, Talmon, & Zana, 1995). They concluded that the Gemini surfactant tended to form aggregates in aqueous solutions of lower curvature than their corresponding single-tail surfactant. The present results are consistent with their conclusion. It is interesting to note that the minimum R_h value for the 12-2-12-bound alginate is almost the same as the lowest R_h value for the DTAB-bound alginate at 2.0 mM of DTAB. This seems to say that there is a minimum volume for these alginate chains shrunk induced by the bound surfactant.

4. Conclusions

The present study revealed through the *cac* and *cac*/*cmc* values that the cooperative aggregation was much stronger for the Gemini surfactant 12-2-12 than that for the monomeric surfactant DTAB with the same tail length and the

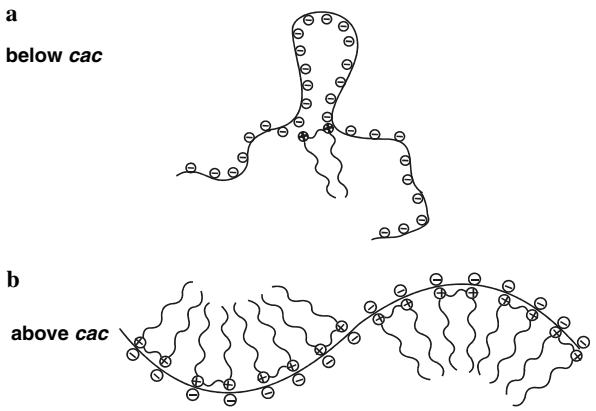

Fig. 9. Schematic illustration for the conformation of alginate binding with Gemini surfactant: (a) hairpin-like below the *cac* and (b) extended above the *cac*.

binding strength of alginate to the both 12-2-12 and DTAB with the same tail length was almost identical. The *cac* was almost independent of the alginate composition and M and G sequence. Dynamic light scattering illustrated that the hydrodynamic radius R_h for a surfactant-bound alginate chain was always smaller than that without binding due to the hydrophobic attraction between the bound surfactant tails, in spite of the surfactant being Gemini or single tail. The change trend for R_h with the surfactant concentration is completely different. Binding with 12-2-12 produced a deep minimum R_h at surfactant concentrations quite lower than its *cac*, while R_h monotonically decreased with increasing DTAB concentration. The appearance of the minimum R_h could be attributed to the hairpin-like conformation of the alginate chain formed due to binding with 12-2-12. The minimum R_h value for the 12-2-12-bound alginate was found to be almost the same as the lowest R_h value for the DTAB-bound alginate at 2.0 mM of DTAB.

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