

Self-assembled Gemini surfactant film-mediated dispersion stability

Y.I. Rabinovich^a, J.R. Kanicky¹, S. Pandey^{b,d}, H. Oskarsson^f, K. Holmberg^f,
B.M. Moudgil^{a,c,*}, D.O. Shah^{b,d,e}

^a Engineering Research Center for Particle Science and Technology, University of Florida, Gainesville, FL 32611, USA

^b Center for Surface Science and Engineering, University of Florida, Gainesville, FL 32611, USA

^c Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA

^d Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

^e Department of Anesthesiology, University of Florida, Gainesville, FL 32611, USA

^f Chalmers University of Technology, Göteborg, Sweden

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Abstract

The force–distance curves of 12-2-12 and 12-4-12 Gemini quaternary ammonium bromide surfactants on mica and silica surfaces obtained by atomic force microscopy (AFM) were correlated with the structure of the adsorption layer. The critical micelle concentration was measured in the presence or absence of electrolyte. The electrolyte effect (the decrease of CMC) is significantly more pronounced for Gemini than for single-chain surfactants. The maximum compressive force, F_{\max} , of the adsorbed surfactant aggregates was determined. On the mica surface in the presence of 0.1 M NaCl, the Gemini micelles and strong repulsive barrier appear at surfactant concentrations 0.02–0.05 mM, which is significantly lower than that for the single C₁₂TAB (5–10 mM). This difference between single and Gemini surfactants can be explained by a stronger adsorption energy of Gemini surfactants. The low concentration of Gemini at which this surfactant forms the strong micellar layer on the solid/solution interface proves that Gemini aggregates (micelles) potentially act as dispersing agent in processes such as chemical mechanical polishing or collector in flotation. The AFM force–distance results obtained for the Gemini surfactants were used along with turbidity measurements to determine how adsorption of Gemini surfactants affects dispersion stability. It has been shown that Gemini (or two-chain) surfactants are more effective dispersing agents, and that in the presence of electrolyte, the silica dispersion stability at pH 4.0 can also be achieved at very low surfactant concentrations (~0.02 mM).

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1. Introduction

Surfactant adsorption onto solid surfaces is a phenomenon of vital importance to various industrial processes ranging from ore flotation, lubrication, and paint technology to enhanced oil recovery [1]. At interfaces, the self-assembly process is influenced by surfactant–surfactant, surfactant–surface, surfactant–solvent, and solvent–surface

interactions. These interactions include the free energy of adsorption, roughness, surface heterogeneities, charge, and crystallinity [1].

Atomic force microscopy (AFM) has been used in the past to directly image and measure forces resulting from surfactant adsorption at the solid/liquid interface [2–8]. Adsorbed surfactant molecules can form bilayers, semi-cylinders, full cylinders, semi-spheres and full spheres (see Fig. 1), and it has been found that the surface has an important influence in controlling the aggregate structure [2–4, 7,8]. For example, in quaternary ammonium surfactant systems, mica leads to the formation of full cylindrical micelles while amorphous silica leads to full spheres [7,9]. Force–

* Corresponding author.

E-mail address: bmoudgil@erc.ufl.edu (B.M. Moudgil).

¹ Present address: DuPont Titanium Technologies, 7685 Kiln-Delisle Road, Pass Christian, MS 39571, USA.

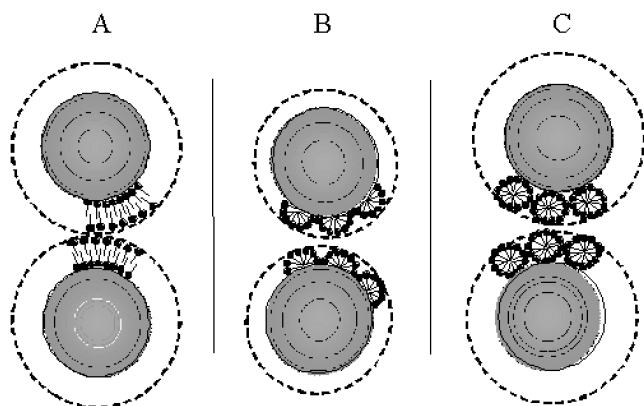


Fig. 1. Schematic diagram showing the possible structures of surfactants adsorbed at the solid/liquid interface. (A) Bilayer formation, (B) semi-cylindrical micelles or semi-spheres, (C) full cylinders or spheres.

distance curves of C_n TAB samples were measured in a fluid cell using AFM contact mode. It was proposed by Patist [10] and Adler et al. [2] that the maximum compressive force of the adsorbed surfactant aggregates, F_{\max} , is directly related to the stability of solid/liquid dispersions. It is clearly demonstrated that as the C_{12} TAB surfactant concentration increases from 8 to 10 mM, the interaction (repulsive) force between the AFM tip and the silica substrate increases significantly and concurrently with the onset of suspension stability [2,3].

It was found that the maximum repulsive force, F_{\max} , increases with the surfactant alkyl chain length. Adler et al. [2] also found additional factors influencing the magnitude of the maximum repulsive force, F_{\max} , including the type of substrate used as well as the presence of added co-surfactant. For example, the repulsive forces are higher and observed at lower concentrations for mica as compared to silica. This is possibly due to the crystalline nature of the mica substrate. Moreover, the addition of small amounts of SDS to a C_{12} TAB solution significantly increases the maximum repulsive force [2]. Similarly to the increased stabilization of bulk micelles caused by charge repulsion, addition of SDS to a C_{12} TAB solution can greatly enhance stability of surfactant film at the solid/liquid interface due to the Coulombic interactions.

Each of the above methods increases the maximum repulsive force, F_{\max} , between the AFM tip and the solid substrate via the surfactant–surfactant, surfactant–surface, surfactant–solvent, and solvent–surface interactions mentioned previously. Another way to increase the maximum repulsive force between particles with adsorbed surfactants is by changing the nature of the surfactant itself, such as in the case of Gemini surfactants. A Gemini (or two-chain) surfactant is a molecule composed of two identical hydrophilic head groups and two hydrophobic tail groups (Fig. 2). It is very similar to two single-chain surfactants linked covalently by a spacer group. The spacer group can vary in length and chemical structure, be flexible or rigid, and be hydrophilic or hydrophobic [11]. Gemini surfactants have three unusual

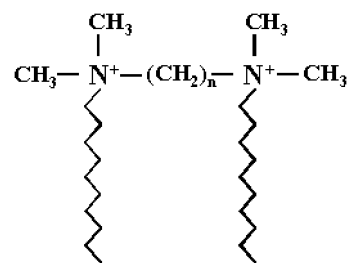


Fig. 2. Molecular schema of Gemini surfactants.

solution and interfacial properties. First, Gemini surfactants have critical micelle concentration (CMC) values one to two orders of magnitude lower than that of corresponding single-chain surfactants [12]. Second, they are much more efficient than their corresponding monomeric surfactants at decreasing the surface tension of water [13,14]. For example, the C_{20} (i.e., surfactant concentration required for lowering the surface tension of water by 20 mN/m) for 12-2-12 Gemini is 0.0083 wt%, while that for C_{12} TAB is 0.25 wt% [15]. Finally, Gemini surfactants with short spacers form large, threadlike aggregates, while the single-chain equivalent forms only small spherical micelles. For example, 12-2-12 Gemini has been shown to form long wormlike micelles at a concentration as low as 1.5 wt% (about 25 mM) [16]. As a result, aqueous solutions of these Gemini surfactants have a very high viscosity at relatively low surfactant concentration and show shear-induced viscoelastic behavior at concentrations as low as 0.7 wt% [17].

Along with the properties mentioned above, Gemini surfactants have been shown to have better solubilizing, wetting, and foaming properties compared to conventional surfactants [12]. Furthermore, the Krafft temperatures of Gemini surfactants with hydrophilic spacers are very low [12], allowing these surfactants to be used in cold water. Finally, Gemini surfactants have been shown to have interesting biological effects. For example, the alkyltrimethylammonium bromide-based Gemini surfactants induce various biological effects such as an inhibition of bacterial activity [18–20] and of photosynthesis [21].

The unusual characteristics listed above make Gemini surfactants a very interesting topic of study. Force/distance curves for 12- n -12 Gemini surfactant on the mica and silica surfaces have been reported in Ref. [22] for two concentrations of Gemini without additional electrolyte. Analysis of obtained results [22] is given only for relatively long distances. The authors drew a conclusion that the measured forces can be attributed to the ion–electrostatic force. However, to reach this conclusion the authors had to assume a tip radius to be of 1000 nm in calculations, while the actual tip radius used was near 20 nm. Therefore, a further investigation of mechanical characteristics of the surface layer of Gemini micelles should be continued. In the present paper, we investigated the aggregation behavior of selected quaternary ammonium Gemini surfactants as dispersants. The results were compared to their single-chain counterparts onto

a mica surface as a function of alkyl spacer group length using atomic force microscopy. Force/distance curves were also obtained for Gemini surfactants on silica surface. Values of F_{\max} were obtained for these surfactant systems and compared with dispersion turbidity results in order to correlate the maximum repulsive force to the stability of a solid/liquid dispersion.

2. Materials and methods

2.1. Materials

Dodecyltrimethylammonium bromide (C_{12} TAB) (99%) was supplied by Acros Organics (Fair Lawn, NJ). Silica particles (200 nm) were obtained from Geltech Corporation (Orlando, FL). Deionized water was passed through a Milli-Q water purification system before use. All experiments were performed at $23 \pm 1^\circ\text{C}$.

2.2. Synthesis of Gemini surfactants

The Gemini surfactant with two methylene groups as a spacer, ethanediyl-1,2-bis(1-dodecyldimethylammonium bromide), was prepared by reacting N,N,N',N' -tetramethyl-1,2-ethylenediamine with 1-bromododecane in a molar ratio of 1.0 to 2.1 in dry ethanol under reflux for 24 h. After the completion of the reaction, ethanol was evaporated under vacuum until a precipitate started to form. The crystals were separated by filtration and recrystallized twice from ethanol/ethyl acetate. The product was identified by ^1H NMR using a Varian 600 MHz instrument. The purity was determined to be in excess of 98%.

Similarly, the Gemini surfactant with four methylene groups in the spacer unit, butanediyl-1,4-bis(1-dodecyldimethylammonium bromide), was prepared from 1,4-dibromobutane and 1-dodecyldimethylamine in a molar ratio of 1.0 to 2.1 in dry ethanol under reflux for 24 h. The recrystallization and identification procedures employed were the same as for 12-2-12 Gemini. The purity of 12-4-12 Gemini was determined to be better than 98%.

2.3. AFM microscopy

Force–distance curves were obtained using a Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) using silicon nitride triangular sharpened contact mode cantilevers (NP-S) with a spring constant of 0.12 N/m. The ultra-sharp pyramidal tip has a radius near 15 nm as measured by scanning electron microscope. Mica substrate was obtained from S&J Trading Inc.; a “flat silica” sample was a silicon wafer with a 2 μm thick coating of CVD silica (Motorola).

The freshly cleaved mica or silica surface were placed in the cell and allowed to equilibrate with the surfactant solution for ten minutes. Manne and Gaub [8] found that mica

immersed for several days showed no difference in the aggregate structure, indicating that the mica surface reaches equilibrium configuration in a few minutes. Our AFM experiments with Gemini surfactant demonstrated no difference between forces measured after ten minutes and one hour equilibration time. Experiments were performed with at least three freshly prepared samples on different days. The variance of the force data obtained in different series of experiments was less than 20%.

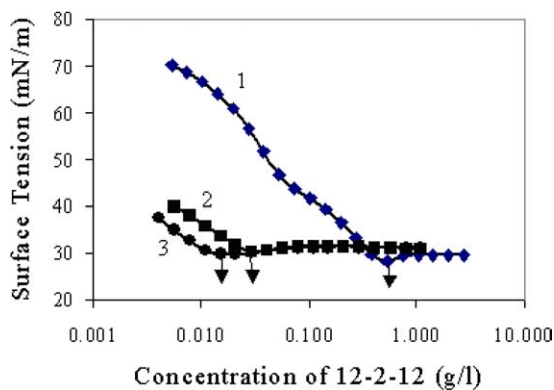
2.4. Turbidity/dispersion stability measurements

The turbidity of dispersions of 200 nm silica particles (0.05 wt% solids at pH 4.0) was measured by a Hach turbidimeter, model 2100A (Hach Chemical Corporation). The intensity of scattered light at 90° was recorded versus time in NTU (nephelometric turbidity units). The procedure of the suspension preparation was as follows. The silica powder was put in the mixture of 12-2-12 Gemini solution (with different concentrations) with 0.1 M NaCl at pH 4.0 and the mixture was sonicated in ultra-sound bath for 10 min. The turbidity was measured immediately after sonication (τ_0) and after 60 min (τ_{60}). Results are given as relative decrease of turbidity, $\Delta\tau/\tau$, vs initial concentration (dosage) of Gemini surfactants.

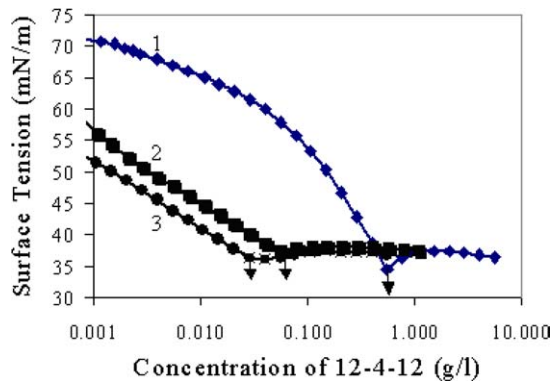
3. Results and discussion

3.1. Surface tension

The surface tension for solutions of the Gemini surfactants was measured using the du Nouy ring method. This method is described, for example, in Ref. [23]. The ring radius is 9.545 mm. The wire diameter is 0.185 mm. The volume of the vessel used for the measurements is 170 ml and the volume of the distilled water used as starting liquid is 50 ml. To this volume of distilled water aliquots of a surfactant solution of 10 g/L are added. We use the simplest equation for calculation of the surface tension. Note, that this equation can be in error by as much as 25% for the absolute value of the surface tension [23]. Moreover, the non-zero contact angle can be the origin of additional error in the absolute value of the surface tension. However, in the present paper we use the dependence of γ vs C only to obtain the CMC values and to check the purity of surfactants. Therefore, the ring method is good enough for this purpose. Figs. 3a and 3b show the surface tension vs surfactant concentration plots for the 12-2-12 and the 12-4-12 Geminis, respectively. Curves for different concentrations of electrolyte (NaCl) are given. The values of CMC obtained from the surface tension measurements are given in Table 1. As per Table 1, CMC for 12-2-12 and 12-4-12 are the same in DI, while for the electrolyte solution the difference is as much as almost 2 times. This may be explained by the electrostatic interaction. However, the relative contribution of



(a)



(b)

Fig. 3. Dependence of surface tension on concentration of 12-2-12 (a) and 12-4-12 (b) Gemini. From graphs follow the values of CMC shown by arrows (see Table 1). Small minimum on some curves near CMC indicates the existence of certain contaminations. Curve 1 is related to the absence of NaCl, curves 2 and 3 are related to the 0.05 M and 0.1 M NaCl, respectively.

Table 1

The CMC values (mM and g/L) for 12-2-12 and 12-4-12 Gemini surfactant in the presence or absence of NaCl. Results are obtained from Fig. 3

Concentration of NaCl (M)	CMC, Gemini 12-2-12		CMC, Gemini 12-4-12	
	mM	g/L	mM	g/L
0	8.7×10^{-1}	5.4×10^{-1}	8.7×10^{-1}	5.6×10^{-1}
0.05	4.9×10^{-2}	3.0×10^{-2}	9.0×10^{-2}	5.8×10^{-2}
0.1	2.6×10^{-2}	1.6×10^{-2}	4.5×10^{-2}	2.9×10^{-2}

this interaction is not the same for molecules with the same length of the hydrocarbon chains but different size of the head groups.

From Fig. 3 and Table 1, it appears that the effect of electrolyte on the CMC is much more pronounced for Gemini surfactants than for ordinary single-chain surfactants. For example, for C₁₂TAB the 15-fold difference was found in CMC between distilled water and 0.1 M NaCl, while for 12-2-12 this difference is 30-fold. Note, that without electrolyte, the CMC of both 12-4-12 Gemini and 12-2-12 Gemini is ca. 0.87 mM. This value is close to the literature data for CMC given by Zana [24,25] of 1.09 mM for 12-4-12 and 0.84 mM for 12-2-12 Gemini. The difference can be related to differences in the synthesis procedure that may lead to dif-

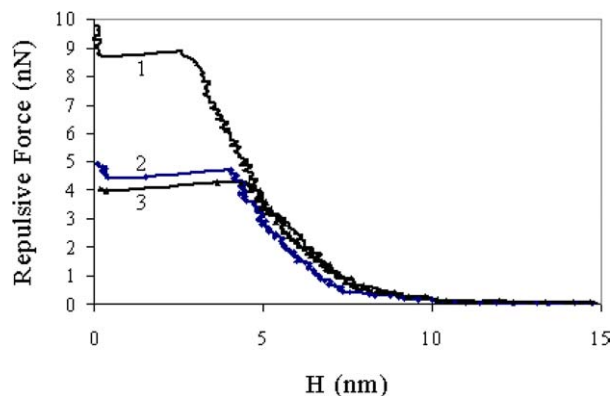


Fig. 4. Repulsive force vs distance between tip and mica substrate in the presence of 0.1 M NaCl. Curve 1—1 mM 12-2-12, 2—0.05 mM 12-4-12, 3—6 mM C₁₂TAB. These concentrations are near or above the surface CMC, where the values of the maximal repulsive force (barrier) achieve the saturation.

ferences in the amount of monoalkylated diamine byproduct, which may not have been removed to the same extent during recrystallization.

The dip in the surface tension vs. surfactant concentration curves around the CMC, for both Gemini surfactants (Figs. 3a and 3b), is most probably due to a small quantity of surface active, hydrophobic byproducts contamination. Likely byproducts for 12-2-12 and for 12-4-12 are 1-bromododecane and 1-dodecyldimethylamine, respectively.

3.2. Surface forces and suspension stability

Force/distance curves for interaction between a silicon nitride tip and mica were measured in Gemini surfactants solutions. Fig. 4 represents force/distance graphs for 12-2-12 (curve 1), 12-4-12 (curve 2), and single C₁₂TAB (curve 3) in the presence of 0.1 M NaCl. This figure demonstrates that slope of these curves in the range of distances 4–7 nm is practically the same for all three surfactants, i.e., the elastic moduli for these surfactants are close to each other. (Explanation of calculation of elastic modulus from force/distance curve is given in Ref. [4].) The size of the micelles (i.e., the thickness of the micellar layer) can approximately be evaluated as maximal distance, at which repulsive force (in the presence of electrolyte) still acts. Fig. 4 also demonstrates that the micelle sizes of all three surfactants are the same in the first approximation and are equal to 7–8 nm. However, the maximal repulsive force (barrier) of 12-2-12 Gemini is almost two times higher than 12-4-12 Gemini and single C₁₂TAB. In agreement with Ref. [4] it means that the yield strength of 12-2-12 Gemini aggregates on mica surface is higher than that of 12-4-12 Gemini or single C₁₂TAB. Note, that the value of the micelle size obtained from the force/distance curve should only be considered as a rough estimation due to the possible contribution of the Coulombic force in the total interaction.

Fig. 5 shows the maximum repulsive force (barrier), F_{\max} , vs surfactant concentration, which has been obtained

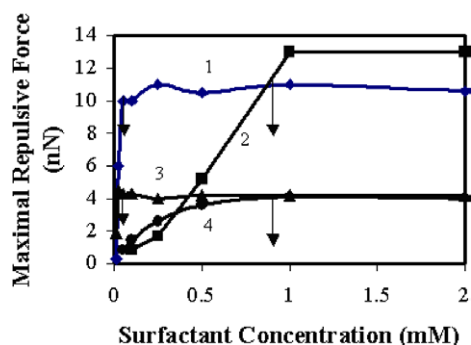


Fig. 5. Maximal repulsive force (barrier) between an AFM tip and a mica substrate in 12-2-12 (curves 1 and 2) and 12-4-12 (curves 3 and 4) alkyldimethylammonium Gemini surfactant solution at pH 4.0. Curves 1 and 3—in the presence of 0.1 M NaCl, 2 and 4—no electrolyte. Arrows show the bulk CMC of Gemini with and without electrolyte.

from force–distance experiments of 12-2-12 and 12-4-12 Gemini surfactants. The arrows show the bulk CMC, with and without electrolyte. The role of electrolyte becomes apparent in Fig. 5. Addition of electrolyte results in a significant decrease of the concentration of Gemini surfactants (both 12-2-12 and 12-4-12), at which the strong repulsive barrier appears. A similar observation was made for C_{12} TAB in Ref. [2]. On the other hand, at higher concentration of Gemini, the role of electrolyte becomes negligible and the barrier vs Gemini concentration dependence reaches the saturation value. It follows from Fig. 5 that the plateau magnitudes of barriers in solutions, with and without electrolyte, are close to each other.

From Fig. 5 and Table 1, it follows that both in the presence and absence of electrolyte, the surfactant concentration, where strong barrier appears, is close to the bulk CMC. It can also be concluded from Table 1 that the CMC decreases with the increasing electrolyte concentration for both Gemini surfactants and the CMC increases as the spacer chain length in the Gemini increases. The width of the transition zone of concentrations, at which the barrier sharply increases, is much larger in the absence of electrolyte. Therefore, the adsorbed film becomes very stiff at lower concentration of Gemini in the presence of electrolytes whereas the barrier increases gradually in the absence of electrolytes. It confirms our previous conclusion about sudden and strong cooperative assembly of Gemini in the presence of electrolytes.

Fig. 6 represents the comparison of the maximum repulsive force (barrier) for 12-2-12 and 12-4-12 Gemini and single C_{12} TAB for the tip/mica interaction in the presence of electrolyte. This figure demonstrates that the maximal repulsive force for 12-2-12 Gemini is approximately twice that of 12-4-12 Gemini. It seems that the self-assembled bilayer [26] formed by 12-2-12 Gemini on mica is much more effective in repelling the AFM tip from the surface than the self-assembled cylindrical micelles formed by 12-4-12 Gemini. This fact can be related to the larger density of the bilayer as compared with adsorbed layer of the cylindrical micelles. The larger density of adsorbed aggregates of

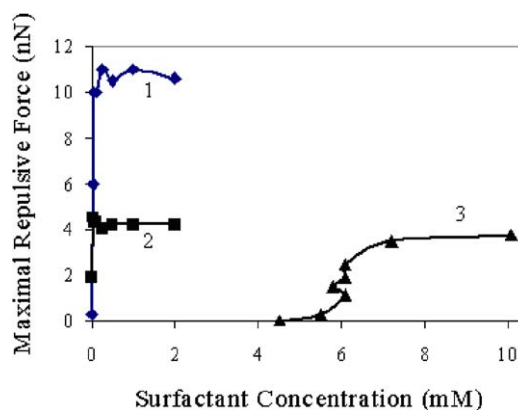


Fig. 6. Comparison of maximum repulsive force of C_{12} TAB (curve 3) on mica with those of 12-2-12 (curve 1) and 12-4-12 (curve 2) Gemini surfactants at pH 4.0 in the presence of 0.1 M NaCl.

12-2-12 can also be explained not only by the flat feature of the bilayer, but also by the smaller size of the molecules with a smaller length of the spacer groups.

It is of interest that the maximum repulsive force of 12-4-12 Gemini is comparable with that of C_{12} TAB. This observation is not surprising since both 12-4-12 and C_{12} TAB form parallel cylindrical micelles on mica surface. Moreover, the adsorption of these species on silica was determined by Atkin et al. [22] to be close to each other. Therefore, the densities of the surface layer of these micelles may be assumed to be close to each other. As a result, the repulsive barriers for 12-4-12 Gemini and C_{12} TAB should also be close to each other. However, one must note the difference in concentration at the onset of the repulsive barrier for 12-4-12 and C_{12} TAB surfactants. C_{12} TAB shows a barrier onset at 6 mM, while 12-4-12 (as well as 12-2-12) shows barrier onset at approximately 0.025–0.05 mM. This difference can be explained by the variation of the CMC of Gemini and single-chain surfactants, and by the stronger adsorption energy of Gemini (due to the presence of two head groups per molecule) as compared with single-chain surfactant.

Figs. 4–6 represent the results of the force measurements between AFM tip and mica. Results for 12-2-12 Gemini on the silica substrate are shown in Figs. 7 and 8. Fig. 7 represents the force/distance dependences for different concentration of Gemini, while Fig. 8 shows the dependence of maximal repulsive force (barrier) on Gemini concentration. Both Figs. 7 and 8 are obtained for Gemini in the presence of 0.1 M NaCl. Comparison of Fig. 7 with Fig. 4 shows that the size of the micelles (i.e., the maximal distance, at which repulsive force still acts) on silica (5–8 nm) is a little smaller than that on mica (9–10 nm). On the other hand, for more than 0.8 mM concentration of Gemini, a second barrier appeared on the force/distance curves for silica surface (Fig. 7); this second barrier was not observed at any concentrations for mica. We propose that this second barrier can be attributed to the adsorption of the layer of micelles on the tip or the second layer of surfactant on the flat silica although we could not prove this unambiguously.

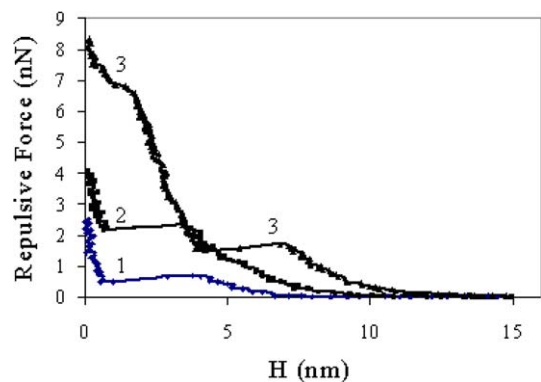


Fig. 7. Repulsive force vs distance between tip and silica substrate in 12-2-12 Gemini solution in the presence of 0.1 M NaCl at pH 4.0. Concentration of surfactant is 0.1 mM (curve 1), 0.4 mM (curve 2), and 0.8 mM (curve 3).

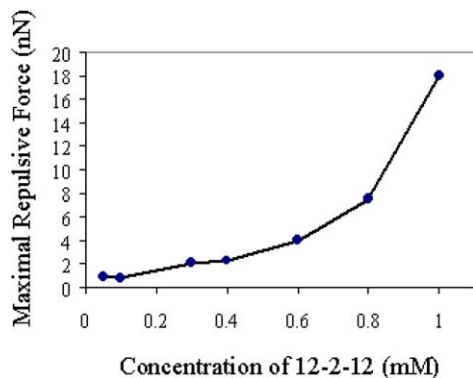


Fig. 8. Maximal repulsive force between tip and silica substrate vs 12-2-12 Gemini concentration at pH 4.0 in the presence of 0.1 M NaCl. The strong repulsive barrier appears already at the Gemini concentration 0.1 mM and increases with C.

From Fig. 8 it follows that similar to the interaction of the tip with mica, for the interaction case of silica, the transition to the strong repulsive barrier occurs at a low concentration of 12-2-12 Gemini (at 0.05 mM, where the normalized force F/R is ca. 60 mN/m). However, in distinction from mica, the steric barrier on silica (coated by Gemini in the presence of NaCl) continues to grow in the wide range of 12-2-12 Gemini concentrations (at least, up to 1 mM). As appears from comparison of Figs. 8 and 5, there is significant difference in the behavior of Gemini surfactant on silica and mica. Actually, on mica the maximal repulsive force (barrier) achieves plateau value near (or even before) CMC, while on silica the barrier continues to grow even for concentrations larger than CMC. We do not have the quantitative explanation for this phenomenon, but qualitatively it can be explained by the difference in (i) the crystalline or amorphous structure, (ii) the adsorption energy, (iii) the anchor size, and (iv) the micellar structure (for example, spherical and bilayer) for mica and silica surfaces. A crucial effect of the substrate material for the repulsive force has been noted in Ref. [2] for single CTAB surfactant. However, in this case growth took place for micelles on mica and was absent for silica. Moreover, ef-

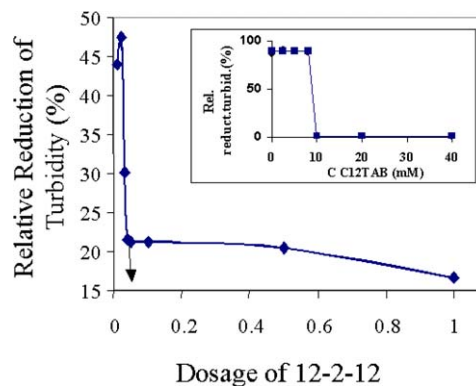


Fig. 9. The relative reduction of turbidity of silica dispersions (%) vs initial concentration (dosage) of 12-2-12 alkyldimethylammonium bromide Gemini surfactants at pH 4.0 in the presence of 0.1 M NaCl after 60 min. The initial concentration of silica particles with size 200 nm was equal to 0.05 wt%. After mixing silica powder with Gemini and electrolyte the mixture was treated in ultra-sound bath. The stability is achieved at dosage 0.04 mM Gemini (shown by arrow), corresponding to the equilibrium concentration 0.02 mM, which is close to CMC in the presence of electrolyte. Inset shows the same graph for C₁₂TAB. (Results are taken from Ref. [2].)

fect of the growth of the barrier magnitude after CMC for single CTAB was significantly smaller, than it is for Gemini surfactant.

It would also be of interest to relate the critical concentrations and mechanical properties of the surface layer of micelles with the shape of micelles on silica and mica surfaces. Shape of 12-2-12 (bilayer) and 12-4-12 (worm-like) micelles on mica are known from Ref. [26]. Unfortunately, for silica only the shape of 12-2-12 Gemini (circular) is known [18], while for 12-4-12 authors of Ref. [18] could not get an image of the surface layer due to a strong attractive force.

Gemini surfactants demonstrate a barrier onset at concentrations (0.02–0.05 mM both on mica and silica in the presence of electrolyte) well below the C₁₂TAB barrier onset concentration (near 10 mM). Therefore, we expect that dispersion stability experiments using Gemini surfactants should show stable dispersions corresponding to these very low surfactant concentrations. Adler et al. [2] reported the formation of a stable silica suspension in the 8–10 mM C₁₂TAB concentration range (see inset in Fig. 9). In the present study, the stability of the silica suspensions has been measured in the solutions of Gemini surfactants. Fig. 9 represents results for the suspension stability as the relative decrease of turbidity, $\Delta\tau/\tau_0$, vs initial concentration (dosage) of Gemini surfactants. It is observed that Gemini 12-2-12 surfactant can be used to form a stable silica suspension at a concentration of 0.04–0.05 mM, i.e., well below above-mentioned concentration of C₁₂TAB, 10 mM. The critical concentration of 12-2-12 Gemini (0.03 mM—Fig. 3a and Table 1) correlates well with concentration range 0.02–0.05 mM (Fig. 5), where the strong repulsive barrier appears between tip and mica (or silica) coated by Gemini. On the other hand, the comparison of Figs. 8 and 9 demonstrates the sensible correlation of the stabilization of the silica suspensions with the appearance of the steric repulsive barrier.

We should also note, that in Figs. 5–8 (where force/distance or barrier/concentration curves are given) the initial concentration of Gemini is equal to its equilibrium concentration, because the adsorption surface in the AFM chamber is very small. On the other hand, for silica suspension (Fig. 9) we could expect a difference between initial concentration (dosage) and equilibrium concentrations of surfactant due to adsorption of surfactant on the solution/particles interface. This adsorption is easy to calculate as follows. The relationship between initial, C_0 , and equilibrium, C_{eq} , concentration can be written as

$$C_{eq} = C_0 - S\Gamma, \quad (1)$$

where S is the surface area of particles in m^2 per liter of the suspension and Γ is adsorption (surface excess) in mol/m^2 . For example, for silica particles with a diameter of 200 nm we have measured the specific surface area to be equal to $14.6 \text{ m}^2/\text{g}$. For a silica suspension with a solid concentration of 0.05 wt%, the value of the silica surface S is found to be equal to $7.3 \text{ m}^2/\text{L}$. The values of the surface excess near CMC for 12-2-12 and 12-4-12 on silica are 1.6 and $1.1 \text{ mg}/\text{m}^2$, respectively [22]. Unfortunately, these data were obtained in the absence of additional electrolyte and data in the presence of electrolyte are not available. However, even in the presence of electrolyte we can use these values of the surface excess as the initial estimation. Then, knowing S and Γ and using Eq. (1), we calculated the difference between equilibrium and initial (dosage) concentration for 12-2-12 and 12-4-12 (near CMC) to be equal to 0.02 and 0.015 mM, respectively. Subtracting this difference from the initial concentration of 12-2-12 Gemini, we found the equilibrium concentration of Gemini. This correction does not play any role near CMC in the absence of salt (ca 0.7 mM), however, it can be significant in the presence of salt. For example, in agreement with our calculations, the critical dosage of 0.04 mM of 12-2-12 Gemini in the presence of 0.1 NaCl (Fig. 9) corresponds to the equilibrium concentration 0.02 mM. Thus, the correction for the surfactant adsorption on the particles does not break the agreement between the surfactant concentration, at which the strong barrier appears, and the concentration, at which the suspension becomes stable.

4. Summary

The force/distance curves of 12-2-12 and 12-4-12 Gemini surfactants on a mica and silica surface obtained by atomic force microscopy were compared with each other and with results for single C12TAB surfactant. It has been shown that strong repulsive barrier for Gemini surfactants appears at significantly smaller concentrations and its value is larger than for the CTAB surfactant. This difference between single-chain and Gemini surfactants can be explained by the stronger adsorption energy of Gemini. It has also been shown that Gemini (or two-chain) surfactants are more effective dispersing agents, and their dispersion stability in the

presence of electrolytes can be achieved at very low surfactant concentrations ($\sim 0.02 \text{ mM}$). The force data for Gemini surfactants correlate well with stability for the silica suspensions.

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