Ultrasonic formation of nanobubbles and their zeta-potentials in aqueous electrolyte and surfactant solutions

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Abstract

The electrokinetic behaviors of nanobubbles internally generated by ultrasonication were investigated in terms of the stability of bubble, size distribution and zeta-potentials. When aqueous solutions were sonicated with a palladium electrode, stable nanobubbles having effective diameters of several hundreds nanometer were formed within a few minutes, and the sizes and size distributions remained stable for up to 1 h. The bubble sizes slightly increased when salts added and significantly reduced when surfactants added. As the chain length of alkyl group of C n TAB increased, the size and size distribution increased with n. A micellar model was proposed to explain the formation of nanobubbles and their size reduction. Zeta-potentials of nanobubbles showed a sharp change at CMC, increasing linearly with surfactant concentrations at low concentrations and invariant at high concentrations. The surface ionization and adsorbed monolayers at a bubble surface would result in a degree of dissociation of a planar air/water interface, but the calculated degree of dissociation at the bubble surface is very low compared with that of micelles. It would be attributed to the counter ion binding at interface or curvature effect.

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1. Introduction

Electrokinetic properties of microbubbles in aqueous solutions are of significance when equilibrium and dynamic behaviors of surface charge, lifetime and mutual interaction with other materials are evaluated. The entrapped gas bubbles in a high density liquid would emerge in many physical and chemical processes [1], while nanobubbles in liquids could deliver a microscopic level of information at liquid–gas interfaces [2]. In any cases, the adsorption of ionic substances onto an air/water interface would play a key role to enhance the efficiency of ore flotation and foam separation processes [3,4] and ultrasonic diagnosis with contrast agents [5]. Meanwhile, the image of nanobubbles was reported by a tapping mode AFM when a hydrophobic surface was immersed in water [6,7], and the time evolution of nanobubbles was by sweeping the surface of a hydrophobic glass substrate in water [8]. Nevertheless, the electrokinetic surface potentials at air/water planar interface could be hardly determined, but the zeta-potentials of bubbles dispersed in water would be directly measured. Further, relatively large and externally injected bubbles (generally greater than 1 μm) might bring about electroosmotic water transports and hydrodynamic effects and consequently make it difficult to analyze the electrophoretic mobilities [2,9–13]. However, zeta-potentials of very small bubbles, i.e., nanobubbles, internally generated with and without alkyl polyglycosides (APG) in aqueous solutions [2], were recently determined without the side effects appeared in electrophoretic measurements such as gravitational forces, convection currents, and many other non-equilibrium effects.

In this paper, we report the formation and stability of nanobubbles in aqueous solutions, which were internally generated by ultrasonication. The nucleation of a gas bubble
could be facilitated by the presence of dissolved gas, or of dust or ions, and surfactants would play a role in the nucleation by lowering the surface tension of aqueous solution. The dispersion stability of nanobubbles could be monitored by the bubble size, bubble density, and surface properties of bubbles. The negatively or positively charged surface depending on the pH of a solution, adsorbed ions, surfactants, and polymers, would control the stability of bubbles, the adsorption of ions, and the bubble hydrodynamics. In fact, the adsorptions, surface tensions, and zeta-potentials of nanobubble surface would be the most important factors to understand the bubble stability and dynamics.

2. Experimental

2.1. Materials

The surfactant series of alkyl trimethylammonium bromide, CnTAB (decyl trimethylammonium bromide; 99%) were purchased from Aldrich Chemical Co. Sodium sulfate (Na2SO4, 99%), C12 TAB (do-decy trimethylammonium bromide; 99%) were purchased from Fluka Co. C12 TAB (dodecyl trimethylammonium bromide; 99%), C12 TAB (hexadecyl trimethylammonium bromide; 99%) were obtained from Aldrich Chemical Co. Sodium dodecyl sulfate (SDS), potassium bromide (KBr, 99%), sodium chloride (NaCl, 95%), calcium chloride (CaCl2, 99%), sodium sulfate (Na2SO4, 99%), all of which were purchased from Aldrich. All surfactant solutions were prepared using de-ionized water (MilliQ water system, Millipore Ltd., Mississauga, Ontario). The de-ionized water had an electrical conductance of 1.5 μS cm−1 and pH of 5.5 when it was saturated with CO2 from air.

2.2. Preparation of nanobubble

Nanobubbles were generated by sonicating the sample solutions with a two-sided 5 mm × 10 mm palladium-coated electrode immersed. Ultrasonic energy was exerted by a Vibra-Cell sonicator (Sonics & Material Instrument) which has a frequency of 20 kHz and an output power of up to 200 W. Every aqueous sample was filtered using 0.2 μm filter (Sterile Acrodics) for dust removal before sonication. Then, generic nanobubbles were sufficiently stable and reproducible for measurements [2].

2.3. Zeta-potential and size measurement of nanobubble

Zeta-potentials of bubbles adsorbed with surface active materials were measured by ZetaPlus (Brookhaven Instruments Co., Holtsville, New York) with Uzgiris, Brookhaven electrodes coated by palladium and He–Ne laser as a light source. Each data point for zeta-potentials was an average of 15 measurements or above at room temperature. The mobility of nanobubbles was determined from a shift in frequency of a laser Doppler spectrum. Consequently, zeta-potential (ζ)

Table 1

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Effective diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>749</td>
</tr>
<tr>
<td>10</td>
<td>745</td>
</tr>
<tr>
<td>20</td>
<td>749</td>
</tr>
<tr>
<td>30</td>
<td>753</td>
</tr>
<tr>
<td>40</td>
<td>774</td>
</tr>
<tr>
<td>50</td>
<td>796</td>
</tr>
</tbody>
</table>

was calculated by the Smoluchowski equation:

\[
\mu = \frac{\varepsilon_0 \varepsilon \xi}{\eta}
\]

where \(\mu\) is the mobility (10−6 m² s⁻¹ V⁻¹), \(\varepsilon_0\) is the permittivity of free space (C² J⁻¹ m⁻³), \(\varepsilon\) is the relative permittivity of water, \(\eta\) is the viscosity of water (g cm⁻¹ s⁻¹), and \(\xi\) is the zeta-potential (mV). The half width at half height of zeta-potential was less than 15 mV in all the cases.

The size of bubbles was measured by a dynamic light scattering method based on the particle size option in ZetaPlus. The scattered intensity was registered at the scattering angle of 90° and temperature of 298.15 K.

2.4. Surface tension and specific conductivity

Table 2 shows the effective diameters of bubbles in pure water upon storage of 90° and temperature of 298.15 K.

3. Results and discussion

3.1. Creation and stabilization of nanobubble

3.1.1. Bubble creation

Fig. 1 shows the size distribution of nano/microbubbles sonicated with a palladium electrode and Table 1 shows the effective diameters of bubbles in pure water upon storage maintaining at 750 nm without significant change of sizes within 1 h. Table 2 shows the effective diameters of bubbles according to sonic powers and sonication time. Size of bubbles increases slightly with increasing power, from 50 to 200 W. At 70 W, bubbles significantly increase within sonication time of 6 min. Also, a tip-type sonicator efficiently generated larger bubbles than a bath-type sonicator did. It is consistent with
that a tip-type sonicator delivers a strong force required for cavitation, cleaning, explosion, and expansion. Therefore, relatively large bubbles were generated in a dip-type sonicator. The high delivery of energy into a solution would apparently enhance the formation of large cavitation in a short time and also the diffusion of volatile components into bubbles expanded the volume exponentially after an adjusting period.

Yet, the mechanism of nanobubble formation with ultrasonic energy is not clear. It is known that a high energy nucleus generated by ultrasonic energy would grow homogeneously in solution or heterogeneously on hydrophobic surfaces, followed by an equilibration between gas in bubbles and dissolved gas in water. Bubbles generated by sonic energy might oscillate with the sound frequency and survive with oscillations. At an instant during sonic compression phase, bubbles might suddenly collapse to a fraction of their maximum size. The gas inside a bubble might be thus compressed and adiabatically heated. Under certain conditions, an imploding shock wave might be driven by collapsing bubble walls, which could increase the temperature and create a rather destructive environment, and thus often used in erosion of metal surface, lithotripsy, ultrasonic cleaning, sonochemistry, and sonoluminescence. [16–21]

When bubbles are generated in a solution by ultrasonic nucleation, a microscopic void of radius, \( R \), grows as long as the bubble pressure, \( P_{\text{out}} \), is greater than a critical value, \( P_{\text{out}} + 2\gamma / R \) calculated by the Young–Laplace equation.

\[
P_{\text{in}} - P_{\text{out}} = \frac{2\gamma}{R}.
\]

where \( \gamma \) is the surface tension and \( R \) is the radius. During the initial cavitation, the ultrasonic energy could be consumed to create the bubble surface and volume, \( 4\pi R^2 \gamma + 4\pi R (P_{\text{out}} - P_{\text{in}}) \). After the nucleation stage, the bulk energies of bubbles would be dissipated into liquid by heat transfer through conduction and condensation and the creation of surface, and so reduced the vapor pressure \( P_{\text{v}} \). If the bubble pressure would be reduced less than \( P_{\text{out}} + 2\gamma / R \), the bubble would be shrunk on the assumption that no gas might be diffused or vaporized into the bubble. However, if a volatile component is diffused in the bubble, the internal pressure of bubble could be readjusted around external pressure so that the bubbles grow to rupture. The curvature effect of 750 nm bubbles at 50 W in water, \( 2\gamma R \) is 3.79 atm \( (2 \times 7.2 \times 10^{-3} \text{N/m} \times 0.375 \times 10^{-6} \text{m}^2) = 3.84 \times 10^{15} \text{N/m}^2 \) = 3.79 atm, while it is 2.95 atm for 200 W, where the size of bubble is 965 nm for 1 min sonication. Therefore, the total energy difference of two stable bubbles could be evaluated by \( (P_{\text{out}} V) + (\gamma V) \),

For 750 nm bubble:

\[
(1 + 3.79) \times 1.013 \times 10^3 \text{N/m}^2 \times (4\pi/3) \times (0.750/2) \times 10^{-6} \text{m}^3 + 4\pi (0.750/2 \times 10^{-6} \text{m}^3)^2 \times 72 \times 10^{-3} \text{J/} \text{m} = 2.34 \times 10^{-15} \text{J}.
\]

For 965 nm bubble:

\[
(1 + 2.95) \times 1.013 \times 10^3 \text{N/m}^2 \times (4\pi/3) \times (0.965/2) \times 10^{-6} \text{m}^3 + 4\pi (0.965/2 \times 10^{-6} \text{m}^3)^2 \times 72 \times 10^{-3} \text{J/} \text{m} = 3.99 \times 10^{-15} \text{J}.
\]

It is apparent that 965 nm bubbles require the intense energy of 1.65 times greater than that of 750 nm bubbles. Table 2 indicates that the energy conversion of sonic energy to nanobubble would not be efficient. Further, as the sonication continued, the bubble size significantly increased because of the evaporation of volatile components.

### 3.1.2 Growth and surface effects

The ultrasound energies would be immediately transformed into the work of cohesion by forming bubble and its surface. This process might be composed of the creation of surface, evaporation of gases to fill vacuoles, and the adsorption of impurities from bulk phase. It is extremely difficult to observe the initial creation stage and dynamics of internal pressure. Table 3 shows that the pH and ion effects on nanobubbles in solutions are relatively small. The bubble

---

**Table 2**

<table>
<thead>
<tr>
<th>Effective diameters of bubbles in pure water when sonic power and time varied</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (1 min) (W)</td>
<td>750</td>
<td>935</td>
<td>921</td>
<td>965</td>
</tr>
<tr>
<td>Time (750 W) (min)</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Effective diameter (nm)</td>
<td>202</td>
<td>890</td>
<td>920</td>
<td>4250</td>
</tr>
<tr>
<td>Polydispersity</td>
<td>0.32</td>
<td>0.32</td>
<td>0.35</td>
<td>0.37</td>
</tr>
</tbody>
</table>

---

Fig. 1. Log-normal size distribution of nanobubbles prepared by sonicating the pure water with a two-sided 5 mm × 10 mm palladium-coated electrode immersed.
Table 3

<table>
<thead>
<tr>
<th>pH of water</th>
<th>2</th>
<th>4</th>
<th>5.8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective diameter (nm)</td>
<td>749</td>
<td>745</td>
<td>749</td>
<td>753</td>
<td>774</td>
</tr>
<tr>
<td>NaCl concentration (mM)</td>
<td>0.001</td>
<td>0.01</td>
<td>0.1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Effective diameter (nm)</td>
<td>897</td>
<td>827</td>
<td>804</td>
<td>850</td>
<td>885</td>
</tr>
<tr>
<td>Na₂SO₄ concentration (mM)</td>
<td>0.001</td>
<td>0.01</td>
<td>0.1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Effective diameter (nm)</td>
<td>839</td>
<td>843</td>
<td>921</td>
<td>853</td>
<td>794</td>
</tr>
<tr>
<td>CaCl₂ concentration (mM)</td>
<td>0.001</td>
<td>0.01</td>
<td>0.1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Effective diameter (nm)</td>
<td>890</td>
<td>934</td>
<td>826</td>
<td>850</td>
<td>950</td>
</tr>
</tbody>
</table>

diameter had no dependency on pH, but it seemed that added salts increased the effective diameter 10–20% and the bubble volume 30–70%. The creation and dispersion processes of bubbles were independent of protons, nature of salts and their concentrations, but bubble sizes increased in salt solutions. Added salts reduced the solubility of volatile components like air and vapor, while slightly induced high surface tensions. Therefore, it seems that the increase of bubble sizes might be attributed to the diffusion and vaporization of volatile components.

Fig. 2 shows the effective diameters of bubbles with surfactant (SDS) concentrations at 70 W of sonication energy. Bubble sizes were reduced from 1200 to 450 nm, while the surface tension was reduced from 72 to 38 dyn/cm. The critical micelle concentration (CMC) of SDS and its surface tension were 8.2 × 10⁻³ M/L and 38 dyn/cm, respectively, at 25 °C [23]. The curvature effect of 450 nm bubble, 2γ/R is 3.33 atm [2 × 38 × 10⁻⁵ (N/m) × 0.452 × 10⁻⁹ m² = 3.33 atm], but the total energy of bubble is 4.51 × 10⁻¹⁴ J [(1 + 3.33) × 0.131 × 10⁻⁵ N/m² × (4π/3) × 0.452 × 10⁻⁹ m³] + 4πr² (0.452 × 10⁻⁹ m²) × 38 × 10⁻⁵ (N/m) = (2.09 + 2.42) × 10⁻¹⁴ J. The bubble size remained invariant at three times of surfactant concentration higher than CMC. It means that three times of CMC is the proper concentration for the formation of nanobubble.

![Fig. 2. Effective diameters of bubbles with SDS concentration (CMC= 8.2×10⁻³ M).](image)

![Fig. 4. Size log-normal distribution of bubbles with alkyl chain length](image)
at \( n = 12 \), 331 nm at \( n = 14 \), and 495 nm at \( n = 16 \), respectively. The thickness of their palisade layer could be estimated by \( L = 0.15 + 0.1265 n \) (\( n \) is alkyl chain length), where \( L \) is approximately the hydrophobic core length (in nm) according to the Tanford relation \([23]\). The thickness of nanobubbles increased with the chain length such as 1.42 nm at \( n = 10 \), 1.67 nm at \( n = 12 \), 1.92 nm at \( n = 14 \), and 2.17 nm at \( n = 16 \). The cone angles created by the chain length and hydrophilic head group would contribute to stabilize the curvature of lamellar and form bubbles.

### 3.2. Zeta-potentials of nanobubbles in electrolyte and surfactant solutions

Fig. 5 shows the zeta-potentials of nanobubbles in aqueous solutions of different pHs. The nanobubbles were sufficiently stable with no significant change of zeta-potentials during the measurements. The zeta-potentials of nanobubbles dispersed in a solution of 1 mM KCl were observed in a function of pH, when the size of bubbles was unchanged. At low pH, the zeta-potential was positive, but changed its sign at high pHs. The point of zero zeta-potential (isoelectric point) was located between pH 3.0 and 3.5. For pH greater than 6, zeta-potential became less than \(-20\) mV because of the adsorption of \( \text{OH}^- \) ions. It is well recognized that the electrokinetic property of interface could be modified because of the adsorption of anions (\( \text{OH}^- \)) and the desorption of cations (\( \text{H}^+ \)).

Fig. 6 shows that zeta-potentials of nanobubbles increase with salt concentrations. Since bubbles would usually bear a negative charge, an increase of NaCl solution concentration would not only cause more \( \text{Na}^+ \) ions to adsorb onto the gas–liquid interface, but also compress the electrical double layer thickness of a bubble. In the presence of bivalent \( \text{Ca}^{2+} \) ions, the zeta-potential would become less negative with \( \text{CaCl}_2 \) concentration than with \( \text{NaCl} \) solution. Also, it is observed that the magnitude of the bubble zeta-potential would be influenced by anion type between \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \).

At dilute concentrations of bivalent anions, the zeta-potential of bubbles would be significantly negative, indicating the significant selective adsorption of negative ions, but the negative mobility of each salt could be monotonically depressed with increasing concentration of each salt. \( \text{Na}_2\text{SO}_4 \) would have the more pronounced effect on the mobility than \( \text{NaCl} \) and \( \text{CaCl}_2 \). In low concentration, there would appear that hydration anionic energies of \( \text{SO}_4^{2-} \) were larger than that of \( \text{Cl}^- \), but the 2:1 electrolyte was expected to produce the lower electrophoretic mobilities because of its effect on the reciprocal Debye length to that of 1:1 electrolytes at high concentration \([24]\).
3.3 Adsorption and surface ionization of CnTAB at the nanobubble surface

Fig. 7 showed zeta-potentials of nanobubbles with the concentration of ionic surfactants, CnTAB. As its concentration increased, zeta-potentials increased linearly with log concentration, and unchanged at the concentrations greater than CMC because monolayer adsorption was completed. In fact, nanobubbles were surrounded by an electrical double layer as ionic surfactants and electrolytes were adsorbed onto the air–water interface. The Gouy–Chapman treatment enabled the surface potential, $\psi$, to be related with surface charge density, $\sigma_s$, of a charged surface and Debye length $\kappa$, and electrolytically relevant zeta-potential $\zeta$ was often used as an approximate. Assuming that $\psi$ is equal to $\zeta$, the surface charge density for a 1:1 electrolyte can be calculated by the following equation [14,15]:

$$\sigma_s = \frac{2kT\sigma_s e^2}{e} \sinh \left( \frac{\varepsilon_0 \varepsilon w z e \zeta}{2kT} \right)$$  \hspace{1cm} (3)

where $k$ is Boltzmann constant (J/K), $T$ is absolute temperature(K), $\varepsilon$ is the inverse of the Debye length (m$^{-1}$), $z$ is the valency of ions, $e$ is the magnitude of charge on a single electron, $\varepsilon_0$ is the permittivity of free space (C$^2$ J$^{-1}$ m$^{-1}$), $\varepsilon_w$ is the relative permittivity of water, and $\zeta$ is the zeta-potential (V) obtained from electrophoretic mobility measurements. Alternatively, the surface number density of charged molecules can be converted to the surface charge density. The surface charge density, $\sigma_s$, at the curved air–water interface of bubbles can be expressed by the amounts of ionized surfactants [25,26]:

$$\sigma_s = [C_n\text{TA}^+]_s$$  \hspace{1cm} (4)

where $[C_n\text{TA}^+]_s$ is the surface concentration of dissociated surfactants. Meanwhile, the number of surfactant molecules at surface could be given as the sum of bound and unbound surfactants, designated by $[C_n\text{TA}^-]_s$, and $[C_n\text{TABr}]_s$, respectively [25,26]:

$$\Gamma = [C_n\text{TA}^-]_s + [C_n\text{TABr}]_s$$  \hspace{1cm} (5)

Degree of surfactant dissociation at the air–water interface, $\alpha_n$, can be defined by the fraction of dissociation as in the Eq. (6):

$$\alpha_n = \frac{[C_n\text{TA}^+]_s}{\Gamma}$$  \hspace{1cm} (6)

Though CnTAB surfactant monomers are almost ionized in a bulk solution, the ionized amounts of molecules at interface are limited as the degree of dissociation. The average number densities of molecules at interface $\Gamma$ can be determined from the surface tension of air–water interface. At a dilute solution, however, ionic surfactant molecules would be completely ionized and adsorbed at interface. The adsorption of surfactants can be given by measuring the equilibrium surface tension and from the Gibbs adsorption equation [26]:

$$\Gamma = \frac{1}{yRT} \left( \frac{dy}{d \ln [C_n\text{TA}]_s} \right)$$  and

$$y = 1 + \left( \frac{[C_n\text{TAB}]_s}{[C_n\text{TAB}]_s + [KBr]_s} \right)$$  \hspace{1cm} (7)

where $\Gamma$ is the surface excess of surfactant (mol/cm$^2$). Molecular area of surfactant at the air–water interface, $A (\AA^2)$, can be calculated from the Eq. (8) [26]:

$$A = \frac{\Gamma 10^15}{N}$$  \hspace{1cm} (8)

where $N$ is the Avogadro number and $\Gamma$ (mol/cm$^2$) is surface excess of surfactant. Surface excess was determined by measurements of surface tension of CnTAB. The surface adsorption near CMC was saturated with surfactant. Table 4 shows the significant increase in maximum surface number density of CnTAB as the chain length increased, whereas molecular area, $A_{\text{max}}$, were reduced from 47 to 32 $\AA^2$, closely packed at air–water interface [27].

Degree of dissociations $\alpha_n$ at the bubble interface and $\alpha_m$ on CMC are shown in Table 5, both calculated using Eqs. (4)–(8). Shorter alkyl chains could contribute higher dissociation of molecules at the air–water interface at CMC as expected. Surfactant monomers would adsorb onto the air–water interface after binding with counter ions very strongly in a very low

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Zeta-potential (mV)</th>
<th>$\alpha_m$</th>
<th>$\alpha_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12TAB</td>
<td>24.5</td>
<td>0.046</td>
<td>0.328</td>
</tr>
<tr>
<td>C14TAB</td>
<td>26.0</td>
<td>0.024</td>
<td>0.277</td>
</tr>
<tr>
<td>C16TAB</td>
<td>28.4</td>
<td>0.015</td>
<td>0.217</td>
</tr>
<tr>
<td>C18TAB</td>
<td>27.9</td>
<td>0.013</td>
<td>0.176</td>
</tr>
</tbody>
</table>

Table 4: Surface excess and molecular area of CnTAB at CMC at 0.01 M KBr.

Table 5: Zeta-potential, dissociation degree of air–water interface ($\alpha_m$), dissociation degree of micelle ($\alpha_n$) at 0.01 M KBr.
surfactant concentration range, while surfactant monomers would reside as a fully ionized state in aqueous solutions. Conductivity of nanobubbles was compared with that of micelles. It would be attributed to the counter ion binding at interface or curvature effect.

4. Conclusions

Surfactant adsorption and ionization at the curved air–water interface was investigated in a stable nanobubbles system generated by ultrasonication with palladium electrode. Nanobubbles of 750 nm for pure water were formed with bath-type sonicator and stable for 1 h, and the sizes shifted a little with ions. As power and time of sonication increased, the size of bubble increased. Adding surfactants, the surface tension drops to 38 dyn/cm and the bubble size increased, the size increased with $n$. A micellar model was proposed to explain the formation of nanobubbles and size reduction. Zeta-potentials of nanobubbles showed a sharp change at CMC, increasing linearly with surfactant concentrations at low concentration and invariant at high concentration. The surface ionization and adsorbed monolayers at the bubble surface would result in a degree of dissociation of a planar air–water interface, but the calculated degree of dissociation at the bubble surface is very low compared with that of micelles. It would be attributed to the counter ion binding at interface or curvature effect.

References