Study of the interfacial array behaviour of surfactant at very low concentration by second harmonic generation and molecular dynamic simulation

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Abstract: The array behaviour of anionic surfactant sodium dodecylbenzenesulfonate (SDBS) on the air/water interface was investigated using non-resonant surface second harmonic generation (SHG) and molecular simulation. It was found that the SHG intensities changed with surfactant concentrations non-monotonously under Critical Micelle Concentration (CMC). The mean orientational angle of SDBS molecule at the air/liquid interface was calculated, and the molecular array behaviour was analyzed by molecular dynamics (MD) simulation. The simulated results agreed with the experimental results very well, which provided the detailed information about the interfacial molecular configuration of surfactant, not only indicating the SHG intensity related to the N_s and $r(\theta)$, but also demonstrates that the microscopic information presented by the MD simulation method is reliable. According to the results, the surfactant molecules get clustered even at very low concentration far lower than the CMC.

Keywords: surfactant; interfacial behaviour; second harmonic generation; molecular dynamic simulation

1. Introduction

As a powerful tool for surface and interface study, SHG has recently gained much interest. In the early 1960s, SHG at the surfaces was first observed as a function of an applied dc electric field in the crystal calcite [1]. Then based on the experiment results, the basic principle of surface nonlinear generation was explored and a comprehensive theory of surface nonlinear optics was established by Bloembergen et al [2, 3]. In the 1980s, there had been significant advances in the application of spectroscopic methods to the field of electrochemistry.

Apart from the advantage including simple and sensitive, SHG is surface-specific. In the electric dipole approximation, SHG is forbidden in media with inversion symmetry. However, it can arise from the surface of bulk material with inversion symmetry or the interface of two media, since inversion symmetry is absent at the surface or the interface. So SHG was one of the specific entrants to study the microscopic interactions that occur at the interface [4, 5]. For example, it was used to detect the formation of individual monolayers and also used as a surface probe for molecular adsorption and orientation [6]. Many physical and chemical interactions on the surface of different media were traced by this method, e.g. electron-transfer reactions occurring at interfaces, electrostatic properties of interfaces, dynamics of dye molecule adsorbed to liposomes, charge-transfer spectrums of a semiconductor-dye surface complex, etc. [7-9]. It was realizable that the vibrational properties of adsorbed molecules in either frequency or time domain can be explored by surface SHG laser beam. After 2000, nonlinear crystals had been introduced for the study of different interface mechanisms, such as solid/solid, liquid/liquid and liquid/gas interfaces [10, 11]. Surfaces of different materials including metal, semiconductor and nonconductor were used to generate surface SHG radiation [12].

SHG study of surfactant solution can provide a lot of information about the properties of molecules at the interface, for example, the molecular second-order polarizability and information of the molecular ordering, symmetry, and orientation.

A detailed analysis of the SHG data for SDBS solutions is presented in this paper. The SHG intensities for different concentrations of SDBS solutions are obtained. Then the microscopic molecular structures are studied by comparing with the variation of SHG intensities, and the mean orientational angle of SDBS molecules at the air/liquid interface is calculated by the method we presented. The interface information, including

the molecular orientational order and the behaviour of interfacial molecules, are analyzed by MD simulation. It can be found that the simulated results are correspondent with experimental results.

2. Materials and methods

2.1 Materials

Sodium dodecylbenzenesulphonate SDBS (purity >95%) was purchased from Tianjin Kermel Chemicals Corp, China. All the vessels are cleaned by chromic acid lotion, and then cleaned with Millipore water for several times. All solutions are freshly made before experiment. To further make an accurate experimental measurement, the last 20ml of SDBS sample solution is transferred to the sample dish by pipetting in order to clear away potential surface-active contaminants on the surface. To ensure that the adsorption of the surfactant molecules at the air/liquid interface get equilibrium, the SHG measurement get started after at least 30 minutes. Milli-Q water was used to prepare all the solutions.

2.2 Methods

2.2.1 Experimental setup

A schematic of the experimental apparatus is given in Figure 1. All SHG experiments have been performed using a 10Hz Nd: YAG laser, with 10ns pulses at 1064nm. The trigger frequency is controlled by a sync signal generator (DG645). The output of the laser is *P*-polarized and a long-pass filter F_1 is placed in the probe beam next to the laser to block any spurious source of SHG. Then the fundamental beam is adjusted by two beam reflectors, M_1 and M_2 . As a result, the fundamental beam is focused to the sample interface at the incident angle of 70° from the surface normal. This beam passes through a Glan prism (GL) to purify the polarization of the beam and through a half-wave plate

(HWP) to control the polarization direction by rotation. A second long-pass filter F_2 is used before the sample to cut off any of the possible 532nm harmonic wave which may generate on the former optical components. For polarization measurement of SHG light, an analyzer (P) is inserted in the light path. After the reflection by beam reflector M_3 and the elimination of the unnecessary laser light using a short-pass filter (F_3), the probing SHG light is spectrally resolved with a monochromator (MC) (DS-100,resolution=1nm). The second harmonic output from the monochromator is directed into a photoelectric detector (PT), whose signal is pre-amplified and then processed by a boxcar (SR250) to increase the signal-to-noise ratio. The resulting signal is acquired by a personal computer. The room temperature is controlled at $22.0\pm1.0\text{ }^{\circ}\text{C}$ and the humidity in the room is controlled around 40%.The whole experimental apparatus and sample are enclosed in a black ABS box, with input apertures to prevent dust from settling on the sample surface. The inside of apertures is inserted a long-pass filter F_1 to reject the possible 532nm harmonic wave generated inside the laser but lets the fundamental beam reach to the the sample.

Figure 1. Experimental Setup.

2.2.2 Molecular Dynamics Simulation

A reasonable double-layer film model was prepared for the simulation and the details of the molecular model and the simulation method used in this paper were described in ref [13]. To construct the model of each surfactant, 16 surfactant molecules were disposed to form a surfactant monolayer at first, with space suitable for hexagonal close packing in a simulation box imposed to periodic boundary conditions in all three spatial directions similar to those shown previously [14, 15]. The adsorption area data per molecule of SDBS are $86.60 \text{ \AA}^2$, $70.14 \text{ \AA}^2$, $55.42 \text{ \AA}^2$, $48.71 \text{ \AA}^2$ and $42.43 \text{ \AA}^2$, respectively. The corresponding concentrations are from 0.001% to CMC (0.042%). A $25 \text{ \AA}$ thick slab of the water phase (the number of water molecules is changed as the changed adsorption area data as shown in Table 1.) using the flexible SPC model with the same cell parameters as those of the surfactants cell was set, and two surfactant monolayers were placed on opposite sides of the water phase with hydrophilic head groups of surfactants inserted [16]. In the initial configuration, a more than $15 \text{ \AA}$ thickness of water slab was chosen, the density being close to real water, which ensured that the molecular model held up abundant liquid and that the two monolayers of surfactant did not just interact with each other.

All the systems were equilibrated using MD, the charges and potentials of surfactant molecules are assigned to the alkyl tail and the hydrophilic polar head of the surfactant based on the parameters given by the Compass force field [13, 17]. The total energy was given as the combination of valence terms and nonbonding interactions, and the summation of energies are listed in Equation (1) [13]:

$$U = U_{bonds} + U_{angles} + U_{dihedrals} + U_{cross} + U_{VDW} + U_{elec} \quad (1)$$

The nonbonding interaction terms include an LJ-9-6 function for the van der Waals (vdW) term and a Coulombic function for an electrostatic interaction. The long-range

electrostatic interactions were described by the Ewald summation method [18]. The system was carried out in the NVT ensemble with a time step of 0.001 ps. The temperature was controlled using a Hoover-Nose thermostat [19] with a relaxation time of 0.2 ps. The simulations were performed at $T = 298$ K, being the same as experimental conditions. To avoid the possible molecule overlap of the initial built configurations, 20000 steps of minimized optimization were first run. Molecular dynamic simulation was then carried out starting with the minimized configuration. The MD simulations were carried out for 3ns, and the results of the last 1ns were used to analyze and evaluate the properties. All the simulations were performed in the software Material studio 4.4 by Accelrys.

Table 1. Details of Simulated Systems.

system	The area of single molecule ($\text{\AA}^2$)	a=b ($\text{\AA}$)	The number of water molecules	Lx ($\text{\AA}$)	Ly ($\text{\AA}$)	Lz ($\text{\AA}$)
SDBS	42.43	7	455	24.248	28	95.42
	48.71	7.5	525	25.980	30	94.40
	55.42	8	590	27.712	32	95.63
	70.14	9	750	31.176	36	95.63
	86.60	10	930	34.640	40	95.66

The array behaviour of surfactants at interface was quantitatively described by P_2 which is defined as the orientational function of the tail chain [20]:

$$P_2 = \frac{3}{2} \langle \cos^2 \phi \rangle - \frac{1}{2} \quad (2)$$

Where ϕ is the angle between the interface normal and the molecular axis defined as the united vector from the first to the last carbon atom of the tail.

2.2.3 Theory of surface SHG

Generally, the SHG response, $I(2\omega)$, for a thin layer should be related to the intensity of input light, $I(\omega)$, by the equation [21-25]:

$$I(2\omega) = \frac{32\pi^3 \omega^2 \sec^2 \beta}{c_0^3 n_1(\omega) n_1(\omega) n_1(2\omega)} |\chi_{eff}|^2 I(\omega)^2 \quad (3)$$

$I(\omega)$ is the incoming laser intensity, c_0 is the speed of the light in the vacuum, β is the incident angle from the surface normal, and $n_1(\omega)$ is the refractive index at the frequency ω of the medium, in which the laser beam propagates. χ_{eff} is the effective macroscopic second order susceptibility. There are three independent χ_{eff} terms for an achiral rotationally isotropic interface ($C_{\infty v}$), namely, s -in/ p -out (χ_{sp}), 45° -in/ s -out ($\chi_{45^\circ s}$) and p -in/ p -out (χ_{pp}). Here, p denotes the polarization in the incident plane, while s the polarization perpendicular to the incident plane. These χ_{eff} terms are directly related to tensorial Fresnel factor L_{ii} and the interfacial macroscopic susceptibilities χ_{ijk} tensor elements as the following [26]:

$$\begin{aligned} \chi_{eff,sp} &= L_{zz}(2\omega) L_{yy}^2(\omega) \sin \beta \chi_{zyy} \\ \chi_{eff,45^\circ s} &= L_{yy}(2\omega) L_{zz}(\omega) L_{yy}(\omega) \sin \beta \chi_{yzy} \\ \chi_{eff,pp} &= L(2\omega) L_{xx}^2(\omega) \sin \beta \cos^2 \beta \chi_{zxx} \\ &\quad - L_{xx}(2\omega) L_{zz}(\omega) L_{xx}(\omega) \sin \beta \cos^2 \beta \chi_{xzx} \\ &\quad + L_{zz}(2\omega) L_{zz}^2(\omega) \sin^3 \beta \chi_{zzz} \end{aligned} \quad (4)$$

In which the surface nonlinear susceptibility $\chi^{(2)}$ is a third-rank tensor. In general it can have 18 distinct non-zero complex elements, χ_{ijk} , where i, j and k refer to Cartesian axes defined with the surface normal as the $+Z$ direction. For most systems, the number of non-zero elements is greatly reduced by the surface symmetry. For example, if the surface is rotationally isotropic about the surface normal, as in the case of a achiral liquid surface, there are only three distinct independent non-zero tensor elements: χ_{zzz} , $\chi_{zxx} = \chi_{zyy}$, and $\chi_{xxz} = \chi_{xzx} = \chi_{yyz} = \chi_{yzy}$, where the indices x, y, z refer to

laboratory coordinates such that Z is along the surface normal. χ_{eff} in any experimental configuration with linearly polarized light can be directly expressed into the linear combination of these three independently measureable χ_{eff} terms as the following

$$\chi_{eff} = \sin^2 \alpha \cos \gamma \chi_{eff,sp} + \sin 2\alpha \sin \gamma \chi_{eff,45^\circ s} + \cos^2 \alpha \cos \gamma \chi_{eff,pp} \quad (5)$$

Here, α and γ are the polarization angle of the incident laser beam and the detection polarization angle of the signal beam, respectively.

The tensorial Fresnel factor L_{ii} is a second-rank tensor, for reflex SHG. By diagonalization method, it can be expressed as [22, 26, 27]:

$$\begin{aligned} L_{xx}(\omega) &= \frac{2n_1(\omega) \cos \beta_r}{n_1(\omega) \cos \beta_r + n_2(\omega) \cos \beta_\omega} \\ L_{yy}(\omega) &= \frac{2n_1(\omega) \cos \beta_\omega}{n_1(\omega) \cos \beta_\omega + n_2(\omega) \cos \beta_r} \\ L_{zz}(\omega) &= \frac{2n_1(\omega) \cos \beta_\omega}{n_1(\omega) \cos \beta_r + n_2(\omega) \cos \beta_\omega} \left(\frac{1}{n'(\omega)} \right)^2 \end{aligned} \quad (6)$$

In which $n'(\omega)$ is the refractive index of interface layer when the frequency of the beam is ω ; β_ω and β_r denote the incident angle and the refraction angle of the beam, respectively, satisfying the following equation:

$$n_1(\omega) \sin \beta_\omega = n_2(\omega) \sin \beta_r. \quad (7)$$

In our SHG measurement, polarization is usually fixed at either p or s , while the polarization angle α of the incident laser beam is varied by the half-wave plate rotating through 360° . The SHG intensity can be expressed as [28]:

$$\begin{aligned} I_p &= \left[A \cos^2 \alpha + B \sin^2 \alpha \right]^2 \\ I_s &= \left[C \sin(2\alpha) \right]^2 \end{aligned} \quad (8)$$

The relative value can be obtained from fitting the experimental data with Equation (8) by knowing the relative signs between them. The parameters A , B and C depend on the assumption of the surface SHG and the symmetry of the interface. The numerical values depend on the experimental geometry and the linear optical properties of the bulk phases.

For molecules with C_{2v} symmetry, there are seven nonzero microscopic polarizability tensor elements β_{ijk} ($i, j, k = a, b, c$) in molecular coordinates system (a, b, c): namely, β_{ccc} , β_{caa} , β_{cbb} , β_{aca} , β_{aac} , β_{bcb} and β_{bbc} , with $\beta_{aca} = \beta_{aac}$ and $\beta_{bcb} = \beta_{bbc}$ for the SHG process. When the optical frequency is far below the resonance, β_{ccc} is usually negligible. By defining $R = (\beta_{caa} + \beta_{cbb})/(\beta_{aca} + \beta_{bcb})$, we obtain [29],

$$\begin{aligned}\frac{\chi_{zxx}}{\chi_{xzx}} &= \frac{(R-2)D + (R+2)}{-RD + (R+2)} \\ \frac{\chi_{zzz}}{\chi_{xzx}} &= \frac{2(R+2)D - 2(R+2)}{-RD + (R+2)}\end{aligned}\quad (9)$$

Here $D = \langle \cos \theta \rangle / \langle \cos^3 \theta \rangle$ is the interfacial order parameter with θ as the tilt angle of the water dipole axis from the interface normal, $\langle \rangle$ denotes the ensemble average of the whole orientational distribution. After quantitative evaluation of the effective microscopic local field factors on the interface layer, the two ratios χ_{zzz}/χ_{xzx} and χ_{zzz}/χ_{xzx} can be accurately obtained from the polarization SHG measurement. Then the R and D values can be readily obtained with good accuracy, using Equation (9). Now with the interfacial order parameter D known, the relative number of water molecules contributing to the measured SHG signal from the interface of the different electrolytes as well as different electrolyte concentrations can be calculated from the changes of the corresponding SHG intensities. Simply stated,

$$I_{2\omega} \propto |\chi_{eff}|^2 \propto N_s^2 |r(\theta)|^2 \quad (10)$$

Here N_s is the number density of the interfacial molecules and $r(\theta)$ is the orientational distribution function directly related to the interfacial order parameter D [30]. Since $r(\theta)$ inherits all the orientational information of χ_{eff} , it naturally contains the full information of the orientational order of the molecular monolayer in surface SHG [25].

3. Results and discussions

3.1 The variation of SHG intensity of the SDBS solution as a function of SDBS concentration

Figure 2. The SHG intensity of SDBS.

Figure 2 shows the variation of the SHG intensity of SDBS solution at air/water interface as a function of SDBS concentration. It is very interesting that the SHG intensity did not increase monotonously as the SDBS concentration increasing before CMC. The SHG intensity increased initially and got to the first peak value at 0.001%, then declined until got to minimum at 0.015%. Then the SHG intensity increased as the

concentration increasing, after got peak value at 0.04%, the SHG intensity decreased a little and then kept as a plat.

This intensity variation regularity is related with the SDBS molecules configuration at the interface. As it was well known, the amount of the adsorbed SDBS molecules at the interface increases with the increasing concentration of SDBS under CMC, and it was reasonable that the SHG intensity increase corresponding to the increase of the amount of molecules at the interface. So the non-monotonously variation of the SHG intensity hinted that the configuration of the SDBS molecules at the interface might change in the concentration range, especially at very low concentration. In order to get information about the molecular orientation on the interface, the measurement results of SHG was analyzed.

3.2 The mean orientational angle of molecule at the air/liquid interface

The SHG intensity determined for 0.001%SDBS solution with different polarization combinations of input light and the second-harmonic signal was determined, as shown in Figure 3. The *s*- and *p*-polarized second-harmonic signal is measured under a variation of incident polarization angle changing from 0° to 360°. The incident angle of input light is set to 70°. I_{pp} and I_{sp} can be obtained from the *p*-polarized fitting curve,

$I_{45^0_s}$ can be obtained from the *s*-polarized fitting curve. i.e.

$I_{pp} = 0.899, I_{sp} = 0.534, I_{45^0_s} = 0.399$. For simplicity, we adopt the refractive index of

air $n_1 = 1$, the refractive index of SDBS solution and the solution interface layer $n' = n_2 = 1.35$. The incident angle of input light is $\beta_o = 70^\circ$. According to Equation (7), the refraction angle of SH wave can be obtained $\beta_r = 44^\circ$.

Figure 3. SHG intensity as a function of incident polarization angle for SDBS in a concentration of 0.001%.

From the Equation (6), we obtain

$$L_{xx}(\omega)=1.217, \quad L_{xx}(2\omega)=1.217, \quad L_{yy}(\omega)=0.522, \quad L_{yy}(2\omega)=0.522, \quad L_{zz}(\omega)=0.318, \\ L_{zz}(2\omega)=0.318$$

Utilizing the Equation (4), yields

$$\begin{aligned} L_{zyy} &= L_{zz}(2\omega)L_{yy}(\omega)L_{yy}(\omega) \sin \beta_{\omega} n'(2\omega)^2 = 0.148 \\ L_{yzy} &= L_{yy}(2\omega)L_{zz}(\omega)L_{yy}(\omega) \sin \beta_{\omega} n'(\omega)^2 = 0.148 \\ L_{zxx} &= L_{zz}(2\omega)L_{xx}(\omega)L_{xx}(\omega) \cos^2 \beta_{\omega} \sin \beta_{\omega} n'(2\omega)^2 = 0.094 \\ L_{xzx} &= L_{xx}(2\omega)L_{zz}(\omega)L_{xx}(\omega) \cos^2 \beta_{\omega} \sin \beta_{\omega} n'(2\omega)^2 = 0.094 \\ L_{zzz} &= L_{zz}(2\omega)L_{zz}(\omega)L_{zz}(\omega) \sin^3 \beta_{\omega} n'(2\omega)^2 n'(\omega)^4 = 0.162 \end{aligned} \quad (11)$$

According to Equation (3), the relation for effective second-order polarization and SHG intensity can be written as

$$\frac{\chi_{sp}}{\chi_{45^\circ s}} \propto \sqrt{\frac{I_{sp}}{I_{45^\circ s}}} \quad \frac{\chi_{pp}}{\chi_{45^\circ s}} \propto \sqrt{\frac{I_{pp}}{I_{45^\circ s}}} \quad (12)$$

Considering that the response efficiency for p - and s -polarized input light of incidence is different, the detection efficiency correction should be added, Equation (12) can be reformulated as

$$\frac{\chi_{sp}}{\chi_{45^\circ s}} = \sqrt{\frac{I_{sp}}{I_{45^\circ s} \sqrt{\frac{P}{S}}}} \quad \frac{\chi_{pp}}{\chi_{45^\circ s}} = \sqrt{\frac{I_{pp}}{I_{45^\circ s} \sqrt{\frac{P}{S}}}} \quad (13)$$

Where the ratio $P/S=1.3$.

Combining Equation (4) and Equation (11), the expression concerning macroscopic effective second-order polarizability and macroscopic second-order polarizability tensors can be obtained:

$$\begin{aligned} \frac{\chi_{zxx}}{\chi_{xzx}} &= \frac{n'(2\omega)^2 \chi_{sp}}{n'(\omega)^2 \chi_{45^\circ s}} \\ \frac{\chi_{zzz}}{\chi_{xzx}} &= \left(\frac{\chi_{pp}}{\chi_{45^\circ s}} - \frac{L_{zxx} \chi_{sp}}{L_{yzy} \chi_{45^\circ s}} + \frac{2L_{xzx}}{L_{yzy}} \right) \frac{n'(2\omega)^2 n'(\omega)^2 L_{yzy}}{L_{zzz}} \end{aligned} \quad (14)$$

Then substituting the above calculated results into Equation (14), yields

$$\frac{\chi_{zxx}}{\chi_{xzx}} = 1.083 \quad \frac{\chi_{zzz}}{\chi_{xzx}} = 6.056$$

According to the Equation (9), it is convenient to determine $R=1.021$, $D=1.991$.

If the molecules of interface follow δ distribution, the mean orientational angle of SDBS molecule at the air/liquid interface can be given by $\theta = \arccos \sqrt{\frac{1}{D}}$. As a result, it can be determined $\theta = 44.87^\circ$. In other words, the SDBS molecules in 0.001%

solution adsorbed and arrayed at the air/liquid interface in an average tilt angle of 44.87

°.

3.3 Array behaviour of SDBS molecules described by MD simulation

Figure 4. Equilibrated configuration snapshots of systems with different SDBS solution concentrations. (A) For clarity, the surfactants and the gas (N₂, O₂, CO₂) are drawn as van der Waals spheres, shown as small coloured sphere and water molecules drawn in line style. The atom colouring scheme is C, gray; H, white; O, red; N, blue; S, yellow; Na⁺, violet. The benzene ring is marked in blue, and shown as small coloured sphere and the others drawn in line style. (B) The corresponding adsorption area per molecule to each figure is a, 346.41 Å²; b, 86.60 Å²; c, 70.14 Å²; d, 55.42 Å²; e, 48.71 Å²; f, 42.43 Å², respectively.

Figure 4 is the MD snapshots of systems with different SDBS solution concentrations, and the increase of adsorption area of single molecule represents the decrease of concentration. The occupied area of per molecule of SDBS was settled to be from 42.43 to 346.41 Å², corresponding to the interfacial array state from very closely packing at SDBS concentration being above CMC to the discretely adsorption at very

low concentration. Figure 4(a) reflected that the adsorbed SDBS molecules at the interface were not independent and the distribution was not even, even if the amount of the molecules was little, the hydrophobic tails of the surfactants clustered and lied on the surface almost flatly, the benzene rings stretched into the water phase perpendicularly to the interface. In snapshot of Figure 4(b), some of the adsorbed SDBS molecules at the interface clustered together and the distribution tended to be even, the hydrophobic tails of surfactants lied in almost same angle to the interface, some of the benzene rings linked together and stood exposed to air. Obviously, in Figure 4(b) the arrangement of interfacial molecules was more orderly. In snapshot of Figure 4(c) the distribution of adsorbed SDBS molecules at the interface was more even with the amount of the molecules increasing, the hydrophobic tails of surfactants interlaced together and stretched out into the air with a variety of angles to the interface, the benzene rings lied on the surface with different form. It can be seen that the arrangement of interfacial molecules become less orderly. In snapshots of the last figures, from Figure 4(d) to Figure 4(e) and then to Figure 4(f), the distribution of adsorbed SDBS molecules at the interface tended to be more even with the amount of molecules increasing, the hydrophobic tails of surfactants became more stretched, the arrangement of interfacial molecules became more orderly with increasing amount of molecules at the interface.

Figure 5. The orientation correlation $P_2(r)$ of hydrophobic tail of SDBS in the systems with different concentrations. Note: $\text{\AA}^2$ is the unit of the maximum adsorption area of single molecule. The decrease of the maximum adsorption area of single molecule represents the increase of adsorption amount of surfactant molecules.

The orientation correlation $P_2(r)$ of hydrophobic tail of SDBS in different systems was calculated, as shown in Figure 5. It can be seen from Equation (2) that the ϕ becomes smaller when the P_2 become larger. The smaller ϕ means that different molecules tend to be the similar orientational distribution, that is to say the arrangement of interfacial molecules becomes more orderly. In a word, the P_2 gives an index to the orientational order. The average P_2 versus adsorption area per surfactant for SDBS was shown in Figure 6.

Figure 6. The average P_2 versus adsorption area per surfactant for SDBS.

It was clearly that the P_2 changed non-monotonously with the concentration decreasing. At very low concentration, the area occupied by per molecule was large, with the concentration increasing, the order degree of interfacial molecules tend to be more orderly at the beginning, but then become more disorder, because of the clustering of the SDBS molecules on the interface, as shown in Figure 4(c), after that the order degree of the molecules increase again as the molecular density at interface increasing along with the bulk phase concentration increasing. The variation of P_2 in Figure 5 has exactly the same trend as the SHG intensity in Figure 2. So it was certain that the arrangement of the interfacial molecules actually go through a transformation even at very low concentration. It intuitively explained why the SHG intensity reached a peak at the concentration of 0.001%, which is far lower than the CMC, as shown in Figure 2. Meanwhile, the mean orientational angle of interfacial molecules of SDBS in system of Figure 4(b) was statistically analyzed, the results were shown in Figure 7.

Figure 7. The statistic result of mean orientational angle of interfacial molecules in system of Figure 4b.

It can be seen in Figure 7 that the most probable orientational angle is exactly 45° . This result was very consistent with the mean orientational angle calculated according to the SHG measurement in section 3.2, which was 44.87° .

Above all, the MD simulation result provides sufficient microscopic information about the interfacial molecular array behaviour of surfactant SDBS, and the MD simulation result was consistent well with the measurement data of SHG experiment data. By combining SHG experimental results and MD simulation results, the interfacial molecular behaviour of SDBS was determined, and the arrangement transformation occurred at very low concentration was clarified.

Conclusions

The behaviour of interfacial molecules of SDBS at very low concentration is studied by combining second harmonic generation and molecular dynamic simulation. It was found that the SHG intensities of SDBS change non-monotonously at very low

concentration under CMC. Using the measurement data, the mean orientational angle of interfacial molecules of SDBS solution was calculated. The MD simulation results correspond very well with the experimental results, not only indicating the SHG intensity related to N_s and $r(\theta)$, but also demonstrates that the microscopic information presented by the MD simulation method is reliable. In summary, the combination of SHG and MD simulation will make a great contribution to the interface molecular configuration study of surfactant solution, especially at very low concentration.

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Table 1. Details of Simulated Systems.

system	The area of single molecule (Å ²)	a=b (Å)	The number of water molecules	Lx (Å)	Ly (Å)	Lz (Å)
SDBS	42.43	7	455	24.248	28	95.42
	48.71	7.5	525	25.980	30	94.40
	55.42	8	590	27.712	32	95.63
	70.14	9	750	31.176	36	95.63
	86.60	10	930	34.640	40	95.66