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Citation: *The Journal of Chemical Physics* **142**, 224704 (2015); doi: 10.1063/1.4922304

View online: <http://dx.doi.org/10.1063/1.4922304>

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# Molecular interactions at the hexadecane/water interface in the presence of surfactants studied with second harmonic generation

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(Received 10 March 2015; accepted 26 May 2015; published online 9 June 2015)

It is important to investigate the influence of surfactants on structures and physical/chemical properties of oil/water interfaces. This work reports a second harmonic generation study of the adsorption of malachite green (MG) on the surfaces of oil droplets in a hexadecane/water emulsion in the presence of surfactants including sodium dodecyl sulfate, polyoxyethylene-sorbitan monooleate (Tween80), and cetyltrimethyl ammonium bromide. It is revealed that surfactants with micromolar concentrations notably influence the adsorption of MG at the oil/water interface. Both competition adsorption and charge-charge interactions played very important roles in affecting the adsorption free energy and the surface density of MG at the oil/water interface. The sensitive detection of the changing oil/water interface with the adsorption of surfactants at such low concentrations provides more information for understanding the behavior of these surfactants at the oil/water interface. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922304>]

## I. INTRODUCTION

To understand the functionality of a surfactant in the adjustment of chemical and physical properties of an oil/water interface, it is crucial to investigate the interactions of molecules including surfactants at the interface. Obtaining such information is not an easy task. Recently, second order nonlinear spectroscopic techniques, including second harmonic generation (SHG) and sum frequency generation-vibrational spectroscopy (SFG-VS), have been demonstrated capable for *in situ* detection of buried interfaces,<sup>1-9</sup> particularly the interfaces in colloids and emulsions.<sup>10-16</sup> With the aid of SHG and SFG-VS, the adsorption of surfactants at oil/water interfaces has also been intensively studied.<sup>14,17-23</sup> Such studies mostly focus on flat oil/water interfaces, with only a few paying attentions to micro- and nano-sized curved oil/water interfaces within emulsions.<sup>14,16</sup> The influence of surfactants on the structure and dynamics of other molecules at oil/water interfaces, especially at the surface of oil droplets, has been rarely reported.

An important parameter of interest is the concentration of surfactant in a solution required to notably affect the properties of the interface. For example, the widely used surfactant sodium dodecyl sulfate (SDS) has been reported to change the interfacial tension of air/water and oil/water interfaces at concentrations in hundreds of micromolar range.<sup>24-28</sup> It was also reported that the size and zeta potential of oil droplets in hexadecane/water emulsions could be influenced

by the presence of SDS with concentrations as low as tens of micromolars.<sup>14</sup> The dynamic process of hen egg-white lysozyme adsorption at the air/water interface was also observed to be influenced by SDS with concentrations in tens of micromolar range.<sup>29</sup> Could the effect of surfactants with substantially lower concentrations at the oil/water interface be detected? In this work, we investigate the adsorption of charged organic molecules at the surfaces of oil droplets in hexadecane/water emulsions, in the presence of surfactants such as SDS, polyoxyethylene-sorbitan monooleate (Tween80), and cetyltrimethyl ammonium bromide (CTAB). The results showed that surfactants with concentrations as low as the micromolar range, that is, two to three orders of magnitude smaller than their critical micelle concentrations, greatly influenced molecular adsorption at the hexadecane/water interface.

Because surfactants typically have relatively small nonlinear polarizability,<sup>12</sup> there are only a few reported applications of SHG in the study of surfactant behavior at solid/liquid and liquid/liquid interfaces.<sup>12,16,17,19,30</sup> To probe the adsorption structure and free energy of surfactants with small nonlinear polarizability at the solid/water interface in colloids, malachite green (MG) has been used as a SHG probe.<sup>12</sup> It has been demonstrated that SHG chromophores with concentrations in the bulk as low as sub-micromolar could be sensitively observed after adsorbing at the interfaces.<sup>12,13,19</sup> In this work, the influence of pre-adsorbed surfactants on the adsorption of MG at the hexadecane/water interface was also used to analyze the induced changes in interfacial property and the molecular interactions at the hexadecane/water interface.

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## II. METHODS

### A. Materials

Deionized water (DI water, 18.25 M $\Omega$ -cm) was obtained from a water purification system (Water Purifier, WP-UP-UV-20, Sichuan water technology development Co. Ltd, China). Hexadecane (99%, Sigma-Aldrich) was purified with six passes through basic alumina columns with procedures presented in previous reports.<sup>9,31,32</sup> SDS (99%, Sigma-Aldrich) was recrystallized three times in a mixed solvent of ethanol (99.7%, Tianjing Baishi Chemical Co. Ltd, China) and DI water with a volume ratio of 9.5:0.5. The purity of SDS was confirmed by surface tension measurements with its aqueous solution. The absence of a clear dent at the surface tension—SDS concentration curve around 4 mM was used as an indicator of a purified SDS sample.<sup>22,25</sup> CTAB (99%, Shanghai Shanpu Chemical Co. Ltd, China) was recrystallized three times in a mixed solvent of acetone (99.5% Tianjing Zhiyuan Reagent Co. Ltd, China) and ethanol with a volume ratio of 1:1.<sup>21</sup> Tween80 (CR, Tianjing Fuyu Reagent Co. Ltd, China) was used as received. Malachite green chloride (MGCl, 96%, Sigma-Aldrich) was dissolved in water to make a 2 mM stock solution. Before each experiment, this solution was adjusted to pH 6 with solution of NaOH (99.99%, Sigma-Aldrich), filtered by an Omnipore membrane filter with 1.0  $\mu$ m aperture size, and diluted to desired concentration. The emulsions and the MG solution were all adjusted to pH 6 to avoid the change of the acidity during the titration experiments. The concentration of MG ions in the solution of pH 6 was calculated and used for the calculation of the adsorption density of MG ions at the oil/water interface, as described in the supplementary material.<sup>45</sup>

Glassware were cleaned with piranha solution (H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> with a volume ratio of 3:7), then thoroughly rinsed with DI water and dried before each experiment. *Please be noted that piranha solution is strongly oxidizing and must be handled with care.*

### B. Preparation of the emulsions

40  $\mu$ l hexadecane was mixed with 2 ml DI water, stirred at 500 rpm in a thermostatic water bath for 15 min and sonicated (KQ-300DE, 300 mW, 40 kHz, Kunshan ultrasonic instrument Co. Ltd, China) for another 10 min with the temperature controlled at  $25 \pm 3$  °C. The emulsion was then diluted 100 times with DI water for the experiments.

### C. Dynamic light scattering (DLS) and zeta potential measurements

The size and the surface zeta potential of the oil drops in the emulsions were measured with DLS method (ZS90, Malvern). The laser wavelength used was 633 nm and the measuring angle was 90°. The results are calculated based on the average of three measurements.

### D. SHG measurements

A Ti:sapphire oscillator laser (Spectra Physics, Mai Tai SP) with a pulse width of approximately 100 fs and a repetition

rate of 84 MHz was used for the SHG measurements. The laser wavelength was centered at 810 nm. The ambient temperature of the lab was set at  $22 \pm 1$  °C for the stability of the laser system.

A cylindrical quartz cell with diameter of 1.3 cm was used to hold emulsions in the SHG experiments. Stirring was applied to avoid the heating effect from the laser. The stirring was controlled with a relatively low speed to avoid the generation of any air bubbles. The horizontally propagating 810 nm fundamental laser was passed through a high pass filter ( $>750$  nm) to eliminate the second harmonic light in the laser and focused at the center of the cell. The SH signal at the forward direction was collected and passed through a filter (BG-39, 300 nm–600 nm band pass) to eliminate the residual light at the fundamental frequency. Because the second harmonic (SH) signal scattered from spherical interfaces with diameters as hundreds of nanometers is normally away from the forward direction of the pumping laser,<sup>33–35</sup> the SH scattering within a relatively wide spatial angle of 40° in both horizontal and perpendicular directions was collected by lens. The signal was then acquired by a monochromator (Andor, SR-500I) before being detected with a photomultiplier tube (PMT, Hamamatsu R-1527p). The output of the PMT was amplified by a factor of 5 with a preamplifier (Stanford Research, SR445A) and analyzed by a photon counter (Stanford Research, SR400). The obtained photon counts were then recorded by a computer. The experiments were performed with a laser power of 300 mW and high-voltage supply for the PMT of  $-900$  V. The polarization of the pump laser was set with the electronic field of the light parallel to the horizontal plane.

## III. RESULTS AND DISCUSSION

### A. The adsorption of MG at the oil/water interface in hexadecane/water emulsions

Fig. 1 shows the SH intensity of adsorbed MG at the surfaces of oil droplets in a hexadecane/water emulsion during a titration experiment. The preparation procedure of the hexadecane/water emulsion, which is detailed in the supplementary material,<sup>45</sup> generates emulsions with droplet diameters ranging from 200 to 300 nm. Because the adsorption of the positively

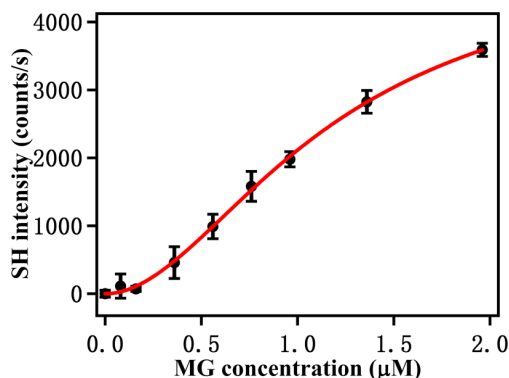


FIG. 1. SH intensity radiated from MG adsorbed at the surfaces of oil droplets in a hexadecane/water emulsion. The MG concentration was kept below 2  $\mu$ M to ensure the stability of the emulsion. The solid line is the fitting with the modified Langmuir model, as detailed in the supplementary material.<sup>45</sup>

charged MG ions neutralizes the negative charges at the hexadecane/water interface, which contribute towards stabilizing the emulsion,<sup>32,36–40</sup> the addition of MG was kept below  $2\ \mu\text{M}$  to ensure emulsion stability during the SHG measurement. Also, in all the titration experiments, the MG concentration was controlled within certain range. More detailed discussion on the stability of the emulsion and the selection of experimental conditions is described in the supplementary material.<sup>45</sup>

The intensities of the nonlinear scattering from the surfaces of spherically shaped objects in colloids or emulsions are influenced by factors including the effective surface area (or molecular density at the surface), the orientational ordering of molecules at the surface, the refractive indices at the interface, or in the bulk phase, the size, and size distribution of the objects.<sup>11–14,34,35,41</sup> However, as demonstrated in these work, with relatively stable colloids/emulsions during the titration experiments ensured, the obtained nonlinear strength (the square root of the nonlinear intensity) can be treated in proportional to the effective surface area or the molecular density at the surface. This treatment can significantly simplify the analysis of the nonlinear scattering from spherically shaped objects and be used to investigate the adsorption dynamics of molecules on the surfaces. The increase in SH intensity shown in Fig. 1 was the result of adsorbed MG ions at the surfaces of oil droplets in the hexadecane/water emulsion and can be fitted with the modified Langmuir model as reported by the Eisenthal group.<sup>11</sup> With measurements repeated in triplicate, we obtained an adsorption free energy of  $-11.4 \pm 0.3\ \text{kcal/mol}$  and a maximum MG adsorption of  $0.9 \pm 0.2\ \mu\text{M}$ . So, the saturated surface coverage of MG ions at the oil/water interface was  $0.1 \pm 0.02\ \text{MG/nm}^2$  for an oil/water interfacial area of approximately  $50\ \text{cm}^2/\text{ml}$  in the emulsion. Titration experiments with the emulsions further diluted by water up to 4 times were also performed. The obtained adsorption free energy and the saturated surface coverage of MG ions kept almost unchanged in these trials, similar as that demonstrated by Wang *et al.*<sup>11</sup>

## B. The effect of SDS on the adsorption of MG at the oil/water interface

The adsorption of a charged organic molecule at a surface is influenced by several factors, including chemical adsorption, charge-charge interactions, hydrogen bonding, hydrophobic effects, and van der Waals interactions.<sup>13,15,42</sup> The extent to which charge-charge interactions influence the adsorption process of MG ions at the oil/water interface could be investigated by adjusting the surface potential with surfactants bearing different charges. For this purpose, we measured the adsorption free energy and the saturated surface coverage of MG at the hexadecane/water interface in the presence of three surfactants with different charges, i.e., positively charged CTAB, neutral Tween80, and negatively charged SDS (see Fig. 2 for molecular structures of the three surfactants).

Fig. 3(a) shows the change in the maximum adsorption density of MG ions at the hexadecane/water interface upon pre-adsorption of SDS at the oil/water interface, as obtained from the titration curves shown in the supplementary material.<sup>45</sup> The maximum adsorption density initially increases drastically with SDS concentration then rapidly decreases.

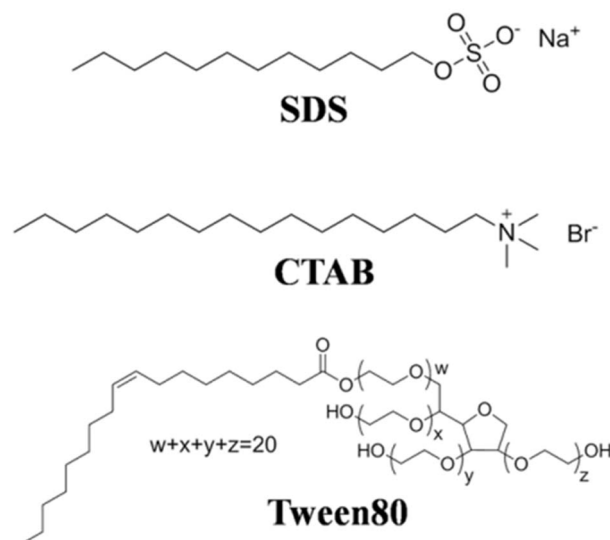


FIG. 2. Molecular structures of the three surfactants.

The charge-charge attraction between positively charged MG ions at the hexadecane/water interface and pre-adsorbed, negatively charged SDS molecules accounts for the initial increase in the maximum surface density. However, the rapid decrease of the MG density at the oil/water interface with further increase in SDS concentration beyond  $100\ \mu\text{M}$  is contradictory to this behavior. Previous SFG-VS and zeta potential measurements showed an increase in SDS population at

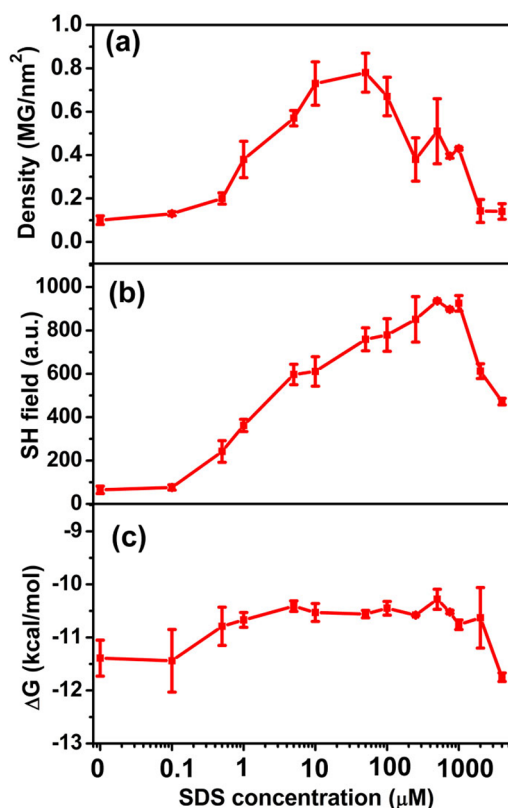


FIG. 3. The saturated surface coverage (a), saturated SH field (b), and the adsorption free energy (c) of MG ions at surfaces of oil droplets in a hexadecane/water emulsion in the presence of SDS at various concentrations. The lines joining the data points track the changes.



this oil/water interface when the bulk concentration increased from 55  $\mu\text{M}$  to 10 mM.<sup>14</sup> The decrease in adsorption density of the positively charged MG ions observed with an increase in the negative surface potential therefore seems implausible. To check the reliability of the MG adsorption density obtained from titration experiments, we plotted the maximum SH field in Fig. 3(b) corresponding to the square root of the maximum SH intensity radiated from the emulsion. The value of the SH field is proportional to the number density of MG at the interface provided that the orientation of MG ions is not changed.<sup>10,11,13,16</sup> It can be seen from Fig. 3(b) that the SH field curve follows a similar SDS concentration-dependent trend as the maximum surface density curve of Fig. 3(a) except for some difference at SDS concentrations in 100-1000  $\mu\text{M}$  range. This confirms the trends observed in the maximum MG density at the oil/water interface. It also suggests that MG ions at the surfaces of oil droplets maintain a similar orientation, with only some change at SDS concentration in 100-1000  $\mu\text{M}$  range.

The decrease in MG adsorption density with increasing SDS population at the oil/water interface in the high SDS concentration range suggests that MG tends to adsorb at “free” hexadecane/water interfaces rather than at interfaces covered by SDS molecules. At the low SDS concentration range, i.e., with low SDS coverage, the “free” oil/water interface is still easily accessible; the charge-charge attraction between negative SDS molecules and positive MG ions notably increases the adsorption density of MG ions at the hexadecane/water interface. At the high SDS concentration range, the increased SDS coverage at the interface prevents MG ions from being adsorbed to the oil/water interface. Hence, the MG adsorption density at the oil/water interface is dependent upon the balance of two factors, i.e., charge-charge interactions and competition adsorption.

The factors affecting the MG adsorption density also influence the adsorption free energy of MG ions at the oil/water interface. Fig. 3(c) shows that as the SDS concentration increases from zero to micromolar levels, smaller adsorption free energy values are obtained. However, in the presence of highly concentrated SDS, a relatively larger adsorption free energy of MG ions at the oil/water interface was observed.

Smaller free energies in the presence of small amounts of SDS seem contradictory because an increased maximum adsorption density suggests a stronger interaction between MG and the oil/water interface. To understand this observation, we need to consider the free energy change of MG ions during the adsorption process. Titration experiments measure the average free energy difference between MG ions in solution and at the interface, taking into account all adsorbed molecules. It is reasonable to assume that the MG ions are initially adsorbed at the oil/water interface with a larger free energy decrease because of the hydrophobic interactions between hexadecane and MG as well as the charge-charge attraction between positively charged MG ions and the negative potential of the interface irrespective of the presence of SDS.<sup>9,32,36-40</sup> The latter portion of MG ions adsorbed may correspond to a smaller free energy decrease because of the hydrophobic interactions between hexadecane and MG ions weakening as a result of the drastic increase in the surface coverage of MG ions. Previous investigations on the adsorption of charged dye molecules

at polystyrene surfaces showed that hydrophobic interactions were so strong that the adsorption of positively charged dyes at a positively charged surface was able to occur.<sup>13,42</sup> So, in the presence of low SDS concentrations, further adsorption of MG ions with weak hydrophobic interactions may cause a decrease in the adsorption free energy.

There are also other factors that affect the free energy difference in the adsorption process which includes the repulsion between the adsorbed MG ions, as well as the synergetic effects of adsorption owing to the interactions between positively charged MG ions and negatively charged SDS molecules. The synergetic effects at the interface may be of particular benefit during certain conditions (i.e., at concentrations around 10  $\mu\text{M}$ , as shown in Fig. 3(a)). With the adsorption of positively charged MG ions at the oil/water interface, the surface coverage of the negatively charged DS ions may also increase. In Sec. III D, we also show that the adsorption of MG ions at the oil/water interface with a relatively high SDS coverage may include an ion exchange process between the  $\text{MG}^+$  in the solution and the  $\text{Na}^+$  that was attracted by  $\text{DS}^-$  at the interface. The  $\text{MG}^+$  and  $\text{DS}^-$  may form neutral complexes at the oil/water interface and influences the  $\text{MG}^+$  adsorption density and free energy. So, quantitative interpretation of the adsorption free energy under the influence of these interactions requires further experimental and theoretical investigations.

Relatively larger adsorption free energies at the oil/water interface in the presence of high SDS concentrations are attributed to increases in charge-charge interactions despite the decrease in the number of MG ions adsorbed at the interface owing to the formation of the SDS adsorption layer. This explanation is supported by zeta potential measurements that indicate an notably increased negative charge density at the oil/water interface at SDS concentrations beyond 0.4 mM.<sup>14</sup>

### C. The effect of Tween80 and CTAB on the adsorption of MG at the oil/water interface

For comparison, Fig. 4 shows the adsorption free energy and the saturated density of MG at the hexadecane/water interface in the presence of Tween80. The measured maximum MG adsorption density decreases with the pre-adsorption of

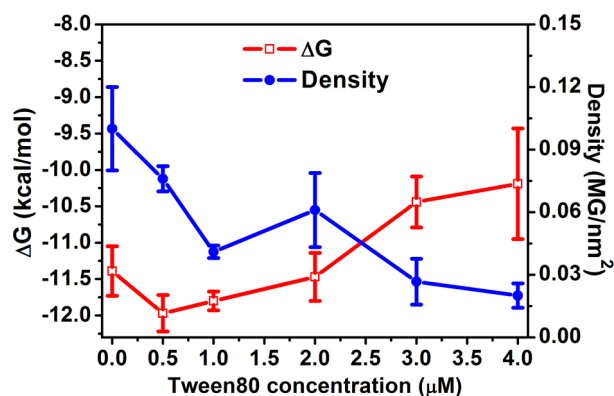


FIG. 4. The adsorption free energy (solid circles) and the saturated density (empty squares) of MG at the surfaces of oil droplets in a hexadecane/water emulsion in the presence of Tween80 at various concentrations.

Tween80. This supports the assumption that the adsorption of MG at the hexadecane/water interface is hindered by the surfactant coverage. Without charge-charge attraction, the measured maximum MG adsorption density and the adsorption free energy values both show a monotonically decreasing trend with an increase in Tween80 concentration. It was also observed that without charge-charge attraction, MG was not able to attach to the oil/water interface in the presence of Tween80 beyond 4  $\mu\text{M}$ , as evident in a barely detectable SH intensity during titration experiments (see the supplementary material<sup>45</sup>).

Experiments were also performed with the pre-adsorption of CTAB at the oil/water interface. Limited by the stability of the emulsion, only measurements with the addition of 0.5  $\mu\text{M}$  and 1  $\mu\text{M}$  CTAB were achieved. The fitting of the titration curves leads to an adsorption free energy of  $-9.2 \pm 0.2$  kcal/mol at both CTAB concentrations, and maximum MG densities at the interface of  $0.05 \pm 0.01$  and  $0.03 \pm 0.01$  MG/nm<sup>2</sup>, respectively. The adsorption free energy value was notably smaller than the values measured in the absence of surfactant and in the presence of the other two surfactants at the hexadecane/water interface.

#### D. Further discussion on the effect of surfactants and counter ions in the adsorption process

The zeta potential at the surface of the oil droplets in the emulsions used in the measurements was checked to verify the surface charge in the presence of surfactants and MG. The measurements confirm that the adsorption of SDS at the oil surface drives the surface potential to more negative values and the adsorption of Tween80 barely changes the surface potential, while the adsorption of CTAB or MG gradually changes the negative surface potential to relatively more positive values, as one would expect.

The change of the zeta potential at the oil surface during the titration experiments in the presence of surfactants was also monitored, with the typical data shown in Fig. 5. The results show that the adsorption of MG at the surface covered by Tween80 still drives the negative zeta potential towards zero. However, the adsorption of MG at the surface covered by SDS or CTAB does not change the zeta potential as expected. This observation reveals that the adsorption of the MG ions at these surfaces, which is evident by the increased SH scattering, has to be accompanied/affected by the counter ions in the solutions.

For the CTAB case in Fig. 5(c), the adsorption of positive MG ions at the interface is accompanied by a decrease, instead of an increase in the surface potential. This implies that the adsorption of MG<sup>+</sup> on this surface is accompanied either by the adsorption of more counter ions (Cl<sup>-</sup>) in the emulsions or a replacing of the positive CTAB ion at the surface, or both of them. For the SDS cases in Fig. 5(b), the adsorption of MG<sup>+</sup> barely causes reliable change in the surface zeta potential. This implies that the adsorption of MG ions at the oil/water interface covered by SDS with relatively high density may include an exchange between the MG<sup>+</sup> in the solution and the Na<sup>+</sup> that attaches with DS<sup>-</sup> at the interface. The adsorption of negatively charged Cl<sup>-</sup> to the surface together with MG<sup>+</sup> adsorption is less possible because of the charge-charge repulsion.

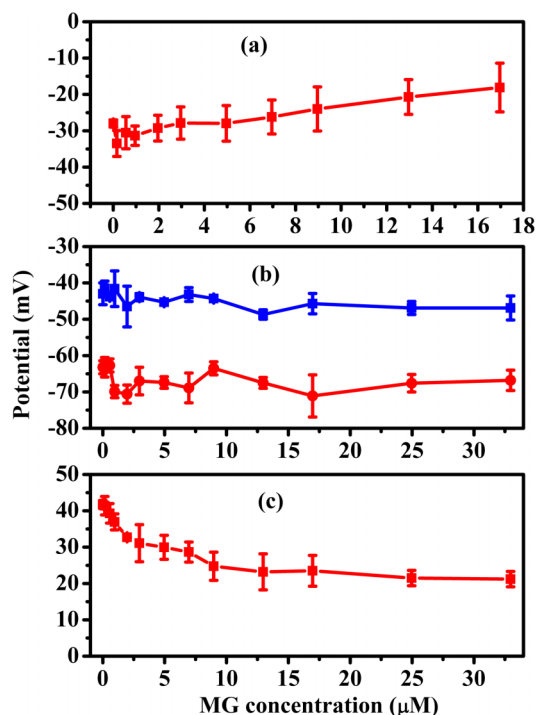


FIG. 5. The change of the zeta potential of the oil surface during the titration experiments in the presence of surfactants at typical concentrations (a) 3  $\mu\text{M}$  Tween80, (b) 0.1 mM and 2 mM SDS for blue and red curves, respectively, and (c) 1  $\mu\text{M}$  CTAB.

Based on above assumption, we performed a MG titration experiment with the emulsion containing 1 mM SDS and 1 mM NaCl. The saturated surface MG density value obtained in this experiment is essentially the same as that obtained without NaCl in the emulsion. The adsorption free energy is, however, slightly smaller ( $-9.9$  kcal/mol compared with  $-10.7$  kcal/mol). This comparison confirms the effect of counter ions in the titration experiments; it also supports that MG<sup>+</sup> may replace Na<sup>+</sup> during the titration experiment.

It has been reported by the Dai group that for polystyrene/water interfaces in colloids, the adsorption free energy of MG was reduced from  $-12.67$  to  $-10.46$  kcal/mol when the surface charge of the polystyrene changed from negative to positive.<sup>13</sup> Here, we also observed a change of approximately 2 kcal/mol in the adsorption free energy of MG ions at the hexadecane/water interface for emulsions containing surfactants of different charges. The measured change in the MG adsorption density at the interfaces is, however, significantly different from that at the polystyrene/water interface. At the polystyrene/water interface, the adsorption density of MG varies over a relatively small range of 0.25–0.37 MG/nm<sup>2</sup>. At the hexadecane/water interface, the adsorption density of MG varies over a relatively large range of 0.02–0.8 MG/nm<sup>2</sup>. This significant difference may be a result of several factors. First, the interaction between MG and hexadecane may differ from the interaction between MG and polystyrene and lead to different MG adsorption densities at their respective water interfaces. Also, we could assume that the charges at the oil/water interface are homogeneously distributed and with high mobility during the adsorption process, which makes them easily influence the adsorption process. In contrast, the

charge distribution at the surface of polystyrene may not be as homogeneous. So, there are local surface areas with low charge distribution and only weakly subjected to the influence of the surface charges. This assumption may also explain the observation that the adsorption of MG at the polystyrene/water interface is always with medium density (around 0.3 MG/nm<sup>2</sup>), compared with that at the oil/water interface (from 0.02 to 0.8 MG/nm<sup>2</sup>).

#### IV. CONCLUSION

Researchers have made extensive efforts to observe the behavior of surfactants at the oil/water interfaces of emulsions. Small angle neutron scattering and surfactant electrode measurements have been used to study the adsorption of SDS at the interfaces of oil/water emulsions at millimolar concentration levels.<sup>43</sup> The conformational structure and molecular dynamics of SDS at the oil/water interface with millimolar concentrations has also been investigated with the aid of an electron paramagnetic resonance probe.<sup>44</sup> SFG-VS studies have demonstrated the ability to obtain interfacial vibrational spectra of SDS, CTAB, and other surfactants with concentrations as low as tens of micromolars.<sup>14,18,21,23</sup> These reports contributed extensively towards understanding the structures and energetics of surfactants at oil/water interfaces. They have also demonstrated the difficulties in directly probing surfactants with low concentrations at oil/water interfaces in emulsions. In this work, we demonstrated that significant differences in adsorption free energy and molecular density of MG at the oil/water interface could be induced by surfactants at micromolar concentrations. The sensitive determination of the changed interfacial environment using SHG measurement provided more detailed information for the understanding of molecular interactions at the oil/water interface.

#### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21273277 and 21473249), the “1000 Talent Program” (The Recruitment Program of Global Experts), the “One Hundred Talents Project Foundation Program” and the “Western Action Plan (KGZD-EW-502)” from the Chinese Academy of Sciences, and the “Young Creative Sci-Tech Talents Cultivation Project of Xinjiang Uyghur Autonomous Region (Nos. 2013711016 and 2013711012).”

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