

Re-Evaluating the Surface Tension Analysis of Polyelectrolyte-Surfactant Mixtures Using Phase-Sensitive Sum Frequency Generation Spectroscopy

Dan Hu and Keng C. Chou*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

S Supporting Information

ABSTRACT: Surface tension (ST) has been the most important measure of a molecule's surface activity. However, in many cases the complex behaviors of ST are challenging to interpret. For example, aqueous solutions of sodium dodecyl sulfate (SDS) and poly(diallyldimethylammonium chloride) (PDADMAC) show dramatic changes in ST when the concentration of SDS varies. Although surfactants are generally described as “substances that reduce surface tension”, new evidence shows that ST may have little changes when a significant amount of SDS is present at the water surface. The decrease of surface entropy resulting from a better ordering of interfacial molecules, such as water, counteracts the decrease of surface enthalpy and is able to keep the ST nearly unchanged. The dramatic ST decrease and recovery of the SDS-PDADMAC mixtures was discovered to be a result of a surface charge reversal. Similar surface charge reversal was also observed in cationic surfactant and anionic polyelectrolyte mixtures.

Surfactants are amphiphilic compounds that contain both hydrophobic and hydrophilic groups. They adsorb at interfaces of hydrophobic and hydrophilic media, such as air/water or oil/water interfaces extending the hydrophobic group out of the bulk water into the air (oil), while the hydrophilic group stays in the water.¹ The presence of surfactants at an interface often significantly changes the properties of the interface. For example, the wetting and penetration effect, emulsification, dispersion, foaming, and detergency are some of the important properties of surfactants. Because of their broad applications, understanding surface activities of surfactants is an ongoing effort in both academic and industrial research.^{2,3}

Surface tension (ST) analysis is the most popular technique for studying surface activities of surfactants.^{4–6} While surfactants are generally described as “substances that reduce surface tension”, the situation is not so straightforward when other molecules, such as polyelectrolytes, are presented in the solution.^{7–9} The interaction between the surfactant and the polyelectrolyte produces a complex ST behavior, and a clear interpretation has been difficult. For example, one of the most studied systems is the mixture of the anionic surfactant sodium dodecyl sulfate (SDS) and the cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC). (Structures shown in the inset of Figure 1.) The SDS-PDADMAC mixture has been extensively studied partly

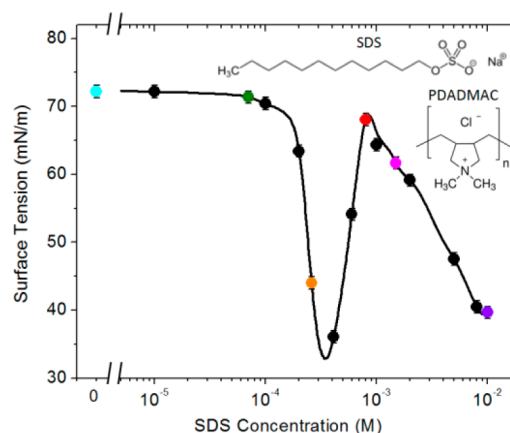


Figure 1. ST of aqueous PDADMAC solution (50 ppm) with various SDS concentrations. The solid line is a guide to the eye. The colored data points indicate the corresponding colored SFG spectra in Figure 3. The insets are the molecular structures of SDS and PDADMAC.

because the interaction becomes particularly pronounced for oppositely charged surfactants and polyelectrolytes.^{10–12} Figure 1 shows the ST of aqueous PDADMAC solutions with various SDS concentrations. PDADMAC is believed to be surface-inactive as it does not induce a ST change without a surfactant.^{7,13} Based on the ST measurements, both the SDS and PDADMAC remain surface-inactive until the SDS approaches 10^{-4} M. Above 10^{-4} M, ST shows a sharp decrease followed by a steep increase and a subsequent decrease. Previous studies by neutron reflectivity suggested that the adsorbed amount decreased by a factor of 2 in the 10^{-4} – 10^{-3} M region.¹⁰ However, a molecular-level understanding of the complex ST behavior is nonexistent because there has been no good analytical tool to obtain molecular-level information at the liquid surface.

Recent developments in phase-sensitive sum-frequency generation (SFG) spectroscopy have provided a new opportunity to study the surface activity of surfactants. While the traditional SFG vibrational spectroscopy measures only the amplitude of the second-order nonlinear optical susceptibility $|\chi^{(2)}|$,^{14,15} the phase-sensitive SFG spectroscopy also measures the phase of $\chi^{(2)}$. The advantage of the phase-sensitive SFG is that the spectrum of the imaginary $\chi^{(2)}$, $\text{Im}(\chi^{(2)})$, characterizes

Received: May 16, 2014

Published: October 9, 2014

surface vibrational resonances and their averaged orientations.^{16–18} In the current study, we re-evaluate the ST analysis with the new information obtained from the phase-sensitive SFG spectra and present a molecular-level understanding of the ST. We found that ST is a misleading indicator for the surface activity of the surfactant. The complex behavior of the ST in Figure 1 is related to a surface charge reversal at the water surface.

Before looking into the ST of SDS-PDADMAC mixtures, it is useful to understand the ST of pure SDS solutions, as shown in Figure 2I. Figure 2II,III shows the SFG spectra of SDS

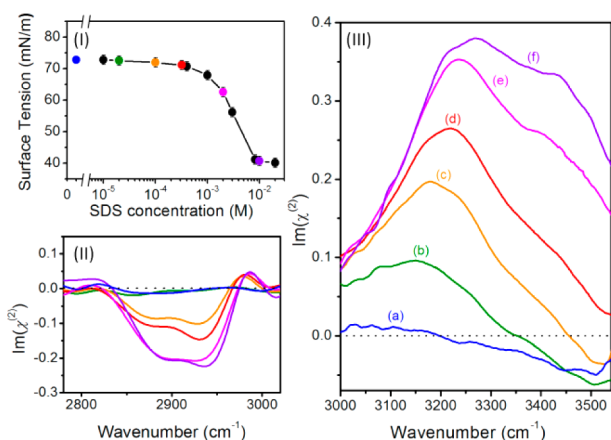


Figure 2. (I) ST of water with various SDS concentrations. (II) $\text{Im}(\chi^{(2)})$ spectra of air/water interfaces in the CH stretch region. Deuterated water was used to avoid interference with the OH stretch. The peaks near 2875 and 2930 cm^{-1} were assigned to the CH_3 symmetric stretch and Fermi resonance. The CH peaks appear negative when the CH_3 pointing up.¹⁹ (III) $\text{Im}(\chi^{(2)})$ spectra in the OH stretch region. Data of the same color indicate the same SDS concentration: (a) 0 M (blue), (b) 2×10^{-5} M (green), (c) 1×10^{-4} M (orange), (d) 3.2×10^{-4} M (red), (e) 2×10^{-3} M (magenta), (f) 1×10^{-2} M (purple).

solutions in the CH and OH regions, respectively. Figure 2I suggests that SDS is nearly surface-inactive until its concentration reaches $\sim 5 \times 10^{-4}$ M. However, Figure 2II shows that a significant amount of SDS has been observed on the water surface at 1×10^{-4} M (orange), and Figure 2III shows that the spectrum of water has significantly changed at 2×10^{-5} M (green). These SFG spectra suggest that ST is a lagging indicator for the surfactant's surface activity.

A big puzzle was how the ST of SDS solutions near 3.2×10^{-4} M (red color) could remain similar to that of pure water when the SFG spectra indicated that a significant amount of SDS was present on the surface and the structure of water had dramatically changed. Answering this question requires a better understanding of the $\text{Im}(\chi^{(2)})$ spectra. The pure water

spectrum in Figure 2III,a has two distinguishable OH bands: a positive OH band near 3100 cm^{-1} and a negative OH band near 3450 cm^{-1} . For the OH symmetric stretch, the $\text{Im}(\chi^{(2)})$ can be positive or negative, depending on the sign of the OH projection with respect to the surface normal: a positive peak indicates water molecules with the hydrogen pointing toward the air (up), and a negative peak indicates the OHs pointing toward the bulk (down).^{20–22} (See Supporting Information (SI).) Nihonyanagi et al., using phase-sensitive SFG along with molecular dynamics (MD) simulation, showed that the H-bonded OH groups near the surface, on average, point down toward the bulk, causing the negative OH band to be at a frequency similar to that of bulk water (3410 cm^{-1}).²³ The origin of the low-frequency peak near 3100 cm^{-1} has been controversial. Tian et al. proposed that “ice-like” tetrahedrally bonded water molecules have a dominating contribution to the positive band near 3100 cm^{-1} .²⁴ Nevertheless, in Nihonyanagi's MD simulation, the positive peak was attributed to water dimers, which generates a vertically induced dipole pointing toward the air,²³ rather than tetrahedrally coordinated water molecules. On the other hand, the MD simulations carried out by Pieniazek et al. using a three-body interaction model showed that the positive peak at the lower frequency is a result of cancellation between the positive contributions from four hydrogen-bonded (H-bonded) molecules and the negative contribution from those molecules with one or two broken H-bonds.²⁵ In the current study, the origin of the low-frequency band is not of a particular concern because flipping the 3450 cm^{-1} band from negative to positive has to involve flipping the averaged water orientation from pointing down to pointing up.¹⁸ It has been experimentally shown that an all-negative spectrum was observed when the water surface was occupied by positively charged surfactants, and an all-positive spectrum was observed when the water surface was occupied by negatively charged surfactants.^{19,26,27} Therefore, the broad positive bands in Figure 2III,d–f indicate that the negatively charged SDS induced an upward averaged OH orientation. When the SDS concentration increased, a more ordered water structure formed as indicated by the enhanced OH peaks. The origin of the OH frequency shift is not clearly known, but it could be related to a change in the strength of H-bonds or vibrational coupling.¹⁵

The formation of a more ordered water structure induced by SDS provides an explanation of how the ST can remain nearly constant at a lower SDS concentration. ST is the Gibbs free energy per unit surface area: $\gamma \equiv (\partial G/\partial A)_{T,P}$ where A is the surface area, T is the temperature, and P is the pressure. Since $\gamma = H^s - TS^s$, where H^s is the surface enthalpy and S^s is the surface entropy, the change of ST, $\Delta\gamma$, is a combined effect of ΔH^s and ΔS^s . The ΔH^s is negative for the adsorption process. On the other hand, the formation of more ordered water and SDS structures suggests a decrease in the surface entropy (ΔS^s

Table 1. Surface Tension, γ , Surface Entropy, S^s , $-TS^s$, and Surface Enthalpy H^s of SDS Solutions Measured at $T = 293 \text{ K}^a$

[SDS] (M)	γ (mN/m)	S^s (mN/m·K)	$-TS^s$ (mN/m)	H^s (mN/m)
0	72.7 ± 0.2	0.15 ± 0.04	-44 ± 12	117 ± 12
2×10^{-5}	72.5 ± 0.2	0.14 ± 0.04	-41 ± 12	114 ± 12
3.2×10^{-4}	71.1 ± 0.2	0.10 ± 0.04	-29 ± 12	100 ± 12
2×10^{-3}	62.5 ± 0.2	-0.05 ± 0.04	15 ± 12	48 ± 12
1×10^{-2}	40.6 ± 0.2	0.04 ± 0.04	-12 ± 12	52 ± 12

^a $-TS^s$ and H^s are calculated values using γ and S^s .

< 0 or $-TS^s > 0$), which counteracts the negative ΔH^s and can potentially keep the ST stable. The ST would then drop after S^s reaches its minimum. To test this model, the surface entropy and surface enthalpy were measured using $S^s = -(\partial\gamma/\partial T)_P$ and $H^s = \gamma + TS^s$, respectively. (Derivations given in the SI.) Table 1 summarizes the measured S^s and H^s . It is clear that the ST shows little decrease at SDS concentration below 2×10^{-3} M because the decrease in H^s is compensated by the decrease in S^s (or the increase of $-TS^s$). Since the surface entropy is an excess property relative to the entropy of bulk water, S^s can become negative. The surface entropy reached its minimum near 2×10^{-3} M which is consistent with the onset of the ST drop in Figure 2I. Theoretically, the adsorbed SDS molecules also contribute to the ΔS^s , but its contribution cannot be separated from that of water in the measurements. The small increase of H^s from 48 mN/m at 2×10^{-3} M to 52 mN/m at 1×10^{-2} M can be explained by the electrostatic repulsive force between SDS as a closely packed SDS layer is enthalpically unfavorable. The S^s increases from -0.05 mN/m·K at 2×10^{-3} M to 0.04 mN/m·K at 1×10^{-2} M cannot be explained by the SFG spectra of water and SDS as both SDS and water show the highest SFG intensities at 1×10^{-2} M. It is possible that the S^s increase at 1×10^{-2} M SDS is related to the relative geometry between water and SDS because the relative position of water and SDS cannot be seen from the separate spectra of SDS and water. This assumption is consistent with fact that the critical micelle concentration (CMC) of SDS is around 8×10^{-3} M.²⁸

With the addition of PDADMAC, the behavior of water is significantly different. Figure 3 shows the SFG spectra of the

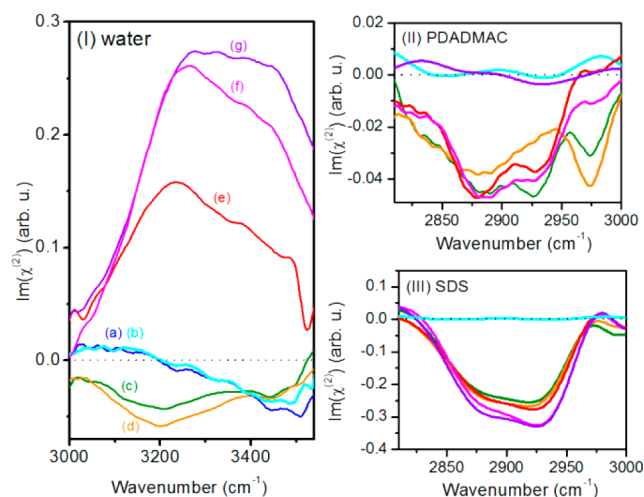


Figure 3. (I) $\text{Im}(\chi^{(2)})$ spectra of (a) pure water (blue) and PDADMAC solutions (50 ppm) with (b) 0 M (cyan), (c) 7×10^{-5} M (green), (d) 2.5×10^{-4} M (orange), (e) 8×10^{-4} M (red), (f) 1.6×10^{-3} M (magenta), and (g) 10^{-2} M (purple) of SDS. Spectra of (II) PDADMAC and (III) SDS. Spectra of the same color have the same SDS concentration.

aqueous PDADMAC solutions (50 ppm) with various SDS concentrations in the OH and CH regions. The CH spectra in Figure 3II were obtained with deuterated SDS in the solutions, therefore the spectra represent the CH peaks from PDADMAC. Because deuterated PDADMAC was unavailable, Figure 3III contained signals from both PDADMAC and SDS. However, it was dominated by SDS because the signal of SDS was one order-of-magnitude larger than that of PDADMAC. A higher SFG intensity from SDS is expected because SDS forms

a much more ordered surface layer in comparison to PDADMAC. The peaks at 2875, 2925, and 2970 cm^{-1} were assigned to the CH_3 symmetric stretch, Fermi resonance, and CH_3 asymmetric stretch, respectively.

The SFG spectra in Figure 3I,b and II (cyan) confirmed that the PDADMAC is not surface-active without SDS. Figure 3I,b is nearly identical to the spectrum of pure water, and Figure 3II (cyan) shows PDADMAC was undetectable without SDS.

Surprisingly, adding 7×10^{-5} M of the negatively charged SDS makes the surface positively charged as indicated by an all-negative water spectrum in Figure 3I,c (green). A reasonable explanation is that SDS at the surface attracted the positively charged PDADMAC to the surface. Since SDS is monovalent and the polyelectrolyte is multivalent, a single SDS molecule at the water surface can attract multiple positive charges carried by a PDADMAC molecule, making the surface overall positive, as illustrated in Figure 4a. This is consistent with previous ST

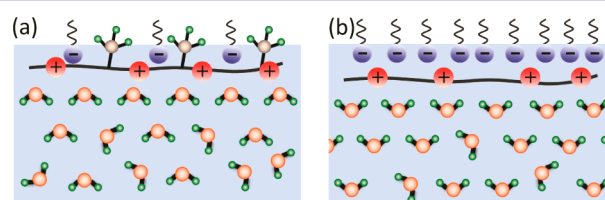


Figure 4. Illustration of the proposed models. (a) A small amount of SDS attracts the PDADMAC to the surface, making the surface overall positively charged and the net orientation of water's OHs points down. (b) A larger amount of SDS on the surface makes the surface negatively charged, and the net orientation of OHs points up.

studies suggesting that the SDS and PDADMAC complex formed at this low concentration is between an isolated SDS and PDADMAC.^{9,29} Figure 3II,III also confirmed that both PDADMAC and SDS were observed at the water surface with 7×10^{-5} M of SDS (green curves). A comparison between Figure 2II and Figure 3III indicates that at the same SDS concentration significantly more SDS was attracted to the surface in the presence of PDADMAC.

The dramatic decrease and recovery of the ST between 10^{-4} M and 10^{-3} M of SDS, as shown in Figure 1, has been difficult to explain with hypotheses developed based on ST and neutron reflection studies.^{8,29–31} The SFG spectra in Figure 3 suggest that the rapid ST decrease and recovery originate from a surface charge reversal. From 2.5×10^{-4} M to 8×10^{-4} M of SDS, the spectra of water changed from an all-negative OH spectrum in Figure 3I,d (orange) to an all-positive spectrum in Figure 3I,e (red), which indicated that the surface charge changed from positive to negative. Above 8×10^{-4} M SDS, the ordering of water increased with increasing SDS concentration and eventually reached its maximum where the ST drops again above 1×10^{-3} M, similar to that of pure SDS solution in Figure 2I. Figure 3II shows that the increased adsorption of SDS at the surface depleted PDADMAC from the surface. At 10^{-2} M SDS (purple curves), PDADMAC became undetectable, whereas the SDS signal reached maximum. It has been observed that the strong interaction between polyelectrolytes and surfactants leads to formation of aggregates and phase separation in the bulk at a higher concentration (see ref 32 for a review). The detailed structure of the SDS-PDADMAC complex at the surface is not well understood.³³ However, the current study suggests that PDADMAC is located below the top SDS layer as illustrated in Figure 4b. Previous neutron

reflectivity studies have shown that the thickness of the surface layer stayed within 17–19 Å when SDS was varied from 10^{-6} to 10^{-1} M.¹⁰ Because the length of a SDS molecule is about 18 Å, the study suggested that surface aggregation or phase separation did not occur at the water surface. The SFG spectra suggest that during the process of the surface charge reversal, the surface charge density decreases, which causes an increase in the surface entropy and a decrease in the ST. As the surface accumulates more SDS and becomes negatively charged, the entropy decreases again, and the ST recovers. To correlate the SFG spectra with thermodynamic functions, measurements of the S^s and H^s were attempted. However, the measurements were unreliable because of a well-known slow decrease of ST over time in surfactant-polyelectrolyte mixtures.³⁴ Although the time dependence is only a few percent, it is larger than the temperature dependence. Since the SFG spectra had a background fluctuation of 5–10%, the time-dependence showed little effect on the SFG spectra.

To test the generality of the observed surface charge reversal, mixtures of cationic surfactant cetyltrimethylammonium bromide (CTAB) and anionic polyelectrolyte poly(sodium styrenesulfonate) (PSS) were studied. In this case, flipping of the SFG spectrum from positive to negative was observed between 10^{-4} M and 10^{-3} M of CTAB (data shown in SI). Therefore, the surface charge reversal is a common phenomenon of surfactant-polyelectrolyte mixtures, not linked to the specific properties of SDS and PDADMAC.

In conclusion, ST was found to be an inaccurate indicator for the surface activities of surfactants because the decrease of surface entropy counteracted the decrease of surface enthalpy and kept the ST nearly unchanged at a lower surfactant concentration. The phase-sensitive SFG spectra showed that the origin of the dramatic changes in the ST of ionic surfactant-polyelectrolyte solutions is a charge reversal at the water surface.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, theoretical derivations, and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

kcchou@chem.ubc.ca

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Institute for Oil Sands Innovation, the Natural Sciences and Engineering Research Council of Canada, and the Canada Foundation for Innovation. The authors wish to thank Dr. Murray R. Gray for his support with this project.

■ REFERENCES

- (1) Nagarajan, R.; Ruckenstein, E. *Langmuir* **1991**, *7*, 2934.
- (2) Lu, J. R.; Thomas, R. K.; Penfold, J. *Adv. Colloid Interface Sci.* **2000**, *84*, 143.
- (3) Alexandridis, P.; Hatton, T. A. *Colloids Surf., A* **1995**, *96*, 1.
- (4) Eastoe, J.; Dalton, J. S. *Adv. Colloid Interface Sci.* **2000**, *85*, 103.
- (5) Claussen, W. F. *Science* **1967**, *156*, 1226.
- (6) Li, D. C.; Wagner, N. J. *J. Am. Chem. Soc.* **2013**, *135*, 17547.

(7) Bain, C. D.; Claesson, P. M.; Langevin, D.; Meszaros, R.; Nylander, T.; Stubenrauch, C.; Titmuss, S.; von Klitzing, R. *Adv. Colloid Interface Sci.* **2010**, *155*, 32.

(8) Taylor, D. J. F.; Thomas, R. K.; Penfold, J. *Adv. Colloid Interface Sci.* **2007**, *132*, 69.

(9) Bahramian, A.; Thomas, R. K.; Penfold, J. *J. Phys. Chem. B* **2014**, *118*, 2769.

(10) Penfold, J.; Tucker, I.; Thomas, R. K.; Taylor, D. J. F.; Zhang, X. L.; Bell, C.; Breward, C.; Howell, P. *Langmuir* **2007**, *23*, 3128.

(11) Campbell, R. A.; Angus-Smyth, A.; Arteta, M. Y.; Tonigold, K.; Nylander, T.; Varga, I. *J. Phys. Chem. Lett.* **2010**, *1*, 3021.

(12) Nizri, G.; Lagerge, S.; Kamyshny, A.; Major, D. T.; Magdassi, S. *J. Colloid Interface Sci.* **2008**, *320*, 74.

(13) Lieske, A.; Jaeger, W. *Macromol. Chem. Phys.* **1998**, *199*, 255.

(14) Rao, Y.; Li, X.; Lei, X. G.; Jockusch, S.; George, M. W.; Turro, N. J.; Eisenthal, K. B. *J. Phys. Chem. C* **2011**, *115*, 12064.

(15) Tyrode, E.; Johnson, C. M.; Kumpulainen, A.; Rutland, M. W.; Claesson, P. M. *J. Am. Chem. Soc.* **2005**, *127*, 16848.

(16) Stiofkin, I. V.; Weeraman, C.; Pieniazek, P. A.; Shalhout, F. Y.; Skinner, J. L.; Benderskii, A. V. *Nature* **2011**, *474*, 192.

(17) Ji, N.; Ostroverkhov, V.; Tian, C. S.; Shen, Y. R. *Phys. Rev. Lett.* **2008**, *100*, 096102.

(18) Nihonyanagi, S.; Mondal, J. A.; Yamaguchi, S.; Tahara, T. *Annu. Rev. Phys. Chem.* **2013**, *64*, 579.

(19) Mondal, J. A.; Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. *J. Am. Chem. Soc.* **2010**, *132*, 10656.

(20) Shen, Y. R. *Annu. Rev. Phys. Chem.* **2013**, *64*, 129.

(21) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. *J. Chem. Phys.* **2009**, *130*, 204704.

(22) Hu, D.; Yang, Z.; Chou, K. C. *J. Phys. Chem. C* **2013**, *117*, 15698.

(23) Nihonyanagi, S.; Ishiyama, T.; Lee, T.; Yamaguchi, S.; Bonn, M.; Morita, A.; Tahara, T. *J. Am. Chem. Soc.* **2011**, *133*, 16875.

(24) Tian, C. S.; Shen, Y. R. *Chem. Phys. Lett.* **2009**, *470*, 1.

(25) Pieniazek, P. A.; Tainter, C. J.; Skinner, J. L. *J. Chem. Phys.* **2011**, *135*, 044701.

(26) Mondal, J. A.; Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. *J. Am. Chem. Soc.* **2012**, *134*, 7842.

(27) Chen, X. K.; Hua, W.; Huang, Z. S.; Allen, H. C. *J. Am. Chem. Soc.* **2010**, *132*, 11336.

(28) Fuguet, E.; Rafols, C.; Roses, M.; Bosch, E. *Anal. Chim. Acta* **2005**, *548*, 95.

(29) Staples, E.; Tucker, I.; Penfold, J.; Warren, N.; Thomas, R. K.; Taylor, D. J. F. *Langmuir* **2002**, *18*, 5147.

(30) Taylor, D. J. F.; Thomas, R. K.; Li, P. X. *Langmuir* **2003**, *19*, 3712.

(31) Merta, J.; Stenius, P. *Colloid Polym. Sci.* **1995**, *273*, 974.

(32) Piculell, L. *Langmuir* **2013**, *29*, 10313.

(33) Monteux, C.; Williams, C. E.; Meunier, J.; Anthony, O.; Bergeron, V. *Langmuir* **2004**, *20*, 57.

(34) Noskov, B. A.; Grigoriev, D. O.; Lin, S. Y.; Loglio, G.; Miller, R. *Langmuir* **2007**, *23*, 9641.