

Charge Inversion at the Surface by Adsorption of Trivalent Cations on a Langmuir Monolayer

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IR-visible sum-frequency generation (SFG) spectroscopy was used to study cation adsorption and charge inversion behavior at the water/lipid interface of a 1, 2-dimyristoyl-*sn*-glycero-3-phosphatidic acid (DMPA) monolayer. At low subphase salt (LaCl_3) concentrations, the sum-frequency signal from interfacial water molecules decreased with increasing salt concentration of the subphase water. At around $\sim 1 \mu\text{M}$ of bulk LaCl_3 concentration, the SFG signal was at its minimum, suggesting charge neutrality at this specific salt concentration. With further increase in the salt concentration, a small SFG signal from the interfacial water molecules was again observed. This phenomenon was explained by an overcompensation of the surface charge by trivalent cations causing an inversion of surface charge, which caused an alignment of the interfacial water molecules at high salt concentrations.

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I. INTRODUCTION

Processes and structures involving electrostatic interactions are abundant in soft matter, and they play an important role in colloidal, polymeric, and biological systems [1]. For example, electrostatic interactions determine many of the membrane structural properties such as rigidity, structural stability, lateral phase transitions, and dynamics [2,3]. Electric charges also have an important role in processes involving more than one membrane, such as membrane adhesion and cell-cell interaction, as well as in the overall interaction of the membranes.

In electrolytes, one of the interesting phenomena due to the electrostatic interaction in soft matter is charge inversion, where charges at an interface attract multivalent counterions in excess of their own normal charge density, causing a sign change of the net surface charge [1]. For example, in the presence of positive multivalent ions (*e.g.*, polycations), the DNA double helix acquires a net positive charge and drifts as a positive particle in an electric field. Analogies of charge inversion in other fields of physics are abundant [4]. In a recent X-ray reflectivity study, a 1, 2-dimyristoyl-*sn*-glycero-3-phosphatidic acid (DMPA) lipid monolayer at an air-water interface was investigated as the concentration of LaCl_3 at the sub-

phase water was changed [5]. The result of that study showed that even very small ($< 1 \mu\text{M}$) bulk LaCl_3 concentrations, the La^{3+} cations adsorbed from the solution to the lipid headgroups would make the interface positively charged. Recently, a theoretical study proposed several mechanisms to account for this phenomenon [6].

The interfacial water in the subphase could be a very sensitive probe for this charge inversion phenomenon, as the surface charge and the induced electric field would be strong enough to align the water dipoles near the interface [7]. The net orientation of these interfacial water molecules could be conveniently monitored by using a surface-sensitive nonlinear optical technique [8]. Infrared-visible sum-frequency generation (SFG) was used in this study to probe the water molecules below the DMPA Langmuir monolayer under different concentrations of LaCl_3 in the subphase. As a second-order nonlinear optical process, SFG is forbidden in an isotropic medium, but is allowed when the symmetry is broken [9]. Thus, it is an ideal technique to monitor the orientation of water under different conditions.

In this study with a DMPA Langmuir monolayer having charged headgroups on top of the water subphase with varying LaCl_3 concentrations, the SFG signal in the OH stretch vibration region at first decreased with increasing salt concentration, reached a minimum, and increased a bit with further addition of LaCl_3 to the solution. This SFG minimum is thought to be caused by

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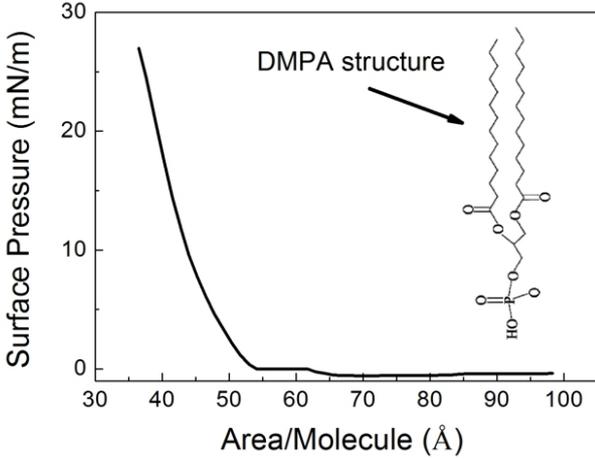


Fig. 1. Surface pressure vs. molecular area for the DMPA monolayer system. Inset: chemical structure of DMPA.

a condition where the interfacial layer becomes charge-neutral due to cation adsorption on an initially negatively charged surface. The slight increase afterwards indicates that the interfacial water molecules become more ordered, suggestive of charge inversion due to overcompensation of adsorbed cations.

II. EXPERIMENT

1,2-dimyristoyl-*sn*-glycero-3-phosphatidic acid (DMPA) lipid molecules (chemical structure shown in the inset of Figure 1) were purchased from Avanti Polar Lipids. The DMPA was spread from a chloroform-methanol (3 : 1, both from HPLC grade) solution onto ultrapure water (18.2M Ω -cm resistivity) of pH 5.7 in a homemade Langmuir trough. The π - A isotherm in Figure 1 recorded at a barrier speed of 0.8 $\text{\AA}^2/\text{min}$ (per molecule), is similar to the published results [5,10]. All the SFG measurements were performed at a surface molecular density $n_s \sim 1/40 \text{\AA}^2$, which also corresponds to the charge density as the DMPA headgroup dissociates 1 of the 2 protons available in our pH condition [11]. The barrier in the Langmuir trough was controlled to maintain a constant surface pressure during the SFG measurement. The SFG experiments were carried out with LaCl₃ (99.9% Aldrich LTD) concentrations in the subphase water ranging from 10^{-7} mol/L to 10^{-5} mol/L. The sample temperature was room temperature (21 $^\circ\text{C}$) for all the measurements.

The SFG experiment employed a home-built optical parametric generator/amplifier (OPG/OPA) system pumped with a picosecond Nd:YAG laser (Continuum PY61-10, 10-Hz repetition rate) [12]. The OPG/OPA based on a LiNbO₃ crystal generated tunable IR pulse from 2.5 to 4 μm , and the second harmonic of the Nd:YAG laser fundamental beam was used as the visible input beam. Typical input energies were 1 mJ/pulse

and $\sim 150 \mu\text{J}/\text{pulse}$, and incident angles were $\theta_{vis} = 49^\circ$ and $\theta_{IR} = 60^\circ$ for the visible and the tunable infrared beams, respectively. The pulsewidths of the input beams were about 30 ps. The two beams were focused and overlapped at the air/liquid interface, and the sum-frequency output in the reflection direction was spatially and spectrally filtered and detected by using a photomultiplier tube. Typically, the data for the spectrum were taken at every 5 cm^{-1} , and at least 200 laser shots were averaged for each data point. The spectrum was normalized to the sum-frequency spectrum from a z -cut quartz sample. The frequency of the infrared beam was calibrated by measuring the absorption spectrum from a polystyrene film.

III. RESULT AND DISCUSSION

To obtain quantitative result, the SFG spectrum is usually fitted by using the following Lorentzian profile;

$$I(\omega_{SFG} = \omega_{ir} + \omega_{vis}) = \left| \chi_{NR}^{(2)} + \sum_q \frac{A_q}{(\omega_{IR} - \omega_q + i\Gamma_q)} \right|^2,$$

where χ_{NR} , and ω_{IR} , are the nonresonant contribution to the susceptibility and the laser frequency, and A_q , ω_q , and Γ_q refer to the strength, the resonance frequency, and the damping constant of the q th vibrational mode, respectively. A_q is nonvanishing only if there exists a net polar orientation of molecules as in the surface or interface. If the orientational distribution is isotropic, A_q vanishes [7].

The surface pressure versus molecular-area (π - A) isotherm of DMPA shown in Figure 1 was used to control the surface charge density, in particular, to identify conditions under which the DMPA surface charge density ($\sigma_s \sim 1e^{-}/40 \text{\AA}^2$) was independent of the LaCl₃ bulk concentration [14]. In the present study, the surface pressure was set at 15 mN/m and was maintained at that value during the measurements to within 1% by adjusting the barrier.

Figure 2(a) is the SFG spectra from the Langmuir monolayer with various LaCl₃ concentrations under S-SFG, S-vis, P-ir polarization conditions (SSP). Four resonant peaks of vibration modes were found in the range from 2800 to 3600 cm^{-1} . The two dominant peaks originated from the terminal methyl group of DMPA, and were assigned to the CH₃ symmetric stretch (2875 cm^{-1}) and the CH₃ Fermi resonance (2942 cm^{-1}) [15]. There is no intensity from the CH₂ symmetric stretch and CH₂ asymmetric stretch, which indicates that the molecules in the monolayer are very well ordered with little gauche defects.

We are more interested in the peaks of the OH vibration mode of interfacial water molecules observed above

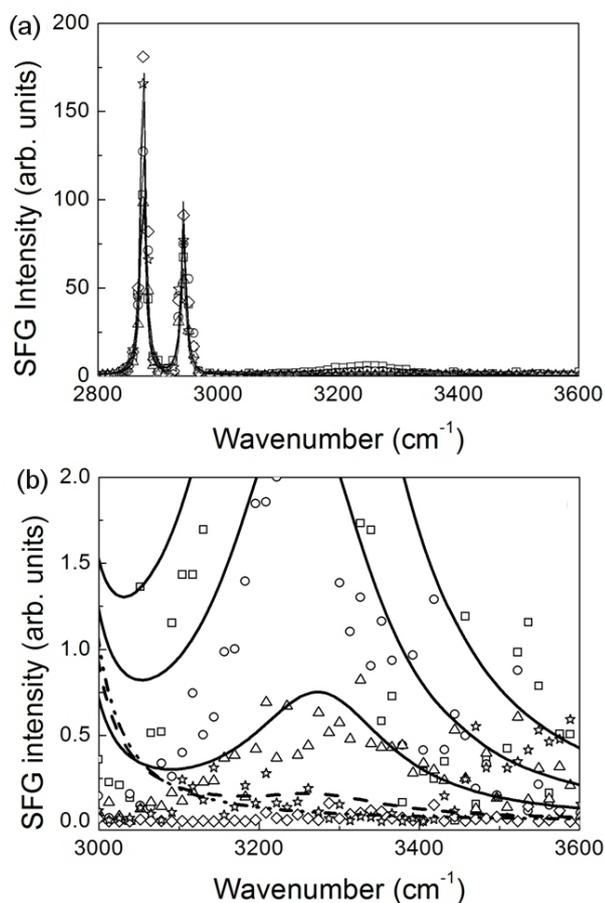


Fig. 2. (a) SFG spectra from the lipid/water interface of a monolayer (at surface pressure ~ 15 mN/m) of DMPA at different LaCl_3 bulk concentrations. Square, Circle, Triangle, Diamond, and Star indicate pure water, 1.0×10^{-7} , 3.1×10^{-7} , 7.1×10^{-7} and 1.4×10^{-5} (M/L) LaCl_3 solutions, respectively (b) SFG spectra in the OH region, magnified by 100 times. The dash-dot-dot line and the dashed line are fitted results at 7.1×10^{-7} (M/L) and 1.4×10^{-5} (M/L) LaCl_3 bulk concentrations (M/L), respectively.

3200 cm^{-1} , which have been assigned to the OH ice-like (3250 cm^{-1}) and the OH liquid-like (3450 cm^{-1}) peaks [15]. It is because the focus of this study is the charge inversion behavior at the lipid/water interface of a DMPA monolayer, in which the alignment of interfacial water molecules can be a signature of a possible electric field produced from the surface charges adsorbed at the lipid/water interface. Figure 2(b) shows the SFG spectra in the OH-stretch vibration region for several different bulk LaCl_3 concentrations. The peak of the OH vibration modes decreased as the LaCl_3 concentration increased from 1×10^{-7} to $\sim 7 \times 10^{-7}$ mol/L, but above 7×10^{-7} mol/L, the spectrum increased slightly. Admittedly, the data is noisy due to the weak SFG signal. The SFG signal, in general, is expected to decrease in strong electrolyte because the electrostatic interactions are exponentially screened beyond the Debye screening

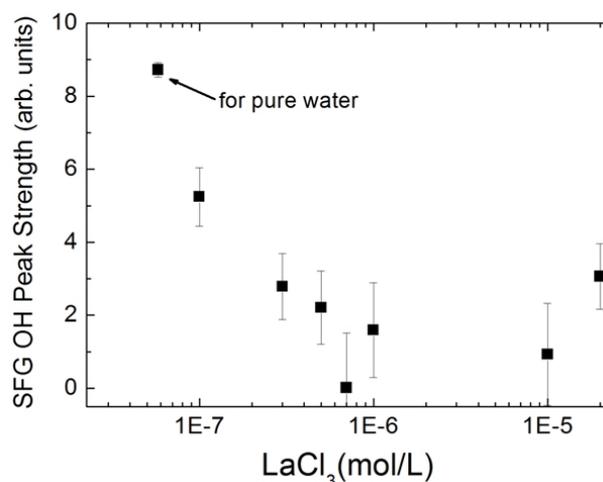


Fig. 3. Sum of the SFG peak strengths of two OH modes vs. LaCl_3 bulk concentration.

length $\lambda_D = (8\pi e^2 I / \epsilon k_B T)^{-1/2}$ (I is an ionic strength) [2]. These spectra in the OH region were fitted, and the sums of two OH-vibration peak strengths are plotted as a function of LaCl_3 concentration in Figure 3.

Starting from the ultrapure water subphase, SFG signal from interfacial water molecules was large, indicating interfacial water molecules are well ordered by the strong electric field from the negatively charged surface of the bare DMPA headgroups [16]. We expect most of the first protons in the PO_4H headgroup to be dissociated as the local pH is expected to be higher than $\text{pK}_{a1} = 2.1$ [17]. As the subphase LaCl_3 concentration was increased, the sum-frequency signal from interfacial water molecules decreased. As the salt concentration was increased, negative charges at the headgroup of DMPA were compensated for more by the cations (La^{3+}) to reduce the net negative charge at the lipid/water interface. This would weaken the strong electric field from the negative charges of the DMPA headgroups at the interface, and alignment of interfacial water molecules due to this electric field would be gradually disturbed, causing a reduction in the SFG signal. At this point, the second proton of the DMPA headgroup would be removed as the local (interfacial) pH would be larger than $\text{pK}_{a1} = 7.21$ [5].

At around an $\sim 1 \mu\text{M}$ bulk LaCl_3 concentration, the SFG signal in Figure 3 was minimized, suggesting charge neutrality at this specific salt concentration. Cation adsorption at this concentration serves to disrupt the strong polar ordering of water molecules within the interfacial region, with $\sim 2 \text{ La}^{3+}$ cations bound to ~ 3 DMPA headgroups [5].

With a further increase in the salt concentration, a small SFG signal from the interfacial water molecules was seen again, as in Figure 3. This phenomenon was explained by an overcompensation of the surface charges by trivalent La^{3+} cations, causing an inversion of the

surface charges, which caused an alignment of interfacial water molecules (in a direction opposite to that for pure water) at higher salt concentrations.

IV. CONCLUSION

Proposed charge inversion upon the adsorption of multivalent cations by the headgroup of a Langmuir monolayer was investigated by monitoring the alignment of interfacial water molecules at different salt concentrations. The slight increase in the SFG signal at high subphase salt concentrations suggested a charge inversion behavior, demonstrating the complex nature of the adsorption process, which includes monolayer adsorption, surfactant restructuring, surface charge inversion, and water reorientation.

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REFERENCES

- [1] See, for example, G. Caracciolo, D. Pozzi, R. Caminiti and H. Amenitsch, *Chem. Phys. Lett.* **429**, 250 (2006).
- [2] J. N. Israelachvili, *Intermolecular and Surface Force* (Academic Press, London, 1990).
- [3] J. S. Hwang, M. H. Son, J. H. Oh, D. Ahn, S. H. Hong, H. K. Kim and S. W. Hang, *J. Korean Phys. Soc.* **50**, 902 (2007).
- [4] A. Y. Grosberg, T. T. Nguyen and B. I. Shklovskii, *Rev. Mod. Phys.* **74**, 2 (2002).
- [5] J. Pittler, W. Bu, D. Vanin, A. Travesset, D. J. McGillivray and M. Löche, *Phys. Rev. Lett.* **97**, 046102 (2006).
- [6] J. Farauto and A. Travesset, *J. Phys. Chem. C* **111**, 987 (2007).
- [7] Y. R. Shen and V. Ostroverkhov, *Chem. Rev.* **106**, 1140 (2006).
- [8] J. Sung, K. Park and D. Kim, *J. Phys. Chem. B* **109**, 18507 (2005).
- [9] See, for example, R. W. Boyd, *Nonlinear Optics* (Academic Press, 2002).
- [10] J. Zhang, D. Mandler and P. R. Unwin, *Chem. Commun.* **4**, 450 (2004).
- [11] In stoichiometry, the dissociation constants of the first and the second protons of DMPA are $pK_{a1} = 2.1$ and $pK_{a2} = 7.21$, respectively [13].
- [12] J. Sung and D. Kim, *J. Korean Phys. Soc.* **51**, 145 (2007).
- [13] P. W. Atkins, *Physical Chemistry* (Oxford University Press, 1998).
- [14] M. Lösche and H. Möhwal, *J. Colloid Interface Sci.* **131**, 1 (1989).
- [15] S. Roke, J. Schins, M. Müller and M. Bonn, *Phys. Rev. Lett* **90**, 128101 (2003).
- [16] D. E. Gragson, B. M. McCarty and G. L. Richmond, *J. Am. Chem. Soc.* **119**, 6144 (1997).
- [17] A. Travesset and D. Vaknin, *Europhys. Lett.* **74**, 181 (2006).