Effect of charge on the mechanical properties of surfactant bilayers

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Charge effects on the mechanical properties of surfactant bilayers have been measured, for a system with a low ionic strength, using small-angle neutron scattering and neutron spin echo spectroscopy. We report that, not only does increasing the surface charge density lead to greater structural ordering and a stiffening of the membrane, which is consistent with classical theory of charge effects on membranes, but also that the relaxation rate of the membrane thickness fluctuations decreases without affecting the fluctuation amplitude. From the relaxation rate we demonstrate, using recent theory, that the viscosity of the surfactant membrane is increased with surface charge density, which suggests that the amount of charge controls the diffusion behavior of inclusions inside the membrane. The present results confirm that the thickness fluctuation relaxation rate and amplitude are tuned independently since the membrane viscosity is only influencing the relaxation rate. This work demonstrates that charge stabilization of lamellar bilayers is not merely affected by intermembrane interactions and structural ordering but that intramembrane dynamics also have a significant contribution.

1 Introduction

The mechanical properties of soft membranes, such as surfactant or biological membranes, have been intensively studied in order to better understand membrane structural and morphological transitions.\textsuperscript{1} These membranes have long been a foundation of self assembly on a nanoscale\textsuperscript{2–4} and a significant focus of soft matter research due to their applications in industry, such as household products, medicine, such as drug delivery systems and general understanding of biological processes. A theory concerning the elasticity of membranes was proposed by Helfrich\textsuperscript{5} whereby the surfactants or lipids comprising these membranes arrange in the form of a smectic A type liquid crystal and can thus be modelled as a thin undulating elastic sheet. This initial theory was further developed to model the membrane as two compressible monolayer leaflets coupled to the bending of the bilayer in order to demonstrate time dependencies,\textsuperscript{6,7} and then subsequently to consider the dynamics of the bending and peristaltic motions as a function of the monolayer leaflet character.\textsuperscript{8} These theories connect the structural and dynamical parameters to the mechanical properties of the membrane. As such, experimental determination of these parameters would help understand the membranes’ intrinsic properties. For example, recent work on stem cell differentiation, has shown that the stiffness of the extracellular matrix has a significant impact on the ultimate fate of the stem cell.\textsuperscript{9} The precise mechanisms for the triggering of the cell differentiation by the extracellular elasticity are as yet unknown, but the mechanical properties of the membranes themselves offer important information towards potential mechanism development.

The elastic bending modulus of a membrane, $\kappa$, has long been a focus of studies concerning the elastic properties of membranes with calculations of $\kappa$ in aqueous mixtures of ionic and nonionic surfactants, where the ionic surfactant content was low,\textsuperscript{10,11} displaying an increase in the membrane rigidity with charge. This was supported by classical theories based on the Poisson–Boltzmann (PB) approach.\textsuperscript{12–17} This theory, concerning Coulombic forces in a mean-field approximation, has been successfully employed to explain electrostatics for monovalent ions and conditions of weak surface charge.\textsuperscript{18} In contrast to the indirect measurement of $\kappa$ in the work of Schomäcker and Strey,\textsuperscript{19} a variety of experimental techniques have made more direct measurements of $\kappa$ for both surfactant and lipid bilayers.\textsuperscript{19–24} Though the results from these experiments display some consistency with theory regarding the mechanical properties of membranes, it is still not wholly conclusive as to how charge affects membrane structure and dynamics.

Recently, fluctuations in the bilayer thickness – as distinct from the bending undulations, have been measured for both pseudo nonionic surfactant bilayers,\textsuperscript{25–27} and zwitterionic lipid bilayers in water.\textsuperscript{28,29} Furthermore, a non-charged bilayer membrane model which predicts the time scale of peristaltic fluctuations (equivalent to thickness fluctuations) as a function of the...
inhaphe undulations of the monolayer components in a bilayer, has been developed. This theory predicts a connection between the time scale of the fluctuations and membrane viscosity, which could potentially contribute to the determination of the latter, a long term experimental challenge as noted in recent publications. This progress, both in theory and experiment, now allows examination of the effect of charge on the dynamics of single membranes in more detail.

Here, we discuss the effect of varying the bilayer charge density on the structure and dynamics of surfactant membranes under classical Debye–Hückel conditions, i.e. monovalent ions with low surface charge. Previous experiments to measure thickness fluctuations did not include charged surfactant component in the membrane, while here, surface charge density is controlled by replacing a portion of the nonionic surfactant with a charged species. The membrane bending modulus increases with surface charge density, which is consistent with classical PB theories. In addition, internal collective membrane dynamics, here demonstrating thickness fluctuations, indicate a significant effect of the surface charge density on the membrane viscosity. This indicates the charge in membranes alters not only the inter-membrane interactions but also the intra-membrane dynamics.

2 Experiments

In order to obtain a stable lamellar structure over an appropriate range of included charge density, a model surfactant system, containing a tetraethylene glycol monododecyl ether (C\(_{12}\)E\(_{4}\)) bilayer swollen with octane and dispersed in water (D\(_2\)O), is used. This system serves to model single membrane dynamics under varying surface charge density. The nonionic surfactant in the bilayer was progressively replaced with a charged surfactant, sodium dodecyl sulfate (SDS), where the mass fraction of SDS to C\(_{12}\)E\(_{4}\), \(C_s\), was varied as 0.001 \(\leq C_s \leq 0.05\). A mixture containing volume fractions of surfactant, \(\phi_s = 0.05\), oil, \(\phi_o = 0.03\) and water, \(\phi_w = 0.92\) produces a stable lamellar phase across a substantial range of SDS concentrations at 20 °C, which was the temperature used for all measurements in this study. SDS was selected as it has the same hydrocarbon tail length as C\(_{12}\)E\(_{4}\) and both surfactants have the same area per polar head group (\(\approx 54\) Å\(^2\)).

The structure of these samples was quantitatively characterized by small angle neutron scattering (SANS) measurements which were conducted on the NGB-30m SANS instrument\(^{38}\) at the NIST Center for Neutron Research (NCNR). Data were collected over a momentum transfer, \(q\), range between 0.003 Å\(^{-1}\) and 0.45 Å\(^{-1}\) with \(q = 4\pi/\lambda\sin(\theta/2)\) where \(\lambda\) is the incident wavelength and \(\theta\) is the scattering angle. The samples were contained in 1 mm thick demountable cells. In order to clearly see the structural modification of the membranes, \(n\)-octane-d\(_{18}\) (C\(_8\)D\(_{18}\)) was used to form the oil layer so that the neutron scattering contrast of the surfactant–surfactant correlations among the monolayers that comprise the oil swollen bilayers is enhanced. A standard procedure was used to correct the obtained data to an absolute intensity using the SANS data reduction software developed at NIST\(^{36}\) with the reduced data displayed in Fig. 1.

The dynamic properties of the system were measured using the neutron spin echo (NSE) technique, with experiments conducted on the NGA-NSE instrument\(^{37}\) at the NCNR. The \(q\) range covered was between 0.04 Å\(^{-1}\) and 0.25 Å\(^{-1}\) while the measured time scale was between 0.1 ns and 100 ns. The cells used for the NSE measurements had a path length of 1 mm. The measured data were reduced using the DAVE reduction software\(^{38}\) to correct resolution and background. NSE measurements featured mixtures containing \(n\)-octane-h\(_{18}\) (C\(_8\)H\(_{18}\)) to calculate the bending fluctuations while C\(_8\)D\(_{18}\) was used to calculate thickness fluctuations.

Electrophoresis measurements were conducted on a Brookhaven ZetaPlus\(^{39}\) zeta potential analyzer instrument. Plastic cuvettes with a 1 cm path length were used while the zeta PALS cell constant was 0.429 cm\(^{-1}\). The solution conductance and electrophoretic mobility were measured for each of the studied SDS concentrations from \(C_s = 0.001\) to \(C_s = 0.05\). The correct level of SDS dissociation was ascertained from the conductance since the conductivity assuming total SDS dissociation could be calculated. In order to calculate the surface charge density the zeta potential of the solutions first needed to be calculated from the measured electrophoretic mobility values. This can be done by evaluating a modified version of the Helmholtz–Smoluchowski (HS) equation, which is given by,

\[
\mu_{\text{mob}} = \frac{2}{3} C(K\eta) \frac{e\zeta}{\kappa D^{-1}}
\]

where \(\mu_{\text{mob}}\) is the electrophoretic mobility, \(\zeta\) is the zeta potential, \(\eta\) is the solution viscosity and \(\kappa D^{-1}\) is the Debye length, defined as \(\kappa D^{-1} = (e^2\kappa_0 T / 2N_A e^2) \text{ } 1/2\).
where \( \varepsilon_r \) is the dielectric constant of the solution, \( \varepsilon_0 \) is the vacuum permittivity, \( N_A \) is the Avogadro constant, \( e \) is the electric unit charge, \( k_B T \) is the thermal energy and \( I \) is the ionic strength. The coefficient \( C(\kappa, \rho) \) varies between 1 and 1.5 as \( \kappa \rho \) varies between \( \kappa \rho^* < 1 \) and \( \kappa \rho^* > 200 \). The limiting value \( \kappa \rho^* \approx 1 \) is typically applicable for simple ions and is known as the Hückel limit.1 The Smoluchowski limit,42 however, is when \( \kappa \rho^* > 200 \), requirements which are satisfied for a wide range of colloidal particles, including this system. Thus, using the Smoluchowski limit value of \( C(\kappa, \rho) = 1.5 \) in eqn (1) to calculate the zeta potential values, the surface charge density for each mixture was obtained, as suggested by Makino and Ohshima.43

Since \( C_{12}E_4 \) is in a liquid state at 20 °C, we measured the bulk viscosity of \( C_{12}E_4 \) in the presence and absence of SDS and octane, using a conventional rheometer. These measurements were conducted on an Anton Paar MCR301 rheometer39 using a cone and plate technique. The titanium cone had a diameter of 25 mm with an angle of 1° and a zero gap of 48 μm. The viscosity was measured over a range of shear rates from 4000 s\(^{-1}\) to 10 s\(^{-1}\), with the lower shear rate constrained by the torque limit of the rheometer. As the mixtures are Newtonian fluids, the viscosity did not vary as a function of shear rate and so values for the bulk viscosity were able to be extracted. A typical value for \( C_{12}E_4 \) at 20 °C was \((36 \pm 1) \) mPa s. As the membrane viscosity, \( \mu \), can be expressed by \( \mu = d_m \eta_l \) where \( \eta_l \) is the bulk fluid viscosity,31 measurements of the bulk viscosity allow comparison with the membrane viscosity extracted from the NSE data.

### 3 Results and discussion

As Fig. 1 shows, the main Bragg peak in the SANS data (at \( q \approx 0.01 \) Å\(^{-1}\)) is shifted to higher \( q \) as \( C_s \) increases along with a sharpening in the peak definition. This shift in \( q \) has been observed before in similar systems10,11 while the peak sharpening is a distinctive feature associated with increased ordering of the bilayers. The Bragg peaks were fitted to a Gaussian function to ascertain the interlayer repeat distance, \( d = 2\pi/q_p \) (where \( q_p \) is the peak location) while the bilayer thickness, \( d_m \), was calculated by fitting the data over the form factor region (solid lines in Fig. 1), using a geometric model proposed by Lemmich et al.44 Both \( d_m \) (circles) and \( d \) (squares) are displayed in Fig. 2(a) as a function of \( C_s \) with the dashed lines representing values predicted by the ideal dilution law \( d_m = 50 \) Å and \( d = 625 \) Å. (b) Change in bilayer area, \( (\Delta A/A)_1 - (\Delta A/A)_2 \) as a function of \( C_s \), displaying values predicted by the ideal dilution law (square) and De Vries theory (circle). The error bars exhibited in each plot represent ±1 standard deviation. The vertical dashed line represents the boundary of charged surfactant content in the bilayer, below which the change in undulation dominate the area change, while above this point the primary driving force for this area change are modifications to the structure.

The mean repeat distance with charge related to the change in the undulation fluctuations as,

\[
\left( \frac{d}{d_m} \phi \right)_1 - \left( \frac{d}{d_m} \phi \right)_2 = \left( \frac{\Delta A}{A} \right)_1 - \left( \frac{\Delta A}{A} \right)_2
\]

where \( (\Delta A/A)_n \) is given by,

\[
(\Delta A/A)_n = \frac{1}{4\pi \kappa \rho_0} \int_{x_{\min}}^{x_{\max}} \frac{d x}{x} \left( 1 + \frac{d_{w,n} f_{e}(x, A)}{\pi \kappa \rho_0 x^4} \right)^{-1/2}
\]

where \( x_{\min} = q_{\text{max}} d_{w}/2 \) with \( q_{\text{max}} = 2\pi/d_m \), \( d_{w,n} \) is the water-layer thickness of species \( n \), \( l_{\text{Bj}} \) is the Bjerrum length given by \( l_{\text{Bj}} = e^2/4\pi \kappa \rho_0 k_BT \), \( \kappa_n \) is the bending modulus of species \( n \) and \( \Lambda = 2d_w/l_{\text{GC}} \) where the Gouy–Chapman length is defined as \( l_{\text{GC}} = e/2\pi l_l \sigma \) with \( \sigma \) the surface charge density. Here we use the values of \( \kappa \) measured by NSE as explained later. The dimensionless
function $f_c(x, A)$ refers to the even mode of the undulation while the expression for $f_s(x, A)$ pertains to the odd mode.45 Values for the difference in the bilayer area change for a given mole fraction of SDS, $(AA/A_2)$, with respect to a reference value, $(AA/A_1)$, are calculated, as has been done previously.45–47 Values calculated using both the ideal dilution law (eqn (2)) and De Vries theory (eqn (4)) are plotted in Fig. 2(b). At $C_s \leq 0.03$, experiment and ideal dilution theory match well which indicates that the reduction of $d$ (or change in area) is primarily due to the suppression of the undulation fluctuations. On the other hand, at $C_s > 0.03$, the difference between the experimental and theoretical values is much greater. This suggests that there is another cause for the change in $d$, other than the undulations, such as structural modifications. As a matter of fact, at $C_s \geq 0.04$, the SANS data shows a clear increase in low-$q$ intensity, corresponding to coexistence with longer length scale structures, which support previous assertions of the emergence of a vesicle phase.10,15 In the absence of charge, on the other hand, the $C_{12}E_4$ solution is a function of charge (circle). The $C_{12}E_4$ solution phase separates. Due to these unclear phase boundaries we have used the $C_s = 0.01$ mixture to provide the $(AA/A_1)$ value since we can be sure that the parameters are not being influenced by structural modifications.

In order to estimate the bending modulus of the membrane, $C_{12}E_4$/SDS/C$_{6}$H$_{14}$/D$_2$O solutions are measured using NSE. NSE is a technique that measures the normalized intermediate scattering function, $I(q,t)/I(q,0)$, as demonstrated in Fig. 3(a). The data are fitted to a model predicting single membrane dynamics, as proposed by Zilman and Granek (ZG),48,49

$$\frac{I(q,t)}{I(q,0)} = \exp\left[-(\Gamma t)\beta\right]$$

where $\beta$ is the stretching exponent ($\beta = 2/3$) and $\Gamma$ is the relaxation rate. ZG theory predicts that the single membrane undulation dynamics describe a relationship between the relaxation rate, $\Gamma_{ZG}$, and $\kappa$ as,

$$\Gamma_{ZG} = 0.025\gamma_\kappa \left(\frac{k_B T}{\kappa}\right)^{\frac{1}{2}} k_B T \eta_{eff} q^3$$

where $\gamma_\kappa$ is a function of $\kappa$ and approaches unity for $\kappa/k_BT > 1$ and $\eta_{eff}$ is the effective solvent viscosity. When $\kappa \approx k_BT$, it has been suggested that the full form of $\gamma_\kappa = 1 - 3 \ln(q_{z_{ext}})k_B T/4\pi\kappa$, where $q_{z_{ext}}$ is a correlation length, be used.48 However, in this system, setting $\gamma_\kappa$ equal to one and applying an effective solvent viscosity as three times the D$_2$O viscosity, produces more physically reasonable values for the bending modulus of the membrane.

Values for $\kappa$, calculated using eqn (6), are displayed in Fig. 3(b). It can be seen that increasing $C_s$ corresponds to a stiffening in the bilayer (increase in $\kappa$). Both the trend and the magnitude of $\kappa$ are comparable with the previous work on surfactant systems mentioned earlier.10,11

Returning to Fig. 2(b), it is important to note the correlation between the values for the bilayer area change calculated using a mixture of dynamical and structural parameters and those from the purely structural measurements up to $C_s = 0.04$ as this suggests that the present assumptions used to estimate $\kappa$ when applying the ZG model are appropriate for this system.

In order to model the charge dependence of $\kappa$, the true ionic strength and surface charge density were determined by electrophoresis measurements at 20 °C. The measurements yielded a dissociation rate of SDS of between 25% and 30%. In Fig. 3(b), the solid line displays values for $\kappa$ calculated by the Schomäcker model, $\kappa = k_g + \kappa_c$ assuming the measured degree of dissociation where $k_g$ and $\kappa_c$ are the contributions from geometry and charge. The $k_g$ term was set to 1.01$k_BT$ which was calculated by extrapolating the experimental values for $\kappa$ to $C_s = 0$. The electrostatic contribution is predicted as $\kappa_c = 3k_BT/4\pi\kappa_D q_D^3$. The predicted values explain the experimental results quite well. This is another indication that the absolute values of $\kappa$ estimated in the present method are reasonable. It is noted that, when the SDS is treated as being completely dissociated, the correspondingly higher surface charge density affects $\kappa_c$ significantly while the increased ionic strength alters $k_g$, resulting in a significant modification of $\kappa$ to larger values.
The electrostatic contribution to the bending modulus can also be modelled using the approach of Fogden et al.\textsuperscript{16} (Fig. 3(b) dashed line) which, like the aforementioned Schomäcker model, originates from the work of Harden et al.\textsuperscript{15} It is a perturbative solution to the PB equation for two undulating sheets with intervening counterions and purports to cover all values of surface charge density and interlayer spacing featured in the Harden model. The model considers a system comprising a periodic stack of alternating hydrocarbon and aqueous planar slabs. Each monolayer bears uniform and equal $\sigma$ separated by an aqueous layer of thickness $d_w$. Fogden et al. consider both the in and out of phase undulations but here we are only concerned with those that are in phase as,\textsuperscript{16}

$$
\kappa_{el}(k_B T) = \frac{d_w}{\pi d_h} \left[ A(2A + 1 - \phi^2) - \left( 1 + \frac{\phi^2}{3} \right) \right]^{1/2}
$$

(7)

where $A = \phi \tan \phi$. The out of phase undulations involve not only the bending of the membrane but also compression of the ionic solution between the membrane.\textsuperscript{15} This compression costs a lot of energy with large values for $\kappa$ resulting. As such this mode is energetically less favourable and has been neglected as in previous studies.\textsuperscript{15} Once again the measured values for the surface charge density were used in the Gouy–Chapman contribution to $\Lambda$. As is evident in Fig. 3(b), the values for $\kappa$ from this model slightly overestimate the experimental data at 0.01 $\leq C_s \leq 0.03$, though the trend of increasing $\kappa$ with $C_s$ still reflects the suppression of the bending fluctuations with charge. This overestimation compared to the Schomäcker model is due to the presence of a bilayer geometry component, $d_w$, in the estimation of $\kappa$, while Schomäcker and Strey only considered electrostatic contributions. For the conditions studied here, a dilute system where the interlayer spacing is comparatively large, the contribution from the geometric component is considered to be low. This however is still accounted for in the Fogden model with the result that it overestimates the overall bending modulus. It is noted that the electrophoresis measurements confirmed that the surface charge density continued to increase above $C_s = 0.04$ despite the experimentally measured values for $\kappa$ that indicate a softening in the bilayer. This confirms that in this region it is the structural changes that are now dominating the mechanical properties, which suggests that the distribution of the charge density in the system has changed, and therefore PB theory is no longer applicable.

Now, we turn to the internal membrane fluctuations, which were measured using $C_{12}$Ea/SDS/CaD2H/D2O. The decay function was well reproduced for this scattering contrast case by again using eqn (5). Looking at the data from the ZG theory in the form of a $\Gamma(q)/q^3$ vs. $q$ plot, as shown in Fig. 4, it is clear that there is a deviation from the $q^3$ dependence. This deviation was attributed as membrane thickness fluctuations, which was also observed in uncharged surfactant and lipid systems.\textsuperscript{25–29} We assume a linear combination of the distinct contributions from the undulations and thickness fluctuations and a Lorentz function is utilized, as in the previous studies, to quantify the contributions from thickness fluctuations, given by,

$$
\frac{\Gamma}{q^3} = \frac{\Gamma_{ZG}}{q^3} + \frac{\Gamma_{TF}}{q^3} \left( \frac{\Gamma_{ZG}}{\Gamma_{TF}} \right) \frac{1}{1 + (q - q_0)^2/\xi^2}
$$

(8)

where $\Gamma_{TF}$ is the contribution to the relaxation rate from the membrane thickness fluctuations, $q_0$ denotes the position of the peak maximum for the $\Gamma/q^3$ plots and $\xi^{-1}$ denotes the half width at half maximum of the Lorentz function. The thickness fluctuation amplitude, $\delta_a$, is estimated from $\xi^{-1}$ and $q_0$ as $\delta_a = 2d_m \xi^{-1}/q_0$ with $d_m$ calculated from the SANS data.\textsuperscript{26} The surface charge density dependence of $\delta_a$ is shown in Fig. 5(a), indicating values that are almost constant with $C_s$ at $\delta_a \approx 14$ Å.

The magnitude of $\Gamma_{TF}$, which is the reciprocal of the relaxation time, $\tau$, exhibits values at low $C_s$ consistent with a previously studied analogous nonionic system.\textsuperscript{26} The overall trend however, decreases with increasing $C_s$ as shown in Fig. 5(b), indicating a slowdown of the fluctuations with increasing $C_s$ for $C_s \leq 0.03$. Increasing the charge density above $C_s = 0.03$ appears to speed up the fluctuations but structural changes now control the behavior.

Recent work by Bingham et al.\textsuperscript{8} on asymmetric bilayer lipid membranes, has proposed that $\Gamma_{TF}$ varies with the area compressibility modulus, $K_A$, which is damped by the viscosities of the membrane, $\mu$, and solvent, $\eta_s$, by,

$$
\frac{\mu}{K_A} = \frac{2\eta_s}{d_m^2}
$$

(9)

where $d_m$ is the Fourier wavelength of the fluctuations. The bending of a bilayer involves a compression of one surface and an extension of the other, the magnitude of the strain being governed by $K_A$. If the two membrane leaflets are free to slide past each other, one can assume a relation $K_A = 48\kappa/d_m^2$.\textsuperscript{52} Thus, we know the value of $K_A$ from the measured bilayer thickness, $d_m$ and the bending modulus, $\kappa$. As described in the original paper,\textsuperscript{8} when the membrane viscosity dominates the
dissipation, where the Saffman–Delbrück length, \( l_{SD} = \mu / \eta_s \), is larger than the fluctuation wavelength, then eqn (9) becomes \( \mu_{rel} = K_\mu / \Gamma_{TF} \). The values for this relative membrane viscosity are plotted in Fig. 6. It is clear that increasing the surface charge density causes a significant increase in the viscosity of the membrane due to the charged headgroups arranging in the bilayer so as to minimize their interaction with each other.

In order to verify the validity of the obtained values of \( \mu_{rel} \), the estimated membrane viscosity, \( \mu_s \), of C_{12}E_{4}/SDS mixtures are also plotted in Fig. 6, as \( \mu = d_m \eta_s \), by assuming \( d_m = 50 \) Å and using the bulk viscosity of the C_{12}E_{4}/SDS/octane mixtures, \( \eta_s \), from the rheology measurements. Both the presence (triangles) and absence (squares) of octane, generated values that are in the range of \( \mu_{rel} \) which suggests that the experimentally estimated values (by NSE) for the membrane viscosity are realistic. At \( C_s > 0.03 \), \( \mu_{rel} \) displays an overall decrease, contrasting the increasing trend observed below \( C_s = 0.03 \), while the values of \( \mu \) calculated from bulk measurements change linearly at \( C_s > 0.03 \) (data not shown for clarity). We have described earlier in the paper that changes at \( C_s > 0.03 \) occur due to structural modifications in the membrane, in particular that the charge distribution is changing. This result suggests that an increase in the heterogeneous distribution of charged species can significantly modify the properties of the membrane.

The present result indicates that this method is a potential technique for quantifying the membrane viscosity purely from thermal membrane fluctuations without having any additional probe molecules added to the system. However, care should be taken when applying this method. In the present system, \( \eta_s \approx 1 \) mPa s, and therefore \( 10 \) nm \( \leq l_{SD} \leq 80 \) nm is estimated. When the fluctuation wavelength is much shorter than these lengths the present result holds well, while in the case of long wavelengths the value might be affected. Considering the limitations of the applied experimental techniques the fluctuation wavelengths are not currently measurable. This point has to be solved in future studies, but use of the present method should provide access to another interesting membrane parameter, the membrane viscosity.

4 Conclusions

In the present study, we demonstrated that increasing the charge density in a surfactant bilayer rigidifies the membrane as well as enlarging its viscosity. Both of these factors contribute to slow down the membrane dynamics. In physical terms, increasing the proportion of charged head groups in the bilayer, with their associated electrostatic interactions, not only makes it more difficult for molecules to diffuse through the bilayer, thus increasing \( \mu \) and slowing down the dynamics normal to the bilayer plane (thickness fluctuations), but also increases the resistance to deformation in the plane of the bilayer (bending fluctuations). The present result indicates potentially independent control of the thickness fluctuation rate and amplitude as the thickness fluctuation rate is characterized by the membrane viscosity while the amplitude is independent of \( \mu \). This independent
control was theorized in a previous study of mixed lipid systems\textsuperscript{29} which are supported by this study. Charge is known to modify the interlayer membrane interactions, but it also alters the intra-membrane dynamics significantly which could be another contributing factor to the stabilization of lamellar phases. Incidentally, when charge density is decreased further, the lamellar phase is disrupted which results in structural modification of the bilayer, destabilization and eventually dissolution of the lamellar structure.

This study shows the effect that charge plays in modifying the mechanical properties of the surfactant membranes. The most impressive result of a change in the membrane viscosity is the potential alteration to the diffusive behavior of the particles in the membrane. We may speculate that in biological membranes, protein or other molecular diffusion is affected, or controlled, by the charge interaction of the membranes. This speculation should be applicable for a wide variety of surfactant systems and the present result opens up the opportunity to strive to control the diffusion properties in the membrane using specific interactions within the membrane itself. Indeed, electrostatic interactions have gained significant attention in studies on lipid–protein interactions.\textsuperscript{54–56} We hope that the presented methodology could potentially help in better understanding some of the complex behavior of charged membranes such as the aforementioned mechanism of stem cell differentiation or how the distribution of charge inside a cell membrane affects its functionality and permeability.

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39 Certain commercial equipment is identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment identified is necessarily the best available for the purpose.


