*Research paper*

# Impact of anions on the surface organisation of lipid monolayers at the air–water interface

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**Environmental context.** Lipids released from lysis of phytoplankton cells are enriched in the sea surface microlayer. Such surface-active organics can be transferred through bursting bubbles to sea-spray aerosols where they can influence atmospheric chemistry. The results presented here suggest that phospholipids combine more readily with $SO_4^{2-}$ than with $Br^-$, leading to enrichment of organic-coated sulfate salts in marine aerosols.

**Abstract.** Inorganic salts and organic matter are known to be present at higher levels in the sea surface microlayer and marine aerosols; however, the impact of common anions on their surface properties is not well understood. Here, a 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) monolayer was enriched with the sodium and ammonium salts of different anions ($Br^-$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $CH_3COO^-$, and $HCO_3^-$), and the effects on the surface properties of the monolayer were investigated. The monolayer phase behaviour and the structure of the lipid phases were studied by surface pressure–area ($\pi$–A) isotherms and infrared reflection-absorption spectroscopy (IRRAS). The presence of salts in the subphase was found to increase the surface pressure of the DPPC monolayer at a fixed area per molecule. The effect of the anions follows the order of the Hofmeister series. The higher concentration of salt solution caused the $\pi$–A isotherm to shift to larger area. The IRRAS spectra demonstrate that the ordering of the DPPC molecules in the liquid condensed phase remains essentially unaffected, even at higher electrolyte concentrations. DPPC molecules combined with $SO_4^{2-}$ could be transferred from the ocean to sea spray aerosol. The present study finds that the anions have significant influence on the surface organisation and, consequently, the interfacial properties, of the surface-active species at the air–water interface, a finding that has further implications for atmospheric aerosol nucleation.

## Introduction

The oceans, atmosphere and clouds are all interconnected through the release and deposition of chemical species.[1] Breaking waves formed through wind-driven mechanisms generate air bubbles that scavenge organic matter from the surrounding sea water. When ejected into the atmosphere, these bubbles burst, yielding sea spray aerosols (SSA) enriched in organic matter, relative to the sea water.[2–4]

The ocean represents a major source of primary aerosols; an estimated $2-100 \times 10^{15}$ g of SSA is emitted from the ocean each year.[5] SSA is a globally important source of particulate matter, although its effect on the atmosphere is largely undetermined.[6] The composition of aerosols in the marine boundary layer has been extensively studied.[7] During phytoplankton bloom periods, the organic fraction dominates, contributing 63 % to the submicrometer aerosol mass, of which ~45 % is water-insoluble.[8,9] Film drops (<1 μm in diameter) produced by bursting of the bubble film efficiently transfer surface-active species that reside at the air–water interface into the atmosphere; this explains the presence of surfactants in fine SSA particles (<2.5 μm in diameter).[10] Given that the relative concentration of organic matter to inorganic salts in the ocean is extremely low (60–90 μM

organic matter compared with approximately 460 000 μM $Na^+$),[3] the high relative fraction of organic matter in SSA shows that the transfer of organic species from the ocean to SSA proceeds through selective processes. To better understand the biogeochemical connections between the ocean and atmosphere, it is critical to improve our understanding of the processes that control SSA composition in order to determine their effects on atmospheric chemistry and climate.[1]

The sea surface microlayer, defined as the uppermost tens to hundreds of micrometres of the ocean surface, is a thin film between the ocean and the atmosphere. It covers more than 70 % of the Earth's surface.[11] The sea surface microlayer is mainly composed of surface-active, biogenically derived organics, such as carbohydrates, fatty acids, lipids and proteinaceous materials.[12] The most important source of surface-active substances is the sunlight-promoted production of organic substances by phytoplankton and bacteria. Phospholipids, glycolipids and triacylglycerides are mainly released during cell lysis of the phytoplankton.[13,14] Coastal and oligotrophic slicks are typically rich in these and other lipids.[12] There is evidence to show that naturally derived surfactants, such as fatty acids and their derivatives, may accumulate in the sea surface microlayer,

showing a greater affinity than other soluble organic molecules for the air–water interface.[13] The air–water interface, having different chemical, physical and biological properties from subsurface waters, plays a significant role in biogeochemical processes on a global scale, a role that needs to be better understood for fundamental research on marine chemistry.[15]

Sea spray aerosol has been shown to comprise more than just sodium chloride; it contains other inorganic salts as well as biologically produced organic species.[16] While the majority of submicrometre SSA particles contain mostly sea salts (i.e. NaCl, KCl, $MgCl_2$ and $CaCl_2$), SSA particles contain increasing levels of organic species (relative to inorganic species) as particle diameter decreases to submicrometre sizes. Mean enrichment factors for major ions demonstrate significant enrichment in fine SSA for $K^+$ (1.3), $Mg^{2+}$ (1.4), and $Ca^{2+}$ (1.7), likely because of their interactions with organic matter.[5] The significant enrichment of $Ca^{2+}$ was observed in submicrometre SSA particles when particles were generated both from seawater sources in the laboratory and from ambient aerosol samples.[17]

Investigations into the role of ions in SSA indicate that cations such as $Mg^{2+}$ and $Ca^{2+}$ can enhance organic species at the interface, which has implications for the surface packing of organic molecules and subsequent interfacial reactivity.[18,19] Further, various chemical properties (e.g. surface activity, solubility, interfacial molecular structure) have been observed to play a role in defining the transfer of chemical matter from the ocean to SSA.[1] Most of these studies have used cations (e.g. $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) as the main inorganic salts, thus neglecting the importance of marine-relevant anions, such as $Br^-$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$. Few studies have investigated how these anions affect surface films and the formation of SSA. Nonetheless, $SO_4^{2-}$, $NH_4^+$, $Cl^-$ and $NO_3^-$ are the dominant ions for marine cloud water collected over the eastern Pacific Ocean.[20–24] They also contribute 24.5 % of PM2.5 mass from continental sources.[25]

Based on the Hofmeister series, ions can be divided into kosmotropes and chaotropes, which have opposing affinities towards the interface.[26] Numerous experiments over several decades have shown that the Hofmeister series plays a significant role in a dramatic range of biological and physicochemical phenomena, affecting the solubility of hydrophobic solutes in water, the diffusion behaviour and interfacial molecular packing of surfactants, the activities of various enzymes, and the surface tension of electrolyte solutions.[26,27] In addition, the ion concentration becomes an important parameter since the relative concentration of ions will change as the marine aerosol loses or adsorbs water in the atmosphere.[19,28]

Although the chemical composition of the sea surface microlayer has been extensively studied, there is still a lack of knowledge about the interfacial properties of the sea surface microlayer and the physicochemical processes governing the formation of SSA. In attempts to explore the interaction between anion and surfactants at the air–water interface, the Langmuir method and infrared reflection-absorption spectroscopy (IRRAS) have been commonly used for the investigation of surface-active substances in different solutions. Langmuir monolayers of zwitterionic phospholipids are used as model systems to understand anion effects in physicochemical and biological systems. 1,2-Dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) is a representative lipid at the air–seawater interface. The sea surface microlayer is known to be enriched in DPPC , and DPPC is therefore likely to be found in marine aerosols.[29,30] The sodium and ammonium salt concentrations used here varied from 0.001–1.0 M to represent different stages of marine aerosol evaporation and different degrees of ion enrichment at the interface. The question we wish to address here is to how the Hofmeister and concentration effects of sodium and ammonium salts with selected anions influence the ordering of DPPC Langmuir monolayers.

## Experimental

### Materials and sample preparation

1,2-Dipalmitoyl-sn-glycerol-3-phosphocholine (DPPC) (98 % purity, Sigma-Aldrich) was dissolved in chloroform at 1 mM without additional purification and sealed from the ambient environment. All isotherms were collected within three weeks of sample preparation to minimise the effect of solvent evaporation and lipid oxidation. $Na_2SO_4$, $NaNO_3$, $NaHCO_3$, $NH_4Br$, $(NH_4)_2SO_4$ were purchased from Alfa Aesar (purity >99 %). NaCl, NaBr, $NaCH_3COO$, $NH_4Cl$, $NH_4HCO_3$, $NH_4CH_3COO$ were purchased from Acros (purity >99 %). Sodium and ammonium salts were dissolved in ultrapure water (specific resistivity of 18.2 MΩ cm) produced by Millipore filtration device to prepare stock solutions. The concentrations of salts used here are below the threshold of saturation. To keep the stability of solutions, all the solutions were prepared immediately before use. The salts of strong acids, such as NaCl, NaBr, $NaNO_3$ and $Na_2SO_4$, were maintained at nearly constant pH values. It would have been possible to precisely control the pH of $NaCH_3COO$, $NaHCO_3$ and ammonium salts solutions through the addition of buffers; however, the resulting mixture of ions would have complicated the interpretation of the experiments. Therefore, the pH values of all salt solutions were not adjusted with buffer: pH 8.4 for 0.001 M $NaHCO_3$, pH 8.2 for 0.001 M $NaCH_3COO$, pH 5.5 for 0.001 M $(NH_4)_2SO_4$, pH 5.8 for 0.001 M $NH_4Cl$, pH 6.3 for 0.001 M $NH_4Br$, pH 7.0 for 0.001 M $NH_4CH_3COO$, pH 8.0 for 0.001 M $NH_4HCO_3$. All experiments were conducted at ambient temperature (25 ± 2°C) and relative humidity (45 ± 2 %).

### Monolayer spreading and surface pressure–area (π–A) isotherms

Surface pressure–molecular area (π–A) compression isotherms were measured on a computer-controlled Langmuir trough. It has a maximum trough area of 210 cm² and two barriers that move symmetrically from both ends towards the trough centre.

In the Teflon-coated film trough, a known volume of a 1 mM solution of DPPC in chloroform was spread dropwise onto the surface of the water subphase or aqueous salt solution using a 50 µL microsyringe with the trough barriers initially in the fully expanded position. After 10–15 min to allow for complete solvent evaporation, the compression of the two hydrophobic barriers was initiated. The surface pressure was measured during compression by using a Wilhelmy plate made of filter paper hung to the surface pressure sensor. The films were compressed at a constant speed of 3 mm/min. The trough was cleaned by repeatedly rinsing with ethanol and Millipore water before use. The procedure followed to obtain the π–A isotherms has been described previously.[31] The measurements were performed three times to ensure consistent results.

### Infrared reflection–absorption spectroscopy (IRRAS)

All spectra were obtained using a Vertex 70 FTIR spectrometer (Bruker, Germany) with a liquid-nitrogen cooled HgCdTe (MCT) detector for a single-beam measurement. The external reflection-absorption spectrum of ultrapure water was used as a reference. Sample (film-covered surface) and reference (film-free surface)

troughs were fixed on a shuttle device driven by a computer-controlled stepper motor for allowing spectral collections from the two troughs in an alternating fashion. A time delay of 60 s was allowed for film equilibrium between trough movement and data collection. Spectra covered a range from 400 to 4000 cm$^{-1}$ and were averaged over 2000 scans with a resolution of 8 cm$^{-1}$. Surface pressure changed slightly for the monolayers ($\leq$ 0.2 mN/m) during the data collection. Measurements were performed at least three times to ensure reproducibility.

## Results and discussion

### Phase behaviour and packing of DPPC monolayer

Surface pressure–area isotherms of Langmuir DPPC monolayers on pure water and sodium salt solution subphases are shown in Fig. 1. The isotherm of DPPC on pure water reveals distinct phases that have been previously identified.[32] Four phases of DPPC monolayer on pure water can be observed: a gas phase (G, >105 Å$^2$/molecule), a liquid-expanded phase (LE, 75–105 Å$^2$/molecule), a liquid-condensed phase (LC, <55 Å$^2$/molecule), and a typical LE–LC transition phase (LE–LC, 55–75 Å$^2$/molecule) defined by a plateau at ~13 mN/m, which is in agreement with the literature.[19] The DPPC monolayer on pure water collapsed at 45 Å$^2$/molecule and 55 mN/m, following a sharp surface-pressure increase. This indicates that DPPC forms a rigid and condensed monolayer at the air–water interface.

All phases described above are also present for DPPC monolayers on sodium salt solutions. For sodium salts, anions have been ordered into a Hofmeister or lyotropic series, which is a classification of ions in order of their ability to salt out or salt in proteins.[33] The Hofmeister series orders anions with decreasing salting-out potency from left to right, as follows: SO$_4^{2-}$, HPO$_4^{2-}$, OH$^-$, F$^-$, HCOO$^-$, CH$_3$COO$^-$, Cl$^-$, Br$^-$, NO$_3^-$, I$^-$, SCN$^-$, ClO$_4^-$. An underlying molecular-level description of the Hofmeister effect is still far from complete.[26,34,35] Two basic hypotheses on how Hofmeister ions affect the aggregation and self-assembly behaviour of macromolecular solutes in aqueous solution have been put forward: (1) indirect mechanism of action – by interacting with water around the macromolecules; (2) direct mechanism of action – by interacting directly with the macromolecules.[36] Anions were found to have a much greater impact on protein solubility than cations.[37] The indirect mechanism concerns the various ions' ability to make or break

hydrogen bonds (known as kosmotropic or chaotropic behaviour, respectively). Kosmotropic anions cause water molecules to favourably interact, which also in effect stabilises intramolecular interactions in macromolecules such as proteins. Chaotropic anions have the opposite effect, disrupting water structure, increasing the solubility of nonpolar solvent particles, and destabilising solute aggregates.[38] Another theory suggests that ions have little effect on the overall hydrogen-bonding of water in bulk solution and do not display the thermodynamic behaviour predicted by recent experiments.[39] A strong non-specific penetration of anions into the lipid phases has been found in recent molecular dynamics simulations by Sachs and Woolf.[40] Adsorption through strong local binding or dispersion forces plays a role in the interaction of anions with lipid interfaces.[41] Our results, based on increasing area for the DPPC monolayer from left to right, show the order of the series as follows: SO$_4^{2-}$, Cl$^-$, Br$^-$, NO$_3^-$. This sequence is in good agreement with Hofmeister.[42]

With 0.001 M or 0.1 M Na$_2$SO$_4$ as subphase, the isotherm (Fig. 1.) shows that the DPPC molecules are able to pack more tightly because the compression of the air–water interface enabled the surface area to reach 52 Å$^2$/molecule at 20 mN/m. In contrast, the DPPC monolayers on NaBr and NaNO$_3$ subphases were much less compressed. Chloride was found to have only a marginal interaction with DPPC monolayers at relatively low concentration (0.001 M). This is not inconsistent with previous work, which has shown chloride to exhibit 'indifferent' behaviour, locating it on the border between kosmotropic and chaotropic anions.[33,43] Given the little change in the π–A isotherms between 0.001 M and 0.1 M Na$_2$SO$_4$, we further measured the π–A isotherms for DPPC monolayers on NaCl and Na$_2$SO$_4$ solutions with varying concentrations (Fig. 2) to investigate the concentration effect.

The phase behaviour of DPPC on NaCl solutions has been studied extensively. As reported in previous work, it was concluded that Cl$^-$ ions do not affect the surface pressure of DPPC monolayer in any significant way, with very low electrolyte concentrations (0.001–0.01 M) in the subphase.[37,44] As can be seen from Fig. 2, the π–A isotherms of DPPC monolayers at various NaCl and Na$_2$SO$_4$ concentrations changed quite substantially with salt concentration. The concentration of NaCl giving rise to the change of lifting area where the surface pressure starts to increase is larger than 0.001 M, while the analogous concentration of Na$_2$SO$_4$ appeared to be larger than
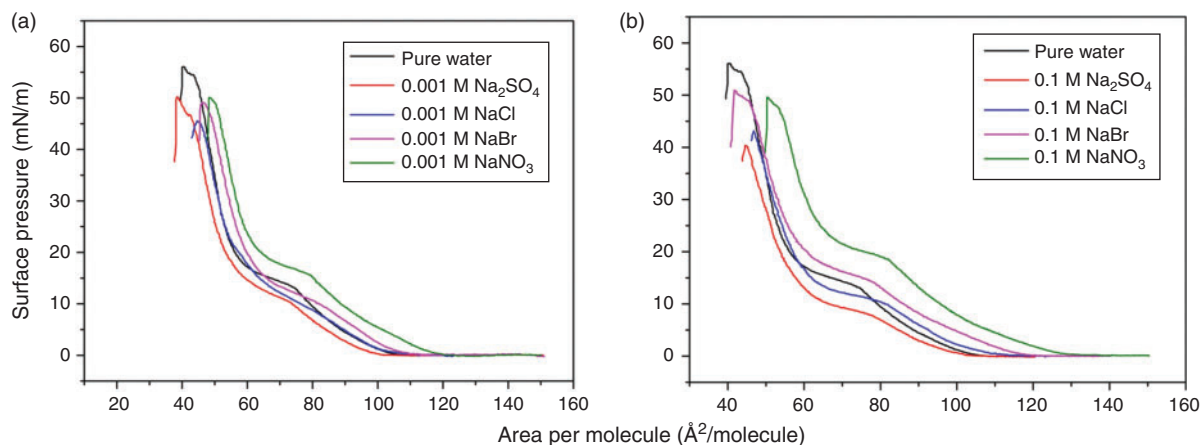


**Fig. 1.** Surface pressure–area isotherms of DPPC monolayers on water and sodium salt solutions (SO$_4^{2-}$, Cl$^-$, Br$^-$ and NO$_3^-$) at concentrations of (a) 0.001 M and (b) 0.1 M.
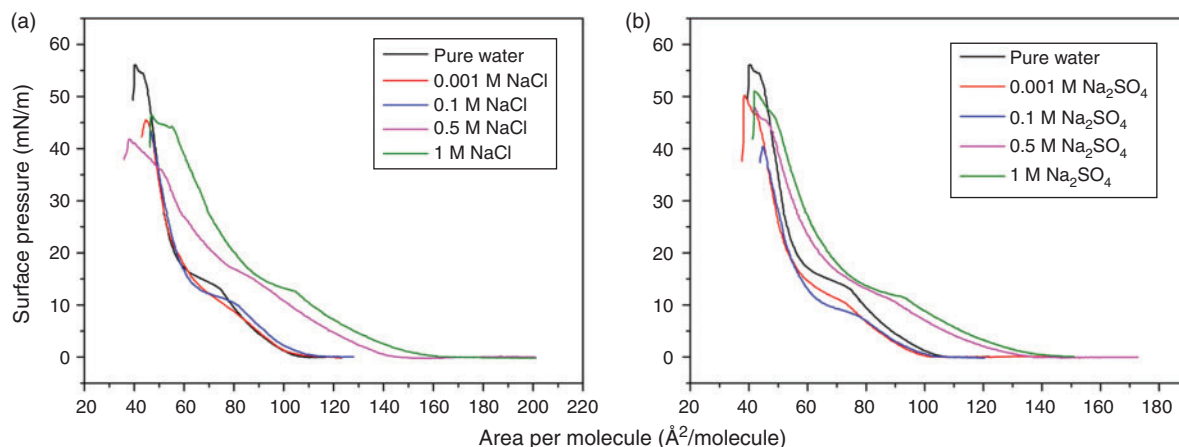
**Fig. 2.** Surface pressure–area isotherms of DPPC monolayers on (a) NaCl and (b) Na$_2$SO$_4$ solutions at various salt concentrations.

0.1 M. Relative to water, an increase in mean molecular area occurs in the low surface-pressure region, and the LE–LC transition phase at ~10 mN/m is lower for 0.1 M NaCl. As the DPPC monolayer is compressed to higher surface pressures (>20 mN/m), DPPC molecules occupy the mean molecular area as on water, suggesting that excess NaCl ions are squeezed out of the monolayer. The isotherm obtained for 0.5 M NaCl has a similar form but with a less well-defined transition. A total expansion of the monolayer occurred on the $\geq$ 0.5 M NaCl solution, where a larger mean molecular area relative to water occurred at all surface pressures. Similar to the NaCl solutions, 0.5 and 1 M Na$_2$SO$_4$ solutions caused the DPPC monolayer to expand at all surface pressures compared with water. It should be noted that all salt solutions had identical ionic strength with the exception of the Na$_2$SO$_4$ solution, the ionic strength of which was three times higher than the others because of the divalent nature of the anion. Control experiments at a third of the Na$_2$SO$_4$ concentration used for the main experiment showed that the higher ionic strength did not change the ordering of any of the results with respect to the other ions.[39] The high film-collapse pressures of DPPC monolayers at various Na$_2$SO$_4$ concentrations reveal that the SO$_4^{2-}$ ions appear to be ejected out of the DPPC monolayers near the collapse point. Results shown in Fig. 2 indicate that, at high concentrations, Cl$^-$ and SO$_4^{2-}$ interact similarly with DPPC molecules, where expansion of the monolayer is likely due to increased electrostatic repulsions in the interfacial region.

The impacts of HCO$_3^-$ and CH$_3$COO$^-$ on the phase behaviour of DPPC in general have been less studied than those of SO$_4^{2-}$, Cl$^-$, Br$^-$ and NO$_3^-$. More specifically, the role of the HCO$_3^-$ ion may include: (1) participation in the hydrogen-bonding network, invoking enhanced condensation, (2) ion-pair formation to mitigate like-charge repulsion, and (3) Hofmeister related HCO$_3^-$/water interactions.[45,46] As shown in Fig. 3, the extent of the mean molecular-area shift appears to be concentration-dependent; it increases by 8–10 Å$^2$/molecule for 0.1 M solution and by 18–20 Å$^2$/molecule for 1 M solution. Despite the strength of the interfacial interaction, the DPPC monolayer was very unstable on the 1 M NaHCO$_3$ subphase, exhibiting relatively low collapse pressure. The π–A isotherms shown in Fig. S1 (available as the Supplementary material to this paper) indicate that CH$_3$COO$^-$ behaves similarly to HCO$_3^-$. In conclusion, the main transition pressure depends on the salt concentration and the type of anion in the subphase.
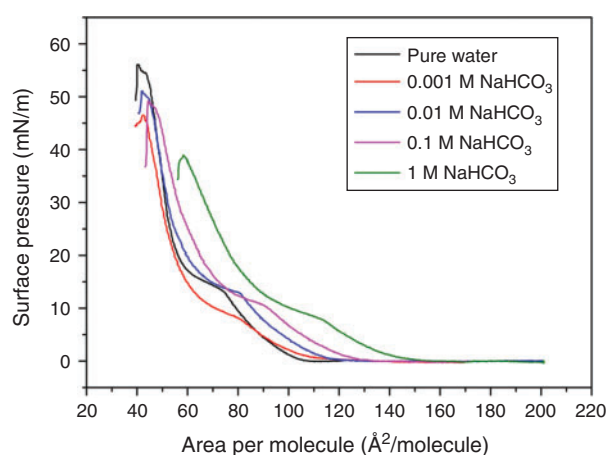


**Fig. 3.** Surface pressure–area isotherms of DPPC monolayers on NaHCO$_3$ solutions at various salt concentrations.



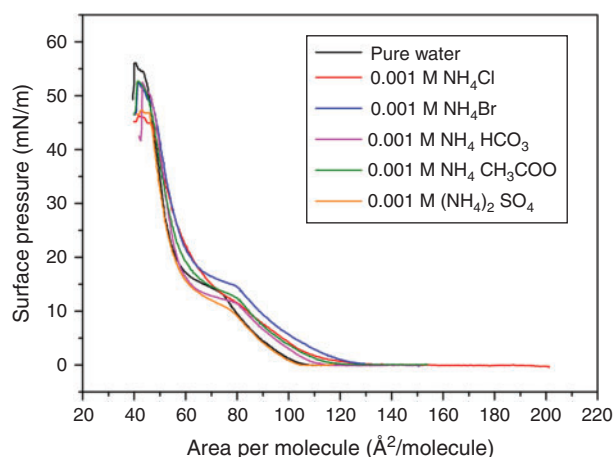**Fig. 4.** Surface pressure–area isotherms of DPPC monolayers on water and 0.001 M ammonium salt solutions.

Sodium is thought to be an indifferent cation in the Hofmeister series.[47,48] The effect of cations follows the order of the Hofmeister series, with NH$_4^+$ appearing in front of Na$^+$.[49] It can be observed that the increase in surface pressure in Fig. 4 is different for different anions. The magnitude of the increase
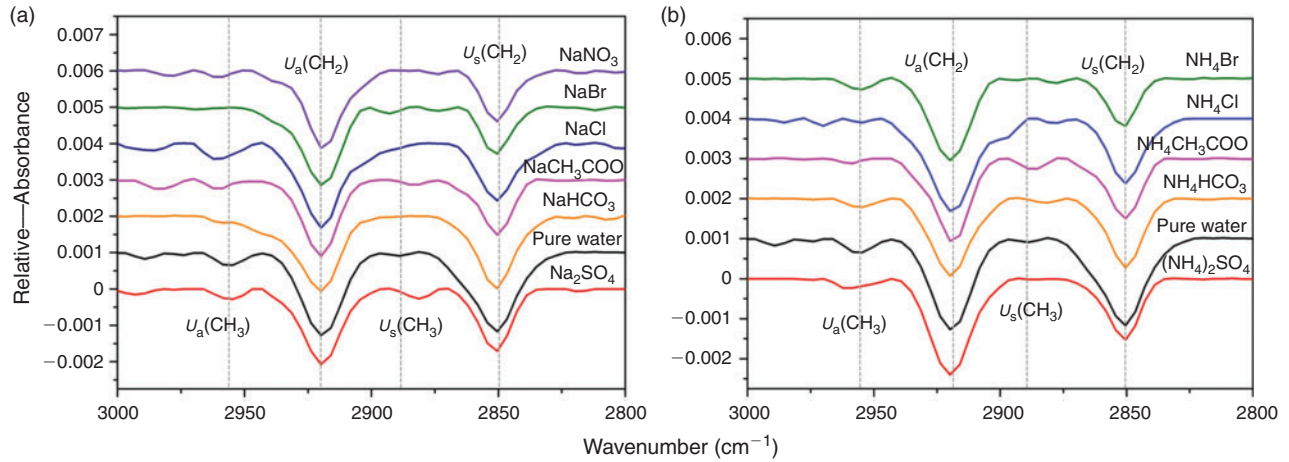
**Fig. 5.** IRRAS spectra (2800–3000 cm$^{-1}$) of DPPC monolayers on water: (a) sodium salt solution and (b) ammonium salt solutions at 0.001 M.

follows the order: $SO_4^{2-}$ < $HCO_3^-$ < $CH_3COO^-$ < $Cl^-$ < $Br^-$.[50] The LE–LC phase-transition pressure in the DPPC monolayer also increases according to the Hofmeister sequence. Along with sodium salts, ammonium salts – which are major components of tropospheric aerosols – have been extensively studied in atmospheric aerosol nucleation.[51–53] The addition of ammonium salts (except ammonium sulfate) in the subphase of DPPC monolayer leads to a general increase in the surface pressure at a fixed molecular area. Ammonium sulfate is the traditional kosmotropic salt for the salting out of protein from an aqueous solution.[54] The general increase in the surface pressure for all electrolytes implies that the salts adsorb at the DPPC monolayer in some way. It is worthy to note that the sequences at higher concentrations of ammonium salt solutions behave differently from the Hofmeister sequence in this work (Fig. S2). At a fixed surface area in the LC phase, the surface pressure of the DPPC monolayer on 0.1 M ammonium salts increases according to the Hofmeister sequence. The difference in the sequence of ammonium salts between low and high concentrations implies that anions affect the ordering of the lipid chain and their tilt angle in the LC phase.[55] The expansions of the monolayers at fixed surface pressure follow the Hofmeister sequence at very low ammonium salt concentrations.

*Conformation of the alkyl chain in the DPPC monolayer*

Besides using $\pi$–A isotherms to observe anion effects on the phase behaviour of DPPC monolayers, we have examined the alkyl chain packing and conformation by using IRRAS. The IRRAS spectra of the methyl ($CH_3$) and methylene ($CH_2$) region (2800–3000 cm$^{-1}$) for DPPC monolayers on water and sodium salt solutions are shown in Fig. 5a. IRRAS spectra were collected in the LC phase (at 30 mN/m) to provide information about the effect of anions on a DPPC monolayer. IRRAS is sensitive to the alkyl chain conformation of the monolayer. Peak positions of $CH_2$ vibrational modes are sensitive to the conformational order of the alkyl chains, and can provide insight into the relative number of *trans* and *gauche* conformations in the monolayer; i.e., a shift to lower wavenumbers indicates that the alkyl chains have more *trans* bonds.[19,56] It was observed that, during the transition from the LE–LC phase to the LC phase in the DPPC monolayer on pure water, the symmetric $CH_2$ stretching frequency decreased from 2855 to 2851 cm$^{-1}$ and the asymmetric $CH_2$ stretch decreased from 2924 to 2919 cm$^{-1}$,

**Table 1.** Assignment of the main vibration bands (2800–3000 cm$^{-1}$) of DPPC monolayer on pure water and salt solutions

| subphase | $\upsilon_a(CH_3)$ | $\upsilon_a(CH_2)$ | $\upsilon_s(CH_3)$ | $\upsilon_s(CH_2)$ |
|---|---|---|---|---|
| pure water | 2956 | 2920 | 2888 | 2850 |
| $Na_2SO_4$ | 2955 | 2919 | 2880 | 2850 |
| NaCl | 2960 | 2920 | | 2850 |
| NaBr | 2968 | 2920 | 2892 | 2850 |
| $NaNO_3$ | 2960 | 2920 | | 2850 |
| $NaHCO_3$ | 2960 | 2919 | | 2850 |
| $NaCH_3COO$ | 2960 | 2920 | 2883 | 2850 |
| $(NH_4)_2SO_4$ | 2958 | 2920 | | 2850 |
| $NH_4Cl$ | 2955 | 2920 | | 2850 |
| $NH_4Br$ | 2955 | 2920 | 2879 | 2851 |
| $NH_4HCO_3$ | 2956 | 2920 | 2882 | 2850 |
| $NH_4CH_3COO$ | 2958 | 2920 | 2886 | 2850 |

indicating an increase in *trans* relative to *gauche* conformations and a higher degree of order.[19,37] Such a trend can be observed in Table 1, where the vibration modes of $CH_3$ asymmetric ($\upsilon_a(CH_3)$), $CH_2$ asymmetric ($\upsilon_a(CH_2)$), $CH_3$ symmetric ($\upsilon_s(CH_3)$) and $CH_2$ symmetric ($\upsilon_s(CH_2)$) at 2955, 2919, 2880 and 2850 cm$^{-1}$, respectively, are shifted to lower wavenumbers when DPPC is compressed on the $Na_2SO_4$ solution. The $\upsilon_a(CH_2)$ values below 2920 cm$^{-1}$ are typical for *all-trans* conformations (Fig. S3).[55] It can be seen that the alkyl chains are slightly more ordered in the presence of $SO_4^{2-}$. The $CH_3$ symmetric stretch at 2888 cm$^{-1}$ on pure water shifted to higher frequency (2968 cm$^{-1}$) in the presence of NaBr. This observation confirms that *gauche* defects exist within the alkyl chain, as the existing IRRAS polarisation is sensitive to the orientation of the terminal methyl, which indirectly reports on *gauche* versus *trans* bonds in the alkyl chains.[19] The frequencies of the $CH_3$ and $CH_2$ groups show that, in the presence of NaBr, the order of the hydrocarbon chains is decreased with respect to DPPC molecules on pure water, indicating a higher content of *gauche* conformations. These findings are in accordance with results obtained in the $\pi$–A isotherms. Previous experimental studies have found that concentrated NaI solutions disrupt chain ordering at low surface pressures,[37] which demonstrates that chaotropic anion's ability to disorder the alkyl chain region, as is typical for $Br^-$. In the case of ammonium salt solutions, the intensities of the $\upsilon_a(CH_2)$
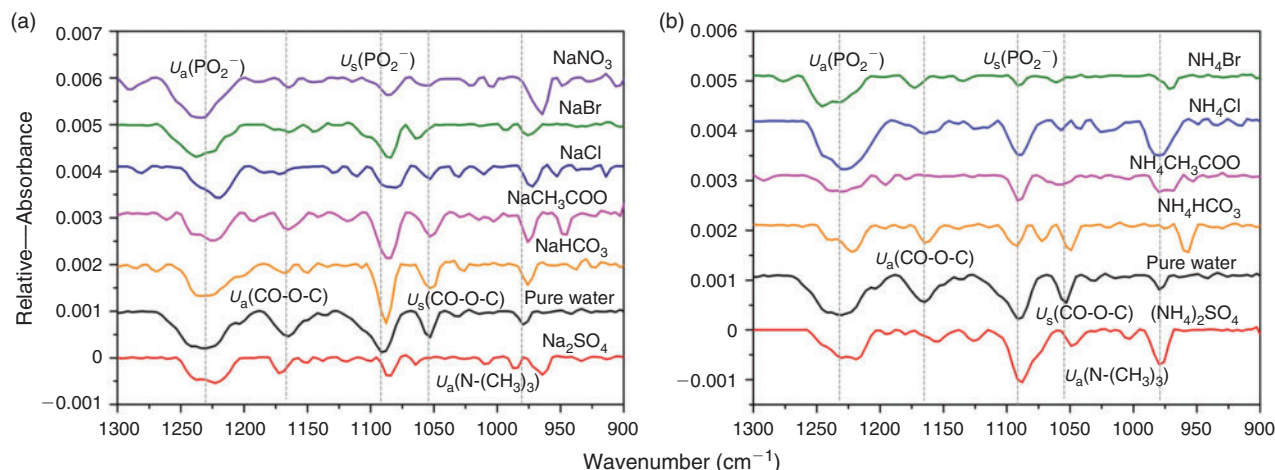
**Fig. 6.** IRRAS spectra (900–1300 cm⁻¹) of DPPC monolayers on water: (a) sodium salt solution and (b) ammonium salt solutions at 0.001 M.

and $\upsilon_s(CH_2)$ bands of DPPC monolayers are lower than those on the pure water (Fig. 5b). Only in the presence of $(NH_4)_2SO_4$ is the intensity of the $\upsilon_a(CH_2)$ band a little stronger than that on pure water, as the DPPC molecules are packed closer together.

A novel Hofmeister effect was demonstrated by Gurau et al. in an octadecylamine monolayer spread on salt solutions by using vibrational sum frequency spectroscopy. The ratios of oscillator strengths from the $CH_3$ symmetric stretch to the $CH_2$ symmetric stretch for the anions follow a series from most ordered to least ordered monolayer, as is consistent with the Hofmeister series.[39] The peak-height intensity ratio between the antisymmetric and symmetric bands of the $CH_2$ groups $(I_{as}/I_s)$ has been demonstrated to be a measure of the order/disorder parameter of the phospholipid chains in the lipid layer.[57–59] The shifts in the peak position of the DPPC alkyl chain $CH_2$-asymmetric mode are less than 1 cm⁻¹ from the value measured on water (Fig. S4). The $I_{as}/I_s$ ratio for the DPPC monolayer at the different concentrations of NaCl solutions remains practically constant. Similar to the previous IRRAS study of NaI, [37] I⁻ anions do not affect the LC phase, which is recovered unchanged at high pressures. However, the LE–LC phase-transition pressure of the DPPC monolayer increases with I⁻ concentration.[37] The LE phase appears to be favoured in the presence of anions. The grazing incidence X-ray diffraction results also imply that Br⁻ ions do not penetrate into or bind to the LC phase.[37] At higher concentrations of NaHCO₃, the positions of the methylene peaks do not change (Fig. S5), indicating that the shape of the LC phase domains is not strongly influenced by the concentrations of anions. This observation suggests that the LC phase appears to be less impacted by anions than the LE–LC phase.

The region between 1300 and 900 cm⁻¹ gives information about the vibrations of the phosphate ($PO_2^-$) headgroup. Spectra of the phosphate vibrational modes of DPPC on pure water and salt solutions are shown in Fig. 6. The asymmetric and symmetric $PO_2^-$ stretching ($\upsilon_a(PO_2^-)$ and $\upsilon_s(PO_2^-)$) modes of DPPC on pure water were observed at 1233 and 1090 cm⁻¹, respectively. Peaks at 1171 and 1053 cm⁻¹ can be attributed to the CO-O-C asymmetric and symmetric stretches ($\upsilon_a(CO\text{-}O\text{-}C)$ and $\upsilon_s(CO\text{-}O\text{-}C)$) of the carbonyl esters, respectively. The feature at 978 cm⁻¹ is attributed to N-(CH₃)₃ asymmetric stretches of the choline group ($\upsilon_a(N\text{-}(CH_3)_3)$). Comparison of the spectra in the presence as well as in the absence of salts shows a marked difference in the absorption frequencies of the phosphate groups

**Table 2.** Assignment of the main vibration bands (900–1300 cm⁻¹) of DPPC monolayer on pure water and salt solutions

| subphase | $\upsilon_a(PO_2^-)$ | $\upsilon_s(PO_2^-)$ | $\upsilon_a(CO\text{-}O\text{-}C)$ | $\upsilon_s(CO\text{-}O\text{-}C)$ | $\upsilon_a(N\text{-}(CH_3)_3)$ |
|---|---|---|---|---|---|
| pure water | 1233 | 1090 | 1166 | 1053 | 978 |
| Na₂SO₄ | 1228 | 1085 | 1171 | 1064 | 966 |
| NaCl | 1224 | 1083 | 1173 | 1054 | 972 |
| NaBr | 1236 | 1086 | 1165 | 1062 | 976 |
| NaNO₃ | 1235 | 1085 | 1165 | 1055 | 968 |
| NaHCO₃ | 1231 | 1087 | 1167 | 1052 | 976 |
| NaCH₃COO | 1226 | 1086 | 1165 | 1052 | 974 |
| (NH₄)₂SO₄ | 1227 | 1086 | 1156 | 1068 | 977 |
| NH₄Cl | 1228 | 1089 | 1164 | 1058 | 978 |
| NH₄Br | 1235 | 1091 | 1171 | 1060 | 970 |
| NH₄HCO₃ | 1229 | 1089 | 1162 | 1050 | 958 |
| NH₄CH₃COO | 1230 | 1089 | 1179 | 1057 | 971 |

(Table 2). These adsorption bands undergo shifts to diminished peak frequencies and intensities in the presence of salt solutions. The asymmetric $\upsilon_a(PO_2^-)$ stretching frequency at 1230 cm⁻¹ decreases slightly in the presence of anions, indicating an increase in the average hydration of the phosphate group.[39]

A much weaker Na⁺/DPPC interaction has been proposed recently, as found by molecular simulations involving monolayers and bilayers.[26] The influence of concentrated ammonium nitrate on monolayers of some carboxylic acids and their derivatives at the air–water interface has been studied earlier.[60,61] $NH_4^+$ and $NO_3^-$ participate as bridging components between the headgroups of dicarboxylic acid at the interface.[60,62] The separation between the $\upsilon_a(PO_2^-)$ and $\upsilon_s(PO_2^-)$ modes $(\triangle = \upsilon_a(PO_2^-) - \upsilon_s(PO_2^-))$ increases according to the Hofmeister series. In the presence of Na₂SO₄, the separation between the $\upsilon_a(PO_2^-)$ and $\upsilon_s(PO_2^-)$ frequencies ($\triangle = 143$ cm⁻¹) is smaller than the presence of NaBr ($\triangle = 180$ cm⁻¹). The smaller separation suggests that the interaction of $SO_4^{2-}$ with DPPC is stronger.[28] For the ammonium salt solutions, the separations in the range of 139 to 144 cm⁻¹ are much smaller than the sodium salt solutions. The interactions of $NH_4^+$ and $SO_4^{2-}$ with the polar headgroups of DPPC shift the peaks to lower frequencies (1227 and 1086 cm⁻¹). The separation between the $\upsilon_a(PO_2^-)$ and $\upsilon_s(PO_2^-)$ for (NH₄)₂SO₄ solution ($\triangle = 139$ cm⁻¹) is smaller than that for Na₂SO₄ ($\triangle = 144$ cm⁻¹). The separation for NH₄Br ($\triangle = 144$ cm⁻¹) is also smaller than that for NaBr

( $\triangle = 180\,\mathrm{cm}^{-1}$ ). A possible explanation for this difference is the position of $NH_4^+$ (to the right of $Na^+$) in Hofmeister sequences for a fixed anion.[34] $NH_4^+$ adsorption on the surface is stronger than the other monovalent cations.[63] The introduction of those ions with relatively strong Hofmeister effects, such as ammonium and sulfate, can enhance the stabilities of the monolayers.

*Atmospheric implications*

Lipids such as DPPC molecules released from cell lysis of phytoplankton can spread on the sea surface microlayer, and then be transferred into the atmospheric aerosols through bursting bubbles. The formation of organic coatings can affect the surface properties of aerosols. In particular, highly ordered organic films coated on aerosols can disrupt the transport of volatile species and reactive free radicals such as OH and $HO_2$ from the gas phase into particles. They could also reduce the evaporation of water from aerosol surfaces.[53] In addition, they could reduce the scavenging efficiency of particles by formation of larger cloud and rain droplets.[64] In the last case, organic films would enhance the atmospheric lifetime of aerosol relative to that expected if organic films were not present.[65] In general, the properties of organic-coated aerosols depend on the nature and concentration of the ions present.

Thus, the results presented here have implications for organic-coated aerosols, as several of the ions studied here have been found at higher levels in marine aerosols, especially $SO_4^{2-}$, which has been found in large quantities.[22,66] $SO_4^{2-}$ is considered a much stronger kosmotropic anion than other anions;[34] its $\pi$–A isotherms show that it can facilitate the formation of highly ordered organic films. As discussed above, the formation of highly ordered organic films on aqueous aerosol surfaces could hinder the transport of volatile species through the interface. The IRRAS spectra suggest that $NH_4^+$ and $SO_4^{2-}$ are likely be more attracted to – and have a higher binding affinity for – DPPC headgroups. As illustrated in Fig. 7, preferential adsorption of $SO_4^{2-}$ with the DPPC monolayer may result in the transport of DPPC monolayer into the atmosphere. These results obtained in the present study could also explain the enrichment of these ions in marine aerosols.[67] The presence of $Br^-$ in the subphase disordered the packing of the DPPC alkyl chains; i.e., it would lower the stability of organic films on an aerosol surface, resulting in defect sites in the DPPC monolayer. Experimental studies of water uptake by hydrophobic surfaces suggest that water uptake does indeed occur on these surfaces, preferentially at the defect sites.[68–70] If a small amount of water does adsorb to the surface, it can then diffuse through the coating or through coating defects and activate the inorganic core.[51]

Inorganic and organic acids also have received attention recently in terms of their roles in $Cl^-/Br^-$ depletion reactions in marine aerosols.[71] $SO_4^{2-}$ has been shown to substitute for $Cl^-$ more effectively than $NO_3^-$ in fine marine particles.[72,73] Surface-active species in marine aerosols are suggested to combine with $SO_4^{2-}$ more tightly than $NO_3^-$. Organic acids, such as $CH_3COO^-$, have been shown to be more active in the $Cl^-/Br^-$ depletion reactions for the smallest marine particle size ($<1\,\mu\mathrm{m}$).[74] Based on the Hofmeister sequence, our results also show that the interactions of $CH_3COO^-$ ions with DPPC molecules are stronger than those of $Cl^-$ and $Br^-$. These selective processes can alter the chemical composition of marine aerosols and, consequently, their hygroscopic and radiative properties.

Furthermore, the increased concentration of salt solution causes destabilisation of the surface film, as the $\pi$–A isotherms of DPPC monolayers are shifted to large areas. Concentrated
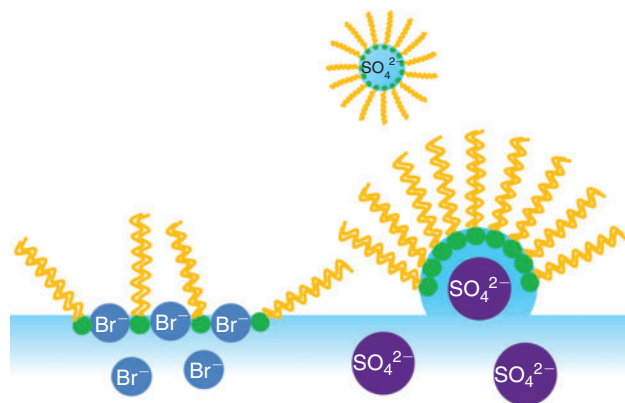


**Fig. 7.** Schematic representation of the behaviour of $Br^-$ and $SO_4^{2-}$ ions in a DPPC monolayer.

sodium and ammonium solutions impact the surface morphology of lipid films, which will influence the rate of water exchange with the atmosphere. Surface tension also depends on solution concentration and the presence of complex aqueous mixtures in aerosols, including both surface-active organic solutes and inorganic electrolytes.[75,76] The thickness of a lipid monolayer depends on the concentration of ions in solution.[28] The refractive index of organic-coated aerosols will change with the concentration of ions as the particle experiences loss or uptake of water from the environment.[19] The water retention combined with the organic shell on the particles can potentially impact light scattering by these particles. It could also affect their activity as cloud condensation nuclei, as well as their heterogeneous chemistry and photochemistry on the particle surfaces.[77] The results found here provide some insight into the interfacial properties of marine aerosols and their atmospheric implications.

## Conclusions

The goal of this study was to ascertain how anions in marine aerosols impact the interfacial organisation and structure of organic lipid films, and to understand the effects of concentration and of the Hofmeister series. The $\pi$–A isotherms and IRRAS measurements reveal that sodium and ammonium salts expand the DPPC monolayer and destroy the ordering of the lipid packing at a certain concentration. The increase in surface pressure follows the Hofmeister series for different anions with a fixed cation. The shape of the LC phase domains is independent of salt concentration, which indicates that the anions do not penetrate into or bind to the domains of the LC phase.

The presence of $Br^-$ reduces the stability of the DPPC monolayer, and suggests that defect sites may exist at the interface. The condensed monolayer and lower separation of phosphate vibrational modes imply that aerosols are enriched in $SO_4^{2-}$ ions, but not significantly in other anions. The concentration and nature of anions impact the surface morphology of lipid films, which will influence the air–water exchange, the evaporation of water and the refractive index of organic-coated aerosols in the atmosphere.

## Supplementary material

The following information is available on the Journal's website: surface pressure–area isotherms of DPPC monolayers on NaCH₃COO solutions with varying salt concentrations (Fig. S1); surface pressure–area isotherms of DPPC monolayers on 0.1 M

ammonium salt solutions (Fig. S2); the *all-trans* structure of DPPC molecule (Fig. S3); IRRAS spectra of the CH-stretching region of DPPC monolayers on NaCl (Fig. S4) and NaHCO$_3$ (Fig. S5) solutions with varying salt concentrations.

## Conflict of interest

The authors declare that they have no conflicts of interest.

## Acknowledgements

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