Investigating the Surface Structure of Liquids Containing Ionic Species

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Abstract

In this work liquid systems containing ionic species are investigated in order to further understand the forces that govern the surface structure of liquids. The distribution of ions along the surface normal, or charge distribution, is especially important in foam films (such as soap bubbles) where the electrostatic forces generated from the separation of charges at the liquid/air interfaces play a pivotal role in stopping the film from collapsing.

Many powerful techniques for investigating surfaces require the samples to be measured under ultra-high vacuum. The volatile nature of liquids makes their use in these instruments difficult, especially so in the case of foam films which are already in a fragile, metastable state. Specialised equipment and experimental techniques are developed for the investigation of foam films under vacuum. A glass film holder is used to generate and hold the film. This film holder is held inside an enclosed cell designed to minimise the evaporation of solvent from the film and aid film stability. Variations to the setup are designed and tested which allow for greater stability of the foam film, along with the means to measure the films under altering conditions.

Foam films of a cationic surfactant, hexadecyltrimethylphosphonium bromide, were investigated. A range of measurements were performed that demonstrated the thinning, and consequential surface rearrangement, of the foam film over time. These results also indicated a decrease in the surface potential upon foam film formation, partially owing to the reorientation of surfactant molecules at the surface.

Foam films containing a non-ionic surfactant, dodecyldimethyl phosphine oxide, were also investigated using the above technique. These films were studied with no added electrolyte as well as added salts, where the anion was varied. Comparing the concentration depth profiles of the foam films to the corresponding bulk liquid surfaces for the various systems studied allowed for the determination as to how the liquid surface changes upon foam film formation. It was found that the addition of salt increased the surfactant adsorption at the surface of both the foam film and bulk liquid. Additionally, it was seen that while iodide was detected as a surface excess at the bulk liquid, chloride was not. Both are detected as a surface excess at the foam film surface.

Surfaces of ionic liquids were also investigated, as they represent a unique situation of a liquid being comprised totally of charged species. Thus, the charge distribution is not mediated by an additional species, as is the case with aqueous solutions. The effect of small amounts of water as a surface impurity in [C_6mim][Cl] was investigated. Increasing the water content lead to an increase in the amount of anion adsorbed at the surface, indicating how forces other than the electrostatic interaction between ions governs surface structure. It was seen that for both protic and aprotic ionic liquids that the cation aliphatic chain length had a significant influence on the surface structure. Increasing the chain length caused increased adsorption of the cation, with subsequent cation reorientation at the surface.

Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Christiaan Ridings

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List of publications

Peer-reviewed journals

[1] Ridings, C. & Andersson, G. Determining concentration depth profiles of thin foam films with neutral impact collision ion scattering spectroscopy. *Review of Scientific Instruments* **81**, 113907-113915 (2010).

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Book chapters

Ridings, C. & Andersson, G. in Innovations in Nanomaterials, **Under review,** (Nova Science Publishers, Inc., 2014).

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Abbreviations

Abbreviations	
AIL	Aprotic ionic liquid
CBF	Common black film
cmc	Critical micelle concentration
DLVO (theory)	Derjaguin Landau Verwey Overbeek (theory)
DRS	Direct recoil spectroscopy
EDL	Electrical double layer
FPDT	Foam pressure drop technique
FWHM	Full-width half-maximum
HOMO	Highest occupied molecular orbital
IL	Ionic liquid
IMFP	Inelastic mean free path
ISS	Ion scattering spectroscopy
LEIS	Low energy ion scattering
MD	Molecular dynamics
MIES	Metastable induced electron spectroscopy
MO	Molecular orbital
NBF	Newton black film
NICISS	Neutral impact collision ion scattering spectroscopy
NLO	Non-linear optical
NMR (spectroscopy)	Nuclear magnetic resonance (spectroscopy)
NR	Neutron reflectivity
PIL	Protic ionic liquid
QMS	Quadrupole mass spectrometer
RBS	Rutherford backscattering spectroscopy

RTIL	Room temperature ionic liquid
SFA	Surface force apparatus
SFG	Sum frequency generation vibrational spectroscopy
TFPB	Thin film pressure balance
TOF	Time of flight
UHV	Ultra high vacuum
UPS	Ultraviolet photoelectron spectroscopy
VSFS	Vibrational sum frequency spectroscopy
XPS	X-ray photoelectron spectroscopy
XR	X-ray reflectivity

Frequently discussed chemical abbreviations	
C_nTAB	(alkyl)trimethylammonium bromide
C_nTPB	(alkyl)trimethylphosphonium bromide
C_{12}DMPO	(alkyl)dimethylphosphine oxide
$[C_n\text{mim}]^+$	1-(alkyl)-3-methylimidazolium$^+$
$[BF_4]^-$	tetrafluoroborate$^-$
POPC	1-palmitoyl-2-oleoylphosphatidylcholine
EAN	ethylammonium nitrate
PAN	propylammonium nitrate
EtAN	ethanolammonium nitrate

Contextual Statement

This thesis presents the investigations into the surface structure of liquids containing ionic species as performed as part of the author's PhD project. It also contains some grounding work from the author's preceding Honours project that directly flows onto the PhD project, which justifies its inclusion.

The Introduction chapter contains a literature review of the current field directly concerning the project, while the Experimental chapter contains the experimental details of the project, along with a discussion of the experimental methods used as part of the project. Given that such a large portion of the project was involving the NICISS technique, a particularly in-depth discussion and review of the method is given in that chapter.

The results chapters 3 – 7 are reformatted versions of the published peer-reviewed papers of the same title, while chapters 8 and 9 are reformatted versions of papers either under review or sent to journals for review.

The author of this thesis was the primary author of all papers used as results chapters. All experimental work was completed by the author. Exceptions involve: Dr. V. Lockett who carried out the Karl Fisher titration to determine the water content in the aprotic ILs; and Dr. E. Carey who performed TFPB measurements (in addition to those completed by the author) in order to test data reproducibility. The author also completed all data evaluation, but acknowledges the input of the respective co-authors in the final interpretation of results.