REVIEW

Surface Potential of the Air/Water Interface

Cuong V. Nguyen¹, Hiromichi Nakahara², and Chi M. Phan^{3*}

¹ Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, VIETNAM

² Department of Industrial Pharmacy, Daiichi University of Pharmacy, 22-1 Tamagawa-cho, Minami-ku Fukuoka 815-8511, JAPAN

³ Discipline of Chemical Engineering and Curtin Institute of Functional Molecules and Interfaces, Curtin University, GPO Box U1987, Perth, WA 6845, AUSTRALIA

Abstract: The surface charge/surface potential of the air/water interface plays a key role in many natural and industrial processes. Since the first decade of the 20th century, there are many theoretical proposals to describe the surface charge in the presence of different moieties. However, a complete and consistent description of the interfacial layer remains elusive. More recently, the theoretical frameworks and experimental data get complementary support from the simulation at a molecular level. This paper reviews the recent developments from the theoretical, experimental and simulation aspects. The combined results indicated that the interaction between hydration shells of adsorbed ions and the H-bonds network of surface water plays a critical role in the ionic adsorption. The factor should be incorporated into the conventional theories to correctly predict the ion distribution near the air/water surface.

Key words: surface charge, air/water surface, surface potential

1 Introduction

Since the early 20th century, the adsorption of the electrolytes is often modelled via surface tension measurement. While the tension reduction is well-accepted for surfactants, the changes for electrolytes are small and rather controversial¹. By applying the Gibbs equation to electrolytes, the adsorption should be negative². However, Jones and Ray published the data showing a minimum surface tension for different electrolytes³. The results indicated that there is negative and then positive adsorption as the concentration changes. Langmuir attributed to experimental errors due to the wetting film on the capillaries⁴, which would be corrected by other experimental methods⁵. Yet it was confirmed that the experimental errors are insignificant and the effect is apparently controlled by the anions⁶. Since the adsorption layer of the charged moieties is the same order of the molecular size, one can expect a non-neutral charge of the surface⁷. Hence, the surface charge of electrolytes is critical to explain the impact on the adsorption of electrolytes⁸⁻¹⁰. The surface charge and ionic adsorption play deterministic roles on the adsorption of macromolecules¹¹, bio-reagents¹², or non-soluble agents¹³ at the air/water surface. Consequently, a proper description of ionic charge of the air/water surface will provide important insights for many natural and industrial processes.

While significant numbers of studies have focused the Jones-Ray effect, i.e. surface tension, the theoretical works are not critically examined for surface potential. One of the earlier exceptions was the study by Warszynski and co-authors¹⁴, in which the surface charge was coupled with surface tension. This review focuses on the latest studies on interfacial layer using the surface charges/surface potential and on the quantitative modelling of the surface charge. More importantly, the structure was obtained by a combination of the simulation and experiment.

2 Experimental Studies on Surface Charge

Comparing to solid surfaces, the measurement of the surface potential has been far more difficult. The available methods measure the change in surface potential, induced by adsorbed molecules. Since the change in surface potential is in the magnitude of millivolts, many factors such as the cleanliness of the surface, the equilibrium state of the interface and the stability of electronic and mechanical equipment would significantly affect the accuracy of the data. In the literature, the change in the surface potential was measured directly using two different methods.

* Correspondence to: Chi M. Phan, Discipline of Chemical Engineering and Curtin Institute of Functional Molecules and Interfaces, Curtin University, GPO Box U1987, Perth, WA 6845, AUSTRALIA

E-mail: c.phan@curtin.edu.au

Accepted February 14, 2020 (received for review January 28, 2020)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjocs>

Fig. 1 Vibrating condenser for studying Volta effect in liquids (Reprinted with permission from reference¹⁵).

2.1 Vibrating plate method

The vibrating plate method was first introduced by Yamins and Zisman¹⁵ to determine the surface potential as well as the electrical properties of monomolecular films floating upon a liquid. This method is based on the usual null method and rigorously described elsewhere¹⁶. A description of the apparatus can be seen in Fig. 1. A flat electrode A, which is made of gold is adjusted to be parallel to the water surface B. A platinum wire, W, is dipped into the solution deep enough to complete the electrical circuit thanks to sufficiently good conductivity of water. Three thin slips of a non-conductive and heat-resistant plastic (Bakelite) K_1K_2 with a fine screw SP near the end are cemented upon the upper surface of the electrode A to form three spokes 120° apart. The vibration of electrode A to and away from the water interface (as close to the interface as possible without any contact) is controlled by the flexible diaphragm, DD, of a loudspeaker vibrator. The parallelism and proximity between the surfaces of A and B are obtained by adjusting the height of Pyrex tray containing water until each screw point seems to touch its image reflected in the water.

It is noted that the capacity of the A and B's surfaces is changed periodically by altering the separation of the surfaces, which leads to the alteration of the current between A and B. This alternating current is then detected by connecting an audiofrequency amplifier in the circuit to the output where a telephone is connected. By using a potenti-

ometer to adjust the potential difference applied to A and B until no signal is heard, one can measure the Volta e.m.f., which is equal in magnitude but opposite in polarity to the potentiometer reading.

Applying this apparatus on air/water and air/oil-film interfaces, Yamins *et al.*¹⁵ gained the time-independent potential difference (dV) for the intervals ranging up to 1 hour, except for a miniature increase by 5 mV in the first several minutes caused by the condensation of water upon the gold surface. The obtained results were steady-state with the repeatability of within 3 mV. In addition, this method had a significant reproducibility with a highly satisfactory manner, which can be seen clearly in Table 1.

2.2 Ionization method

The ionization method has been extensively used to measure the potential difference between two opposing interfaces for decades^{17, 18}. In comparison with vibrating plate method, ionization method setup is simpler with a source to ionize the air space between the two surfaces and a high impedance electrometer as an indicating device¹⁹. In principle, the potential difference between the surfaces is determined based on the average energy to produce an ion pair, that is related to the ionization produced in air by a known-energy α -particle²⁰.

An addition to a common electrometer and calomel electrode (used as a reference electrode), the α -particle emitter is required. Originally, polonium-210 (^{210}Po) was firstly used by Guyot²¹, and Jarvis²² for the ionizing electrode in the schematic diagram showed in Fig. 2. A number of ^{210}Po strips were attached to the surface of a 5×5 cm brass plate to form this electrode, that was mounted about 1 cm above the liquid's interface. This experimental instrument was employed to measure the surface potential of various electrolyte solutions, such as NaCl, Na_2SO_4 , NH_4Cl , and $\text{Mg}(\text{NO}_3)_2$ with a reported sensitivity of ± 1 mV.

Another type of the ionizing electrode use by Bewig¹⁹ consists of a 6×6 mm foil activated with radium-226 (^{226}Ra), which is placed between a gold over-layer and a silver base-plate. This apparatus was used to investigate the impacts of the distance between two surfaces on the accuracy of the measured results. It is noted that both

Table 1 The potential difference (mV) between gold and oil-films measured by vibrating plate method¹⁵.

Oil films	1 st	2 nd	3 rd	4 th	5 th
	run	run	run	run	run
Oleic acid on water	163	162	165		
Palmitic acid in benzene on water	291	298			
Palmitic acid in benzene on 1/100 normal H_2SO_4	380	394	380	383	379
Tricaprylin on water	407	408			
Tricaprylin on 1/100 normal H_2SO_4	426

Fig. 2 Experimental setup for Ionizing-electrode method: (1) Calomel electrode; (2) Brass plate with a series of thin polonium-210 strips attached to the surface; (3) Aqueous solution; (4) High impedance electrometer.

Fig. 3 Experimental setup for surface potential measurement using an ionizing ^{241}Am electrode.

^{210}Po and ^{226}Ra are able to pose adverse effects on living organisms due to their intense radioactivity and chemical reactivity. As a result, these ionization probes are not used recently.

Recently, the ionizing Americium-241 (^{241}Am) electrode has been popularly used in potential instruments owing to its relatively little harmful alpha and gamma radiation^{23–31}. As can be seen in Fig. 3, while a reference electrode is immersed in the liquid phase, the ionizing ^{241}Am electrode is positioned at a certain level (1–2 mm) above the air/liquid interface. The surface potential is calibrated to zero for just the air/water interface before starting the measurements. These experimental facilities have been utilized to determine the surface potential of solutions of electrolytes, surface-active agents, and proteins. The ionization method remains the most practical and reliable methods.

It is important to note the two features of the obtained data. First, the actual surface potential of pure water is unknown. Second, the change in the surface potential can be induced by the adsorption of charged molecules as well

Fig. 4 Density distribution for uni-univalent electrolytes in the interfacial zone, calculated from Equation (1).

as water reorientation.

3 Theoretical Frameworks

In the literature, there exist several proposed models for the electrical structure of the air/liquid interface with the presence of electrolytes and surface-active agents. These models are based on the surface tension and surface potential to quantify the adsorption of surfactant molecules, counter-ions and electrolytes, and can be briefly reviewed below.

3.1 Simple structure models

Originally, the experimental result found by Heydweiller and co-workers³²) showed that the surface tension of the solution of inorganic salts is greater than that of pure water. Thermodynamically, this increment indicates the deficiency of electrolytes within the interfacial zone. Based on this result, Onsager and co-worker⁸) proposed a simple theory to describe the structure of the interface layer and compute the surface tension of electrolytes, that could be compared to experimental data. In the systems of uni-univalent electrolytes, the density distribution in the interfacial zone was described by below equation, and one example was tabulated in Fig. 4.

$$\frac{c(x)}{c} = e^{\frac{-e^2 q^2 - 2k_B T x}{4Dk_B T x}} = e^{\frac{-q e^{-2k_B T x}}{2x}} \quad [1]$$

Where $c(x)$ is the concentration of solute at a distance x from the surface boundary; $c = c(\infty)$ is the bulk concentration of the solute; k_B is Boltzman constant; T is temperature; D is dielectric constant of solution.

It is noted that the analysis of Eq. 1 is independent on the nature of ions, and the density distribution of electrolytes is just dependent on the charge and concentration. Therefore, this theory predicted a zero surface charge, and consequently, a zero surface potential for electrolyte solu-

Fig. 5 A description of adsorption layer structure (left) and the variation of counter-ion and head group concentrations near the air/water surface (right) by Borwankar and Wasan model.

tions. However, experimental results clearly demonstrated significant surface potential, which depends on the salt's concentration³³). Moreover, experiments with several salts conducted by Jones *et al.*³⁴) indicated slight decreases in surface tension at extremely low concentrations before following a positive slope. These discrepancies encouraged the introduction of many surface structure models.

The simplest structure model was developed by Davies *et al.*³⁵) which considered the effect of a double layer on the adsorption. However, this model was not in quantitative agreement with some obtained experimental results, especially surface tension of ionic surfactants³⁶), and accordingly was improved by Borwankar and Wasan³⁷). In Borwankar-Wasan model (as described in Fig. 5), all adsorbed headgroups are assumed to be concentrated in an infinity thin layer, while other head groups are strongly compelled away due to the charged layer. Meanwhile, counter-ions are attracted to this charged layer and form an ion-concentrated region, which significantly contributes to the total adsorption.

As the adsorption layer is infinity thin, the surface charge density, σ is proportional to the surface excess concentration, Γ and can be computed by Grahame equation.

$$\sigma = z_1 \Gamma_1 = \frac{\sqrt{8\epsilon\epsilon_0 k_B T c_{2\infty}}}{e} \sinh\left(\frac{e\psi_s}{2k_B T}\right) \quad [2]$$

Where ψ_s is the surface potential of the charged adsorption layer, 1 and 2 is for surfactant head group and for counter-ion respectively. In this model, the surface excess was determined by the Frumkin isotherm, and the relation between the surface tension and surface excess obeys the Gibbs adsorption isotherm, described by the analytical equation:

$$Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp(-2\beta \frac{\Gamma_1}{\Gamma_\infty}) \quad [3]$$

Where β is the intermolecular interaction constant. If β is positive, adsorbed surfactants enhance the adsorption and vice versa. c_{1s} is the headgroup concentration at the adsorption layer, and can be calculated from the bulk concen-

tration using the Boltzmann equation.

$$c_{1s} = c_{1\infty} \exp\left(-\frac{z_1 e\psi_s}{k_B T}\right) \quad [4]$$

$$\gamma_0 - \gamma = -k_B T \Gamma_\infty \left[\ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right) + \beta \left(\frac{\Gamma_1}{\Gamma_\infty}\right)^2 \right] + \frac{4k_B T \sqrt{2\epsilon\epsilon_0 k_B T c_{2\infty}}}{e} \left[\cosh\left(\frac{e\psi_s}{2k_B T}\right) - 1 \right] \quad [5]$$

In general, the adsorption layer can be characterized by fitting eqs. 3, 4 and 5 to the experimental results of surface tension and surface potential using K , β , and Γ_∞ as fitting parameters. However, it is reported that these constants cannot be obtained reliably by curve fitting techniques due to the uncertainty and instability³⁸⁻⁴²). Besides, this simple model utilized the Grahame equation, which is still questionable for asymmetric electrolytes, and may not be applicable for low surfactant concentrations.

3.2 Ionic binding models

The assumption of simple structure models that all adsorbed head-groups stay in an infinity layer results in high surface potentials, which cannot be verified by reported experimental observations^{14, 19, 28, 37}). More importantly, current-developed techniques showed that there exist counter-ions closely interacting with the headgroups within the interfacial zone. Therefore, researchers proposed that a part of counter-ions should account for the structure of the adsorption layer, and developed the formulation of the ionic binding models accordingly.

From the above models (Fig. 6), it can be seen that the surface potential is a complicated function of the surface charge. The non-neutral charge of the interfacial layer is balanced by the charge distribution in the diffuse layer. The quantification of surface charge/surface potential requires non-measurable properties of the interfacial layer: the thickness and emissivity. The current models require additional information on the adsorbed ions, for instance, ionic headgroups surfactants^{14, 43}).

The summary, the current models on the surface charge is based mostly on surface tension. In most cases, the adsorption of ionic surfactant was obtained from surface tension and used as the ionic binding sites for ionic adsorption. Such information is not accessible for non-ionic surfactants nor electrolytes. Furthermore, the models require some information on the molecular arrangement between moieties.

4 Molecular Simulations

With the recent advance in computing, the molecular dynamics have been simulated for many different systems. The simulations can reveal molecular insights into the surface layer. Instead of verifying the proposed theory, however, the simulations present a more complicated ar-

Fig. 6 A description of adsorption layer structure with ionic binding¹⁴⁾.

range near the air/water surface.

4.1 Density distribution and the Gibbs dividing plane

Molecular simulations have been applied extensively to the air/water surface to describe the relative position of all moieties near the surface^{44, 45)}. In the current theories, the surface is typically defined by the Gibbs dividing plane^{12, 46)}, in which a model system of two phases with the same volumes are assumed homogeneous up to the dividing plane. By conceiving the dividing plane, Gibbs introduced a well-known adsorption isotherm for the interface state.

$$d\gamma = -\sum \Gamma_i d\mu_i \quad [6]$$

Where Γ_i and μ_i are the surface excess concentration and the thermodynamic potential of the i th component, respectively.

According to this approach, the location of the dividing plane is based on solvent distribution. The concept has been used to predict surface adsorption of surfactants and ions⁴⁷⁾. Hence, it is interesting to observe the distribution of molecules around the dividing plane. Contrasting to the conventional theory, the simulations demonstrated continuous variations of spatial distributions around the water surface as can be seen in Fig. 7^{48–51)}.

From the simulations, the dividing plane can be determined

by an error function:

$$\rho(z) = \frac{\rho_0}{2} \left(1 - \operatorname{erf} \left(\frac{z - z_0}{\sqrt{2} w} \right) \right) \quad [7]$$

Where ρ_0 is the density of water, z_0 is the Gibbs dividing plane (GDP) location, w is the width of the surface.

It is important to note that the width of the surface is around 0.5 nm, which is similar to ionic hydration shells. In addition to the thickness of the water surface, the simulations also demonstrated two distinguished layers of water molecules. While water molecules in the outer monolayer orient toward the vapor side, ones in the inner layer point to the liquid side^{52–54)}.

Unlike the well-structured arrangement of water or surfactant molecules at the interface, the distribution of inorganic ions is significantly varied. The molecular simulation dispute conventional theory, which depicts a gradual reduction for all ions as in Fig. 4. Instead, some ions are significantly present at the air/water surface (Fig. 8)⁵⁵⁾. Small inorganic halides, such as F^- or Cl^- are dimly present; meanwhile large anions including Br^- and I^- show an enrichment near the surface. Nevertheless, there is significant disagreement on the quantification of the depletion of the enhancement of these ions, either experimentally or theoretically.

Furthermore, the water surface has its own roughness, that would increase the surface area by approximate 15%, and form nanoscopic surface waves (capillary waves)⁵⁶⁾. In order to exclude the effect of capillary waves on the distribution of species within the interface, a new intrinsic method, call identification of truly interfacial molecules was proposed and successfully applied^{25, 57–60)}. In this method, molecules that form the interfacial layer and the subsequent molecular layers beneath the surface are searched by a sphere of a chosen radius moving along a number of test lines perpendicular to the surface (Fig. 9). Hence, it was verified that the distribution of ions is influenced by the surface roughness²⁵⁾.

4.2 Kinetics of ionic interactions at the surface

Motivated by the phenomena of selective ion adsorption at the aerosol interface, many studies have focused on understanding the behaviour of adsorbed ions at the air/liquid interface^{61–63)}. Despite much attention spent on ion polarizability as a critical factor for surface activity^{64–67)}, few studies have coped with the interfacial solvation of ions at the interface. Molecular dynamics simulation results recently have revealed important understanding of the hydration shell thickness and kinetic of ion-surface interaction.

Investigating the systems of sodium iodine and sodium chloride in water, Dang *et al.*⁶⁸⁾ indicated that the surface water molecules considerably affect the kinetics of ion pairing. Specifically, the association of ion pair at the interface is stronger than that inside the bulk, leading to the re-

Fig. 7 Density distributions of species within near water surface for alcohol/NaCl mixture. The density profile demonstrates strong interaction between ions and hydroxyl group of the alcohol. *Reproduced from reference 24. Copyright 2017 with permission from Elsevier.*

arrangement of the H-bond network of interfacial water molecules to accommodate this ion pair. Moreover, the large induced dipole of I^- would further enhance the pairing with Na^+ at the interface⁶⁵. The pairing is more likely to be determined within the first two solvation shells of the ions.

4.3 Interfacial layer defined by H-bonds structure

From the density distribution, the molecular simulations have not been able to verify the theoretical models in section 3. On the other hand, the simulated ions are clearly located further from the outmost water layer. Furthermore, the interaction between ionic hydration shells and the water surface is very strong comparing to those in bulk. As it can be seen clearly from **Fig. 7**, the Gibbs dividing plane is not appropriate for quantifying adsorbed ions. To quantify the ions adsorption, a new interfacial limit is required. The new limit needs to account for the H-bonds interaction. Consequently, we proposed a newly-defined limit of the interfacial zone⁵², which is positioned at the positive peak of the water dipole order as can be seen in **Fig. 10**.

The basis of the limit is that water molecules on the right of this limiting plane are constrained by the asymmetric interfacial arrangement, while water molecules on the left start moving in all direction as with water in the bulk. The exact position of this plane was found by fitting the profile of the dipole water moment against a polynomial function. It is worth noting that the presence of non-ionic surfactants⁶⁹ disrupted the well-structured arrangement of the interface, and shifted the positive peak further outside in response to increasing the surfactant's concentration. More importantly, the new limit allows quantitative models of the surface potential. In particular, the limit can be used to calculate the adsorbed ions for non-ionic surfactant/electro-

Fig. 8 Distribution of four sodium halides near the air/water surface: (A) to (D) shows ionic distribution for NaF, NaCl, NaBr and NaI (the blue circles represent Na^+ , and color circles represent the corresponding halide). (E) to (H) presents to density profiles of ions for corresponding systems. *Reprinted with permission from reference 55. Copyright 2004 American Association for the Advancement of Science.*

lyte mixture and electrolyte systems.

For the non-ionic surfactant/ions systems, we focused on MIBC and 1-hexanol²⁴. These two isomers have similar physiochemical properties, such as solubility, surface tension and z -potential. Yet, the surface potentials are completely different: one increased with NaCl and the other decreased. In these cases, the ion-binding model¹⁴ is applied to the polar group of the alcohol.

As revealed by the simulation, the contrasting behaviour was caused by the carbon chain (**Fig. 11**). In this instance, the carbon structure can alter the relative distribution between Na^+ and Cl^- . By using the new limits, the interfacial adsorption of ions were quantified and correlated very well with the contrasting experimental observation (**Fig. 11**)⁵².

Similar to the previous case, the new interfacial limit was also applied NaCl and NaI solutions. The ionic adsorption

Fig. 9 Water layers at the air/water interface analyzed by ITIM method.

Fig. 10 Newly-proposed limiting plane of the interfacial region based on the water dipole order⁵²⁾. Reprinted with permission from reference 52. Copyright 2015 American Chemical Society.

was inputted from the simulations before combining with the classical Grahame equation (Equation (2)). The adsorbed concentration clearly reflects the opposite experimental observation in the surface potential: increasing for NaCl and decreasing for NaI (Fig. 12)²⁵⁾. In these cases, the hydration shells of halides alter the interaction with H-bonds of surface water and consequently the relative anion/cation adsorption. The combined results also predict the surface potential of pure water at +13 mV.

In the absence of ionic surfactants, the ionic adsorption is governed by the interaction between hydration shells and H-bonds structure near the surface. The observation is consistent with the increased ionic binding near the surface⁴¹⁾. The role of H-bonds at water-liquid interface was explored in details by Sakurai and co-authors⁷⁰⁾. This factor was not included in the conventional theories as summarized in the theoretical section.

5 Conclusions and Outlooks

The surface charge is an important property of the air/water interface, which determines many industrial and natural processes. Despite of numerous studies, the surface charge is still not fully understood. The obstacles arise from the gap between experimental and theoretical models: most theories require multiple parameters which cannot be independently verified. Furthermore, the conventional models tend to depict a reduced ionic concentration near the surface, which was not observed in molecular simulations. Recently, a better modelling was obtained by a combination of the simulations and experimental data. The combined methods provide a quantifiable correlation between the adsorbed moieties and changes in surface potential. The results indicate that the adsorption of ions at the water surface was determined by the interaction between the H-bonds of the surface and hydration shells.

Fig. 11 Change in surface potential of MIBC/1-hexanol. Reproduced from reference 52. Copyright 2015 with permission from Elsevier.

Fig. 12 Comparison between NaI and NaCl systems (a) change in surface potential of NaCl/NaI. (b) net ionic concentration of the interface²⁵. Reproduced from reference 25. Copyright 2019 with permission from Elsevier.

This factor was not included in the conventional theory. Hence, the H-bonds structure should be included into the future theoretical framework to describe the ionic adsorption and the surface charge of the air/water surface.

References

- 1) Levin, Y.; Dos Santos, A.P.; Diehl, A. Ions at the air-water interface: An end to a hundred-year-old mystery? *Phys. Rev. Lett.* **103**, 257802-257806 (2009).
- 2) Petersen, P.B.; Saykally, R.J. On the nature of ions at the liquid water interface. *Annu. Rev. Phys. Chem.* **57**, 333-364 (2006).
- 3) Jones, G.; Ray, W.A. The surface tension of solutions of electrolytes as a function of the concentration II. *J. Am. Chem. Soc.* **63**, 288-294 (1941).
- 4) Langmuir, I. Repulsive forces between charged surfaces in water, and the cause of the Jones-Ray effect. *Science* **88** (2288), 430-432 (1938).
- 5) Wood, L.A.; Robinson, L.B. A test of Langmuir's interpretation of the Jones-Ray effect. *J. Chem. Phys.* **14**, 258-262 (1946).
- 6) Petersen, P.B.; Johnson, J.C.; Knutsen, K.P.; Saykally, R.J. Direct experimental validation of the Jones-Ray effect. *Chem. Phys. Lett.* **397**, 46-50 (2004).
- 7) Petersen, P.B. On the nature of ions at the liquid water surface. *Annu. Rev. Phys. Chem.* **57**, 333-364 (2006).
- 8) Onsager, L.; Samaras, N.N.T. The surface tension of Debye-Hückel electrolytes. *J. Chem. Phys.* **2**, 528-536 (1934).
- 9) Sakurai, M.; Tamagawa, H.; Inoue, Y.; Ariga, K.; Kunitake, T. Theoretical study of intermolecular interaction at the lipid-water interface. 1. Quantum chemical analysis using a reaction field theory. *J. Phys. Chem. B* **101**, 4810-4816 (1997).
- 10) Xiao, Y.; Zhao, J.K.; Xu, T.; Liu, S.W.; Wang, H.Z. Review of the technology of electrostatic enhancement of coalescence of water droplets in oil. in *Petrochemical Equipment*, Elsevier, pp. 49-53 (2009).
- 11) Ariga, K.; Mori, T.; Li, J. Langmuir nanoarchitectonics from basic to frontier. *Langmuir* **35**, 3585-3599 (2019).
- 12) Yunoki, T.; Kimura, Y.; Fujimori, A. Maintenance properties of enzyme molecule stereostructure at high temperature by adsorption on organo-modified magnetic nanoparticle layer template. *Bull. Chem. Soc.*

- Jpn.* **92**, 1662-1671 (2019).
- 13) Liu, X.; Riess, J.G.; Krafft, M.P. Self-organization of semifluorinated alkanes and related compounds at interfaces: Thin films, surface domains and two-dimensional spherulites. *Bull. Chem. Soc. Jpn.* **91**, 846-857 (2018).
 - 14) Warszynski, P.; Barzyk, W.; Lunkenheimer, K.; Fruhner, H. Surface tension and surface potential of Na Iz-dodecyl sulfate at the air-solution interface: Model and experiment. *J. Phys. Chem. B* **102**, 10948-10957 (1998).
 - 15) Yamins, H.G.; Zisman, W.A. A new method of studying the electrical properties of monomolecular films on liquids. *J. Chem. Phys.* **1**, 656-661 (1933).
 - 16) Noblet, A.; Ridelaire, H.; Sylin, G. Measurement of surface potentials. *J. Phys. E* **17**, 234-239 (1984).
 - 17) Schulman, J.H. Colloid chemistry. *Annu. Rev. Phys. Chem.* **11**, 169-186 (1960).
 - 18) Patai, I.F.; Pomerantz, M.A. Contact potential differences. *J. Franklin Inst.* **252**, 239-260 (1951).
 - 19) Bewig, K.W. Ionization method of measuring contact potential differences. *Rev. Sci. Instrum.* **35**, 1160-1162 (1964).
 - 20) Jesse, W.P. *The Ionization by Polonium Alpha Particles in Air and the Average Energy to Make an Ion*, Vol. 13 (1960).
 - 21) Guyot, J. Effet Volta Métal-Électrolyte et Couches Monomoléculaires. *Ann. Phys. (Paris)* **10**, 506-638 (14924).
 - 22) Jarvis, N.L.; Scheiman, M.A. Surface potentials of aqueous electrolyte solutions. *J. Phys. Chem.* **72**, 74-78 (1968).
 - 23) Phan, C.M.; Nakahara, H.; Shibata, O.; Moroi, Y.; Le, T.N.; Ang, H.M. Surface potential of methyl isobutyl carbinol adsorption layer at the air/water interface. *J. Phys. Chem. B* **116**, 980-986 (2012).
 - 24) Nguyen, C.V.; Phan, C.M.; Ang, H.M.; Nakahara, H.; Shibata, O.; Moroi, Y. Surface potential of 1-hexanol solution: Comparison with methyl isobutyl carbinol. *J. Phys. Chem. B* **117**, 7615-7620 (2013).
 - 25) Nguyen, C.V.; Nakahara, H.; Shibata, O.; Phan, C.M. Adsorption of sodium iodine at air/water interface. *J. Mol. Liq.* **298**, 112076-112082 (2020).
 - 26) Nguyen, C.V.; Phan, C.M.; Nakahara, H.; Shibata, O. Surface structure of sodium chloride solution. *J. Mol. Liq.* **248**, 1039-1043 (2017).
 - 27) Demé, B.; Rosilio, V.; ronique; Baszkin, A. Polysaccharides at interfaces 2. Surface potential of adsorbed cholesteryl-pullulan monolayers at the solution-air interface. *Colloids Surf. B* **4**, 367-373 (1995).
 - 28) Baszkin, A.; Deyme, M.; Couvreur, P.; Albrecht, G. Surface pressure and surface potential studies of poly (Isobutylcyanoacrylate)-ampicillin interactions at the water-air interface. *J. Bioactive.Compat. Polym.* **4**, 110-123 (1989).
 - 29) Nakahara, H.; Shibata, O.; Moroi, Y. Examination of surface adsorption of sodium chloride and sodium dodecyl sulfate by surface potential measurement at the air/solution interface. *Langmuir* **21**, 9020-9022 (2005).
 - 30) Nakahara, H.; Shibata, O.; Rusdi, M.; Moroi, Y. Examination of surface adsorption of soluble surfactants by surface potential measurement at the air/solution interface. *J. Phys. Chem. C* **112**, 6398-6403 (2008).
 - 31) Nakahara, H.; Shibata, O. Interfacial behavior of pulmonary surfactant preparations containing egg yolk lecithin. *J. Oleo Sci.* **63**, 1159-1168 (2014).
 - 32) Heydweiller, A. Über Physikalische Eigenschaften von Lösungen in Ihrem Zusammenhang. II. Oberflächenspannung Und Elektrisches Leitvermögen Wässeriger Salzlösungen. *Ann. Phys.* **338**, 145-185 (1910).
 - 33) Markin, V.S.; Volkov, A.G. Quantitative theory of surface tension and surface potential of aqueous solutions of electrolytes. *J. Phys. Chem. B* **106**, 11810-11817 (2002).
 - 34) Jones, G.; Ray, W.A. The Surface Tension of Solutions of Electrolytes as a Function of the Concentration II*. *J. Am. Chem. Soc.* **63**, 288-294 (1941).
 - 35) Davies, J.T.; Rideal, E.K.; Bender, M. Interfacial phenomena. *J. Electrochem. Soc.* **109**(7), 175C (1962).
 - 36) Lucassen-Reynders, E.H. Surface equation of state for ionized surfactants. *J. Phys. Chem.* **70**, 1777-1785 (1966).
 - 37) Borwankar, R.P.; Wasan, D.T. Equilibrium and dynamics of adsorption of surfactants at fluid-fluid interfaces. *Chem. Eng. Sci.* **43**, 1323-1337 (1988).
 - 38) Daen, J. Insoluble monolayers at liquid-gas interfaces. *J. Colloid Interface Sci.* **22**, 309 (1966).
 - 39) Dang, L.X. Computer simulation studies of ion transport across a liquid/liquid interface. *J. Phys. Chem. B* **103**, 8195-8200 (1999).
 - 40) Phan, C.M.; Le, T.N.; Yusa, S. A New and consistent model for dynamic adsorption of CTAB at air/water interface. *Colloids Surf. A* **406**, 24-30 (2012).
 - 41) Truong, V.N.T.; Wang, X.; Dang, L.X.; Miller, J.D. Interfacial water features at air-water interfaces as influenced by charged surfactants. *J. Phys. Chem. B* **123**, 2397-2404 (2019).
 - 42) Nguyen, C.V.; Nguyen, T.V.; Phan, C.M. Adsorption of alkyltrimethylammonium bromide surfactants at the air/water interface. *Int. J. Heat Mass Transf.* **106**, 1035-1040 (2017).
 - 43) Phan, C.M.; Nguyen, C.V.; Nakahara, H.; Shibata, O.; Nguyen, T.V. Ionic nature of a gemini surfactant at the air/water interface. *Langmuir* **32**, 12842-12847 (2016).
 - 44) Jungwirth, P.; Tobias, D.J. Specific ion effects at the air/water interface. *Chem. Rev.* **106**, 1259-1281

- (2006).
- 45) Gao, G.; Nguyen, C.V.; Phan, C.M. Molecular arrangement between electrolyte and alcohol at the air/water interface. *J. Mol. Liq.* **242**, 859-867 (2017).
 - 46) Cofman, V. The Scientific Papers of Willard Gibbs. *Science* **66**(1717), 510(1927).
 - 47) Butt, H.-J.; Graf, K.; Kappl, M. *Physics and Chemistry of Interfaces*. John Wiley & Sons (2006).
 - 48) Björneholm, O.; Hansen, M.H.; Hodgson, A.; Liu, L.-M.; Limmer, D.T.; Michaelides, A.; Pedevilla, P.; Rossmeisl, J.; Shen, H.; Tocci, G. *et al.* Water at interfaces. *Chem. Rev.* **116**, 7698-7726 (2016).
 - 49) Sun, L.; Li, X.; Hede, T.; Tu, Y.; Leck, C.; Ågren, H. Molecular dynamics simulations of the surface tension and structure of salt solutions and clusters. *J. Phys. Chem. B* **116**, 3198-3204 (2012).
 - 50) Hub, J.S.; Wolf, M.G.; Caleman, C.; Van Maaren, P.J.; Groenhof, G.; Van Der Spoel, D. Thermodynamics of hydronium and hydroxide surface solvation. *Chem. Sci.* **5**, 1745-1749 (2014).
 - 51) Jungwirth, P.; Winter, B. Ions at aqueous interfaces: From water surface to hydrated proteins. *Annu. Rev. Phys. Chem.* **59**, 343-366 (2008).
 - 52) Nguyen, C.V.; Phan, C.M.; Ang, H.M.; Nakahara, H.; Shibata, O.; Moroi, Y. Molecular dynamics investigation on adsorption layer of alcohols at the air/brine interface. *Langmuir* **31**, 50-56 (2015).
 - 53) Yuet, P.K.; Blankschtein, D. Molecular dynamics simulation study of water surfaces: Comparison of flexible water models. *J. Phys. Chem. B* **114**, 13786-13795 (2010).
 - 54) Mountain, R.D. An internally consistent method for the molecular dynamics simulation of the surface tension: Application to some TIP4P-Type models of water. *J. Phys. Chem. B* **113**, 482-486 (2009).
 - 55) Garrett, B.C. Ions at the air/water interface. *Science* **303**(5661), 1146-1147 (2004).
 - 56) Smith, J.D.; Rick, S.W. Ion clustering in aqueous salt solutions near the liquid/vapor interface. *Condens. Matter. Phys.* **19**, 1-10 (2016).
 - 57) Sega, M.; Hantal, G.; Fábíán, B.; Jedlovsky, P. Pytim: A python package for the interfacial analysis of molecular simulations. *J. Comput. Chem.* **39**, 2118-2125 (2018).
 - 58) Hantal, G.; Darvas, M.; Pártay, L.B.; Horvai, G.; Jedlovsky, P. Molecular level properties of the free water surface and different organic liquid/water interfaces, as seen from ITIM analysis of computer simulation results. *J. Phys. Condens. Matter.* **22**, 284112 (2010).
 - 59) Jorge, M.; Hantal, G.; Jedlovsky, P.; Cordeiro, M.N.D.S. A critical assessment of methods for the intrinsic analysis of liquid interfaces: 2. Density profiles. *J. Phys. Chem. C* **114**, 18656-18663 (2010).
 - 60) Pártay, L.B.; Hantal, G.; Jedlovsky, P.; Vincze, Á.; Horvai, G. A new method for determining the interfacial molecules and characterizing the surface roughness in computer simulations. Application to the liquid-vapor interface of water. *J. Comput. Chem.* **29**, 945-956 (2008).
 - 61) Otten, D.E.; Onorato, R.; Michaels, R.; Goodknight, J.; Saykally, R.J. Strong surface adsorption of aqueous sodium nitrite as an ion pair. *Chem. Phys. Lett.* **519-520**, 45-48 (2012).
 - 62) Bian, H.T.; Feng, R.R.; Guo, Y.; Wang, H.F. Specific Na⁺ and K⁺ cation effects on the interfacial water molecules at the air/aqueous salt solution interfaces probed with nonresonant second harmonic generation. *J. Chem. Phys.* **130**, 134709 (2009).
 - 63) Noah-Vanhoucke, J.; Geissler, P.L. On the fluctuations that drive small ions toward, and away from, interfaces between polar liquids and their vapors. *Proc. Nat. Acad. Sci. USA* **106**, 15125-15130 (2009).
 - 64) Petersen, P.B.; Saykally, R.J. Confirmation of enhanced anion concentration at the liquid water surface. *Chem. Phys. Lett.* **397**, 51-55 (2004).
 - 65) Wick, C.D.; Kuo, I.F.W.; Mundy, C.J.; Dang, L.X. The effect of polarizability for understanding the molecular structure of aqueous interfaces. *J. Chem. Theory Comput.* **3**, 2002-2010 (2007).
 - 66) Levin, Y. Polarizable ions at interfaces. *Phys. Rev. Lett.* **102**, 147803 (2009).
 - 67) Jungwirth, P.; Tobias, D.J. Ions at the air/water interface. *J. Phys. Chem. B* **106**, 6361-6373 (2002).
 - 68) Dang, L.X.; Schenter, G.K. Rate theory of ion pairing at the water liquid-vapor interface: A case of sodium iodide. *J. Chem. Phys.* **148**, 222820 (2018).
 - 69) Phan, C.M.; Nguyen, C.V.; Pham, T.T.T. Molecular arrangement and surface tension of alcohol solutions. *J. Phys. Chem. B* **120**, 3914-3919 (2016).
 - 70) Tamagawa, H.; Sakurai, M.; Inoue, Y.; Ariga, K.; Kunitake, T. Theoretical study of intermolecular interaction at the lipid-water interface. 2. Analysis based on the Poisson-Boltzmann equation. *J. Phys. Chem. B* **101**, 4817-4825 (1997).