

CHEMISTRY AT AQUEOUS INTERFACES

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Abstract:

The study of chemical reactivity at liquid/aqueous interfaces occupies an important place in chemistry. Operations like corrosion and the manoeuvre of electrochemical and photo-electrochemical cells, etc. are examples of chemical processes at the liquid/solid interface [6, 7]. For understanding processes such as liquid chromatography, phase-transfer catalysis[8] drug delivery problems in pharmacology[9] and other phenomena in membrane biophysics, electron transfer, ion transfer, and proton transfer at the interface between two immiscible liquids are fundamentally important[10]. While studying any reaction at aqueous interface, the behaviour of solute molecules and their reactivity at the interface between a liquid and a second phase is also needed to be considered as it affects the reactions occurring at the interface. This paper discusses the phenomenon 'On-Water Catalysis'. We review some enthalpic or entropic solvation effects that cause transition-state stabilization and accelerate the reaction, followed by structure of liquid-liquid and liquid-vapour interface. We also discuss some of the techniques for surface tension calculation. Finally, we discuss chemical reactivity at aqueous interfaces.

Keywords —On-Water Catalysis, tensiometer.

I. INTRODUCTION

The molecular structure of aqueous interfaces always had a significant role in various diverse fields such as chemistry, biology, astrophysics and atmospheric and soil sciences, etc. The significance of aqueous interfaces is not limited to any field. Though it's been thoroughly studied, an aqueous interface somehow manages to play a significant role in each field. Modern theories of the origin of life assume that water surfaces played a fundamental role in directing the earliest organic material and organizing it into vesicles, precursors of the simplest cells [1].

Aqueous interface is the place where one of the entity is water. Other entity may vary, i.e. it can be air, vapor, acid, or any other liquid. It is found that when two liquids are in contact, then their

interactions are weak. Also the liquid-liquid interfaces are locally sharp but are widened by capillary waves. These interfaces also affect both equilibrium and dynamic components of any chemical reactions [5].

When water interacts with gases, there are a number of coupled steps such as diffusion of gas to the surface, mass accommodation, diffusion inside the liquid, and possibly reaction in the bulk or at the gas/liquid interface, etc. [5] When acidic gases interact with aqueous systems including ice, processes like acid deposition, polar stratospheric clouds, and the polar snow packs, etc. start to occur. Thus, the structure of water surface has been a subject of research [33]. Most of the current models propose different theories regarding structure of water. The first SFG (Sum Frequency Generation) spectrum of the liquid water-vapor interface [24] depicts that about 20% of water molecules possess

a dangling bond i.e. free OH bonds, which are projected into vapor phase. More recent studies have also supported the fact of a 2D H-bond network at water surface (the ‘water skin’) where OH bonds oscillate around a plane parallel to the instantaneous surface [34]. Figure 1 shows a schematic view of the water with a typical density profile from classical molecular dynamics simulations.

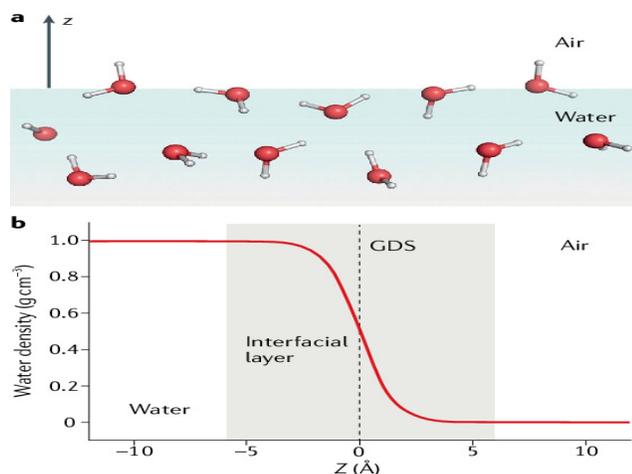


Fig. 1 Schematic structure of the water surface.
1.a | A water surface having free OH groups pointing towards the air/vapor layer [24-29].
1.b | Density profile of water at the air–water interface from molecular-dynamics simulations[23,30-32]. The vertical dashed line indicates the Gibbs dividing surface (GDS), which corresponds to a water density which is half of the density.

These aqueous interfaces accelerates many chemical and photochemical reactions as compared to other interfaces like gas phase or bulk water. This phenomenon is now labelled as ‘On-Water’ Catalysis [1]. The term ‘On-Water’ refers to processes occurring at or near aqueous interfaces.

A. On-Water Catalysis:

When liquid water is used as a solvent, it offers great economic and environmental paybacks to chemical industry due to its inexpensive, nontoxic, and non-flammable nature [35]. Reactions taking place on water are specifically a bunch of organic reactions taking place as an suspension in water and possess an unusual reaction rate acceleration as compared to

the same reaction in an organic solvent or any reaction with dry solvent.

The structure of interfacial water has been studied extensively, by experiment [36-44] and theory [45-56]. All of these studies consistently observe dangling (or free) OH bonds at the surface of liquid water, which overhangs out of water phase. It shows that an increased reactivity of the water surface can facilitate heterogeneous catalysis [57, 58].

Below is a figure showing interaction between oil and water molecules.

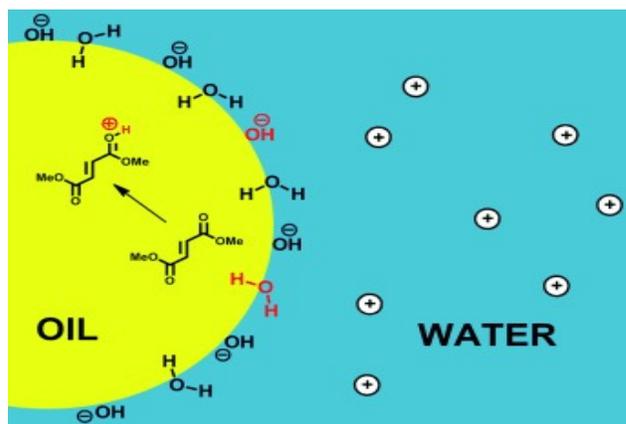


Fig. 2 Mechanism of ‘On-Water Catalysis’ at oil-water interface.

II. INTERFACIAL REACTION KINETICS

The term ‘On-Water Catalysis’ generally describes the observed rate enhancement of many chemical reactions at aqueous interfaces. The rate enhancement at aqueous interface can be described by adsorption, which is a non-catalytic reaction that couples interface and bulk reactions [13]. But interfacial effects other than accumulations of the reactants can lower the activation barriers thus promoting the reaction. We present below some basic theories of interface catalysis. Several enthalpic or entropic solvation effects may cause transition-state stabilization and reaction acceleration.

We discuss some of the major effects below.

A. Hydrogen bonding

Dangling OH groups at water surface need to be at the origin of 'On-Water' catalysis for some processes [11, 18]. These OH groups form hydrogen-bonds with the chemical system along the reaction path. Catalysis would occur only when hydrogen bonds to the transition state become stronger than hydrogen bonds to the reactants. Although the bulk water molecules around hydrophobic groups must first be reorganized before the OH groups become available for catalysis, it is not necessary at the interface thus it results in a lower activation barrier and faster processes. Calculations for the cycloaddition reaction of quadricyclane with dimethyl azodicarboxylate, the number of hydrogen bonds with the dangling OH groups is higher for the transition states than for the reactants.

B. Acid–base catalysis

Interfacial liquid can also have acid–base properties that can majorly influence and drive the process of catalysis. In the study of oligomerization of isoprene, during the electrospray-mass-spectrometry experiments [12], we found that surficial water is super acidic, even for mildly acidic water solutions. Similarly, acid–base chemistry is responsible for On-Water catalysis, which would have strong interface affinity of the hydroxide ion implied by some experiments from the same group [14].

C. Electrostatic fields

Electric fields can drive chemical processes through alteration of their rates or selectivities, according to Diels–Alder reactions [19-21]. Within the crude approximation of dielectric models, the electric field generated by dielectric response of the

solvent to the charge distribution of the solute, interacts with the solute, it then stabilizes the whole system. Moreover, processes having increasing polarity (charge separation) along the reaction path will be preferred more in bulk water than that of gas phase. At the interface, as polarity and its contributions to the solvations are less clearly defined, things are far more complicated. It appears sometimes difficult to establish general and qualitative rules for electrostatic-field effects on interfacial-reaction thermodynamics.

D. Reactivity indices

Both the frontier orbitals HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), as well as other reactivity indices in density functional theory [22] such as chemical potential, hardness and electrophilicity, etc. interpret or predict the doom of chemical reactions. These indices are particularly sensitive to the interface electrostatic potential, which can have larger effects than the potential in bulk water [15-17]. These reactivity indices are highly correlate to the relative orientation of reactant molecules to the interface plane, which gives particular importance to the presence of proton donor or acceptor groups, as illustrated in figure shown below. A good example is the case of the reaction of H_2CO (a proton acceptor) with HO_2 (a proton donor involving a proton-coupled electron transfer [17]). The electron transfer is ideal at the interface with respect to both gas phase and bulk water as the HOMO- (HO_2) -LUMO- (H_2CO) energy gap decreases under the local interface electrostatic potential which is generated by the hydrogen-bonded water molecules.

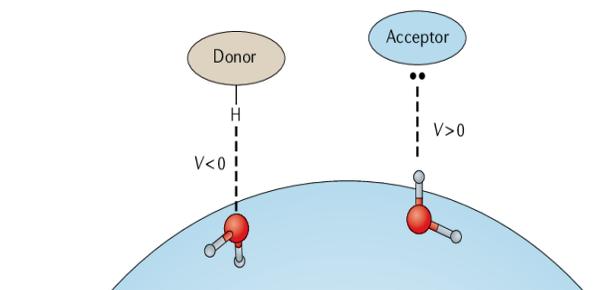
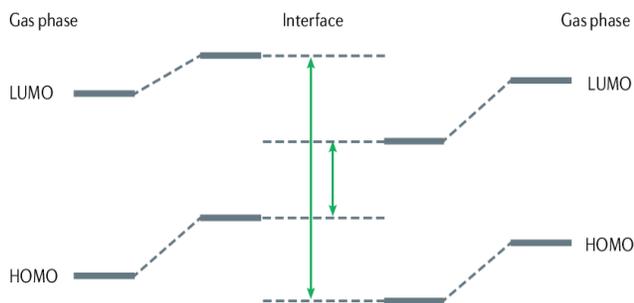


Fig. 3 Reactant molecular orbitals HOMO and LUMO at air/vapour-water interface.

E. Page Layout

Your paper must use a page size corresponding to A4 which is 210mm (8.27") wide and 297mm (11.69") long. The margins must be set as follows:

- Top = 19mm (0.75")
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- Left = Right = 14.32mm (0.56")

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III. STRUCTURE OF INTERFACES

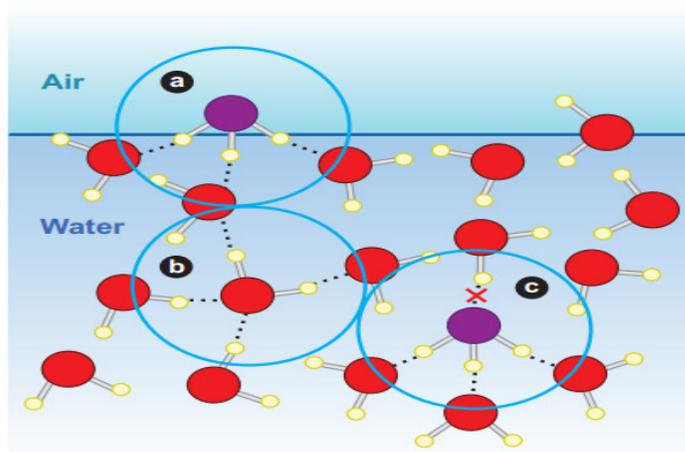
A. Liquid-vapor/air interface

It is known that the water molecules at the liquid-vapor interface are not oriented randomly. The direction of dipole moments of the water molecules is observable and further we can analyse the directions of O-H bonds at the interface. On the vapor side of the interface, one O-H bond points toward the vapor and the other is directed into the liquid, whereas on the liquid side, O-H bonds are mostly oriented parallel to the interface and point towards the liquid [59-61]. The average number of hydrogen-bonded neighbours per water molecule

goes on decreasing rapidly as they enter an interfacial region.

The liquid-vapor interface is distinct at molecular scale. Deviations from random orientation of water molecules are observed near the surface. These deviations can persist for at least 5 Å from the equimolar surface into the liquid

Fig. 4 Ionic movements at liquid/water-air interface.



B. Liquid-liquid interface

Several computer simulations on liquid-liquid interfaces/systems have been performed in recent years such as water-benzene [62], water-dodecane [64] and water-hexane [63, 64] interfaces. The most complete study published to date involved the water-1, 2 dichloroethane (DCE) interface [65] depicting electron transfer reactions at liquid surfaces. Precisely, how the molecules of one liquid penetrate into the other, also orientational and conformational preferences of liquid at equilibrium with water in the interface facial region are of interest [2]. The density profiles of the two liquids limitedly overlap each other's, as these liquids are immiscible. The interfacial dipoles lie mostly parallel pointing towards the liquid. One of the hydrogen atoms of the interfacial water molecules be likely to be away from the aqueous phase. When compared with the bulk liquid, the number of hydrogen bonds per water molecule decreases at the interface but their strength, on average, increases i.e. both are inversely proportional. These results put

forth the fact that the interactions between the two liquids in contact are weak than water-water interactions. They also imply that there is no substantial mixing between the components at interfacial region. It is observed that the interfacial interactions between water and liquids of essentially hydrophobic molecules are weak.

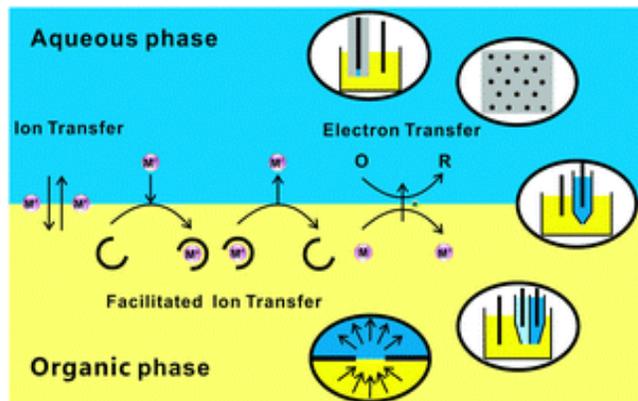


Fig. 5 Chemistry at liquid-liquid interface.

IV. SURFACE TENSION AND SURFACE POTENTIAL

A. Surface Tension

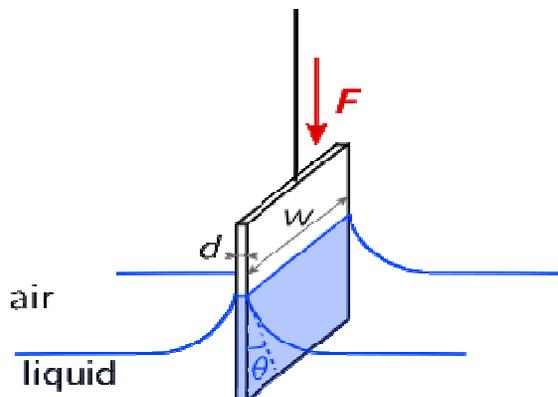
It is defined as the amount of work done per unit area, required to increase the interface at constant temperature and volume [10]. For amphiphilic species extended on an aqueous interface, this is usually termed as surface pressure, π , which is the difference between surface tension at a given surface coverage of surfactant and the surface tension of the pure water liquid-vapor interface, $\pi = \gamma_0 - \gamma$.

Below are some of the methods for calculating surface tension:

1) Wilhelmy Plate method

In this method, a thin plate is oriented perpendicular to the interface (either liquid/liquid or liquid/vapor), and the force exerted on it is measured. The Wilhelmy plate's size is an order of a few square centimeters in area. The plate is made

from filter paper, glass or platinum which may further be roughened to ensure complete wetting of the plate. The result of experiment doesn't depend upon the material used, only required is that the material should be wetted completely by the liquid. The plate is then cleaned thoroughly and attached to a balance having a thin metal wire. The force on the plate due to wetting is measured using a tensiometer or microbalance with a specific equation [5]. Below is a figure showing the plate



with respective parameters.

Figure7. Wilhelmy Plate; where,

- F- force acting on plate
- w- width of plate
- d- thickness of plate
- θ - contact angle between the liquid phase and the plate.

When conducting actual experiments, contact angle is rarely measured, instead either literature values are used, or complete wetting is assumed.

2) Bubble Pressure method

In this method, bubble pressure tensiometer is used which produces gas bubbles (ex. air) at constant rate and blows them through a capillary which is submerged in the sample liquid whose radius is already known.

The pressure (P) inside of gas bubble goes on increasing and the maximum value is recorded when bubble has the completely hemispherical shape having radius exactly equivalent to capillary radius.

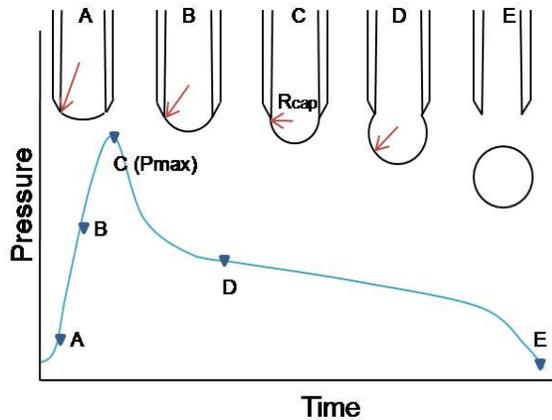


Fig. 8 Time vs. Pressure inside of gas bubble.

3) Spinning drop method

In this method, measurements are carried out in a rotating horizontal tube containing a dense fluid. Then a drop of a less dense liquid or a gas bubble is placed inside the fluid. As the horizontal tube rotates horizontally, a centrifugal force is generated towards the tube walls, the liquid drop will deform into an elongated shape. When the interfacial tension and centrifugal forces are balanced, this elongation of drop stops. The surface tension between the two liquids can then be derived from the drop shape at this equilibrium point. A device used for such measurements is called a ‘spinning drop tensiometer’.

This method is usually preferred for the accurate measurements of surface tensions below 10^{-2} mN/m.

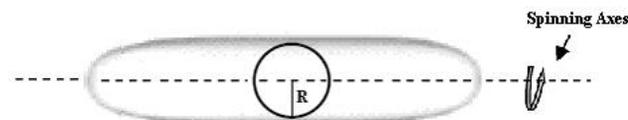


Fig. 9 Horizontal tube with a drop/gas bubble.

4) Capillary Rise method

A liquid of density ‘ ρ ’ and surface tension ‘ σ ’ rises in a capillary of inner radius ‘ r ’ to a height $h = \frac{2\sigma \cos\theta}{\rho g r}$,

Where ‘ θ ’ is the contact angle made by the liquid meniscus with the capillary’s surface. The liquid rises due to various forces such as adhesion, cohesion, and surface tension. If adhesive force (liquid-capillary) is more than the cohesive force (liquid-liquid) then liquid rises as in case of water rise in a glass capillary. In this case, the contact angle ‘ θ ’ is less than 90 degrees and the meniscus is concave. If adhesive force is less than the cohesive force then liquid depresses as in case of mercury in a glass capillary. In this case, the contact angle ‘ θ ’ is greater than 90 degrees and the meniscus is convex.

The formula for capillary rise can be derived by balancing forces on the liquid column. The weight of the liquid ‘ $\pi r^2 h \rho g$ ’ is balanced by the upward force due to surface tension ‘ $2\pi r \sigma \cos\theta$ ’.

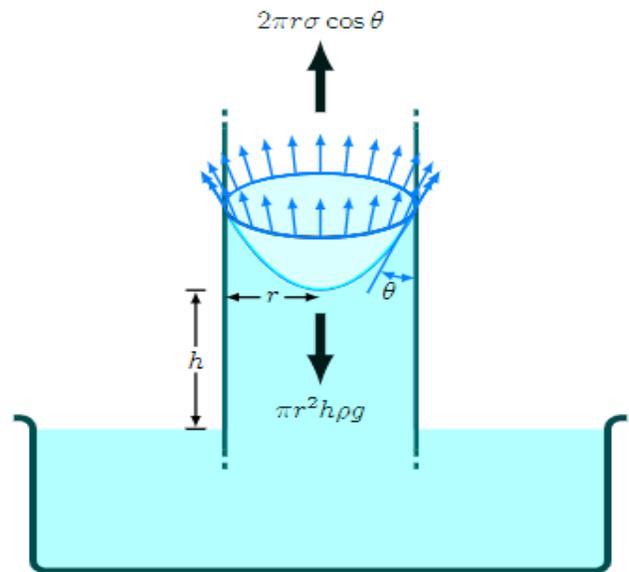


Fig. 10 Capillary rise method for surface tension.

B. Surface Potential

It is defined as the drop in the electrostatic potential when a test charge is moved from one bulk phase to the other.

VI. CONCLUSION

An aqueous interface region is most likely to have some properties, which can be described with the use of bulk liquid concepts, such as effective density and dielectric constant and some without a bulk counterpart, such as surface roughness and microscopic structural constraints, etc. These properties can expressively affect and modify the solvation of molecules, the equilibria and thus the rate of chemical reactions. The free OH-bonds at the water-organic interface majorly affect the energetics of the reaction occurring at interface. It is also noticed that these free O-H bonds imply the stabilization of the transition state as they are less relevant. When the reactants are present over an interface, they do not reduce the free energy barrier of the reaction as compared to the reactants present over “in-water” conditions.

In this paper, we have discussed chemistry at aqueous interfaces, reviewed some techniques for surface tension calculations. We also covered some of the effects of interfacial kinetics followed by structure of liquid-liquid and liquid-air/vapor interface. And thus the simulation of chemical reactions taking place at liquid-water interfaces can be considered to be still in its embryonic stage. Thus, future research should be able to explore this nature of aqueous interface a more. It can also clarify which catalytic processes are due to environmental effects and which are caused by other factors, such as the charge separation or gas-phase chemistry in electrospray experiments, or the diffuse interfaces of emulsions, owing to partial solubility in water [5]. Another topic of great interest can be the study of reactions at aqueous interfaces with non-organic solvents, such as ionic liquids or compressed CO₂, which can be opted for developing new green synthetic methods [5].

REFERENCES

- [1] Molecular reactions at aqueous interfaces.
- [2] Viewpoint 9 - Molecular structure of aqueous interfaces
- [3] Structure and Chemistry at Aqueous Interfaces

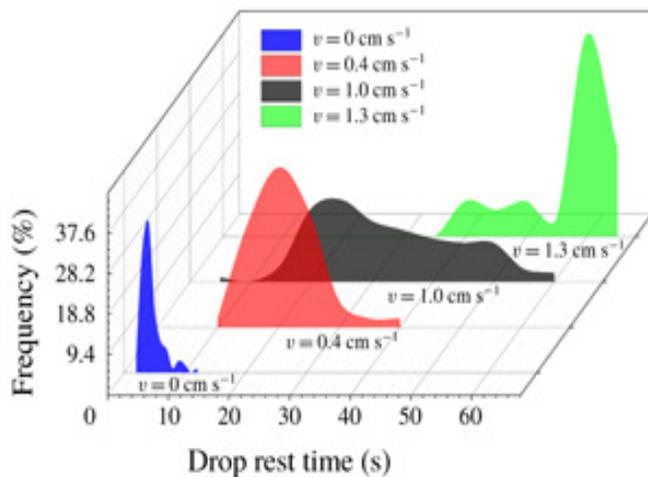


Fig. 6 Surfing of drops on moving liquid-liquid interfaces

V. CHEMICAL REACTIONS AT AQUEOUS INTERFACES

When the reactions occur at any interface, the role of the interfacial structure on the equilibria and rates of chemical reactions are to be majorly considered. When liquid interfacial effects on chemical reaction equilibrium and rate are studied, determination of change in the solvation free energy of the reactants, products, and the transition state, etc. come into picture. The ion-transfer process has solvation of ions at the liquid/liquid interface at its core. A characteristic soft organic-aqueous interface can deeply interpenetrate aqueous and organic phases. Studies going on clearly distinguish the reactions occurring at aqueous interfaces from reactions in bulk water solution. This studies remain largely motivated by concepts indicted in the experiments [67, 68] and by the development of new techniques to investigate reactions at interfaces [66, 69-71]. Polar solvents around the charge transfer centres are able to project into other solvent. Aqueous interfaces have also been evoked as possible environments in which prebiotic processes could happen and led to the origin of life.

- [4] STRUCTURE AND PROPERTIES OF SOFT ORGANIC-AQUEOUS INTERFACES.
- [5] Chemical Reactions and Solvation at Liquid Interfaces: A Microscopic Perspective
- [6] Bockris, J. O'M.; Gonzalez-Martin, A. In Spectroscopic and Diffraction Techniques in Interfacial Electrochemistry; Gutierrez, C., Melendres, C., Eds.; Kluwer Academic Publishers: Dordrecht, 1990.
- [7] Bard, A. J.; Faulkner, L. R. Electrochemical methods: fundamentals and applications; Wiley: New York, 1980.
- [8] Starks, C. M.; Liotta, C. L.; Halpern, M. Phase Transfer Catalysis; Chapman & Hall: New York, 1994.
- [9] Arai, K.; Ohsawa, M.; Kusu, F.; Takamura, K. Bioelectrochem. Bioenerg. 1993, 31, 65.
- [10] Gennis, R. B. Biomembranes; Springer: New York, 1989.
- [11] Jung, Y. & Marcus, R. A. On the theory of organic catalysis "on water". J. Am. Chem. Soc. 129, 5492–5502 (2007).
- [12] Enami, S., Mishra, H., Hoffmann, M. R. & Colussi, A. J. Protonation and oligomerization of gaseous isoprene on mildly acidic surfaces: implications for atmospheric chemistry. J. Phys. Chem. A 116, 6027–6032 (2012).
- [13] Fallah-Araghi, A. et al. Enhanced chemical synthesis at soft interfaces: A universal reaction-adsorption mechanism in microcompartments. Phys. Rev. Lett. 112, 028301 (2014).
- [14] Beattie, J. K., Djerdjev, A. M. & Warr, G. G. The surface of neat water is basic. Faraday Discuss. 141, 31–39 (2008).
- [15] Martins-Costa, M. T. C. & Ruiz-Lopez, M. F. Solvation effects on electronic polarization and reactivity indices at the air–water interface: insights from a theoretical study of cyanophenols. Theor. Chem. Acc. 134, 17 (2015).
- [16] Martins-Costa, M. T. C., Anglada, J. M., Francisco, J. S. & Ruiz-Lopez, M. Reactivity of atmospherically relevant small radicals at the air–water interface. Angew. Chem. Int. Ed. 51, 5413–5417 (2012).
- [17] Martins-Costa, M. T. C., Anglada, J. M., Francisco, J. S. & Ruiz-Lopez, M. F. Reactivity of volatile organic compounds at the surface of a water droplet. J. Am. Chem. Soc. 134, 11821–11827 (2012).
- [18] Jung, Y. S. & Marcus, R. A. Protruding interfacial OH groups and 'on-water' heterogeneous catalysis. J. Phys. Condens. Matt. 22, 284117 (2010)
- [19] Meir, R., Chen, H., Lai, W. Z. & Shaik, S. Oriented electric fields accelerate Diels–Alder reactions and control the endo/exo selectivity. ChemPhysChem 11, 301–310 (2010).
- [20] Aragonés, A. C. et al. Electrostatic catalysis of a Diels–Alder reaction. Nature 531, 88–91 (2016).
- [21] Ruiz-López, M. F., Assfeld, X., García, J. I., Mayoral, J. A. & Salvatella, L. Solvent effects on the mechanism and selectivities of asymmetric Diels–Alder reactions. J. Am. Chem. Soc. 115, 8780–8787 (1993).
- [22] Geerlings, P., De Proft, F. & Langenaeker, W. Conceptual density functional theory. Chem. Rev. 103, 1793–1874 (2003).
- [23] Benjamin, I. Chemical reactions and solvation at liquid interfaces: A microscopic perspective. Chem. Rev. 96, 1449–1475 (1996).
- [24] Du, Q., Superfine, R., Freysz, E. & Shen, Y. R. Vibrational spectroscopy of water at the vapor/water interface. Phys. Rev. Lett. 70, 2313 (1993).
- [25] Wilson, M. A., Pohorille, A. & Pratt, L. R. Molecular-dynamics of the water liquid-vapor interface. J. Phys. Chem. 91, 4873–4878 (1987).
- [26] Townsend, R. M. & Rice, S. A. Molecular dynamics studies of the liquid–vapor interface of water. J. Chem. Phys. 94, 2207–2218 (1991).
- [27] Morita, A. & Hynes, J. T. A theoretical analysis of the sum frequency generation spectrum of the water surface. Chem. Phys. 258, 371–390 (2000).
- [28] Sulpizi, M., Salanne, M., Sprik, M. & Gageot, M.-P. Vibrational sum frequency generation spectroscopy of the water liquid–vapor interface from density functional theory-based molecular dynamics simulations. J. Phys. Chem. Lett. 4, 83–87 (2012).
- [29] Kuo, I. F. W. & Mundy, C. J. An ab initio molecular dynamics study of the aqueous liquid–vapor interface. Science 303, 658–660 (2004).
- [30] Kuo, I. F. W. et al. Structure and dynamics of the aqueous liquid–vapor interface: a

- comprehensive particle-based simulation study. *J. Phys. Chem. B* 110, 3738–3746 (2006).
- [31] Verde, A. V., Bolhuis, P. G. & Campen, R. K. Statics and dynamics of free and hydrogen-bonded OH groups at the air/water interface. *J. Phys. Chem. B* 116, 9467–9481 (2012).
- [32] Taylor, R. S., Dang, L. X. & Garrett, B. C. Molecular dynamics simulations of the liquid/vapor interface of SPC/E water. *J. Phys. Chem.* 100, 11720–11725 (1996).
- [33] Shultz, M. J., Vu, T. H., Meyer, B. & Bisson, P. Water: A responsive small molecule. *Acc. Chem. Res.* 45, 15–22 (2012).
- [34] Pezzotti, S., Galimberti, D. R. & Gageot, M.-P. 2D H-bond network as the topmost skin to the air–water interface. *J. Phys. Chem. Lett.* 8, 3133–3141 (2017).
- [35] P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice* (Oxford University Press, Oxford, 2000).
- [36] 3Q. Du, R. Superfine, E. Freysz, and Y. R. Shen, *Phys. Rev. Lett.* 70, 2313 (1993).
- [37] Q. Du, E. Freysz, and Y. R. Shen, *Science* 264, 5160 (1994).
- [38] L. F. Scatena, M. G. Brown, and G. L. Richmond, *Science* 292, 5518 (2001).
- [39] C. D. Cappa, J. D. Smith, K. R. Wilson, and R. J. Saykally, *J. Phys.: Condens. Matter* 30, 205105 (2008).
- [40] Z. Zhang, L. Piatkowski, H. J. Bakker, and M. Bonn, *J. Chem. Phys.* 135, 021101 (2011).
- [41] P. A. Pieniazek, C. J. Tainter, and J. L. Skinner, *J. Am. Chem. Soc.* 133, 10360 (2011).
- [42] S. Nihonyanagi, T. Ishiyama, T. k. Lee, S. Yamaguchi, M. Bonn, A. Morita, and T. Tahara, *J. Am. Chem. Soc.* 133, 16875 (2011).
- [43] I. V. Stiopkin, C. Weeraman, P. A. Pieniazek, F. Y. Shalhout, J. L. Skinner, and A. V. Benderskii, *Nature* 474, 192 (2011).
- [44] B. Torun, C. Kunze, C. Zhang, T. D. Kühne, and G. Grundmeier, *Phys. Chem. Chem. Phys.* 16, 7377 (2014).
- [45] C. Lee, J. A. McCammon, and P. J. Rossky, *J. Chem. Phys.* 80, 4448 (1984).
- [46] L. X. Dang and T.-M. Chang, *J. Chem. Phys.* 106, 8149 (1997).
- [47] A. Morita and J. T. Hynes, *Chem. Phys.* 258, 371 (2000).
- [48] I.-F. W. Kuo and C. J. Mundy, *Science* 303, 658 (2004).
- [49] I.-F. W. Kuo, C. J. Mundy, B. L. Eggimann, M. J. McGrath, J. I. Siepmann, B. Chen, J. Vieceli, and D. J. Tobias, *J. Phys. Chem. B* 110, 3738 (2006).
- [50] C. D. Wick, I.-F. W. Kuo, C. J. Mundy, and L. X. Dang, *J. Chem. Theory Comput.* 3, 2002 (2007).
- [51] B. M. Auer and J. L. Skinner, *J. Phys. Chem. B* 113, 4125 (2009).
- [52] Y. Fan, L. Yang, P. S. Cremer, and Y. Q. Gao, *J. Phys. Chem. B* 113, 11672 (2009).
- [53] T. D. Kühne, T. A. Pascal, E. Kaxiras, and Y. Jung, *J. Phys. Chem. Lett.* 2, 105 (2011).
- [54] P. A. Pieniazek, C. J. Tainter, and J. L. Skinner, *J. Chem. Phys.* 135, 044701 (2011).
- [55] M. D. Baer, C. J. Mundy, M. J. McGrath, I.-F. W. Kuo, J. I. Siepmann, and D. J. Tobias, *J. Chem. Phys.* 135, 124712 (2011).
- [56] M. Sulpizi, M. Salanne, M. Sprik, and M.-P. Gageot, *J. Phys. Chem. Lett.* 4, 83 (2013).
- [57] C. Zhang, R. Z. Khaliullin, D. Bovi, L. Guidoni, and T. D. Kühne, *J. Phys. Chem. Lett.* 4, 3245 (2013).
- [58] I. Benjamin, *Chem. Rev.* 96, 1445 (1996). 66D. Marx, *Science* 303, 5658 (2004)
- [59] M.A. Wilson, A. Pohoriffe and L.R. Pratt, *J. Phys. Chem.*, 91 (1987) 4873.
- [60] M. Matsumoto and Y. Kataoka, *J. Chem. Phys.*, 88 (1988) 3233.
- [61] R.A. Motakabbir and M.L. Berkowitz, *Chem. Phys. Lett.* 176 (1991) 61.
- [62] P. Lime, *J. Chem. Phys.*, 86 (1987) 4177.
- [63] L.L. Carpenter and W.J. Hehre, *J. Phys. Chem.*, 94 (1990) 531.
- [64] M.A. Wilson and A. Pohorilie, in preparation.
- [65] L Benjamin, *J. Chem. Phys.*, 97 (1992) 1432.
- [66] Y.R. Shen, *Annu. Rev. Phys. Chem.*, 40 (1989) 327.
- [67] D. Chandler, *J. Chem. Phys.*, 68 (1978) 2959. D. Chandler, *J. Stat. Phys.*, 42 (1986) 49. B.J. Berne, M. Borkovec and J.E. Straub, *J. Phys. Chem.*, 92 (1988) 3711. J.N. Onuchic and P.G. Wolynes, *J. Phys. Chem.*, 92 (1988) 6495. J.G. Harris and F.H. Stillinger, *Chem. Phys.*, 149 (1990) 63.

[68] J.T. Hynes, in M. Baer (Ed), The Theory of Chemical Reactions, Vol. 4, CRC Press, Boca Raton, FL, 1984.

[69] E.V. Sitzmann and K.B. Eisenthal, J. Phys. Chem., 92 (1988) 4579.

[70] E.V. Sitzmann and K.B. Eisenthal, J. Chem. Phys., 90 (1989) 2831.

[71] S.R. Meech and K. Yoshihara, Chem. Phys. Lett., 174 (1990) 423.

(2002) The IEEE website. [Online]. Available: <http://www.ieee.org/>