10.1515/umcschem-2015-0013

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA
VOL. LXX, 2 SECTIO AA 2015

Surface potential at the water-air interface

Maria Paluch
Jagiellonian University, Faculty of Chemistry,
Ingardena 3,30-060 Krakow, Poland
email: paluch@chemia.uj.edu.pl

Dedicated to Professor Bronisław Jańczuk
on the occasion of his 70th birthday

A problem associated with the surface potential jump at the air-water interface has been studied for many years. However, to date, there is no consensus both as to its value and sign. This is due to the impossibility of direct measurement of the surface potential, which caused that many scientists have attempted to estimate the value and sign of this potential, indirectly by measuring other physical parameters or using simulation methods. In this review, the most important results concerning this issue were collected and briefly described.

1. INTRODUCTION

Free surface of water and aqueous solutions is present both in mineral and living nature. However, the electrical properties of this phase boundary, despite its wide dissemination, are still poorly understood. Interfacial water molecules at the gas-liquid surface have a strong attraction towards the bulk liquid causing high surface tension. Gas at the air-water behaves like a flat hydrophobic surface. The van der Waals interaction between the liquid and gas surfaces are negligible.

Several techniques, including atomic force microscopy (AFM) [1], optical second-harmonic generation and sum-frequency generation [2] and X-ray and neutron scattering [3] were used for studying aqueous interfaces. Sum-frequency vibrational spectra suggest the coexistence of “ice like” and “liquid like’ hydrogen bonding networks at the air-water interface [2]. It depends on temperature, ionic strength of water solution and presence of surfactants at free water surface [4–6].

The properties of water located between surfaces depend not only directly on the interaction of the surface with water, but also on the number of water molecules. The interfacial water possesses properties of bulk water only for a certain minimum number of water molecules. This problem is especially important in thin water films occurring in industrial processes as flotation, foaming, emulsification, wetting, colloid stability, etc. and in biological systems for which it has been postulated [7] that all the water is in the state profoundly different from normal water.

It is well known that water molecules may form hydrogen bonds between themselves. Such bonding is responsible for special thermodynamical properties of liquid water. In order to explain them, various structural models for water are proposed. Generally speaking, these fall into two categories: continuous models [8–15] and mixed bi-structural models [16–20]. In continuous models structure transformation is considered in terms of changes in bond geometry without bond breaking. In mixed models an assumption is made about possible breaking of bonds in structural changes brought about by external factors. Free water surface has different properties as compared to the interior of liquid phase due to the fact that intermolecular cohesive forces in the surface phase are uncompensated. There is a force perpendicular to the surface and, as a result, the surface layer exerts pressure upon the bulk of water, the so-called surface pressure. Beside this force there is another, tangential force, which counteracts the increase of the surface area: this force per unit length is called surface tension. The dependence of surface tension on the state parameters can provide information which can be deduced from experimental data. Thus, from the temperature dependence of surface tension the value of the surface entropy can be determined, from the dependence of surface tension on the composition, one can determine the composition of surface layer, from dependence of surface tension on pressure one can determine autoadsorption and surface density of water and, indirectly, the structure of surface layer [21–22].

The density, dielectric permittivity [23] and dipole moment of interfacial water change from their bulk water values to that of the gas over a distance of less about a nanometer.

As a result of water dipoles orientation, an electric double layer is formed on the free water surface and an electric potential drop occurs (χ_{H_2O}). Water molecules in the surface layer are in an electric field different from the dipole field in the bulk and, consequently, must have dipole moments different from bulk molecules and also different dielectric permittivity. In the literature no values are given of dielectric permittivity at the water-air interface. The lack of data concerning dielectric permittivity of the interfacial water region is a reason why it is often assumed to be equal 1, hence treating water molecules as isolated entitles, or the value of 1 is taken for the lack of the better value [24–28].

2. THE SIGNIFICANCE OF THE PROBLEM

As it was mentioned above, on the free water surface the electric potential drop exists. It is surface potential χ_{H_2O}.The surface potential χ is generally defined as the difference between the liquid-phase inner (Galvani) potential φ and the vapour-phase outer potential (Volta) ψ and is given by: $\chi = \varphi - \psi$ [29–31].

The Volta outer potential can be determined from the work required to bring an unperturbing unit charge from infinity to a point just outside the vapour-liquid interface. Similarly the Galvani inner potential could be determined from the work required to bring an unperturbing unit charge from infinity through the vapour-liquid interface into the bulk liquid. In practice however, the work required to move a charge through an interface must involve a real, physical charge, i.e. electron, or an ionic atom or molecule. The motion of a physical charge through the interface is associated with changes in the interfacial structure and electronic environment. The value of χ potential is experimentally unobtainable. Many scientists tried to explain the origin of the electric potential at the water-air interface and determine its magnitude. In Table 1 there are the values o surface potential of water given by various authors. The sign of the values of the electric potential drop at air-water interface given by various authors which dealing with this problem is related to the charge of free water surface on the side of the bulk water phase. As can be seen significant differences exist between the magnitude and sign of χ_{H_2O} from

–1.10 V to + 3.63 V. The magnitude of potential drop at the water-air interface cannot be measured directly. The values were determined either indirectly from experiments, or calculated assuming certain orientation of water dipoles on the free surface and adopting appropriate models and mathematical-physical procedures.

Table 1. The values of surface potential at the air-water interface obtained experimentally and calculated for different water models by various authors.

Lp.	Author	Experimental	χ_{H_2O} [v]
1	A.N. Frumkin [53,54]		+0.1 – +0.2
2	B. Kamienski [55,56]		+1.0
3	J. A. Chalmers, F. Pasquil [57]		–0.26
4	H. Strehlow [58]		–0.36
5	N. S. Hush [59]		–0.3
6	G. Passoth [60]		+0.29
7	K. P. Miscenko, E. J. Kwiat [61]		–0.3 – +0.1
8	E. Verwey [62]		–0.48
9	J. E. Randles, D. Y. Schiffrin [63]		+0.07 – +0.13
10	A. Buhl [64]		+0.0055
11	R. Gomer , Tryson [65]		+0.05
12	J. E. Farrell, P. McTique [66]		+0.025
13	S. Trasatti [67,68]		+0.13
14	N. N. Kochurowa, A. I. Rusanov [69]		+0.1
15	M. Solomon [70]		–1.10
16	I.I .Krishtalik [71]		+0.14
17	V.I.Parfenyuk [72]		+0.1

Cont. Table 1.

	Authors	Calculated	Water model
18	V. P. Sokhan, D. Tildesley [73]	SPC/E	–0.55
19	C. G. Barraclough, P. T. McTigue, Y.L.Ng [74]	SPC	–0.53
20	M. Matsumoto, Y. Kataoka [75]	CC	–0.6
21	N. J. Christou, J. S. Whitehouse, D. Nicholson, N.G. Parsonage [76]	RWL	–0.53
22	G. Aloisi, R. Giudelli, R. A. Jackson, M. S. Clark, P.Barnes [77]	TIPS2	–0.89
23	F. H. Stillinger, A. Ben-Naim [78]	dd+QQ	+0.029
24	M. A. Wilson, A. Pohorille, L. R. Pratt [79]	TIP4P	–0.13
25	E. N. Brodskaya, V. V. Zakharov [80]	ST2	–0.11
26	E. N. Brodskaya, V. V. Zakharov[80]	TIPSP	–0.66
27	K. Leung [81]	SPC/E	+3.63
28	S. M. Kathmann, I-F.W. Kuo [82]		–0.018

According to some authors water dipoles passing through the interface in the process of evaporation and condensation become oriented -according to the laws of electrostatics – with that part of the molecule exhibiting greater electric field density pointing towards the medium with greater dielectric permittivity, hence hydrogen atoms pointing towards the water phase (ε ~ 80) and oxygen atoms towards the air (ε ~1). A water molecule has non-linear structure. Two hydrogen atoms are bonded to oxygen atom at an angle of 104.45°. The bond length is 0.958 Å [32]. The water molecule, although uncharged as a whole has the centre of positive charge (hydrogen atoms) which no coincide with the centre of the negative charge (oxygen). The greater electric field density exist close to hydrogen atoms.

In the past decade air-water interface has been intensively investigated both theoretically and experimentally [33–47]. Experimental method such as X-ray reflection can be used to get the liquid surface roughness [35], but orientational structure and dynamics information at molecular level can only be obtained by Sum Frequency Generation (SFG) or Second Harmonic Generation (SHG) because of their submonolayer sensitivity and interface specifity [34]. It has been generally accepted that the interfacial water molecule has one free OH bond protruding out of the interface. However, the existence of water molecules with both OH bonds pointing to the vapour phase is still controversial issue [38, 41–43, 47]. The dynamics of water molecule at air-water interface has also been discussed theoretically in literatures [37, 39–40, 44–47] Quantitative analysis of the SFG spectra by W. Gan et al. [48] in different polarization and experimental configuration for the air-water interface shows that orientational motion of the interfacial water molecule is libratory, as fast as 0.1 ps it may be [48–49], only within a limited angular range of less than 15 with the tilt angle around 30°. Therefore, the air-water interface is quite well-ordered. This picture is significantly different from the previous conclusions.

Fan et al. [50] using Vibrational Sum Frequency Spectroscopy and molecular dynamic simulation for different water models such as SPC/E, TIP3P, TIP4P-Ew, POL3, TIP5P, mPIP5P, which names depend on the parametrization applied in simulations [51–52], suggested that vapour-water interface is well ordered in two interface layers. The top layer arranged such that the OH moiety points upward into the air.

As it results from the data presented in Table 1 up to this time, there is no agreement relative to the sign and the magnitude of surface potential of free water surface [53–82]. It is connected with lack of agreement according to the orientation of water molecules at air-water interface. The sign and the values of electric potential drop χ at the free water surface were obtained by various authors indirectly with some physicochemical quantities such as surface tension of some surfactants solutions , temperature coefficient of surface potential of dilute solutions of some electrolytes , values of chemical and real energies of ion hydration , and some electrochemical measurements .

Considerable progress has been made during the past decade in utilizing computational techniques to understand the equilibrium properties (orientational structure, surface tension, etc.] of the vapour-liquid interface of water [83]. In particular many effort in this area of research have been focused on computing the surface potential using molecular simulation techniques. Improving these simulations the present opinion is that the surface potential of water-air interface is nonzero. Its actual value computed is dependent upon the choice of water model employed. As we can see with Table 1 the surface potential calculated for different models is negative and its value for different computer simulation is between –0.11V to –0.89V, with the exception of values obtained by Leung [81] whose for SPC/E model, using Density Functional Theory obtained the value of +3.63 V at 0,92 g/cm^3 water density, and value obtained by Kathmann et al. [82], whose using ab initio molecular dynamics found that the surface potential $\chi = -0.018$ V. They also give a comparison between theirs quantum – mechanical results and these from previous molecular simulations underscoring the different treatments of the charge distribution (multipole expansion using dipole and quadrupole moments, partial point charges with and without polarizability and quantum-mechanical electronic structure).

The comparison of the surface potential values of free surface of water obtained from experiments and different computed methods shows that investigation on the orientational ordering and electric properties of the vapour water-water remains valid and requires continuation.

As mentioned previously, the value of the potential drop at the water-air phase boundary cannot be measured directly. What can be measured are its changes resulting from the formation on this surface a monolayer of different substances. These changes (ΔV) are sometimes called the surface potential of the solution [30,8 4] and are connected with the changes $\Delta\chi$ – of the potential χ and $\Delta\psi$ – of the potential ψ, $\Delta V = \Delta\chi + \Delta\psi$.

The surface potential ΔV is the sum of changes of potentials χ and ψ only in the case of partly ionized monolayer. In the case of non-ionized monolayer we have $\Delta V = \Delta\chi$.

The ΔV potential is generally given a qualitative interpretation in terms of the analogy between monolayer and condenser. Three possible contribution to $\Delta\chi$ may be distinguished [24]:

- that of permanent dipole of hydrophilic head of the adsorbed molecule,
- that due to a reorientation of the water molecule in the immediate vicinity of the hydrophilic heads, and finally,
- a contribution arising from a dipole moment in the hydrophobic part of the adsorbed molecule.

The detailed data of these contributions to surface potential of surfactants solutions [ΔV] are presented in reviewed articles [85-86].

3. CONCLUSIONS

As we can see from the review outlined in these few pages the free surface of water despite of long and different kind of studies is still fascinating for many scientists. To date, there is no consistency as to the orientation of water molecules at the free water surface, theirs motion and electric potential drop. It is seen therefore, that investigations of surface potential changes at water–air interface and another phase boundaries remain still a live issue.

REFERENCES

[1] M. J. Higgins, M.Polcik, T.Fukuma, J. E. Sader, Y.Nakayama, S. P. Jaris, *Biophys. J.*, **91** 2532 (2006).

[2] Y. R. Shen, V. Ostroverkhov, *Chem. Rev.*, **106**,1140 (2006).

[3] T. Head-Gordon, G. Hura, *Chem.Rev.*,**102**, 2651 (2002).

[4] D. E. Gragson, *J. Phys. Chem.*, **100**, 1427 (1966).

[5] D. E. Gragson,*J. Phys. Chem.*, **119**, 6144 (1997).

[6] D. E. Grakson, *J. Phys. Chem.*, **102**, 387 (1998).

[7] G. L. Ling, *Ann. N.Y.. Acad. Sci.*, **125**, 401 (1965).

[8] J. D. Bernal, R. M. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[9] F. A. Pople, *Proc. R. Soc., A* **205**, 163 (1951).

[10] G. N. Zacepina, *Zh. Fiz. Khim.*, **47**, 2005 (1973).

[11] J. R. O’Neil, L. M. Adanu, *J. Phys. Chem.*, **73**, 1553 (1969).

[12] M. C. R. Symous, Nature, **239**, 257 (1972).

[13] Y. A. Barker, R. O. Watt, *Chem. Phys. Lett.*, **3**, 144 (1969).

[14] A. Rachman, F. H. Stllinger, *J. Chem. Phys.*, **55**, 3336 (1971).

[15] F. H. Stillinger, A. Rachman, *J. Chem. Phys.*, **57**, 1281 (1972).

[16] E. Eucken, *Z. Electrochim.*, **52**, 255 (1948).

[17] M. S. Frank, A. S. Quist, *J. Chem. Phys.*, **34**, 603 (1961).

[18] G. Nemethy, A. Scheraga, *J. Phys. Chem.*, **36**, 3362 (1962).

[19] R. P. Marchi, M. Eyring, *J. Phys. Chem.*, **68**, 221 (1964).

[20] B. R. Lentz, A. T. Hagler, M. A. Scheraga, *J. Phys. Chem.*, **78**, 1531 (1974).

[21] A. I. Rusanow, N. N. Kochuruwa, *Dok. Akad. Nauk. SSSR*, **202**, 380 (1972).

[22] W. N. Chabarow, A. I. Rusanow, N. N. Kochurowa, *Kolloid. Zh.*, **38**, 120 (1978).

[23] O. Teschke, E. F. de Souza, *Phys. Chem. Chem. Phys.*, **7**, 3856 (2005).

[24] J. T. Davies, E. K. Rideal, International Phenomena, Acad. Press, New York and London, 1963.

[25] Z. Koczorowski, in: A. G. Volkov, D. W. Deamer (Eds), Volta and Surface Potential at Liquid/Liquid Interfaces: Theory and Methods, CRC Press, Inc, 1966 p.16.

[26] R. Parsons, in: J. O’M. Bockris, B. M. Conway (Eds), Modern Aspects of Electrochemistry, Ch. 3, Vol 1, Butterworths, London, 1954.

[27] A. J. Demchak T. Fort, *J. Colloid Interface. Sci.*, **46**,191 (1974).

[28] E. Gileadi, E. Kirowa-Eisner, J. Penciner, Interfacial Electrochemistry, Addison-Weseley Publ. Company, Inc, London, 1975, p. 15.

[29] J. Koryta, J. Dworak, L. Kovan, Principles of Electrochemistry, John Wiley and Sons, New York, 1993.

[30] A. W. Adamson, Physical Chemistry of Surfaces, John Wiley and Sons, New York, 1990.

[31] W. R. Fawcett, Liquids, Solutions and Interfaces: From Macroscopic Description to Modern Microscopic Details, Oxford Univ. Press, New York, 2004.

[32] Tables of Interatomic Distances and Cofiguration in Molecules and Ions, Publ. by the Chemical Society, London, 1958.

[33] P. B. Miranda, Y. R. Shen, *J. Phys. Chem. B*, **103**, 3292 (1999).

[34] A. Braslau, M. Deutsch, P. S. Pershan, A. H. Wels, J. Als-Nelson, J. Bohr, *Phys. Rev. Lett.*, **54**, 114 (1985).

[35] A. Braslau, P. S. Pershan, G.Swislow, B. M. Ocko, J. Als-Nielsen, *Phys. Rev.*, A**38**, 2457 (1988).

[36] M. C. Goh, J. M. Hicks, K. Kemnitz, G. R. Pinto, K. Bhattacharyya, K.B. Eisenthal, *J. Phys. Chem.*, **92**, 5074 (1988).

[37] R. M. Townsend, S. A. Rice, *J. Phys. Chem.*, **94**, 2207 (1991).

[38] Q. Du, R. Superfine, E. Freysz, Y. R. Shen, *Phys. Rev. Lett.*, **70**, 2313 (1993).

[39] J. Benjamin, *Phys. Rev. Lett.*, 73, 2083 (1994); Chem. Rev., **96**, 1449 (1996).

[40] A. Morita, J. T. Hynes, *Chem. Phys.*, **258**, 371 (2000).

[41] M. G. Brown, E. A. Raymond, H. C. Allen, L. F. Scatena, G. L. Richmond, *Phys. Chem. A*, **104**, 10220 (2000).

[42] X. Wei, Y. R. Shen, *Phys. Rev. Lett.*, **86**, 4799 (2001).

[43] K. R. Wilson, M. Cavalleri, B. S. Rude, R. D. Schaller, A. Nilson, L. G. M. Pettersson, N. Goldman, T. Catalano, J. D. Bozek, R. J. Saykally, *J. Phys. Condens. Matte*r **14**, 221 (2002).

[44] A. Perry, H. Ahlborn, B. Space, P. B. Moore, *J. Phys. Chem.*, **118**, 8414 (2003).

[45] J. C. Fecko, J. D. Eaves, J. J. Loparo, A. Tokmakoof, P. L. Geissler, Science, **301**, 1698 (2003).

[46] S. Paul, A. Chandra, *Chem. Phys. Lett.*, **373**, 87 (2003).

[47] J-F. W. Kuo, C. J. Mundy, *Science* **303**, 658 (2004).

[48] W. Gan, D. Wu, Z. Zhang, H. Wang, Chin. *J. Chem. Phys.* **19**, 1360 (2006).

[49] Y. L. Yeh, C. Zhang, H. Held, A. M. Mebel, X. Wei, S. H. Lin, Y. R. Shen., *J. Chem. Phys.* **114**, 1837 (2001)

[50] Y. Fan, X. Cen, L. Yang, P. S. Cremer, Y. Q. Gao, *J. Phys. Chem. B*, **113**, 11672 (2009).

[51] J.Zielkiewicz, *J.Chem.Phys.,* **123,**104501(2005).

[52] C.Vega, J. L. F. Abascal, *Phys.Chem.Chem.Phys.,* **13,**19663(2011).

[53] A. N. Frumkin, Z. A. Jofa, M. A. Gerovich, *Zh. Fiz. Khim.*, **30**, 1155 (1956).

[54] A. N.Frumkin.*Electrochim.Acta,* **2,**351(1960).

[55] B. Kamienski, *Wiad. Chem.*, **14**, 619 (1960).

[56] B. Kamienski, *Bull. Int. Acad. Polon. Sci., Cracovie*, Cl.III. Ser. A., 430 (1937).

[57] J. A. Chalmers, F. Pasquile, *Phil. Mag*. **23**, 88 (1937).

[58] H. Strehlow, *Z. Electrochem.*, **56**, 119 (1952).

[59] N. S. Hush, *Aust. J. Sci. Rec.*,**1**, 480 (1948).

[60] G. Passoth, *Z. Phys. Chem.* **203**, 275 (1954).

[61] K. P. Miscenko, E. I. Kwiat, *Zh. Fiz. Khim.*, **28**, 1451 (1954).

[62] E. Verwey, *Rec. Trav. Chim. Pays-Bas*, **61**, 127 (1942).

[63] J. E. B. Randles, D. Y. Schiffrin, *J. Electroanal. Chem.*,**10**, 480 (1965).

[64] B. Buhl, *Ann. Phys.*, **84**, 211 (1927).

[65] R. Gomer, G. Tryson, *J. Chem. Phys.*, **66**, 4413 (1977).

[66] J. R. Farrell, P. Mc Tique*, J. Electroanal. Chem.*, **163**, 129 (1984).

[67] S. Trasatti, *Electrochim. Acta*, **32**, 843 (1987).

[68] S. Trasatti, *J. Chem. Soc. Faraday*, **170**, 1752 (1974).

[69] N. N. Kochurowa, A. I.Rusanov, *J. Colloid Interface Sci.*,**81**, 297 (1981).

[70] M. Solomon, *J. Psys. Chem.*, **74**, 2519 (1970).

[71] I. I. Krishtalik, *Rus. J. Electrochem.*, **44**, 43 (2008).

[72] V. I. Parfenyuk, *Colloid Journal*, **64**, 588 (2002).

[73] V. P. Sokhan, D. J. Tildesley, *Molec. Phys.*, **92** ,625 (1997)

[74] C. G. Barraclough, P. T. McTique, Y. L. Ng, *J. Electroanal. Chem.*, **329**, 9, (1992).

[75] M. Matsumoto, Y. Kataoka, *J. Chem. Phys.*, **88**, 3233 (1988).

[76] N. I. Christou, J. S. Whitehouse, D. Nicholson, N. G. Parsonage, *Molec. Phys.*, **55**, 397 (1985).

[77] G. Aloisi, R. Giudelli, R. A. Jackson, S. M. Clark, P. Barnes, *J. Electroanal. Chem.*, **206**,131 (1986).

[78] F. M. Stillinger, A. Ben-Naim, *J. Chem. Phys.*, **47**, 4431 (1967).

[79] M. A. Wilson, A. Pohorille, L. R. Pratt, *J. Phys. Chem.*, **90**, 5211 (1989).

[80] E. N. Brodskaya, V.V. Zakharov, *J. Chem. Phys.*, **102**, 4595 (1995).

[81] K. Leung, *J. Phys. Chem. Lett.*, **1**, 496 (2010).

[82] S. M. Kathmann, I-F. W. Kuo, C. J. Mundy, *J. Am. Chem. Soc.*, **130**, 16556 (2008)

[83] P.Jungwirth, D. J.Tobias, *Chem.Rev.,***66,**1259(2006).

[84] N. K. Adam, The Physics and Chemistry of Surfaces, Oxford Univ. Pres, London, 1941, p. 133.

[85] P. Dynarowicz-Łatka, A. Dhanabalan, O. N. Oliveira, *Adv. Colloid Interface Sci.*, **91**, 221 (2001).

[86] M. Paluch, *Adv. Colloid Interface Sci.* **84**, 27 (2000).