

A Mathematical Model of Exclusion Zone Behavior

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Abstract—Physical properties of ordered water in the vicinity of various hydrophilic surfaces are different in many areas, such as viscosity, charge, movement and characteristics of molecules in its composition. One of these diversities was shown in the experiments including UV-Vis absorption spectra, where was shown significant absorbance of water in this area at the wavelength of 270 nm. Mathematical model for examined absorption spectra based on the appropriate differential equation and conditions is formulated and presented in this paper. Derived model considerably corresponds to fitted normal (Gaussian) function for absorption spectra.

Keywords— exclusion zone, UV-Vis absorbance, mathematical model.

I. Introduction

Areas of structured water in the vicinity of different hydrophilic surfaces have been recognized in series of recent findings. They remain phenomena of great interest for scientists in different areas of research because of many possible applications. Depending on scientific area these clear structured zones, i.e. exclusion zones (EZ) have different names, so in biology is talked about unstirred layers, in material science is vicinal water, interfacial water, confined water, in physics is water structure, in protein science is interfacial water, bound water, and in common these areas of water are known as organized water [Golubovic, 2012]. Width of these zones is varying depending on surfaces and solutes which are examined, and they may reach even several hundred micrometers [Zheng and Pollack, 2003; Chai and Pollack, 2010; Yoo et al, 2011; Bhalerao and Pollack, 2012]. Different types of hydrophilic surfaces are affecting moving solutes and particles away from them, and regarding that EZ's can be found next to different natural and artificial hydrogels, monolayers, polymer and polymer membranes (Nafion, contact lenses), wires, optical cables, biological tissues (muscles, cornea) [Green and Otori, 1970; Zheng et al, 2006; Pollack and Clegg, 2008;], reactive metals (zinc, tin, lead, aluminum, tungsten) [Chai et al, 2013].

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Exclusion zones are dependent on material, diameter and concentration of particles in examined solutions.

Those colloid particles are diverse by constitution: silt, sand, red blood cells, proteins, bacteria, dyes, microspheres, sugars, salts [Zheng and Pollack, 2003]. It is also important to remark that various solutions show near surface EZ's, such as: aqueous solutions, solutions with hydrogenized nanoparticles, lens solutions, polar solutions (acetic acid, isopropanol, DMSO, D20) [Chai and Pollack, 2010].

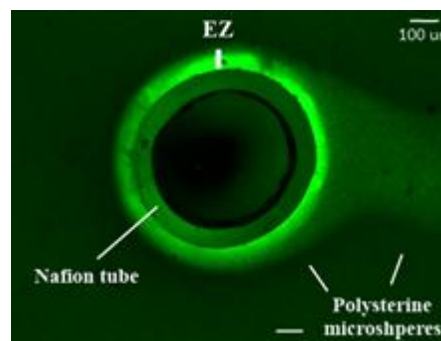


Figure 1. Exclusion zone appeared in interaction of deionized water solution with microspheres and Nafion tube [Golubovic, 2012].

Many different researches which were conducted indicate that phenomena of clear areas next to various hydrophilic structures are of great interest. While measuring the spatial distribution of electrostatic potential inside the exclusion zone for water and aqueous solutions of salts it was shown that potential is negative with values up to -120mV While distance from Nafion (used as hydrophilic surface next to which is formed EZ) is increasing, value of potential is decreasing. Conclusion from these researches is that this zone is negatively charged [Chai and Pollack, 2010]. Behavior of EZ's is examined also regarding the radiant energy. Ez's were observed in all visible, near IR and IR spectra of light, and it is concluded that exposure to radiation causes the increase of its size [Pollack, 2013]. Thermal imaging of these zones was done and it was shown with spatial temperature distribution in EZ that temperature is less than in bulk water [Zheng et al, 2006].

Regarding the thermodynamic parameters, water within the certain range of boundary conditions creates a system which characteristic is coexistence of its two phases that have different parameters, one with high entropy in bulk water, and one with low entropy interfacial coherent exclusion zone domains [Voeikov et al, 2009]. Measurements of birefringence showed that optical properties of EZ's are different, meaning refractive index of this water is 10% higher in comparison to bulk water. One of distinctive properties of the near hydrophilic surface clear areas was obtained by observing UV-Vis spectra of absorbance. It was shown in different researches that peak which appears at 270 nm in several solutions became

so called “signature” of EZ water. Peaks can vary in height or strength, but EZ water always absorb light at the value of 270 nm (± 10 -25 nm) [Chai et al, 2008; Pollack, 2013].

Previously stated difference of exclusion zone was examined through various imaging techniques: NMR, IR, birefringence and thermal. Physical differences were tested by measuring of: electrical potential, viscosity, UV-Vis and IR absorption spectra, thermal properties, and optical properties. After all experiments which were done, many differences between EZ and bulk water were stated: differences in structure i.e. molecular ordering, charge, viscosity, density, alkalinity, refractive index, freezing temperature, relative permittivity, relaxation times.

This paper was motivated with distinctive characteristic of EZ, based on findings of Chai et al (2008) that exclusion zone has anomalous prominent peak of light at 270 nm in UV-Vis absorption spectra. Experimental model in this research showed properties that have not been seen previously. Absorption spectral analyses were made on single beam diode-array spectrophotometer with usage of UV-quartz micro-rectangular cuvette. The spectrophotometer measures wavelengths from 190 nm to 820 nm, and the transmitting range of cuvette is from 170 nm to 2,7 μm . Vertically on wall was placed Nafion sheet in order to observe if EZ will generate. Spectrometer was directed so it sample narrow parallel zones next to Nafion. Among other solutions which were used in various experiments, in paper under consideration are examined absorption spectra's of sodium chloride, potassium chloride and lithium chloride. Absorption of water next to Nafion and in bulk water was completely different. Possibility that these spectral features arose from presence of water-soluble organic impurities is eliminated in series of experiments. The lowest examined concentration was 1M when peak decreased, but it's position remained. Effect of anions and cations on peak was not noted. Variety of situations were explored where ordered water was anticipated, and 270 nm absorbance peak confirmed, and those experiments included mentioned salt solutions, sugar solutions, and Nafion 117 solution/film.

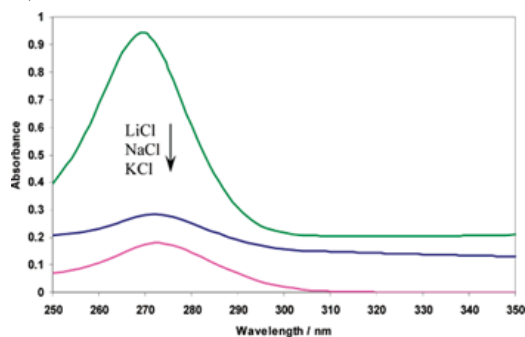


Figure 2. Absorption spectra of NaCl, KCl and LiCl solutions after purification by baking. Inset: amplitude of ~ 270 nm absorbance of LiCl solution as a function of salt concentration [Chai et al, 2008].

Modeling strategy of 270 nm peak absorbance is based on developed model of partial differential equations (PDF), and fitted experimental PDF data. These data are fitted according to the function which represents solution of developed method

of differential equations. In this paper are shown results of height distribution analysis of absorbed peaks, and differential equations accompanied with appropriate additional conditions which describe such kinds of distributions have been formulated and presented. Derived model considerably corresponds to fitted normal (Gaussian) function for absorption spectra.

II. Results

A. Mathematical model

A mathematical method of 270 nm absorption is presented in this paper for experimentally verified phenomena. The problem under consideration can be described by the following partial differential equation of the second order [Rothe, 1984; Grindrod, 1996; Cerrai, 2001; Buerger and Mailer, 2005]:

$$\frac{\partial y}{\partial t} = \frac{w^2}{8} \frac{\partial^2 y}{\partial x^2} \quad (1)$$

where $y = y(x, t)$ is a function which describes the height of the structural elements. x and $t > 0$ are the coordinates of space and time, respectively, and w is a known constant. Now, neither the boundary conditions nor the initial conditions as in classical physics [Kreyszig, E.] are given. A solution of equation (1) having the form

$$y = t^{-\alpha} f[(x - x_c)t^{-\alpha}] \quad (2)$$

where α is an unknown constant should be determined.

The function $f(x)$ can be expressed in the form

$$f(x) = B e^{-g(x)} \quad (3)$$

The unknown function $g(x)$ has continual derivatives of the adequate order and satisfies $g(x_c) = 0$. Simultaneously, $g(x)$ and the unknown constant B obey the normalization condition:

$$B \int_{-\infty}^{+\infty} e^{-g(x)} dx = 1 \quad (4)$$

Furthermore, the scaling condition

$$g(xt^{-\alpha}) = g(x)t^{-1} \quad (5)$$

holds. Using these new relations (2), (3) and (5), $y(x, t)$ must be given by:

$$y = B t^{-\alpha} e^{-g(x)t^{-1}} \quad (6)$$

Inserting this in (1) implies the nonlinear differential equation

$$t g'' - g'^2 + \frac{8}{w^2} g = \frac{8\alpha}{w^2} t, \quad g = g(x) \quad (7)$$

The coefficient of (7) are analytic functions at $x = x_c$. So every solution $g(x)$ is analytic at $x = x_c$ and can be represented by

$$g(x) = c_0 + \sum_{n=1}^{\infty} c_n (x - x_c)^n \quad (8)$$

with radius of convergence $R > 0$. The condition $g(x_c) = 0$ implies $c_0 = 0$. Every power series (8) is uniformly convergent in every closed interval $|x - x_c| \leq r$ of radius $r < R$ and the series (8) can be differentiated term by term with respect of x and the resulting series has the sum. The absolute convergence of $g(x)$ resp. $g'(x)$ allows to use the Cauchy product for calculation of g^2 . Inserting (8) in (7) and equating the coefficients of $(x - x_c)^n t$, $n \geq 0$, to zero yields

$$c_2 = \frac{4\alpha}{w^2} \text{ and } c_n = 0, n \geq 3. \quad (9)$$

Equating to zero the coefficients of distinct powers $(x - x_c)^n t^0$, $n \geq 0$, yields a system of infinitely many recursion formulas

$$\sum_{k=0}^n (k+1)(n-k+1)c_{k+1}c_{n-k+1} - \frac{8}{w^2}c_n = 0, \quad (10)$$

Inserting $c_n = 0$ for $n \geq 3$ for (9), then all relations (10) are fulfilled for $n \geq 3$. The three remaining relations in (10) are

$$c_1^2 = 0, c_1(c_2 - \frac{2}{w^2}) = 0, c_2(c_2 - \frac{2}{w^2}) = 0. \quad (11)$$

Since $c_1 = 0$ the second relation is satisfied. $c_2 = 0$ cannot be taken in the third relation, because then all coefficients c_n vanish, i.e. $g(x) = 0$

So (11) implies

$$c_1 = 0, \quad c_2 = \frac{2}{w^2}. \quad (12)$$

From c_2 in (9) and (12) follows $\alpha = \frac{1}{2}$, and the solution of (7) is

$$g(x) = \frac{2}{w^2} (x - x_c)^2. \quad (13)$$

So, the complete solution (6) becomes

$$y(x, t) = B t^{\frac{1}{2}} e^{-\frac{2(x-x_c)^2}{w^2 t}}, \quad t > 0. \quad (14)$$

Substituting (13) in (4) implies

$$B = \frac{1}{w} \sqrt{\frac{2}{\pi}}. \quad (15)$$

Expression (13) with (14) represents the solution of (1) in the form

$$y(x, t) = \frac{\sqrt{2}}{w\sqrt{\pi}} t^{\frac{1}{2}}. \quad (16)$$

Since the differential equation (1) only includes derives of first and second order

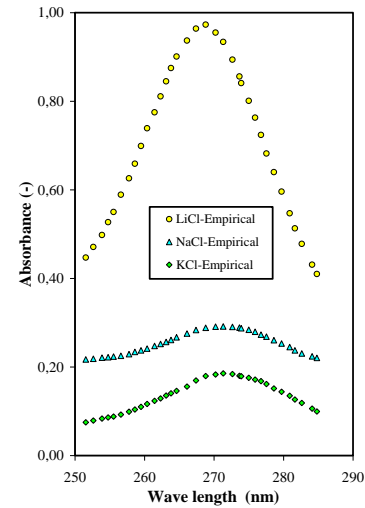
$$y(x, z) = y_c + \frac{\sqrt{2}}{w\sqrt{\pi}} t^{\frac{1}{2}} e^{-\frac{2(x-x_c)^2}{w^2 t}}, \quad y_c = \text{const.} \quad (17)$$

also is a solution of (1).

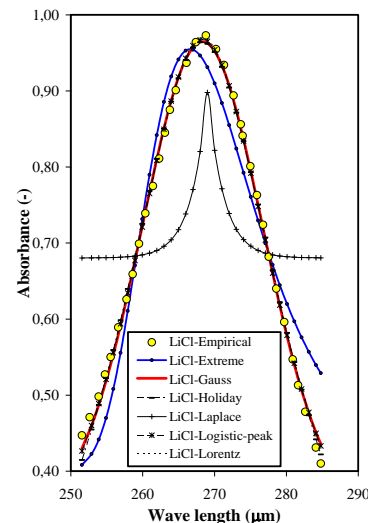
Taking $t = 1$ in (17), the expressions become identical form of Gaussian function (function 2 in table 1).

B. Verification of the model

The applicability of a wide variety of potential functions with respect to analytical describing the LiCl, NaCl and KCl absorption has been tested in present study. Empirical data of Chai et al (2008) where fitted using the software realization of the numerical procedure of Levenberg-Marquardt [Press et al, 2002]. However, only the six model functions that enabled convergence of fitting procedure and which were characterized by the highest accuracy of experimental data approximation are presented in figures 3.4 and discussed in this paper.



(a)



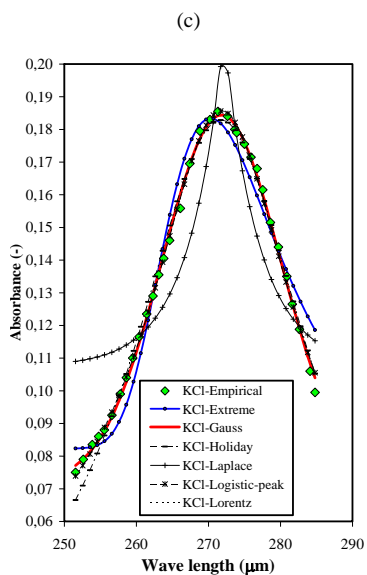
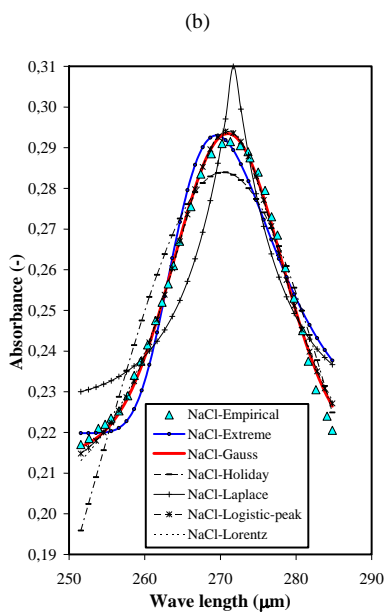
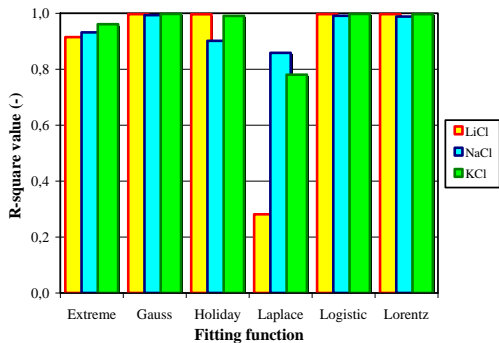
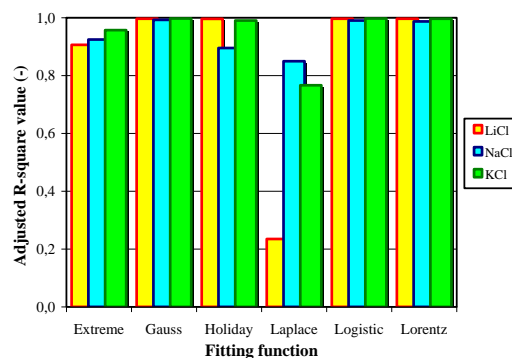


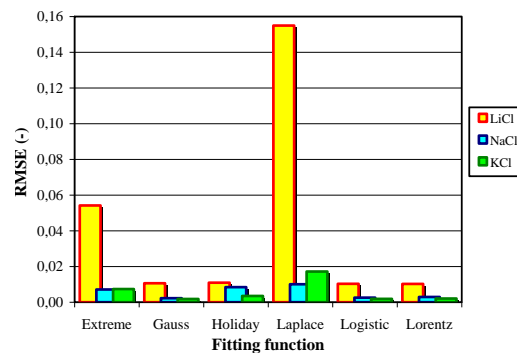
Figure 3. Results of the experimental data fitting.



(a)



(b)



(c)

Figure 4. The fitting accuracy parameters of tested model functions.

TABLE I. MODEL FUNCTIONS.

	Model function	Formula
1.	Extreme	$y = y_0 + A \cdot e^{\left[e^{-z} - z + 1 \right]}$; $z = \frac{x - x_c}{w}$; $y_0, A, x_c; w = \text{const.}$
2.	Gauss	$y = y_0 + \frac{A}{w \cdot \sqrt{\pi/2}} \cdot e^{-z^2}$; $z = \frac{x - x_c}{w}$; $y_0, A, x_c; w = \text{const.}$
3.	Holiday	$y = (a + b \cdot x + c \cdot x^2)^{-1}$; $y = y_0 + \frac{A}{w \cdot \sqrt{\pi/2}} \cdot e^{-z^2}$; $a, b, c = \text{const.}$
4.	Laplace	$y = y_0 + \frac{1}{2 \cdot b} \cdot e^{-\frac{ x-a }{b}}$; $y_0, a, b = \text{const.}$

5.	Logistic peak	$y = y_0 + 4A \cdot \frac{e^{-z}}{(1 + e^{-z})};$ $z = \frac{x - x_c}{w};$ $y_0, A, x_c; w = \text{const.}$
6.	Lorentz	$y = y_0 + \frac{2A}{\pi} \cdot \frac{w}{4(x - x_c) + w^2};$ $y_0, A, x_c; w = \text{const.}$

Among these six models, the functions 2 (Gaussian), 5 (Logistic peak) and 6 (Lorentzian) have achieved the highest accuracy, as it can be seen in the Figure 3. This is also evident from the Figure 4, which shows that using each of these three functions for data fitting resulted in the highest R-square values and adjusted R-square values, reaching the level of about 0,99 (this verifies near the perfect fitting of experimental data). In the same manner, the same three functions resulted in the smallest Root-mean-square errors (RMSE) (Figure 3c).

Presented analysis also verifies that absorption spectra characteristics for exclusion zone are fairly close to normal Gaussian distribution.

III. Summary

Recognition of clear zones of water from which all particles are excluded is differently structured than bulk water is important for biological, medical, biotechnological and other applications. Absorption in narrow part spectra of 270 nm is unique characteristic of the ordered water structure. The most recent finding [So et al., 2012] also experimentally confirmed existence of 270 nm peak in area of the exclusion zone in case of ice melting. This state of intermediate phase which appears between ice and liquid water, i.e. phase of liquid crystalline water is shown to be EZ.

However, pure raw experimental data of absorption spectra with the characteristic peak at 270 nm are not suitable enough for sophisticated analysis of these unique phenomena. With respect to this, an adequate mathematical model has been formulated based on partial differential equations, and corresponding additional conditions. The solution of these PDF's is just the normal Gaussian function which was verified with statistical characterization and data fitting.

This mathematical model is made with purpose of describing the unique characteristic of EZ. It make possible insight and analysis of impacts which may well reflect extensive water structuring, such as concentrations of saturated solutions, aromatic impurities, quasicrystalline nature of water in vicinity of charged of hydrophilic entities etc. Our mathematical analysis represents a valuable basis for further development of mathematical models for analysis of structured water characteristics.

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