

Janina GRODZKA*, Andrzej POMIANOWSKI**

ON THE NECESSITY OF MODIFYING THE DLVO THEORY (IN EQUILIBRIUM SYSTEMS)

Received March 15, 2005; reviewed; accepted May 15, 2005

Almost half of a century has past since the time when I (AP) had the opportunity to meet personally three persons of the authors of the DLVO theory, on one of the first international Surface Activity Congresses. Not so long ago I have paper napkins on which, during one of the banquettes, the fathers of the DLVO theory drew the equipment for removal of disorderly lecturers and for punishment them for the "quality" of their presentations. Among the others, we planned to stick pins in... the bottom of professor Ekwall, for his work on bile acids.

Derjaguin referred its initial studies on the process of the contact between gaseous bubbles in solutions, and he explained the basic difference between the statically stable systems and the dynamics of unstable foams and free films. By the analogy with the surface pressure in monolayers he defined the equilibrium pressure in free films.

Key words: hydrogen bond, water structure, hydrophobicity, soft and hard matter

INTRODUCTION

The DLVO theory - combined with the theory of the structure of the electric double layer - thanks to the Hamaker's works, has become a basis for the description of "stability" of dispersed systems and of many surface phenomena. It is worth to mention that this theory describes only the interactions between two molecules. We say that the interactions are of a short or far range, depending on how fast their energy decays with the distance. When two approaching molecules are "pressed" to each other the energy of the system rapidly increases, showing the repulsive interaction. The molecules behave practically as hard, noncompressible spheres. The commonly accepted theory of the Lennard-Jones interactions assumes that the algebraic sum of their energy values is equal to:

$$U = b/r^{12} + (- a/r^6) .$$

** Emeritus professor of Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Kraków.

* Poznan University of Technology, Institute of Chemical Engineering and Technology, Poznan.

The first (positive) term describes a rapid decrease of repulsive interactions with a distance, r , while the second one (negative) describes a rapid (but 6 orders of magnitude slower) decay of attractive interactions. The latter manifest themselves at the distances comparable with the size of molecules. It remains true for two, neutral molecules, of the total energy which has a sharp minimum on the curve showing its dependence upon the distance. A natural measure of the attractive interactions intensity is $1 kT$, because free molecules participate in chaotic thermal motions. An average kinetic energy of translational motions is equal to $1 kT$ for every degree of freedom. This causes that temperature is a factor determining how much the interactions may affect the motion of approaching molecules.

The terms describing the constants of attractive interactions depend on the nature of molecules. They are different for stable dipoles, for induced dipoles, for nonpolar molecules, but they always decrease with "the 6-th power of a distance". The interactions of ions depend on their charges and may be attractive or repulsive, but they are the far range interactions, contrary to the previously discussed interactions, because following the Coulomb rule they decrease proportionally to the distance between the charges and therefore they are visible at significantly greater distance.

In the years when the DLVO theory was developed the state of the quantum mechanics did not give the opportunity for so precise description of the bonds, both internal and intermolecular, as nowadays (GRABOWSKI; BARBIELLINI). For this reason it was not possible to distinguish for the molecule of water its very characteristic hydrogen bonds!

Why the DLVO theory needs to be further developed?

The most important reason for the attempts to modify the DLVO theory (GRASSO) is to include within the theory the existence of hydrogen bonds explicitly. This is especially important because of the common studies of aqueous solutions. Even in the manuals of the Physical Chemistry it is stated that the quantum mechanical description of interactions between two molecules, which may form a hydrogen bond needs other than the DLVO theory modelling!

Despite the raising conscience that the theory should be supplemented or even that a new look for this problem is required, relatively little number of works are dealing with this question. Why we are trying to present this question here? The review of the present literature shows that in the next future this subject will be rapidly developed (GUILLOT).

There are in Poland many well equipped Scientific Centres, carrying out both experimental and theoretical works on a high level. The development of a wider national co-operation between these centres seems very attractive - it could assure our investigations to take a stable place in the front of basic studies of the "Surface Activity". A well prepared, based on a critical literature review experimental system should also create a basis for verification of the "virtual reality" studies, the models based on the assumed molecular dynamics!

DESCRIBED SYSTEMS

We shall present the selected systems, for which the shortcomings of the "classical" treatment of experimental data have been established.

In this PRESENTATION three words will be of primary importance:

water
silica
protein.

The "theoretical" interpretation of experimental data, concerning the interfacial systems containing the above mentioned substances is generally based either on the classical DLVO theory

or on

the theory developed by Hamaker.

What is the essence of the Hamaker's development? He was interested in the description of the interactions of the surfaces of solids or fluids, i.e. the "sets" of molecules present at the condensed interfaces. He began from the consideration of changes in attraction of bodies in vacuum, and next he replaced vacuum with media of properties differing from the properties of approaching bodies. One of the important conclusions is that the summing up - in practice - the integration of single interactions causes that the range of the attractive "London" and electric interactions becomes similar. These interactions result in aqueous solutions from the creation of electric double layers on the interfaces (they are determined by concentration and kind of the electrolyte, which determines also the charge density on the surface of a condensed phase). In our presentation we would like to prove that consideration of the properties of water, resulting from the existence of hydrogen bonds will have the influence on all phenomena, called the "surface phenomena".

From the above mentioned substances water plays the primary role (in fact its basic properties). From these properties two play a particular role: pH and HLB.

A basic "bulk" property of chemically pure water is its "ionic product". But in the interfacial regions the "thermodynamic activity of hydrogen ions" becomes a local function of a "site". Therefore "surface pH" depends on our model assumptions and on the operational (usually electrochemical) definition of pH. (We know only the average thermodynamic activity values for electrolytes, "activity of hydrogen ions" depends on convention!).

A basic "interfacial" property of chemically pure water is its HLB. (As we know, this term denotes the equilibrium constant for the hydrophilic - lipophilic balance). For the interface between water and its saturated vapour this value may be taken arbitrarily as 7. This equilibrium constant is a basic "distribution constant" for water molecules between the "hydrophobic" vacuum and "hydrophilic" liquid water! It should be noted here that practically all gases dissolve better or worse in water. (Their solubility is also a measure of their hydrophilicity, not properly defined yet)! The so called noble gases, as well as oxygen or nitrogen "enforce the structure" of water (they are hydrophobic)

to a different degree. On the contrary, carbon dioxide breaks the structure of pure water (it is hydrophilic). The older concept of "structure making" or "structure breaking" substances has been replaced now by the more general concepts of cosmotropes and chaotropes (GALINSKI). Let us also remember that by dissolving any amount of any substance in water we change thermodynamic activity of water and pH. Usually it is important only when we discuss a concrete process. Similarly, **every** substance introduced to water will appear in all interfacial layers, contacting with the solution. We are however usually interested only in so called "surfactants" and (eventually) in their HLB!

But every substance (and also every ion, formed by dissociation in water) has its own characteristic HLB value in a particular equilibrium system.

We define these HLB values on a free surface of water (in relation to its saturated vapour) as the adsorption equilibrium constants, determined by thermodynamics and visualized by the changes of the surface free energy.

We have however to remember that usually we measure surface tension in water, that contains dissolved gases, or additional substances. These substances often in a more or less visible way affect the observed equilibrium state, and therefore the correct HLB values, which are necessary to model any particular system with the molecular dynamics. HLB values are as much important for the equilibrium in systems forming stable microemulsions as for free surface of solutions.

The greatest and most interesting challenge is a complete and true description of hydrophilic-hydrophobic equilibrium of micellization and wetting.

The mentioned systems are the most difficult to describe! (For instance because of the hysteresis characteristic for wetting, which accompanies always the heterogeneity of solid surfaces). Thermodynamic considerations are usually carried out for flat surfaces, often neglecting the Kelvin formula, which does not require taking into account the occurrence of the pressure gradient in the interfacial region only for the surfaces of small curvatures, or "coarse" macroscopically. However, when any coarseness in the nanometric or molecular scale appears on the surface, the pressure gradients, determined by surface tension increase abruptly. Following the Gibbs thermodynamics the decisive role begin to play the role of so called burst pressures or linear pressure. The quantitative measure of the thermodynamic "activity" of any substance is its pressure of saturated vapour. The droplet of water, of 1 μm (micron) radius has the saturated vapour pressure of 1 per mille higher than above a flat surface. The droplet of 5 nm radius has the saturated vapour pressure twice higher than above a flat container, and as the radius tends to the molecular dimensions the increase of the activity becomes abrupt! The change of the thermodynamic activity of water in flat, and even more in strongly curved interfacial regions, causes that the molecular description of the energy and structural changes using the "classical" free energy functions ($F_{T,V,N}$ or $G_{T,p,N}$) is not sufficient! Unfortunately - only the Scheludko's school has the clear feeling of necessity to use the rules of the thermodynamics of open systems while describing the interfacial systems. This requires the consideration

of the equilibrium state at the fixed value of the pV product! (Whenever it is possible - with the use of the statistical thermodynamics). Two things should be always remembered:

- HLB - as the equilibrium constant is an additive quantity. Therefore by combining the results of measurements carried out on the correctly selected systems it is possible to determine the additive HLB values even for the functional groups or for the fragments of larger molecules.

The concepts of phases and components are often mistaken or mixed, when considering the processes proceeding in particular systems. Some phases forming the system are sometimes its components.

For instance:

An aqueous solution of a surfactant becomes a multicomponent phase, while a solid covered with a surfactant becomes another phase for a bubble of a gas. On the other hand, a gas is a phase, but for instance water vapour (usually in the equilibrium with an aqueous solution) contains usually also other components dissolved in water. Wetting is an equilibrium property of the systems. Scheludko has thoroughly studied the dynamics of nucleation, very often preceding the equilibration of phases. A particular attention he paid to the relation between the dynamic equilibrium of formation and annihilation of nuclei with the state of hydrophobicity of the interfacial region. The nucleation of a particular gas, in the dynamic equilibrium with the surface is closely related to the HLB value of a particular gas - solid body system, not with HLB of the surface. We must remember, that each equilibrium state has its own barriers, usually different for the opposite direction of a process, which often causes the occurrence of meta stable states!

The HLB values give a phenomenological characteristic of the systems - but the understanding and "molecular" description of these systems needs the "modelling" of the existing interactions of the solvent molecules with the surfaces of solid bodies, and afterwards the studying the influence of substances, which were introduced to modify the nature of the interfacial region. The DLVO theories - both the existing and the modified one - should serve to solve these problems.

The aim of the authors is to show the inadequacies of the present DLVO theory, irrespective of the type of matter, to which this theory is applied.

THE "HARD" AND "SOFT" MATTER

We shall distinguish here two basic types of the matter, in English - hard and soft matter.

The first matter has crystallic lattices, with its nodes occupied by atoms and small molecules or their ions.

In the second matter the nodes, or rather the lattice positions are occupied by large molecules, usually organic ones, or even their crystalline aggregates (in the classical sense).

This second way of arrangement is determined in general by large dimensions and shapes of the molecules.

This classification is obviously a convention!

We shall consider only the selected, equilibrium multiphase systems, of hard and soft materials in the aqueous medium. The HLB theory in its classical form is based on the description of the equilibrium of the substance distribution between the hydrophilic and hydrophobic phase. Let us remember that not all gases contained in air are hydrophobic in relation to the aqueous solution.

The necessity of a rigid definition of the hydrophobicity was formulated in the Davies and Riedel monograph, in a form presented by Davies in 1957 at the II International Congress of Surface Activity (DAVIES). In this period of time people were intensively looking for the theoretical bases determining the minimum on the dependence of the density of liquid water on temperature, at about 4⁰ C. Despite the almost 40 years since that time this anomaly is still explained by the hypothesis of an additional phase transition between two structures of water of a different spatial arrangement of bonds (JHON). The attempts of distinguishing the "complete" (unbroken) hydrogen bonds from those totally broken hydrogen bonds in water have long tradition. In the paper (JHON; SILVERSTEIN) the present opinions are quoted. It is estimated that at 0⁰ C between 7 and 60 % of hydrogen bonds are broken. These estimations were even more deviating previously! Within last several years many papers have appeared that with model calculations have shown the reality of the occurrence of dynamic aggregates of water molecules, differing in the number of molecules and their mutual orientation (SILVERSTEIN; CHEN). The existence of these aggregates makes possible the explanation of all observed "anomalies", accompanying the changes of: temperature, pressure, and dissolving in water molecules and ions - hydrated to various extents, and even the hydrophobicity (DU). A rapid progress of investigations in this area is best illustrated by the fact, that within 100 most interesting publications on the structure of water issued in the years 1990 - 2004, one half was published in the years 2003 - 2004, one third - in the years 2002 and 2001 and only 1/6-th - in the whole previous ten years! From the papers published in the years 1999-2001 two papers have drawn our special attention (WALLQUIST; KANNO).

Which way this huge increase of interest in theoretical explanation of the special position of water and aqueous solutions in practice and research may be most shortly characterized? It may be explained by two reasons. The first - a better understanding of the important role of creating the simplified models, which enable the correct prediction of the properties of systems, which have not been studied yet. The second - a fast development of quantum mechanics, based on progress both in computer hardware and software.

For many tens of years people verbally claimed that the majority of the properties of water result from the presence of hydrogen bonds. However only within last few years it has been shown that the consideration of the factors determining the

specificity of hydrogen bonding in the models of water makes possible showing that the "anomalous" effects are a simple consequence of this bond that was not correctly accounted for (SYMONS). An important factor in the development of the discussed direction of investigations is a fast progress in spectral measurement techniques, which may be used for the verification of the results of the computations. Many known phenomena have appeared to be a simple consequence of the changes, caused in hydrogen bonds by temperature, pressure and the presence of "foreign" molecules. In particular we may say about the breakthrough in the understanding of the processes proceeding in the regions of the contact between water and its solutions and other phases!

The path to precise defining of the hydrophobicity has been opened.

HYDROPHOBICITY

This path should lead to creation the possibility of the quantitative prediction, both theoretical and experimental of the changes of hydrogen bonds in the interfacial area, by the contact of liquid water with any other phase. Moreover, the understanding the quantitative changes in hydrogen bonds around any molecule, either neutral or charged, will create the possibility of the uniform treatment of the "hydrophobicity" in the description of the properties of aqueous solutions, both in bulk and in interfacial regions. The spectacular proof on the possibility of the realization of this aim is the present interest in the behaviour of ions in aqueous solutions. The description of changes in their hydration should be closely correlated with their influence on the behaviour or state of colloidal systems, expressed by the so called "Hofmeister series" (COLLINS).

In such short review it is not possible to consider many particular systems, on which the usefulness of the more precise defining of the hydrophobicity has been proved. Therefore we have chosen one example for the behaviour of water in respect to "hard" and to "soft" matter. Silica and quartz are the examples of the hard matter, crystallizing in various crystallographic systems. The chemical composition of pure SiO_2 determines the variety of spatial arrangement of silicon and oxygen atoms in crystals and its very low solubility (at room temperature and atmospheric pressure) in chemically pure water! It is however sufficient to change temperature and pressure, and in particular pH of water, to obtain gel from the silica crystals. Such drastic change of the form, from poorly soluble silica to well soluble sodium silicate results from the change of the character of hydrogen bonds in the interfacial area of the contact between " SiO_2 " and " H_2O ", " OH^- ", and " Na^+ ", following the variations of pH. The works dealing with the interfacial changes caused by variations of pH has been focused on the measurements of electrokinetic phenomena and potentiometric titration of suspensions of silica grains, since the development of the theory of so called "binding sites". An excellent, critical survey of these problems has been done by M. Kosmulski (KOSMULSKI). Irrespective of the particular example of silica, the works

generalizing the role of water in two states of its structure and density, determining the "gelous" form of the matter have already appeared (WIGGINS). It is suggested that this type of interactions with water may be important for life (POLLACK).

Discussing the question of changes of solubility, both in the particular case of silica, and more generally, we have always to remember whether we are interested in the stable state during the thermodynamic equilibrium of the saturated solution, or also in the dynamics of reaching this state. The thermodynamics defines concentrations in the state of saturation, the kinetics - the velocity of attaining the equilibrium (SCHMID). This latter depends on the barriers of the particular process. The always present barrier is the diffusional limitation, which may be reduced by varying the mixing intensity, and so called activation of dissolution barrier, which may be reduced to some extent by the change of temperature. The dissolution is generally the more difficult the more complex is the frequently multistage process of formation of the new structure of molecule, such structure that the molecule would be able to pass into the solution. In some sense this stage reminds the process of the heterogeneous "nucleation" of the new phase - from aqueous solutions. More and more papers follow the works of the Scheludko's school, which had bound the nucleation process to hydrophobicity of the system: surface - "nucleus", and to the occurrence of the linear tension (YANG; WENNERSTRÖM). The approximation describing liquid water as the substance of a dynamic structure, existing in two forms, is applied also in the description of the interactions of water with the "soft" matter.

PROTEINS

A simple example of such matter may be a molecule of a protein, of a globular structure. In addition to bulk water, at the distances greater than about 15 Å from a molecule of a protein, in diluted solutions we may distinguish also water aggregates of the structure changed by the hydrophobic character of the "surface" of molecules, and so called structural water, necessary for keeping the characteristic spiral structure of the protein. The wide, professional and clearly documented work on these problems may be found in the monograph (HAMLEY). A special internal structure of proteins results from the occurrence of hydrogen bridges, binding every fourth acid group with the amino group of subsequent amino acids. There are some reports claiming that these aqueous bridges differ in energy, depending on the bound groups. Generally the structure of these solutions varies with the concentration of proteins, leading to aggregation of the molecules. The result of the aggregation depends on the mutual interplay between enthalpy factor, of the energy of molecule interactions, and on the entropy factor, depending on their configuration. This however does not lead to crystallization - as in the ionically or covalently bound crystals, but to the aggregation of the micellar type, in which the structural elements take the definite types of the symmetry, but they do not separate as a macroscopic phase. The author of the quoted review (GUILLOT) writes that the present state of knowledge on the bonds existing in

liquid water arouses his doubts. But in accordance with our belief he states in the summary that many papers (URQUIDI; CHO; ROBINSON; KELL) prove the possibility of breakthroughs in the nearest future in the discussed area!

SUMMARY

Dispersed systems and surface phenomena are commonly described using the DLVO theory, together with the theory of the structure of the electric double layer. In this paper the attention was drawn to the fact that the development of investigations on the behaviour of aqueous solutions needs the consideration of the role of hydrogen bonds, and the appropriate modification of the DLVO theory. The acceptance of the role of dynamic aggregates of water molecules, of variable number of the molecules and their orientation, makes possible the explanation of the "anomalies" observed in aqueous solutions, in particular the hydration and hydrophobicity.

By stressing the specificity of hydrogen bonds the path to more complete defining and generalization of the concept of hydrophobicity was shown. Based on the example of silica and proteins - as the representatives of the "hard" and "soft" matter the attention was drawn to the changes of the character of phases, related to the content of water and the nature of its hydrogen bonds, particularly in interfacial regions.

The doubts and the large number of papers in the discussed area hold up the hope that in the nearest future the breakthrough in the description of interactions of water with its surrounding will take place.

ACKNOWLEDGMENT

The authors thank Dr. J. Rodakiewicz - Nowak and dr P. Nowak for the english translation of this paper.

REFERENCES

- GRABOWSKI S.J., *A new measure of hydrogen bonding strength - ab initio and atoms in molecules studies*, Chem.Phys.Lett. **338** (2001) 361-366
- BARBIELLINI B., SHUKLA A., *Ab initio calculations of the hydrogen bond*, Phys. Rev. B **66** (2002) 235101
- GRASSO D., SUBRAMANIAM K., BUTKUS M., STREVETT K., BERGENDAHL J., *A review of non-DLVO interactions in environmental colloidal systems*, Re/Views in Environmental Science & Bio/Technology **1**: 17 – 38, 2002.)
- GUILLOT B., *A reappraisal of what we have learnt during three decades of computer simulations on water*, J. Mol. Liquids **101** (2002) 219-260.
- GALINSKI E.A., STEIN M., B. AMENDT and M. KINDER, *The kosmotropic (structure-forming) effect of compensatory solutes*, Comp. Biochem. Physiol. **117A** (1997) 357-365.
- DAVIES J.T., RIDEAL E.K., *Interfacial Phenomena*, Academic Press, (1961) 371.
- JHON Y.I., KIM H.G., JHON M.S., *Equilibrium between two liquid structures in water: explicit representation via significant liquid structure theory*, J. Mol. Liquids **111** (2004) 141-149.
- SILVERSTEIN K.A.T., HAYMET A.D.J. DILL K.A., *The strength of hydrogen bonds in liquid water and around nonpolar solutes*, J. Am. Chem. Soc. **122** (2000) 8037-8041.
- CHEN B., IVANOV I., KLEIN M.L., PARRINELLO M., *Hydrogen bonding in water*, Phys. Rev. Lett. **91** (2003) 215503.
- ENGLISH N.J., MACELROY J.M.D., *Hydrogen bonding and molecular mobility in liquid water in external electromagnetic fields*, J. Chem. Phys. **119** (2003) 11806-11813.

- DU Q., FREYSZ E., SHEN Y.R., *Surface vibrational spectroscopic studies of hydrogen bonding and hydrophobicity*, *Science*, **264** (1994) 826-82.
- WALLQVIST A., MOUNTAIN R.D., *Molecular models of water: Derivation and description*, *Reviews in Computational Chemistry* **13** (1999) 183-247.
- KANNO H., YOKOYAMA H., YOSHIMURA Y., *A new interpretation of anomalous properties of water based on Stillinger's postulate*, *J. Phys. Chem. B* **105** (2001) 2019-2026.
- SYMONS M.C.R., *Water structure, unique but not anomalous*, *Phil. Trans. R. Soc. Lond. A* **359** (2001) 1631-1646.
- COLLINS K.D., WASHABAUGH M.W., *The Hofmeister effect and the behaviour of water at interfaces*, *Quart. Rev. Biophys.*, **18** (1985) 323-422.
- KOSMULSKI M., *Chemical Properties of Material Surfaces*, in: vol. 102 *Surfactant Science Series*, Marcel Dekker, Inc. N.Y. 2001
- WIGGINS P.M., *High and low-density water in gels*, *Prog. Polymer. Sci.* **20** (1995) 1121-1163.
- POLLACK G.H., *Is the cell a gel-and why does it matter?* *Jap. J. Physiol.* **51** (2001) 649-660.
- SCHMID R., *Recent advances in the description of the structure of water, the hydrophobic effect, and the like-dissolves-like rule*, *Monatsh. Chem.* **132** (2001) 1295-1326.
- YANG J., DUAN J., FORNASIERO D., RALSTON J., *Very small bubble formation at the solid-water interface*, *J. Phys. Chem. B* **107** (2003) 6139-6147.
- WENNERSTRÖM H., *Influence of dissolved gas on the interaction between hydrophobic surfaces in water*, *J. Phys. Chem. B* **107** (2003) 13772-13773.
- HAMLEY Ian W., *Introduction to Soft Matter, Polymers, Colloids, Amphiphiles and Liquid Crystals*, Ed. John Wiley & Sons, Ltd (200).
- URQUIDI J., SINGH S., Cho C.H., ROBINSON G.W., *Temperature and pressure effects on the structure of liquid water*, *J. Mol. Struct.* **485-486** (1999) 363-371.
- CHO C.H., URQUIDI J., GELLENE G.I., ROBINSON G.W., *Mixture model description of the T-, P dependence of the refractive index of water*, *J. Chem. Phys.* **114** (2001) 3157-3162. A. H. Harvey, *Comment on "Mixture model description of the T-, P dependence of the refractive index of water"* [*J. Chem. Phys.* 114 (2001) 3157], *J. Chem. Phys.* **115** (2001) 7795. C. H. Cho, J. Urquidi and G. I. Gellene, *Response to "Comment on 'Mixture model description of the T-, P dependence of the refractive index of water'"* [*J. Chem. Phys.* 114 (2001) 3157], *J. Chem. Phys.* **115** (2001) 7796-7797.
- G. W. ROBINSON, S. -B. ZHU, S. SINGH, M. W. EVANS, *Water in Biology, Chemistry and Physics: Experimental Overviews and Computational Methodologies*, (World Scientific, Singapore, 1996). (The original SPC reference is H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren and J. Hermans, in B. Pullman (ed.), *Intermolecular Forces* (Reidel, Dordrecht, 1981) p331.)
- KELL G.S., *Thermodynamic and transport properties of fluid water*, in F. Franks (Ed), *Water A comprehensive treatise*, Vol. 1, Plenum Press, New York, (1972) pp. 363-412.

Grodzka J., Pomianowski A., *Konieczność modyfikacji teorii DLVO (w układach równowagowych)*, *Physicochemical Problems of Mineral Processing*, 39 (2005), 11-20 (jęz. ang.).

Układy rozdrobnione i zjawiska powierzchniowe są powszechnie opisywane w oparciu o teorię DLVO, wraz z teorią struktury pwe. W pracy zwrócono uwagę, iż rozwój badań dotyczących zachowania roztworów wodnych wymaga wyróżnienia roli wiązań wodorowych, a więc dokonania modyfikacji teorii DLVO. Akceptacja roli dynamicznych agregatów molekuł wody, o zmiennych ilościach drobin i ich ułożeniu, pozwala wyjaśnić obserwowane w układach wodnych "anomalie". W szczególności dotyczy to zagadnienia hydratacji i hydrofobowości.

Podkreślając specyfikę wiązań wodorowych wskazano drogę do pełniejszego zdefiniowania oraz uogólnienia pojęcia hydrofobowości. Na przykładzie krzemionki i białka - jako reprezentantów materii "twardej" i "miękkiej" zwrócono uwagę na zmiany charakteru faz, związane z zawartością wody i natury jej wiązań wodorowych, szczególnie w obszarach powierzchniowych.

Nagromadzone wątpliwości i duży wzrost ilości prac w omawianej dziedzinie - pozwalają spodziewać się, w najbliższej przyszłości, przełomu w opisie oddziaływań wody z jej otoczeniem.