

Janina GRODZKA^{*}, Andrzej POMIANOWSKI^{**}

WETTABILITY VERSUS HYDROPHILICITY

Received June 28, accepted July 3, 2006

Basing on recent works we discuss the issue relating wetting and hydrophilicity pointing out the topics enabling a fast progress in this area. Wetting is a phenomenon that is still the subject of intensive studies, both pure and applied. However, precise definitions of its molecular basis are still lacking and the static and dynamic macroscopic parameters should also be defined. An important role seems to be played by profound investigation on relaxation times of the primary elemental steps of the joined chemical and mechanical processes.

Key word: wettability, hydrophilicity, hydrophobicity, water clusters, flotation, interfacial phenomena, contact angle

INTRODUCTION

Wettability and hydrophilicity are closely related phenomena. Most research groups working on surface activity use these terms in their every-day practice. The wettability and hydrophilicity phenomena are useful in solving practical issue as well as scientific concerns on both molecular and macroscopic scales under static (at thermodynamic equilibrium) and dynamic conditions. During the last few years interest in a better understanding of wettability is systematically growing. For instance discussions at a recent SURUZ (2006) meeting encouraged us to summarize the recent state of knowledge concerning wetting utilizing numerous original and review articles, especially those of Guillot (2002) and Verdaguer et al. (2006).

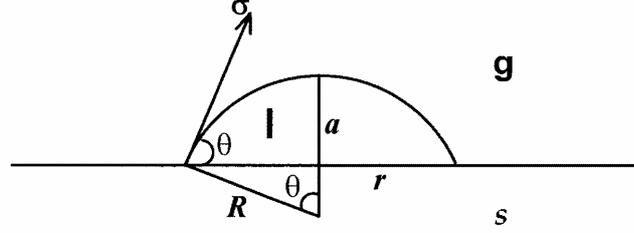
FROM MACROSCOPIC TO MOLECULAR DIMENSIONS

Not long ago Platikanov (Toshev and Platikanov, 2004) remind us a precise thermodynamic analysis of the wetting process. He showed that the simplest model of a wetting system consist of a plane homogeneous surface of an ideally hard and

^{*} Medical Center of HCP Poznań, Poland

^{**} Professor Emeritus of Polish Academy of Sciences, Tenczynek, Poland,
izabela.pomianowska@neostrada.pl

practically insoluble solid being at equilibrium with a liquid or solution and either saturated vapor of the liquid or insoluble neutral gas. The number of conditions concerning the nature of the considered phases directly indicates the number of sources of error and problems in delineation of wetting processes.



$$(d\Omega)_{T,\mu_i} = -\Delta p dV + \sigma dA_{lg} + (\omega_{ls} - \omega_{gs}) dA_{ls}, \quad d\Omega = 0$$

$$V = \frac{1}{6} \pi a (3r^2 + a^2); \quad A_{lg} = \pi (r^2 + a^2); \quad A_{ls} = \pi r^2$$

Fig.1. The state of thermodynamic equilibrium of a wetting system

Figure 1 presents the state of a thermodynamic equilibrium in a system of already mentioned properties. We assume a lack of any external forces, including gravity, event though their introduction to the system is simple. However, it complicates the final formulas resulting from the system geometry and equilibrium of the “surface forces”. Figure 1 shows a drop placed on a flat surface, cut with a plane perpendicular to the diameter of the fragment of the sphere drop. The equations inserted in Fig.1 describe the condition of thermodynamic equilibrium ($d\Omega = 0$). The radius of the sphere is denoted with R , the drop volume V , drop-solid surface area A_{ls} , drop-gas surface area A_{lg} , radius of the “perimeter” (spherical perimeter of wetting) r , and the height of the drop a . We have shown also the vector of force σ , which is tangent to the drop and results from the interfacial tension (gas-liquid) γ , and the angle θ between the tangent and the surface of the solid.

The angle θ observed on a macroscopic scale is commonly called the wetting angle. It is agreed to measure the angle through the liquid phase. It can be seen in the figure that the wetting angle for well wetting liquids (up to a complete, “ideal” wetting) must tend to zero. For the non-wetting liquids the drop contacting the liquid remains spherical and the wetting angle is 180° . In Fig.1 symbols g , l , and s denote the gas, liquid, and solid phases, respectively. The interfacial regions are denoted as l - g , g - s , and l - s , or shortly by lg , gs , and ls .

Equilibrium in this “open” system having $T = \text{const}$, and constant composition ($m_i = \text{const}$) means that the minimum of the free energy Ω of the system can be calculated

for $-pV = \text{const}$ providing $d\Omega = 0$. We omit here mathematical derivation of the equilibrium of open systems based on the Gibbs thermodynamics giving only the sense of symbols and conclusions based on authors considerations. It should be stressed here that there is an essential difference between the nature of a system composed of two liquid phases and a gas and that composed of two solids and a gas, or a system composed of a solid, gas, and liquid. In contrast with the liquid phases, the solid phases (ideally hard and elastic) cannot change their macroscopic shape after a contact with gas, i.e. they cannot change the shape. Practically non-compressible liquids do not show the elasticity of their "form". For a solid body in contact with gas or liquid we must distinguish components of its excess free energy appearing due to interactions with molecules of the gas or liquid of the interfacial region and its "own surface tensions" $_{gs}\gamma$ and $_{gl}\gamma$. We define them using the following formulas: $_{gs}\gamma = _{gs}\omega_s - _s\omega_s$ and: $_{ls}\gamma_s = _{ls}\omega_s - _s\omega_s$. It is worth to notice the question of a wide variation of the names that we come across in the area of the "surface phenomena". An excuse for a lack of precision in theoretical descriptions of surface phenomena is the argument that precise measurements of certain parameters, even those which are very well defined, is often not possible. Large deviations result from both the nature of the "real" phases, the variety of the measuring methods, and from inappropriate conditions of the experiments.

PRECISE NOMENCLATURE AND SYMBOLS

The excess specific (or molar) free energies of the surface are denoted in the following way for one-component condensed phases:

for fixed T and V : $_{l}f_1$ and: f_s (for a liquid and solid phases),

for fixed T and p : $_{l}g_1$ and: g_s

for fixed T and m_i : $_{l}\omega_1$ and: $_{s}\omega_s$.

Strictly speaking the definitions are limited only to the condensed phases at an equilibrium with their saturated vapor, or as we say "in vacuum". However, often we assumed the presence of the so-called inert gas, instead of the vacuum, having a finite volume or pressure. The gas is not soluble in the phases forming the system and is not absorbed at the interfacial regions. So, there is no doubt that for the contact of phases the symbols $_{gs}f_s$, $_{gs}g_s$, and $_{gc}\omega_s$ can be applied along with indication of the type of gas or the vapor, though determination of their values is not always possible. Due to mentioned above inaccuracies of the measurements, as a rule simplifications for "pure" liquids are commonly applied:

$$g^0 \approx _{gl}f_1 \approx _{gl}g_1 \approx _{gl}\omega_1,$$

and for the solutions:

$$_{gl}\omega_1 \approx g = g^0 - \Pi \text{ (for: } T = \text{const.}, \text{ and: } m_i = \text{const}).$$

The "surface pressure" $\Pi = \gamma - \gamma^0$ is obviously a function of the composition of solution, and γ^0 denotes "pure solvent".

A fast development of measuring equipment and a tendency to get more precise results lead us to the conclusion that the technique of measuring the interfacial tensions from the shape of pending or sessile drops is one of the best. The apparatuses make possible the control of the composition of the gas phase, enables thermostating the measuring chamber and does not require the use of any corrections. A precise thermodynamic description based on the equilibrium of forces resulting only from the interfacial tensions and gravity forces makes also possible to determine the contact angles during the same measurement. A maximum precision of the results requires, however, optimization of the drop volume depending on the density of liquid and the value of measured interfacial tension. In the case of solids, because of their hardness and elasticity, their excess specific values of the free energies cannot be replaced with the tensions. In addition, even during unlimitedly slow recrystallization, they do not achieve spherical shape, though they minimize the free energy by the formation of walls. The quasi-static final state depends on cooling conditions. The amorphous solids are usually overcooled liquids or as composition of microcrystalline patches. Only close to the melting temperature, the excess free energies can be determined from the measurements of the interfacial tensions of the saturated liquid phase extrapolated to the melting point. It gives the possibility of determining the $(_{gs}\gamma^0)_{top}$ component. We take here advantage of the fact that the derivatives of the chemical potential are continuous at the temperature of the phase transitions, which however is not the same as the precise determinations of the $_{gs}\omega_s$ values. A rigorous use of appropriate definitions of the considered parameters is important only for accurate understanding of wetting.

A proper form of the Young formula is:

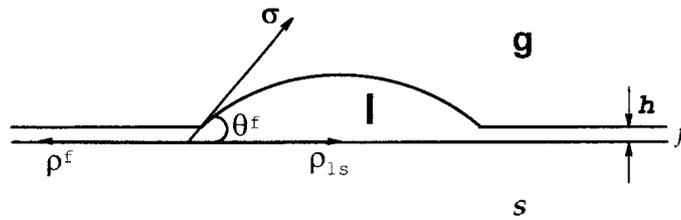
$$\gamma \cos \theta = _{gs}\omega_s - _{ls}\omega_s = \Delta _{ls}\gamma$$

because both the contact with gas and liquid modifies $_s\omega_s$ function of the state defined for vacuum, and therefore is only for the gaseous phase, characterized by the vapor pressure of the solid. We must remember that: $_{gs}\omega_s = _s\omega_s + _{gs}\gamma$.

The components of γ are the tensions that are localized in the Gibbs "tension plane" and act in the interfacial region due to the modification of the interparticle bonds of liquid and solid. Sometimes this region contains an aqueous film of thickness h . It should be remembered that for a direct contact between the solid and liquid is not necessary to attain the equilibrium between saturated vapor of a liquid or solvent and the solid surface. Unfortunately, the process of attaining the equilibrium indirectly by the gaseous phase is usually very slow. In the case of a drop of an aqueous solution, a very important issue is the equilibrium sorption of the saturated vapor of the solution on the initially dry solids at the same temperature. A particularly important is the question of the modification by the water vapor of the surface of such solids as quartz, mica, silica, and silicates because of a particular nature of the bonds with water. The process depends on temperature, pressure, and time. These substances immersed in

water form gel layers, more or less slowly, and depending on the pH. It is worth to remember a remark of Platikanov (Toshev and Platikanov, 2004) who stressed that strictly speaking the assumption of the identity of the excess free energies and interfacial tensions is never true, while it is often used in practice. Only rarely this is nearly true. From very rich Platikanov's material (Toshev and Platikanov, 2004) we have chosen only one fragment, no doubt, a very important one, describing the thermodynamic equilibrium in systems having complete wettability. We limit here the considerations to the situation, in which the volume, size of the plane surface of the solid, and the volume of liquid are such that they allow the formation of the „equilibrium” aqueous interfacial film.

All interested in the description of the „free liquid films” in the form of bubbles or being in the equilibrium with „black films” should consult the Platikanov (Toshev and Platikanov, 2004) lecture.



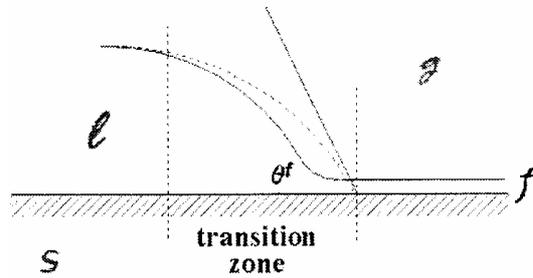
$$\Pi = p_N - p_l = p_g - p_l = \Delta p_c$$

$$\rho^f = \rho_{ls} + \sigma \cos \theta^f = \rho_{ls} + \sigma + \int_h^{\infty} \Pi dh + \Delta p_c h$$

ρ^f is the superficial tension of the film in contact with the solid.

Fig. 2. A scheme of a sessile drop on a plane surface covered with a thin liquid film. $p_g - p_l = \Delta p_c$ is the pressure difference between the gas phase and the liquid in the drop

Figure 2 shows a scheme of the system consisting of a drop sitting on a plane surface covered with a thin liquid film. The macroscopic wetting angle is also shown. The macroscopic view is not able to reveal the presence of an equilibrium aqueous film because its usual thickness is about $0.5 \mu\text{m}$. The formula given in Fig.2 represents a dependence of the wetting angle θ^f in the vicinity of the drop perimeter on the film thickness changing from its equilibrium value h to the “ ∞ ” thickness beneath the drop. The surface tension of the equilibrium film ρ^f is balanced by the sum: $\rho_{ls} + \sigma \cos \theta^f$. The surface pressure Π depends on the solution composition and balances the pressure increase Δp_c caused by the drop surface curvature. dh is the change of the local film thickness.



$$\cos \theta^f = 1 + \frac{1}{\sigma} \int_h^{\infty} \Pi dh + \frac{\Delta p_c h}{\sigma}$$

Fig. 3. Enlarged Platikanov's picture of the "transition region"

Figure 3 presents an enlarged Platikanov's picture of a "transition region", in which the microscopic shape of the interfacial layer is changing within the nanometric scale. Only beyond this region the surface of the drop becomes „identical” with the macroscopic one. The wetting angle, determined macroscopically θ^f , is the wetting angle characteristic for the border of a drop, gaseous phase, and a film covering a well wetted surface of a solid with a thin layer of thickness h . The thickness h is also an important and characteristic feature of well wetted surfaces. Equation given in Fig. 3 was confirmed experimentally by Platikanov (Toshev and Platikanov, 2004). It should be remembered that wettable bodies, beside a visible macroscopic wetting angle, differ in the thickness of the invisible equilibrium surface film.

At this point we would like to make some remarks concerning the measurements of the macroscopic wetting contact angles. It is possible to perform very precise measurements only for a system consisting of two very little mutually soluble phases. An ideal model of such a system is mercury in contact with an aqueous solution having a well defined redox potential. Measurements of macroscopic wetting angles on solid surfaces is a very difficult task due to problems with the nature and preparation of surfaces. These problems sum up and lead to a hysteresis of the wetting angles. This phenomenon is a result of low reproducibility of the results and their variation with time. As for any other phenomenon in which hysteresis appears, we look for the reasons of dependency on the direction of performing the experiments. When a liquid is propagating over the surface, we observe advancing angles. In the contrary to that, withdrawing the liquid creates receding angles. These processes depend not only on direction of medium movement but also on the speed of the process, which always is related to the slow-attaining equilibrium state, and results from the energetic barrier which depends on the nature of the process. Usually, the height of the barriers is related to the sample history, its surface preparation and usually not well known final micro-state inhomogeneity, roughness, contaminations,

etc. The course of a very slow quasi-static detachment of air bubble from selected surfaces was presented by Pomianowski (1960). The fixed wetting angles on galena and mercury in xanthate solutions and on paraffin, called the equilibrium contact angles, assumed 46, 62, and 107 degrees. The investigations were initiated by a hot, at that time, discussions concerning the scale of wetting and its applicability in describing the flotation processes. The nonwetting scale, as other ones applied in thermodynamics, is arbitrary. It may start from zero, but there were also the arguments for 90 degrees as the initial value of nonwetting. The thermodynamic arguments favor zero degree as the starting point of the scale since it represent an ideal wetting. On such surfaces the thickness of a surface wetting film tends to infinity. In practice, the thickness of the film is about 7 water molecules thick, because at this distance the structure of the vicinal water, as is now called the interfacial water, has the structure practically identical with the bulk water. As the hydrophobicity increases, the thickness of the interfacial film h decreases, and finally water takes the form of dynamic "flickering clusters" containing from about 20 to 280 molecules. Water in interfacial regions raises recently more and more interest (Paul and Chandra 2003, 2004; Liu et al., 2005; Tombari et al., 2005; Koga and Tanaka, 2005; Ju and Yang, 2006; Ewing, 2006).

A characteristic feature of flotation systems are dynamic conditions of the contact of air bubbles with mineral particles which are usually significantly lower in dimensions in relation to the bubble. It raises a question to what degree the static wetting angles, measured on plane macroscopic surfaces, can be used for estimating the degree of "hydrophilicity". A setup, consisting of a tensiometer combined with a camera (Pomianowski and Para, 1988) made it possible to record variations in the wetting angle and the perimeter of wetting under the conditions of a slowly increasing force of detachment of a bubble from the surface. The technical equipment at that time allowed to draw only one important, no doubtful, conclusion: it is not the value of the wetting angle itself but its hysteresis is determining floatability. There are two behaviors of the "wetting perimeter". It may easily slide over the surface due to the influence of the external forces acting in the system, or it tends to be rather stably localized. The static angles being below 90° cause that the force needed to detach the bubble results from its perimeter of adhesion and the surface tension of the solution. For larger angles at the moment of detachment the force must be greater. However, it should be remembered that for small grains the so-called "angle of shape" plays an important role. Most easily these relationships can be observed on render, to a different extent, hydrophobic drops of mercury on which the variations in the angle and wetting perimeter caused by an external force are large and easily measurable with modern equipment. The most recent works of Verdaguer et al. (2006) carried out with STM, under precisely controlled conditions (temperature increasing from 4° K) showed that irrespective of the degree of macroscopic hydrophobicity of the metals the two first layers of water have the structure of hexagonal ice. Using a modified AFM technique it was also shown (SIRGHI et al., 2006) that within the nanometric

molecular scale the speed of wetting process is determined by a mechanical equilibrium, because other processes are significantly slower, and under dynamic conditions the system does not gain the minimum of the thermodynamic potential.

A combination of studies of wetting with modern electro- and spectrochemical techniques such as STM, AFM, and the time resolved sum frequency generation, together with a computerized equipment recording variations of wetting angles with time, should lead in the nearest future to a significant development in the theory and practice of wetting.

During the recent SURUZ (2006) workshop, two basic ways of approaching this problem has been presented, that is an “applied” aspect of the investigation of the macroscopic wettability and a typical basic description derived from the principal electrical interactions. Adamczyk (2006) has shown in a systematic and suggestive way that present possibilities of a precise description of the behavior of systems in the interfacial regions are limited by a simple and rarely recognized by many other scientists fact that the interaction of charges is dependent on their distance. There is no doubt about the validity of the Coulomb law. However, a precise formulation of the rules and the values of interactions becomes difficult when the distances between ions, dipoles, and systems of many charges become comparable with the atomic sizes.

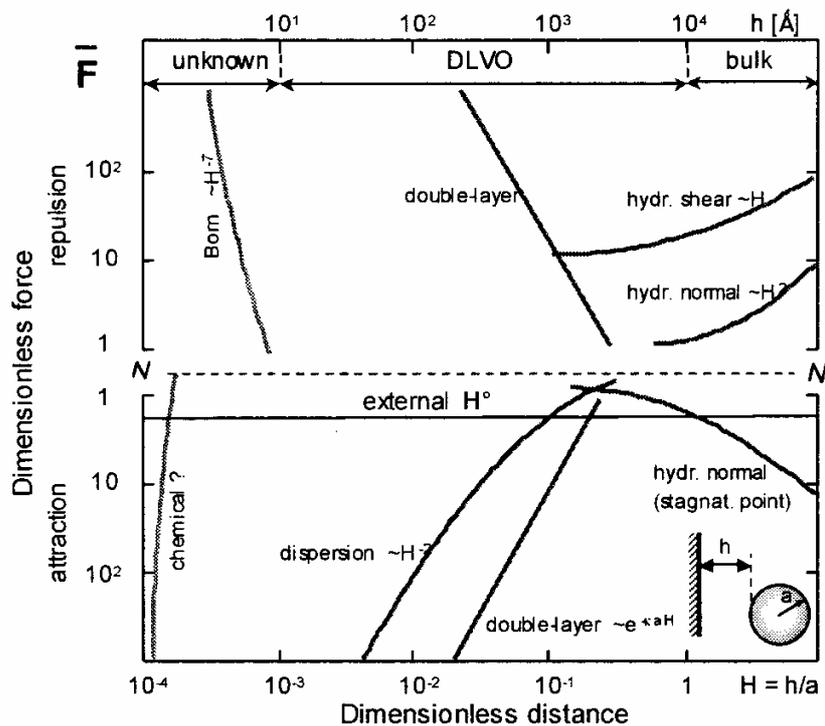


Fig. 4. Relative significance of forces affecting particle adsorption. After Adamczyk, 2006

The data presented in the diagram show clearly, as it has been mentioned in numerous publications recently, that it is not possible to apply strictly the DLVO theory and the resulting from the theory formulas containing the Hamaker parameter (Grasso et al., 2002; Grodzka and Pomianowski, 2005). It becomes more and more commonly recognized that for molecular considerations on a nanometric scale a more precise definition of hydrophobicity, as well as interrelation of "hydrophobic interactions" with changes in the structure of water in the vicinity of the groups and bonds of the dissolved in water foreign molecules, is necessary. These phenomena are, in certain systems, „observed" by the presence in the solutions of dissolved gases and small hydrophobic molecules, as well as by large area of the walls of laboratory vessels (Wennerstrom, 2003; Yang et al., 2003; Attard, 2003; Meyer et al. 2005; Ju and Yang, 2006). There exists a well documented evidence that at low temperatures fluctuating aggregates of water molecules (known - in professional works - as "flickering clusters") contain a measurable contribution of dynamic, bound with hydrogen bonds, "clusters" of a nanometric size.

No later than several years ago it was realized that the hydrogen bonds have the energy of the order of 10 kT, and the London dispersive forces cannot disturb the internal structure of water clusters of a high symmetry. These dynamic structures, based on a characteristic for liquid water pentamer structure (Haraker et al., 2005) are formed at the contacts of water with hydrophobic fragments of systems and they remain statistically stable in the ensemble, with some analogy to the "stability" of micellar aggregates.

WHAT CAN WE PRESENTLY SAY ABOUT WETTING AND TO WHAT EXTENT IS IT TRUE?

The wettability by water, a liquid of a special structure, requires definition of the concept of the hydrophilicity both in a molecular and macroscopic sense. We have to remember that every definition is introduced for a special case. Therefore, it must appropriately broad and detailed. The philosophical school of Vienna positivists assumed that in natural sciences the definitions should be particular recipes for a precise measurement of the value of the defined feature. Therefore, the most difficult task is to formulate cognitive scientific definitions. For instance *natural water* means water of an average isotopic composition containing smaller or greater concentrations of substances with which it either has been or is in contact. *Pure water* means natural water which is free of all substances dissolved in it. *Chemically pure water* means an isotopic mixture of molecules of H₂O, D₂O, and T₂O with prevailing O¹⁶ isotope. Different, though equally rigorous requirements are formulated for applied systems, and still different and rigorous for pure research. Therefore, the most difficult and requiring the best knowledge combined with common sense are works involving both theory and practice.

The Polish Workshop (Suruz, 2006) is an ideal illustration of the necessity of both close contact and a good co-operation between representatives of both approaches to the studied systems. Drzymala (2006) stressed a tendency of accumulation of such information on the nature of complex flotation systems which would allow a good prediction of the results of separation. Adamczyk (2006) presented a primary source of all interactions, including the most complex, considered on atomic as well as macroscopic levels. Both lecturers presented systems for which we are close to describe precisely and quantitatively the occurring there phenomena, but at the same time they showed difficulties in generalization of the conclusions. It is important to stress here that the origin of difficulties is different in applied research and in pure studies. We used this dichotomic classification only to more clearly present our point of view. In reality both types of the investigations are interwoven, and they are distinguished only by their aim formulated by a particular author. Drzymala (2006) revealed a correct ambition to organize and define the concept of the „key role” of the process played by the mineralization of bubbles in a set of primary single processes in the global mechanism of flotation. On the contrary, Adamczyk (2006) showed the source of present limitations, conceptual and mathematical, in calculation of particular interactions appearing in the systems containing particles of various sizes. Such a characteristic gap results from a lack of theoretical delineation of interactions in nano-dispersed systems. It is the largest dynamic clusters of water, being a part of an ensemble of molecules differing in the structure resulting from the existence of hydrogen bonds, which are nanometric in diameter. In applied studies of systems in which the local dynamic conditions (in space and time) fluctuate, the phenomenological thermodynamic predictions are not sufficient. The data on the energy barriers for elemental processes are very difficult to estimate. A very tedious way of the progress seems to be created by computer simulations of these processes and studying the systems that are sufficiently simple and are subjected to the same processes which takes place in real, more complex, systems. Drzymala (2006) gave an example of such simple process. It is for instance the behavior of mercury in the solutions of flotation agents. A.N. Frumkin, an internationally renowned scientist, pointed to this system before the Second World War (Frumkin, 1927). He also pointed out the role of the so-called generalized electrocapillary effect (Frumkin, 1979). It represents a thermodynamic relationship between molecular as well as macroscopic wetting and electrical potential, generated on the surface of the condensed matter by appropriate composition of the solution. Mercury is particularly suitable for studying such effect because only mercury allows to measure precisely the values of all parameters necessary for calculations. The measurement of some isolated surface properties is not possible on solids and studying of some others is more difficult as well as less accurate and less precise than on mercury.

Due to diversity of problems we are dealing with, we shall start from the discrimination between various descriptions of systems on a molecular and macroscopic scale. Here we should return to the fact that there is not possible to make

strictly dichotomous classification, which causes a necessity to apply arbitrary definitions. For instance in the field of strongly dispersed systems, the name of colloid is given to a set of particles or macromolecules of at least one dimension smaller or equal to 1 micron (μm). Even more troublesome is the definition of the difference of a true and colloidal solution. If we take as the criterion the fact that the solution does not disperse the light, also the nature and way of illumination must be taken into account. Due to this fact, the nanometric systems occupy a special place. Depending on the used definition, they may belong either to the colloidal system or to true solution. As a consequence, their equilibrium state may be described as the transition of phases or chemical equilibrium. This is in analogy to the discussion on the nature of light. The difference is only the way of description, not the essence of the question. We always try to choose a simpler description for a particular situation, for obvious reasons. Davies (1957) paved the way leading to the quantitative molecular definition of the degree of hydrophilicity, showing which way the hydrophilic-lipophilic (HLB) equilibrium index should be ascribed not only to the particular substances, but also to the functional groups and types of bonds, in a given system. He showed how these values result from the phase distribution equilibrium constants of substances or their fragments, between water and a desired oil (hydrophobic) phase. We consider it natural to extend the concept of a hydrophobic phase also to gases that are poorly soluble, and first of all to vacuum. In the case of aqueous solutions, it means a space filled with saturated vapors of water and of the studied substance. Furthermore, making use of the additivity rule of the free energies, it is possible to define in the modeling works the functionals of density and the local values as properties of inhomogeneity regions both on free surface and in particulate fine systems, for instance colloidal systems (Meng et al., 2003; Jaqaman et al., 2004). Having numerical data characterizing the degree of hydrophilicity consistent with the generalized HLB index, one could macroscopically define the hydrophilicity through wetting investigations.

The theory and practice of wetting is simple in the systems of two liquids unless (as it was discussed earlier) we do not enter the nanometric level in which the degree of hydrophilicity needs a precise theoretical descriptions using local values of the parameters. Enormous difficulties are met during a precise description of wettability of “real” solids.

We can expect in the nearest future a breakthrough in the theoretical model description of two border type systems, molecularly smooth, practically non-oxidizable, monocrystals of metals in two extreme cases:

- 1: “practically” hydrophobic metals, and
- 2: ideally hydrophilic metals.

In recent years, techniques of synthesis, purification, and observation of deposition of single water molecules and formation of first few layers of water on selected walls of monocrystals have been developed. Also directly an increase in the surface mobility, starting with a single molecule up to the pentamer of water molecules, has

been observed. The already quantitatively known fact that the free energy of sorption of water molecules on many metals are of the same order of value as the free energy of the hydrogen bond between the water molecules has been already confirmed. It was correlated with the results of the above mentioned studies showing that on various metals the structure of water remains similar only in two first molecular layers. The next layers differ more and more, depending on the degree of hydrophilicity of the metal, determined by the structure of water. More hydrophilic metals bind strongly water, competing for its hydrogen bonds, changing their number, structure and energies. It is commonly described as breaking the structure of water, favoring more dense CS structure. More hydrophobic metals favor the formation of an open, more ordered structure of ES water. The speed of a spontaneous self-diffusion motion of interfacial ad-atoms of metal in water and its solutions was also studied deeply. The role of electrical potential in the process has also been reported (Dutkiewicz, 2002).

Metals, similarly to other substances, may behave in solutions in two very different ways. They can be practically non-polarizable semi-cells or be ideally polarized. In both cases their wettability may be theoretically described using the “generalized theory of the electrocapillarity” of Frumkin. Until now, it was not possible to describe the intermediate cases in a strict thermodynamic way. There is only one preliminary work of Para (Pomianowski and Para, 1988), pointing to a possible utilization of the above mentioned phenomena to show the influence of solution red-oxy potential on surface tension of mercury. Such investigations, however, have never been popular. They require a tedious preparation of water, very pure mercury (purified and distilled) and very good anaerobic environment of work. Nowak (2006) has spent many years attempting to show a quantitative relationship between oxidation of the surface of mineral particles and their ability to bind thiol collectors.

We would like to end the paper with a remark concerning the complexity of transferring pure studies into industrial applications. A good example of such difficulty was for us a close observation of implementation works being carried out for many years at the Institute for Non-Iron Metals in Gliwice, Poland.

ACKNOWLEDGEMENTS

The authors wish to thank Janka Rodakiewicz-Nowak for her involvement and valuable help in preparation of the paper.

The support of the SURUZ program and its managers as well inclusions of our papers and lectures into programs of the Physicochemical Problems of Mineral Processing conference and SURUZ activities, especially Young Scientists Forums, are gratefully acknowledged.

REFERENCES

- ADAMCZYK, Z., (2006), *Dynamic aspects of surfactants and particle adsorption, lecture for Young Scientists Workshop on Surfactants in the Environment*, SURUZ 2006, Sudomie near Koscierzyzna, Poland, May 19-25.
- ATTARD P., (2003), *Nanobubbles and hydrophobic attraction*, Adv. Colloid Interface Sci. 104, 75.

- DAVIES J.T., (1957), Proc. 2-nd Intern. Congr. Surface Activity, 1 (1957) 426.
- DRZYMALA, J., (2006), Surfactants in flotation, lecture for *Young Scientists Workshop on Surfactants in the Environment*, SURUZ 2006, Sudomie near Koscierzyna, Poland, May 19-25.
- DUTKIEWICZ E., (2002), *Dynamics of electrochemical surface processes at the monocrystalline electrode/electrolyte solution interface and the theory of structure and properties of the interface*, *Facultatis Chemiae, Universitatis Studiorum Mickiewiczianae Posnaniensis, Annales I*, p. 67-102, Wyd. Nauk. UAM Poznan, Poland.
- EWING G.E., (2006), *Ambient thin film water on insulator surfaces*, *Chem. Rev.* 106, 1511.
- FRUMKIN A.N., (1932), *Physicochemical principles of flotation theory*, *Trudy Uralsko - Kuznieckoj Sesji AN SSSR*, izd. A.N. (1932) Leningrad (in Russian).
- FRUMKIN A.N., (1979), *Potential of zero charge*, *Izdat. Nauka*, (in Russian).
- GRASSO D., SUBRAMANIAM K., BUTKUS M., STREVETT K. and BERGENDAHL J., (2002), *A review of non DLVO interactions in environmental colloidal systems*, *Rev. Environ. Sci. and Biotechn.* 1, 17.
- GRODZKA J. and POMIANOWSKI A., (2005), *On the necessity of modifying the DLVO theory (in equilibrium systems)*, *Physicochem. Problems Min. Proc.* 39, 11.
- GUILLOT B., A., (2002), *Reappraisal of what we have learnt during three decades of computer simulations on water*, *J. Mol. Liq.* 101, 219.
- HARKER H.A., VANT M.R., KEUTCH F.N., MICHAEL E.A., Mc LAUGHLIN R.P. and SAYKALLY R.J., (2005), *Water pentamer: Characterization of the torsional - puckering manifold by tetrahertz VRT spectroscopy*, *J. Phys. Chem. A* 109, 6483.
- JAQAMAN K., TUNCAY K. and ORTOLEVA P.J., (2004), *Classical density functional theory of orientational order at interfaces: Application to water*, *J. Chem. Phys.* 120, 926.
- JU S., YANG S. and LIAO M., (2006), *Study of molecular behavior in a water nanocluster: Size and temperature effect*, *J. Phys. Chem. B* 110, 9286.
- KOGA K., and TANAKA H., (2005), *Phase diagram of water between hydrophobic surfaces*, *J. Chem. Phys.* 122, 104711.
- LIU P., HARDER E. and BERNE B.J., (2005), *Hydrogen bond dynamics in the air - water interfaces*, *J. Phys. Chem. B* 109, 2949.
- MENG S., WANG E.G. and GAOS S., (2003), *A molecular picture of hydrophilic and hydrophobic interactions from ab initio density functional theory calculations*, *J. Chem. Phys.* 119, 7616.
- MEYER E.E., LIN Q. and ISRAELACHVILI J.N., (2005), *Effect of dissolved gas on the hydrophobic attraction between surfactant - coated surfaces*, *Langmuir* 21, 256.
- NOWAK P., (2006), D.Sc. monograph (habilitation), Institute of Catalysis and Surface Chemistry, Polish Academy of Science, Kraków, Poland.
- POMIANOWSKI A. and PARA G., (1988), *Electrocapillarity in the model mercury flotation*, *Materials Sci. Forum* 25-26, 447.
- POMIANOWSKI A., 1960. *Abreisskräfte und Randwinkelhysterese in den Systemen: Lösung / Luftblase / Quecksilber - oder Festkörperoberfläche*, III Intern. Congress of Surface Activity, 4, 435.
- PAUL S. and CHANDRA A., (2003), *Dynamics of water molecules at liquid - vapor interfaces of aqueous ionic solutions: effect of ion concentration*, *Chem. Phys. Lett.* 373, 87.
- PAUL S. and CHANDRA A., (2004), *Hydrogen bond dynamics at vapour - water and metal water interfaces*, and: *Binding of hydrogen bonding solutes at liquid - vapour interfaces of molecular fluids*, *Chem. Phys. Lett.* 386 (2004) 218, and: 400, 515.
- SIRGHI L., SZOSZKIEWICZ R. and RIEDO E., (2006), *Volume of a nanoscale water bridge*, *Langmuir* 22, 1093.
- SURUZ, (2006), *Young Scientists Workshop: Surfactants in the environment, Sudomie near Koscierzyna, Poland, May 19-25*. Organized by Dept. of Chem. Techn., Gdańsk University of Technology
- TOMBARI E., SALVETTI G. and FERRARI C., (2005), *Thermodynamic functions of water and ice confined to 2nm radius pores*, *J. Chem. Phys.* 122, 104712.
- TOSHEV B. and PLATIKANOV D., 2004. *A new approach in the wetting thermodynamics: superficial tension of the film in the contact with solid*, SURUZ Workshop (2004) - Kraków.

- VERDAGUER A., SACHA G.M., BLUHMH. and SALMERON M., (2006), *Molecular structure of water at interfaces: Wetting at the nanometer scale*, Chem. Rev. 106, 1478.
- WENNERSTRÖM H., 2003. *Influence of dissolved gas on the interaction between hydrophobic surfaces in water*, J. Phys. Chem. B 107, 13772.
- YANG J., DUAN J., FORNASIERO D. and RALSTON J., (2003), *Very small bubble formation at the solid - water interface*, J. Phys. Chem. B 107, 6139.

Grodzka J., Pomianowski A., *Zwilżanie a hydrofilność*, Physicochemical Problems of Mineral Processing, 40 (2006), 5-18 (w jęz. ang.).

Opierając się na najnowszych pracach oryginalnych i przeglądowych, omówiliśmy podstawowe zagadnienia hydrofilowości i zwilżalności. Wskazaliśmy problemy, których rozwiązanie umożliwi szybkie postępy w tej dziedzinie. Zwilżalność należy do zjawisk o dużym znaczeniu, zarówno poznawczym, jak i praktycznym. Potrzebne jest sprecyzowanie definicji stosowanych pojęć i skali ich wartości. Należy dokładnie określić skalę zmian struktury wody, zarówno w pobliżu rozpuszczonych w niej cząsteczek, jak też w nanometrycznych oraz mikroskopowych obszarach granic międzyfazowych.