

E. V. Gribanova, A. E. Kuchek

ON SOME IMPORTANT PECULIARITIES OF THE PHENOMENON OF WETTING*

St. Petersburg State University, 199034, St. Petersburg, Russian Federation

The problems of objective approach to the wetting phenomena research are being discussed. The peculiarities of the direct and reverse processes at three-phase-contact (solid—liquid—gas) formation and the inevitability of wetting hysteresis for polar solids and liquids are under consideration. An opinion about the cause of this phenomenon is expressed, the cause being the high values of the energy of solid—liquid interaction (the heat of immersion and the heat of adsorption from the vapor) and as consequence the high values of retention time for the molecules of liquid on the surface that is of the relaxation time for three-phase-contact system. The question of proper purification of the solid surface without changing its composition and properties is analyzed as well. The results of experimental data on estimation of activation energy for wetting glass surface with water are given, the data being obtained from temperature dependence of dynamic contact angles, calculated from the data on capillary rising of water in round glass capillaries having cross-section 104–108 μm . It is shown that the value of activation energy for this system exceeds the one for water evaporation. Inevitability of the occurrence of a number of active sites with different acid-base properties at the surface of solids (OH-groups in the case of metal oxides) is discussed. The data on estimation of dissociation constants (pK_a) of these sites and their content at the surface are given, the data obtained in the experiments with electrometric titration and wetting. It is shown that the values of dissociation constants for the different surface OH-groups, estimated by these two methods agree sufficiently well. The result obtained permits to conclude that the method of electrometric titration in the proposed modification of data treatment as well as the method of measurement of $\theta = f(\text{pH})$ dependence can be used to characterize the acid-base properties of solid surface together with IR-spectroscopy and some other methods. Refs 27. Figs 4.

Keywords: contact angle, direct and reverse processes, wetting hysteresis, activation energy, acid-base surface sites, electrometric titration.

E. V. Грибанова, А. Э. Кучек

О НЕКОТОРЫХ ВАЖНЫХ ОСОБЕННОСТЯХ ЯВЛЕНИЯ СМАЧИВАНИЯ*

Санкт-Петербургский государственный университет,
199034, Санкт-Петербург, Российская Федерация

Обсуждаются проблемы объективного подхода к изучению явлений смачивания. Рассматриваются особенности прямого и обратного процесса при образовании трёхфазного контакта твёрдое тело — жидкость—газ и неизбежность явления гистерезиса смачивания для полярных твёрдых тел и жидкостей. Высказывается мнение, что причиной этого является высокая энергия взаимодействия жидкости и твёрдого тела (теплоты смачивания и адсорбции из газовой фазы), а следовательно, и время удерживания молекул жидкости на поверхности, т. е. время релаксации системы трёхфазного контакта. Затрагивается вопрос очистки поверхности твёрдого тела без изменения его состава и свойств. Приводятся результаты экспериментальных данных по определению энергии активации смачивания поверхности стекла водой при разном состоянии исходной адсорбционной плёнки, полученные в результате исследования температурной зависимости динамического краевого угла, рассчитанного из данных капиллярного поднятия воды в цилиндрических стеклянных капиллярах сечением 104–108 мкм. Обсуждается неизбежность существования на поверхности твёрдых тел (на

* Работа выполнена по программе Президента Российской Федерации «Ведущие научные школы» (гранты № НШ-6291.2010.3 и № НШ-4464.2012.3).

примере оксидов металлов) ряда активных центров (ОН-групп), отличающихся кислотно-основными свойствами. Приводятся данные по оценке констант диссоциации (pK_a) этих центров и их содержания на поверхности, полученные в результате использования методов потенциометрического титрования и смачивания. Показано, что значения констант диссоциации поверхностных ОН-групп по оценке этих двух методов хорошо согласуются между собой, что позволяет сделать вывод о перспективности их использования для характеристики кислотно-основных свойств исследуемой поверхности. Библиогр. 27 назв. Ил. 4.

Ключевые слова: угол смачивания, прямой и обратный процессы, гистерезис смачивания, энергия активации, кислотно-основные центры поверхности, потенциометрическое титрование.

Introduction. Thoroughly made studies on the problems of wetting allow to reveal some aspects, peculiarities of this phenomenon that should be taken into consideration, otherwise neglect of their importance can lead (and really does lead) to not completely correct conclusions and summaries. Thus, ignoring the peculiarities of the direct and reverse processes at three-phase-contact formation is one of the most essential problems in explanation of the wetting as with such view there is a good probability of serious mistakes. As a consequence, practically all textbooks and monographs are stating that contact angle can be measured at putting a liquid drop on the surface of solid body (“sessile drop” method), that is in the direct process as well as at bringing an air bubble under the solid body immersed in liquid that is in the reverse process. Herewith the well known phenomenon of the wetting hysteresis (the difference of values of the contact angles resulting at three-phase-contact formation for these two methods) is considered as something uncertain and demanding special explanation.

Strictly speaking the word “wetting” supposes the direct process for the solid-liquid-gas system, where just liquid is the final interacting phase (it wets the solid body, the last-named being initially in equilibrium with gas phase that is with liquid vapor). At present they usually determine this process as “advancing” one though the term “advancing” has been introduced for another phenomenon, notably for the case of a liquid drop on an inclined surface. It is well known when one inclines a surface with a liquid drop on, the last changes its shape, the lower side of the drop forming contact angle which is greater than the one on the upper side. To identify these angles the terms “advancing angle” and “receding angle” were accepted respectively. It was also found out that the contact angle on horizontal surface is equal to half-sum of advancing and receding angles. Though in principle it’s possible to name the wetting process as “advancing” one with liquid really advancing on the solid surface, one must not use terms “advancing angle” and “receding angle” for the equilibrium contact angle to prevent a confusion, these terms being used for a peculiar state of the system. With using the same principle we can say that the receding process is reverse to the wetting one. At receding the initial state of the system is a two-phase one, the solid body being in equilibrium with the liquid, and the gas phase is the final one that comes into the interaction, the three-phase-contact being formed therewith. As it is well known most of the processes of phase interaction are irreversible (in a varying degree), so we can draw the conclusion that for these two cases the states of the three-phase contact must differ from one another, that is the wetting hysteresis is unavoidable phenomenon, and one should use only the contact angle received (and measured) in the direct process for characterizing the wetting.

We should discuss this question more closely. Let us consider direct and reverse processes for wetting of polar solids with water (or water solutions). At present due to proper calorimetric equipment the heat of adsorption from gas phase and the heat of immersion can be examined with sufficient accuracy. These heat values for the case of water interaction with the polar solids (for example with metal oxides) are rather high. In consequence the

time value of adsorption of water molecules on solid surface is high as well [1], that is the time of the transition between the solid—gas state and the solid—liquid one is reasonably long in the wetting processes (especially in the reverse one), transition process itself needing activation energy [2]. This peculiarity was discussed by Frumkin in his old (now classical) paper [3], where, we can say, nearly by intuition, but absolutely correctly he described the whole process of liquid—solid interaction. One of the most important conclusions made in [3] about the state of thin water films on the surface of polar solids is, on our opinion, as follows: only the adsorption film, formed from the gas phase (water vapor) on such a surface, is thermodynamically stable. The thin wetting films formed on solid surface after receding process are only metastable. These wetting films can keep stability for some (considerable) time depending on conditions of their formation, geometric parameters of the system and the composition of water solution, which this film was formed from [4, 5]. But finally its disruption takes place, with the adsorption film and separate droplets of water or water solution remaining on the surface as a result. The process of water (and especially water electrolyte solutions) receding from the surface of polar solids represents a separate (and very interesting) phenomenon, its theory developed rather extensively [5]. But this concept is unfortunately inapplicable to the direct process of wetting (to the wetting polar solids with polar liquids) the wetting films not being formed in this case.

Another important problem in using wetting to determine the properties of solids is the pretreatment of their surface. This problem arises because of the fixed opinion that the contact angle for hydrophilic solids and water (or water solutions of inorganic electrolytes) should be very small (quite near zero). It is common opinion to correlate the great values of contact angles (much more than zero) for such systems to different (especially fatty) impurities. That's why very hard methods of purification of surfaces as using concentrated acids and bases, chromic acid, hydrogen peroxide, hydrofluoric acid, boiling, and so on were employed. Often such methods gave really the decrease of contact angles [6], but what is the cause of this decreasing? It should be clear for a chemist that any of the listed treatments will result in solid surface modification determined by the processes of chemical interaction (dissolution, leaching out separate components, changing oxidation level of some of them and, finally, precipitating dissolution products on the surface of the solid under investigation).

It is obvious, that if we intend to get a valid description of a given solid applying processes of the wetting phenomenon we cannot use the above-listed methods of treatment. As for cleaning from fatty substances it's sufficient to use more soft treatment (paraffin hydrocarbons, acetone and so on).

The results of research on the dependence of contact angle on velocity. The reason for non-zero value of the contact angles (θ) of water on the surface of hydrophilic solid bodies was (and still is for some scientists) not perfectly clear. This problem was discussed in details in [7]. As it was referred earlier the cause of such a phenomenon is the existence of adsorption film of water vapor on polar solid. Therefore the process of wetting with water should be considered as the process of activated transition of water molecules from the state of adsorption film (adsorbed from water vapor) to the state of bulk water near the surface of a polar solid body. The concept of Blake and Haynes [8] was used to describe this dynamic process.

Blake and Haynes used the approach of Cherry and Holmes which was based on the theory of absolute reaction rates [2]. Following this approach the three-phase-line (TPL) zone of wetting liquid on the solid surface is considered to be the transition state (activated complex), and the system under consideration has to overcome this state in the process of pulling out one liquid state with another one from the surface of solid. This process develops

at the active sites of the surface and the concentration of these sites (Δn) is constant. The value of molecular rate of the process is denoted by K_+ . The application of the theory of absolute reaction rates [2] gives:

$$K_+ = \frac{kT}{h} \frac{z^*}{z^+} \exp\left(-\frac{\varepsilon_+}{kT}\right), \quad (1)$$

where ε_+ is the activation energy for the process at absolute temperature (0 K); z^* and z^+ are the partition functions for the activated and initial states respectively; k is Boltzmann's constant, h_P is Planck's constant; T is absolute temperature.

The molecular rate of the reverse process is:

$$K_- = \frac{kT}{h} \frac{z^*}{z^-} \exp\left(-\frac{\varepsilon_-}{kT}\right). \quad (2)$$

At equilibrium the net rate of exchange is equal to zero and $K_+ = K_-$. The additional force needed to cause flow will not change z^+ or z^- ; it can be regarded as altering the energy barriers ε_+ and ε_- , lowering one and raising the other. The work done by the additional force per unit displacement of unit length of the TPL is given by:

$$W = \gamma_{LA}(\cos \theta_0 - \cos \theta_A), \quad (3)$$

where θ_0 being the equilibrium (static) contact angle.

If this work is used entirely in raising or lowering ε_+ and ε_- then

$$W = \Delta n w, \quad (4)$$

where w is the work done on each site. The net molecular rate of the process is

$$K_{\text{net}} = 2K \sinh\left(\frac{W}{\Delta n k T}\right). \quad (5)$$

Here $K = K_+ = K_-$. If λ is the average distance between centers of adsorption ($\lambda \approx \Delta n^{-1/2}$), then the linear rate of the wetting process is

$$V = K \lambda \sinh\left[\frac{\sigma(\cos \theta_0 - \cos \theta_A)}{\Delta n k T}\right]. \quad (6)$$

If $(\sigma/\Delta n)(\cos \theta_0 - \cos \theta_A) \gg kT$, then

$$V = K \lambda \exp\left[\frac{\sigma(\cos \theta_0 - \cos \theta_A)}{\Delta n k T}\right]. \quad (7)$$

In this case a plot of $\lg V$ against $\cos \theta$ should give a straight line with a slope of $\sigma/2.303\Delta n k T$.

The results of experimental investigations of temperature dependences of dynamic contact angles were presented in [7]. The dependences of contact angles on velocity ($\cos \theta / \lg V$) were calculated from the experimental data on capillary rising of water in cylindrical glass capillaries with a cross-section of 104–108 μm .

Using the equation of capillary rise [9], the dependence of $\cos \theta$ on $\lg V$ was calculated from the h vs. t data:

$$\cos \theta = \frac{g\rho r h}{2\gamma} + \frac{4(\eta h + \eta_a h_a)}{\gamma r} \frac{dh}{dt}; \quad \frac{dh}{dt} \equiv V. \quad (8)$$

Here η is the viscosity of water, η_a the viscosity of air, $h_a = H - h$ (H is the length of the capillary), ρ is liquid density, and g is the acceleration due to gravity. Equation (8) includes the air resistance, which is important for sufficiently long capillaries.

The experiments on capillary rising were performed at temperatures from 20 to 70 °C for juvenile (dehydrated) and hydrated capillaries with different state of adsorption film of water on the surface of glass.

In agreement with the absolute reaction rates theory [2], the value of K in Eqn. (1) can be written as follows:

$$K = \frac{kT}{h_P} \exp\left(-\frac{\Delta H}{kT}\right) \exp\left(\frac{\Delta S}{k}\right). \quad (9)$$

Here ΔH and ΔS are the enthalpy and entropy of wetting activation respectively.

Using Eqn. (9) enables the value of ΔH and ΔS to be estimated from the experimental data for the dependence of $\lg K$ on $1/T$. The experimental points in the plots of $\lg K$ vs. $1/T$ are very close to a straight line. The slope of the line is equal to $(kT + \Delta H)/k$. The value of $(kT + \Delta H)$, which is usually referred to as the experimental activation energy, is constant for the system under investigation and equal to $95 \cdot 10^{-21}$ J per center. The values of ΔH and ΔS , calculated at different temperatures, show that the activation enthalpy of wetting is significant and equal to $5.4 \cdot 10^4$ J/mol (calculated per mole of silanol groups). This value is more than that of the enthalpy of water evaporation ($4.48 \cdot 10^4$ J/mol). The ΔS values of wetting activation were negative in sign and this can be explained by the disordering of the water molecules near the surface during the wetting process. The enthalpy of activation for wetting is significant and depends (as the entropy of activation does) on the state of the adsorption film of water on the glass surface. These results confirm the viewpoint that the cause of non-zero value of contact angles (θ) of water on the surface of hydrophilic solid bodies is the existence of adsorption film of water vapor on polar solid.

The results obtained were in good agreement with the activation model of dynamic wetting by Blake and Haynes.

The dependence of the wetting on solution composition. As is known, the development of a charge on solid surface leads to the decrease of free surface energy. The general equation of electro capillarity can be written as follows [10]:

$$d\sigma = -\varepsilon d\varphi - \sum_i \Gamma_i d\mu_i, \quad (10)$$

where Γ_i is Gibbs surface surplus values; μ_i — chemical potentials of the components of a system except for the one that charges the surface; φ — surface potential; ε — the charge.

In accordance with (10) the value of the energy of solid—liquid interface depends not only on the surface charge, but, to significant extent, on the adsorption-desorption processes for all components of the system including water.

We will cite some results of our previous investigations to demonstrate the above mentioned peculiarities of the wetting phenomena.

Previous investigations [11, 12] proved that contact angle (θ) measurement at solid/liquid/gas interfaces is a very powerful tool not only in characterizing the state of solid surfaces, but also in getting information about all kinds of interactions between liquids and solids [11–16]. In particular the estimation of the dependence of contact angles for solid oxides on the potential-determining ions activity (H^+ and OH^-) shows that variation of contact angles allows one to follow not only the double electric layer (DEL) development [13], but also to detect the existence of the functional groups with different acid-base properties at the surface [11, 12, 15, 16]. Because of the existence of such groups the dependence of

θ on pH shows maxima and minima and this is the case for all examined oxides (SiO_2 , Al_2O_3 , Fe_2O_3 and so on). The $\theta(\text{pH})$ dependences for all examined oxides had many extremums (Fig. 1).

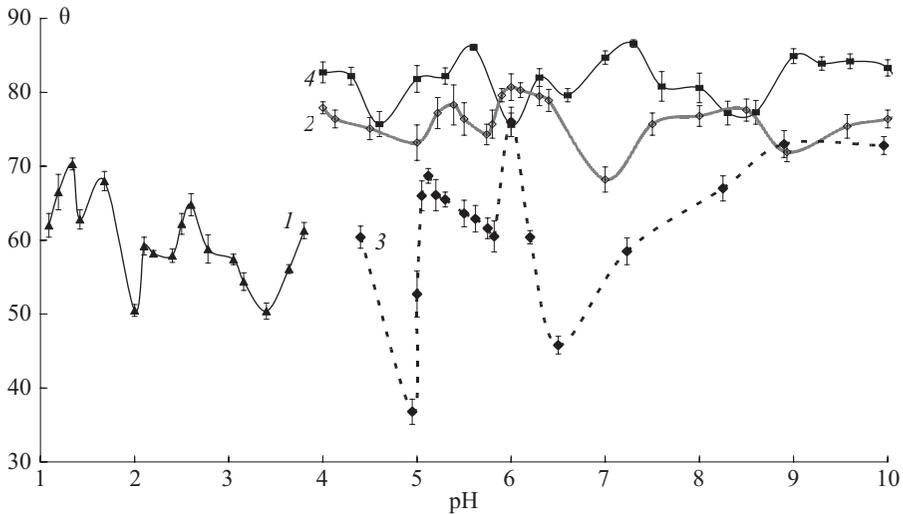


Fig. 1. Dependences of contact angle on pH (HCl, KOH) for solids:
 1 — diamond; 2 — alumina ($\alpha\text{-Al}_2\text{O}_3$) (soft treatment);
 3 — alumina (hard treatment); 4 — yttrium iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$)

The comparison of the results on $\theta(\text{pH})$ dependences with the data on electro surface properties of the oxides under consideration permits to conclude that the many extremum shape of $\theta(\text{pH})$ dependence cannot be explained by the development of surface charge (DEL) only. It is possible that one of the maxima of $\theta(\text{pH})$ dependence is correlated with the point of zero charge (PZC) of the surface. The appearance of other maxima is apparently caused by reducing of the solid surface—solution interaction at pH which ensures the minimum dissociation of individual functional groups (we call it the point of minimum individual charge — PMIC). Reducing of the solid surface—solution interaction for this alone site leads to an increase in θ . Though it is still not completely understood why θ sometimes changes so sharply at the pH corresponding to the PMIC, the existence of this correlation is out of doubt.

The investigation of the dependence of heat of immersion of quartz and some other solids on pH and solute concentration showed that the main factors determining the solid—liquid interaction at wetting were: the nature of the solid (including its crystallinity and the state of the surface), the development of boundary layers of water near the solid surface; the degree of dissociation of surface OH-groups and the development of double electric layer; the influence of electrolytes on the structure of water in boundary layers. The dependences of heat of immersion (Q) on solution pH (HCl—KOH and HCl—KCl—KOH) for the surface of yttrium iron garnet were studied with the aid of micro calorimetry, micro electrophoresis and electrometric titration respectively [16]. The data for dependences of heat of immersion and contact angle (θ) on pH for yttrium iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) are represented in Fig. 2. It's seen that the $\theta = f(\text{pH})$ dependence has many extremum, the position of maxima and minima being contrary to $Q = f(\text{pH})$ dependence (measured earlier) that is maximum of Q is corresponding to minimum of θ and *vice versa*. The value of isoelectric point and that of

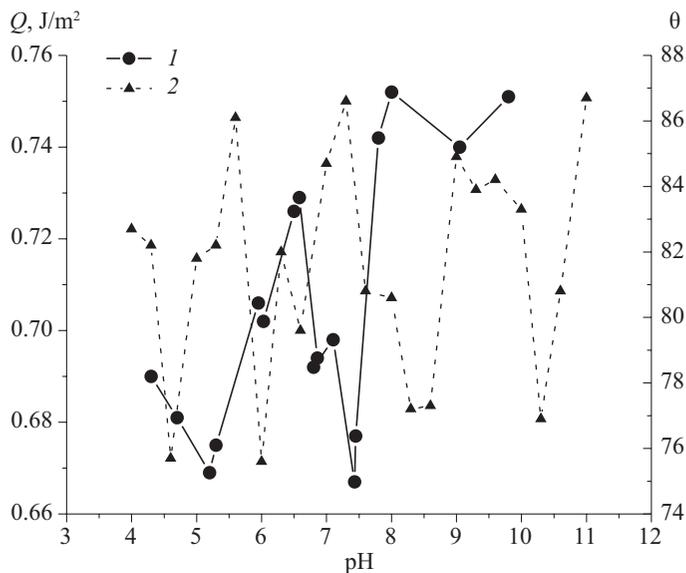


Fig. 2. Dependences of heat of immersion (1) and contact angle (2) on pH for yttrium iron garnet ($Y_3Fe_5O_{12}$)

zero charge were at pH region quite near the position of middle θ -maximum (Q -minimum) at pH = 7.3, that confirms the influence of the charge of the surface. The whole form of the dependences was discussed in [16] from the position of the existence of the sites with different acid-base properties (with different constants of dissociation) at the surface of $Y_3Fe_5O_{12}$.

The electrometric titration. The calculation of acid-base characteristics of the solids is mostly carried out on the data of electrometric titration of the sample with the acid or the base. The meanings of dissociation constants and surface concentration of the sites are obtained with the aid of the treatment of electrometric titration curve in the context of one or another model of acid-base equilibrium in solution—sorbent system. If the qualitative composition of the surface is known the existent methods of calculation permit to estimate both the dissociation constants of surface sites and their concentration (content). In the cases when the solid composition is unknown or the solid surface contains a lot of types of surface sites with close dissociation constants, these methods permit only to estimate total surface concentration and some averaged dissociation constant.

The main disadvantage of existent calculation methods is, on opinion of [17], that they do not perfectly take into account the energy heterogeneity of the surface of every real sorbent. In a number of methods an influence of the surface is not taken into account at all [18, 19]. Usually it is implicitly supposed that the dissociation constants of surface sites do not depend on the place of their attaching to the surface. Such assumption is right only for ideal sorbent having energy homogeneous surface. It is evident that the surface of all real solids is heterogeneous to a greater or lesser extent. So even for the solids with just one type of surface sites the splitting of dissociation constants and the formation of the series of constants are taking place.

It has long been known that the acid-base sites at the oxide surface can both accept and give up the proton (depending on solution pH). For such solids it is common to calculate ΔpK_a i. e. the difference of dissociation constants on acid and base mechanisms in addition to the data on zero point of the charge (ZPC). At the same time, as it was already shown one does not take into account that the sites with different dissociation constants (i. e. with different acid-base properties) as a rule, are coexisting at the same surface. Such a

peculiarity may be correlated to different coordination of the metal atoms to the oxygen, to the defects of the crystal lattice and to the hydration of the surface sites as well. In this case ZPC becomes an averaged value, and ΔpK_a calculations should be done for each type of the sites.

The investigation of the dependence of contact angles θ of different solids on solution pH performed earlier [11, 12] showed that these dependences have many extremums (like spectrum) for all objects under study and can be used to characterize the acid-base properties of the surface. An investigation has been carried out with the aim to reveal possibility to compare the results of electrometric titration on the dissociation constants of separate surface sites of real oxides with the same data on $\theta = f(\text{pH})$ dependence.

In analytical chemistry for determining the dissociation constants of acids and bases in the solution the method of electrometric titration is widely used. It permits to determine more precisely the final point of titration with the aid of differential curve $\Delta\text{pH}/\Delta V = f(V)$ (V is the volume of a titrant). The sharp maximum (peak) at this curve just corresponds to the final point. It's also possible to determine approximate meanings of dissociation constants of the substances under consideration. For weak acid HA we can suppose in the middle point, that

$$[\text{HA}] \cong [\text{A}^-] \quad (11)$$

and

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = [\text{H}^+]; \quad (12)$$

$$\text{p}K_a = \text{pH}_{hn}. \quad (13)$$

The dissociation constants defined in this way differ from the right ones by the value of logarithm of the ratio of activity coefficients:

$$(\text{p}K_a)_{\text{exp}} = \text{pH}_{hn} = \text{p}K_a + \lg \frac{f_{\text{A}^-}}{f_{\text{HA}}}. \quad (14)$$

All expressions cited above are correct for the solutions. To apply these expressions in calculations of the dissociation constants of the sites situated at the solid surface we proposed to use the value of adsorption Γ_{OH^-} or Γ_{H^+} , calculated for each meaning of pH at the titration curve of suspension instead of the volume V .

$$\Gamma_{\text{OH}^-} = \frac{(V_{\text{susp}} - V_{\text{sol}})C_{\text{OH}^-}}{m_S S_s}. \quad (15)$$

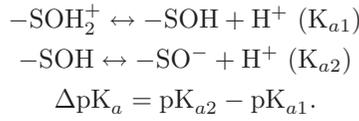
Here V_{susp} and V_{sol} are the volumes of acid or base, used for titration of the suspension and background solution respectively to the same meaning of pH; m_S — the mass of the powder and S_s — its specific surface. The application of the value of adsorption permits to exclude the interaction of the dispersion medium with the H^+ and OH^- ions. Using the obtained meanings of Γ_{OH^-} , first integral ($\Gamma_{\text{OH}^-} = f(\text{pH})$) and next differential ($\Delta\text{pH}/\Delta\Gamma = f(\text{pH})$) and $\Delta\text{pH}/\Delta\Gamma = f(\Gamma_{\text{OH}^-})$ curves of titration are plotting. The position of each peak at the dependences $\Delta\text{pH}/\Delta\Gamma = f(\Gamma_{\text{OH}^-})$ permits to determine the values of adsorption of corresponding final points of titration Γ_{FTP_i} and the points of half neutralization Γ_{hni} as well:

$$\Gamma_{hni} = \frac{\Gamma_{\text{FTP}_i} - \Gamma_{\text{FTP}_{i+1}}}{2}. \quad (16)$$

The meaning of pH_{hn} corresponding to the point of half neutralization, i. e. pK_a of the given type of acid-base site can be found from the integral curve of titration, pK_a for all defined sites having been determined in this way. The estimate of the content of corresponding type of the site at the surface Q_i with the aid of differential curve $\Delta\text{pH}/\Delta\Gamma = f(\Gamma_{\text{OH}^-})$ was also done:

$$Q_i = \Gamma_{\text{FTP}_{i+1}} - \Gamma_{\text{FTP}_i}. \quad (17)$$

From the results of calculations the final graph of the dependence of Q_i on pK_a was plotting. It's necessary to discuss some peculiarities of acid-base properties of solid surface before presenting the detailed analysis of final dependences of Q_i on pK_a . It's known [20, 21], that there are several types of monobasic amphoteric OH-groups at the surface and each of them can dissociate on acid and base types:



The monobasic property of the groups under consideration supposes independence of their acid-base properties from the degree of dissociation of adjoining sites. It's well known that for polybasic acids the dissociation constants for different stages can differ significantly (up to several orders). Crystallographic data show [22, 23] that the existence of metal atoms connected to several OH-groups at the surface of oxides is possible, their dissociation being interdependent. If to take into account the peculiarities of the solid body i. e. the difficulties to rebuild the structure after the dissociation of a site it's hard to tell about the full mutual independence of monobasic adjacent groups. As a result even for the same type of the sites the meanings of the dissociation constants can somehow vary depending on the state of the adjacent site.

It's possible to obtain some data about ΔpK_a of individual sites from the data on contact angles. To elucidate this fact we will carry out some mental experiment. Let us suppose that there is the equal content of three types of acid-base sites at the surface. Their individual ZPC are, for example, 5, 7 and 10 pH and the values of ΔpK_a are identical. We can calculate the part of not dissociated OH-groups of the given type of the site α_0^i using the next formula [21]:

$$\alpha_0^i = 1 - \alpha_-^i - \alpha_+^i = \frac{\text{K}_{a1}^i [\text{H}_s^+]}{[\text{H}_s^+]^2 + \text{K}_{a1}^i \text{K}_{a2}^i + \text{K}_{a1}^i [\text{H}_s^+]}. \quad (18)$$

Here α_-^i and α_+^i are the contents of negatively and positively charged groups. Accordingly, the total content of not dissociated OH-groups will be equal to:

$$\alpha_0 = \frac{\alpha_0^1 + \alpha_0^2 + \alpha_0^3}{3}. \quad (19)$$

The estimation of the dependences of α_0 on pH for different ΔpK_a showed that at low values of ΔpK_a the number of peaks corresponds to the number of the types of acid-base sites, the positions of maxima of α_0 being at pH equal to their individual ZPC. The larger ΔpK_a is, the broader the peaks of the dependences obtained become and the degree of their mutual overlapping increases. This can lead to the junction of several peaks to one, which is much higher than the initial peaks were. In this connection the process of identification of

individual ZPC can be troublesome. Nevertheless, with taking into consideration the profile of such dependence and criteria of intensity and symmetry it's possible to suppose that the peak observed is individual or it arises in the result of overlapping and junction of several ones.

Let us return to contact angles. What can explain the evident existence of many extremums on the curves $\theta = f(\text{pH})$? It is known that the heat of hydration of proton two times higher than that of hydroxyl group [24] and both of them are higher than the heat of water condensation. So the hydration of the surface of solids depends, to a great extent, on the correlation of charged and neutral (not dissociated) functional groups on the surface because the interaction of the water molecules with not dissociated OH-groups is essentially weaker. This should lead to the increase of contact angle.

If there are several types of acid-base sites at the surface, then, as it was discussed higher, the dependence of the content of not dissociated OH-groups on pH should have several maxima. Hence the maxima of the dependence of contact angle on solution pH can correspond to the higher content of not dissociated OH-groups and therefore show the possible position of individual ZPC of surface sites. If there are many maxima (more than three ones) at the θ/pH dependence and these maxima are sufficiently clearly expressed then one can draw the conclusion about rather small value of ΔpK_a of surface sites (no more than 1).

To calculate the values of pK_a from the data of contact angles we should use the value of so called adhesion tension $A = \sigma_{\text{SA}} - \sigma_{\text{SL}} = \sigma_{\text{LA}} \cos \theta$. We should also subtract free energy of double electric layer from specific free energy of solid—liquid solution interface to remove it from consideration. If to calculate electric charge of the surface from the adsorption of potential determining ions one can estimate DEL potential Ψ , using simplified formula (Guy theory) for the case of big potentials in the presence of indifferent electrolyte:

$$\Psi = \frac{2.3rt}{z_i F} \left(2 \lg \sigma_0 + \lg \frac{1}{2\epsilon\epsilon_0 RT} - \lg C \right). \quad (20)$$

Here C is electrolyte concentration; σ_0 — surface charge, calculated from adsorption data at every pH value. The free energy of DEL can be estimated in this case from:

$$G_{\text{DC}} = -\frac{RT}{F} \sqrt{\frac{8\epsilon RT C}{\pi}} \left(\cosh \frac{F\Psi}{2RT} - 1 \right). \quad (21)$$

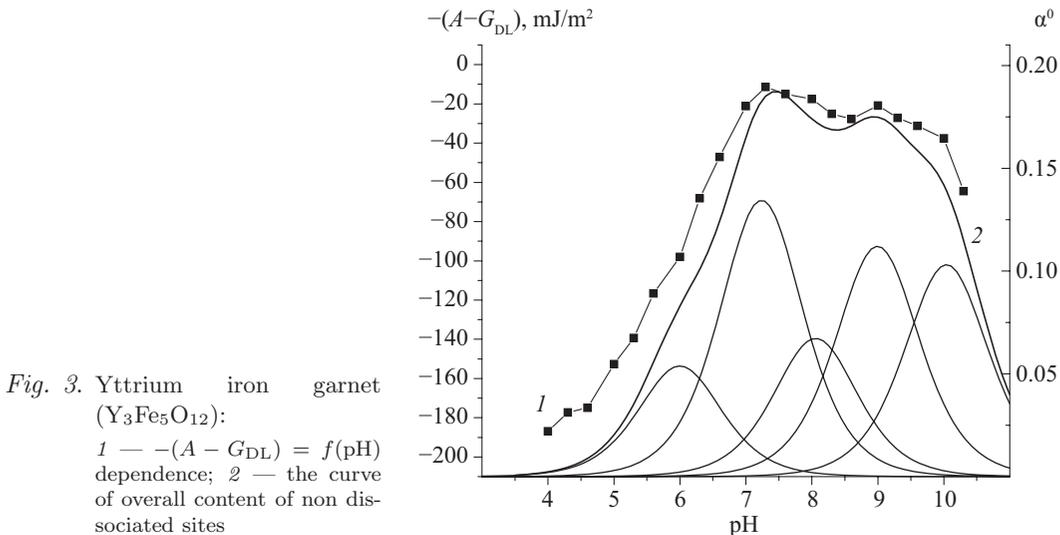
If to suppose that specific free energy of oxide—solution interface depends on pH because of the changing of the oxide surface—water interaction energy (as a result of the changing of no dissociated OH-groups amount at the surface) only, then one can approximate the curve $-(A - G_{\text{DC}}) = f(\text{pH})$ by the curve of summary content of no dissociated surface sites:

$$\alpha^0 = \sum_i q_i \alpha_i^0. \quad (22)$$

Here q_i — the relative content of i -type of OH-groups at the surface.

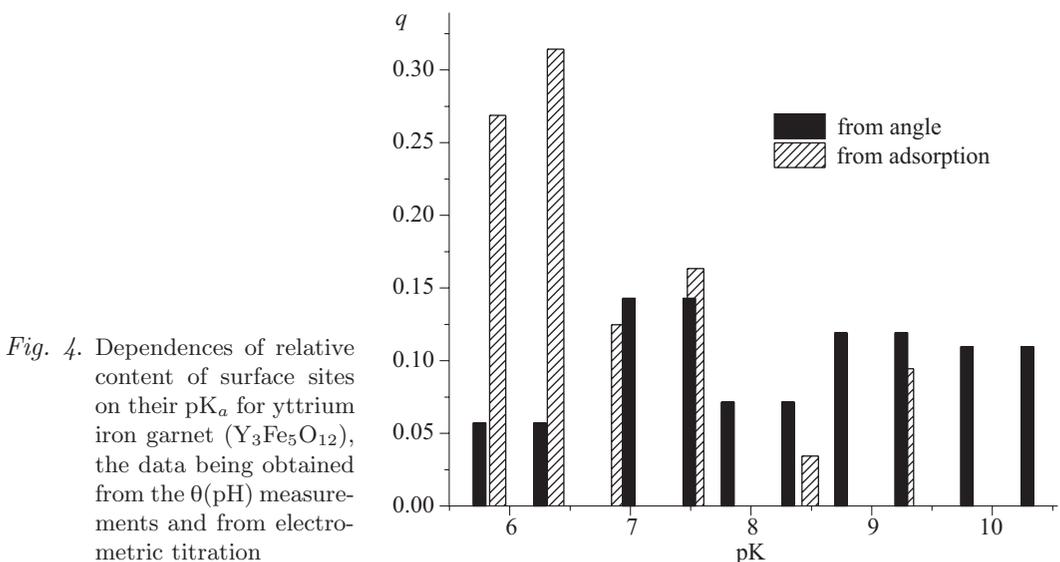
The amount of sites types and their content are chosen in approximation process to receive maximal (highest possible) agreement of both curves. The result of such approximation for the θ/pH data of yttrium iron garnet (YIG) [25] is shown at Fig. 3 [26].

The data of Fig. 2 permit to conclude that there are at least 4 types of surface sites at YIG surface. One can see from Fig. 3, that approximation process gave both the meaning of



pK_{a1} and pK_{a2} for 5 surface sites and their contents. The comparison of the data on pK_a of the sites and their content obtained from electrometric titration and from θ/pH dependence are shown in Fig. 4 [26].

It is seen that there is practically pure coincidence of the values of pK_a in the range of pH from 5 to 7.5 for both methods. As for the range of $\text{pK}_a > 7.5$ it is difficult to make definite conclusion about coincidence because in this case electrometric titration was not sufficiently detailed. It is necessary take in account the possible difference of the state of the surface for the case of plate and powder. Nevertheless it is important that the part of pK_a values for both methods coincides sufficiently well. Similar data were obtained for other oxides (Al_2O_3 , Fe_2O_3) too. This result permits to conclude that the method of electrometric titration in the proposed here modification of data treatment as well as the method of measurement of



$\theta = f(\text{pH})$ dependence can be used to characterize the acid-base properties of solid surface together with IR-spectroscopy and some other methods.

The data cited above show that the main factor defining existence of many extremum at $\theta = f(\text{pH})$ dependences for solid oxides is the influence of chemical reactions on the surface. These reactions (dissociation of surface sites, adsorption from solution, ionic exchange) can change the mechanical state of surface layer of the solid and therefore to change its surface tension [27]. The discovered earlier [12] influence of the hardness of solid plate, on the $\theta = f(\text{pH})$ dependence for solid oxides is indirectly confirms an importance of this factor. The $\theta = f(\text{pH})$ dependences are characteristic of the given solid and one can consider them as a peculiar spectrum of energetic state of its surface in the solution under consideration (at the given pH).

The all aforesaid permits to state that contact angle measurement at solid/liquid/gas interfaces is really a very powerful tool not only in characterizing the state of solid surfaces, but also in getting information about all kinds of interactions between liquids and solids.

References

1. De Boer J. H. The dynamical character of adsorption. Oxford: Clarendon Press, 1953.
2. Glasstone S., Laidler K. J., Eyring H. The theory of rate processes. New York; London: McGraw Hill, 1941.
3. Frumkin A. About phenomena of wetting and bubbles adherence // Zhurn. fiz. khimii. 1938. Vol. 12, N 4. P. 337–345. (In Russian.)
4. Astrakhantseva N. P., Usjyarov O. G. Dependence of electrolytes upon stability of wetting films of different sizes // Collected papers on agronomic physics. 1973. Iss. 31. P. 29–35. (In Russian.)
5. Derjaguin B. V., Churaev N. V. Wetting films. Moscow: Nauka, 1984. 159 p. (In Russian.)
6. Pashley R. M. Multilayer adsorption of water on silica // J. Colloid and Interface Sci. 1980. Vol. 78, N 1. P. 246–248.
7. Frumkin A. N. Potentials of zero charge. Moscow: Nauka, 1979. 260 p. (In Russian.)
8. Gribanova E. V. Dynamic contact angles: temperature dependence and the influence of the state of the adsorption film // Advances in Colloid and Interface Sci. 1992. Vol. 39. P. 235–255.
9. Blake T. D., Haynes J. M. Contact-angle hysteresis // Progr. Surf. Membr. Sci. 1973. Vol. 6. P. 125–138.
10. Gribanova E. V., Molchanova L. I. Velocity dependence of contact angle. Capillary rising of aqueous electrolytes solutions in cylindrical glass capillaries // Kolloid. Zhurn. 1978. Vol. 40, N 2. P. 217–223. (In Russian.)
11. Gribanova E. V., Zhukov A. N., Antonyuk I. E. et al. Effect of the acidity of aqueous solutions on the wettability of various carbon surfaces // Diamond and related materials. 2000. Vol. 9, N 1. P. 1–6.
12. Gribanova E. V., Jadagayeva N. B. The influence of the hardness of solids on the dependence of contact angle for solid surface with oxide nature on solution pH // Vestn. S.-Peterb. Univ. Ser. 4. Fizika, khimii. 2004. Iss. 3. P. 60–64. (In Russian.)
13. Gribanova E. V., Molchanova L. I., Mazitova K. B. et al. Investigation of the dependence of contact angles on quartz and glass on the pH value of solution // Kolloid. Zhurn. 1983. Vol. 45, N 2. P. 316–320. (In Russian.)
14. Gribanova E. V., Schutkevitch V. V., Tikhomolova X. P. Investigation of electro-surface properties and wetting of ferrite materials // Proc. II Int. Meet of highly disperse iron oxides and corrosion. Leningrad, 1983. P. 38–41.
15. Gribanova E. V., Antciferova E. A., Bushenkova I. A. The investigation of the dependence of contact angle on solution pH for Al₂O₃ // Vestn. S.-Peterb. Univ. Ser. 4. Fizika, khimii. 2004. Iss. 4. P. 113–116. (In Russian.)
16. Gribanova E. V., Schutkevitch V. V., Goncharova N. N. The investigation of heat of immersion and electro-surface properties of yttrium iron garnet // Vestn. S.-Peterb. Univ. Ser. 4. Fizika, khimii. 2003. Iss. 3. P. 85–91. (In Russian.)
17. Golikov A. P. The estimation method of acid-base characteristics of a sorbent on results of electro-metric titration // Zhurn. fiz. khimii. 1995. Vol. 69, N 4. P. 664–667. (In Russian.)
18. Riazanov M. A., Doudkin B. N. A study of acid-base properties of α -Al₂O₃ suspension by pK-spectroscopy method // Kolloid. Zhurn. 2003. Vol. 65, N 6. P. 831–836. (In Russian.)

19. *Gorichev I. G., Konykov S. A., Batrakov V. V.* The estimation of acid-base equilibrium constants at the oxide-solution interface by the electrometric titration method // *Electrokhimia*. 1993. Vol. 29, N 3. P. 310–314. (*In Russian.*)
20. *Morrison S.* The chemical physics of surfaces. New York; London: Plenum Press, 1977.
21. *Davis J. G., James R. O., Leckie J. O.* Surface ionization and complexation at the oxide/water interface. 1. Computation of electrical double layer properties in simple electrolytes // *J. Colloid Interface Sci.* 1978. Vol. 63, N 3. P. 480.
22. *Tsyganenko A. A., Mardilovich P. P., Lysenko G. N., Trokhymets A. I.* Hydroxyl cover and electron-acceptor sites of alumina surface // *Usp. fotoniki*. 1987. Vol. 9. P. 28–68. (*In Russian.*)
23. *Kisel'jov V. F.* Surface phenomena in semiconductors and dielectrics. Moscow: Nauka, 1970. (*In Russian.*)
24. *Tarasevich Ju. I., Polyakov V. E., Polyakova I. G.* A study of water interaction with α -Al₂O₃ surface by adsorption calorimetric method // *Kolloid. Zhurn.* 2001. Vol. 63. P. 254–258. (*In Russian.*)
25. *Gribanova E. V., Jadagayeva N. B.* The peculiarities of yttrium iron garnet structure display in the wetting phenomena // *Vestn. S.-Peterb. Univ. Ser. 4. Fizika, khimii*. 2004. Iss. 1. P. 74–79. (*In Russian.*)
26. *Kuchek A. E., Gribanova E. V., Vasutin O. A.* Application of contact angles measurement method for analysis of acid-base properties of the surface // *Vestn. S.-Peterb. Univ. Ser. 4. Fizika, khimii*. 2012. Iss. 2. 89–95. (*In Russian.*)
27. *Rusanov A. I.* Thermodynamic foundation of mechanic chemistry. St. Petersburg: Nauka, 2006. 222 p. (*In Russian.*)

Статья поступила в редакцию 15 октября 2013 г.

К о н т а к т н а я и н ф о р м а ц и я

Грибанова Елена Владимировна — профессор; e-mail: egribanova@yandex.ru; egribanova38@gmail.com

Кучек Анастасия Эдуардовна — старший преподаватель; e-mail: kuchkobrazz@gmail.com

Gribanova Elena Vladimirovna — Professor; e-mail: egribanova@yandex.ru; egribanova38@gmail.com

Kuchek Anastasiya Eduardovna — Senior Lecturer; e-mail: kuchkobrazz@gmail.com