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Potentiometric (pH-Metric) Methods of Studying Acid-Base Properties on the Surface of Dispersed Materials

DANCHENKO Yuliya[1,a*], ANDRONOV Vladimir[2,b], OLIJNYK Halina[3,c], KOSSE Anatoliy[2,d], RASTORHUEVA Mariia[4,e]

[1]National Academy of the National Guard of Ukraine, 3, Zakhysnykiv Ukrainy sq., Kharkiv, 61001, Ukraine

[2]National University of Civil Defense of Ukraine, 94, Chernyshevska str., Kharkiv, 61023, Ukraine

[3]Khmelnytskyi National University, 11, Instytuts'ka str., Khmelnytskyi, 29016, Ukraine

[4]Kherson National Technical University, 24, Beryslavske Shose, Kherson, 73008, Ukraine

[a]u_danchenko@ukr.net, [b]va_andronov@ukr.net, [c]oliinykha@khmnu.edu.ua,
[d]kosse@nuczu.edu.ua, [e]mrastorgueva65@gmail.com

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Abstract. The article presents potentiometric (pH-metric) methods that are used to study the acid-base properties of the surface of dispersed materials of different chemical nature. It is shown that the surface of any solid body has a surface hydroxyl-hydrate layer with a set of active adsorption centers (ACA) of different chemical structure and a wide range of acid-base properties. It has been proven that potentiometric (pH-metric) methods of studying dispersed materials in suspensions allow obtaining the most complete information about surface acid-base properties.

Introduction

Disperse and powder materials of various origins are in great demand in a wide range of industries. This is due to the unique properties of the surface, which depend on the chemical composition and nature of minerals (in the case of crystalline structure), particle size (dispersity), structure of the surface layer of dispersed particles. The surface properties of dispersed materials can also be determined by the chemical nature, storage conditions, dispersion, and the method of preliminary chemical, physical, or mechanical processing. Particular attention needs to be paid to the study of the acid-base properties of the surface of dispersed materials, on which interactions between surface functional groups (acidic or alkaline functionals) and the surrounding environment - gases or liquids - take place. The regularities of interactions on the surface of the phase separation in any case can be described as reactions between acids and bases according to the mechanisms of Bronsted (proton reactions) or Lewis (aproton reactions).

Literature Review

Dispersed particles of materials have excess surface energy, which includes the acid-base (polar) energy of surface adsorption centers [1, 2], which adsorb water molecules from the air, forming a number of functional groups (functionals) with a wide range of acid-base properties [3, 4]. The effect of chemically and physically adsorbed water on the acid-base properties of the surface is confirmed experimentally. It has been proven that during firing or during mechanical processing (grinding) the number and acid-base characteristics of active centers on the surface of dispersed materials change [5]. When water is adsorbed on the solid surface of any structure, a hydroxyl-hydrate layer is formed, which is characterized by a wide range of active adsorption centers (ACA) [6-8], whose acid-alkaline properties are of great scientific interest, but not sufficiently studied.

It is believed that the structure of the surface hydroxyl-hydrate layer consists of chemically bound water molecules that form the first lower hydroxyl layer of OH groups (Brønsted centers), which may also contain a certain number of aprotic Lewis centers (Fig. 1) and the following more distant from the solid surface of hydrate layers of water molecules connected to the hydroxyl layer due to hydrogen and other physicochemical bonds. All types of functional groups are essentially active adsorption centers, which to one degree or another are capable of adsorbing any chemical substances or elementary particles - molecules, atoms, ions, electrons, radicals, etc. from the external gaseous or liquid medium. Therefore, the name "active adsorption center" (ACA) is justified and can be used for any functionality of a solid surface.

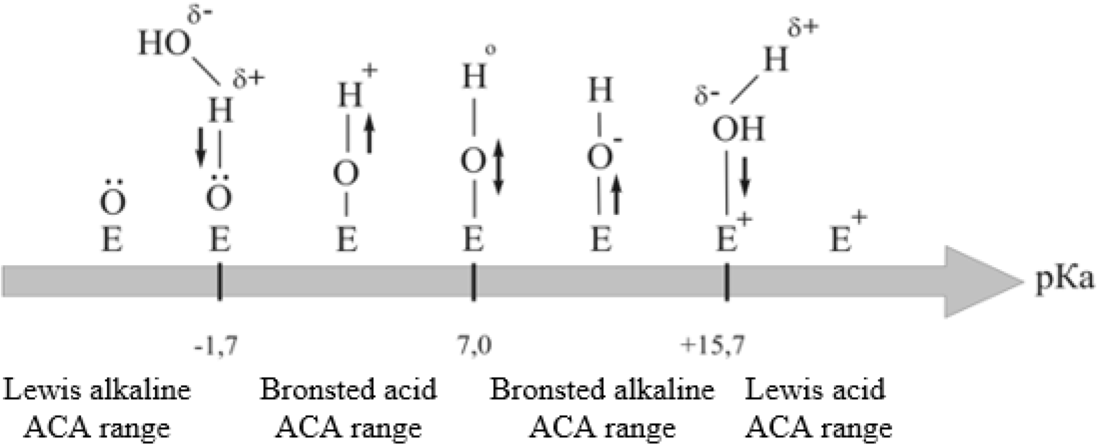

Fig. 1. The structure of the hydroxyl layer of a solid surface

It is known [3] that the hydroxyl layer of a solid surface of an inorganic nature includes several types of ACA: "isolated centers", which contain a central element - a metal atom and one, two or three OH-groups, as well as so-called "vicinal centers" , in which two adjacent hydroxyl groups, which are connected to different central elements, can interact with each other by means of a hydrogen bond. It is possible that the structure of the hydroxyl layer is more complex and the spectrum of ACA is much wider. Regarding the structure of the hydrate layer, it is obvious that the chemical structure of the centers has a much larger spectrum and is more diverse. In addition, it is important not to forget that in addition to water molecules, the surface of a solid can adsorb elementary particles of other substances, forming an even more diverse structure of the surface layer.

Determining the acid-base properties of the ACA of the surface layer of dispersed materials is a complex, but very important scientific and practical task. For this, methods are used that allow determining the amount and acid-alkaline parameters of ACA experimentally or with the help of theoretical calculations. For example, experimental methods of IR spectroscopy [9], adsorption of gas molecules in a gaseous medium [3, 10] or color indicator molecules in liquids [11-14] are used. Experimental methods are informative, but time-consuming, and most of them do not allow determining the chemical nature of ACA. To find out the chemical nature of active centers and to study the regularities of chemical and physicochemical interactions on the surface of solid materials, the method of quantum chemical modeling is used, which is based on the idea of the chemical composition and structure of ACA and allows to calculate the thermodynamic parameters of interactions involving ACA [15- 17]. A quantum-chemical approach for modeling surface ACAs and an algorithm for calculating acid-base parameters can be used for a preliminary assessment of the surface properties of dispersed materials and establishing the chemical nature of ACAs, the amount of which prevails on a particular surface.

The nature and acid-base properties of ACA have been most thoroughly studied for dispersed crystalline materials of an inorganic nature, which is related to the more or less known chemical composition and crystal structure [6-8]. The complexity of studying the surface of dispersed inorganic materials of an amorphous structure or materials of organic origin is caused by the need to identify a surface with a complex chemical structure and unstable composition [18, 19]. The characteristics of the constituents of such materials – density, molecular weight, molecular and supramolecular structure, decomposition temperature, solubility in solvents, heat capacity – have a very wide range. Therefore, most of the chemical and physicochemical experimental methods for studying the surface properties of materials with an amorphous structure are unacceptable.

Potentiometric (pH-metric) methods for the study of acid-base properties of the surface of dispersed materials

Among the experimental methods, the most informative and easy to use are potentiometric (pH-metric) methods, which allow studying the acid-base surface properties of dispersed materials in suspensions, and also do not require complex laboratory equipment [4, 6-8, 18, 19].

The following concepts lie in the theoretical basis of the use of potentiometric methods. The concept of "surface isostate" is used to estimate the degree of integral (total) acidity of the surface of a solid body. Isostate is an equilibrium stable state of inertness of the surface of a solid body in a dispersed system (suspension), which is determined by the absence of mass transfer of charged ions and is characterized by an isopoint. At this point, the equilibrium between the ions of the solid surface and the ions in the liquid phase is maintained for a certain time. From the point of view of mass, an isoadsorption state occurs, from the point of view of charge, the system is characterized by an isoelectric state [4].

The task of potentiometric research includes the determination of the isoadsorption state of the surface, that is, the search for such a state of the dispersed system (suspension) in which the mass transfer of counterions from the liquid phase to the surface of the solid body does not occur. Such a state is called "zero", and the electric potential on a solid body in a solution is the point of zero charge (PZC). This potential is equal to the negative value of the decimal logarithm concentration of the potential determining ion. In the case of OH^- or H^+ potential determining ion (which is the most logical and convenient from the point of view of determining acid-base properties), the isoadsorption state of the surface is characterized by the value of pH_{PZC}. Most often, water is used as the liquid phase of suspensions, which makes it possible to determine the isoadsorption state and, in general, the characteristics of surface ACA in the pH range from 0 to 14. To expand the pH range of the corresponding ACAs that can be on the surface of a solid body (Fig. 1), can be other non-aqueous solvents were used, for example, ethanol (pH ranges from –4 to 18), etc. [20].

The isoadsorption state of the surface of a solid body in suspensions and acid-base properties in dispersed systems are generally most conveniently investigated by potentiometric methods. At the present time, several variants of the potentiometric determination of pH_{PZC} have been developed, which are based on one general principle – the study of the patterns of absorption of OH^- or H^+ ions by the surface of a solid body from liquids (electrolytes) of different acidity and the selection of such a pH value of the electrolyte solution that does not change upon contact with a solid body, that is, it characterizes the equilibrium on the surface of the phase separation. The availability of various options is related to the search for the most informative, expressive and accessible methods. All methods can be divided into two groups: in some, the isoadsorption state is evaluated by the pH values of the suspensions, in others, by the pH of the filtrates of the suspensions. From the first group of methods, the Nechyporenko method and the Parks-Bobyrenko method with the use of potentiometric titration deserve special attention.

Nechyporenko's method is the easiest to perform, express and informative. This methodology considers the regularity of the change in the pH value of the suspension (pH_{susp}) over time, that is, the dependence "$pH_{susp} = f(t)$". Considering the process and regularities of changes in the pH_{susp} over time, it is possible to determine the integral (total) acidity of the solid surface and the distribution and some qualitative characteristics of surface ACA. The value of pH_{susp} indicates the preference of surface acidic or alkaline ACAs: the less acidic properties inherent in the surface in contact with the electrolyte, the greater the value of pH_{susp} in a given electrolyte. But it is necessary to take into account that the presence of water-soluble substances in the composition of solid dispersed materials can complicate the interpretation of the obtained results of experiments. The time factor reflects the processes of hydration and hydrolysis, changes in the composition of the electrolyte and the surface. Therefore, the change in the value of pH_{susp} over time can be viewed as a "composition – properties" diagram with the corresponding features. The extreme points and inflections on the graphical curve of dependence "pH_{susp} = f (t)" correspond to significant changes in the system, for example, the appearance of a new phase, etc. In accordance with the methodology, 10 cm^3 of distilled boiled water with pH_0 = 6.8–7.0 is added to the potentiometric cell with glass and silver chloride electrodes. After stabilization of the potential of the glass electrode (after 2–3 minutes with continuous stirring with a magnetic stirrer), a weight of dispersed material (~0.2 g) is added. At the same time, the stopwatch starts. Measurement of the pH of the solution performed every 5 seconds during the first minute of contact of the solid material with water and every minute during the next 5 minutes. For a more complete picture, after 10 minutes of contact, measurements are taken every 10 minutes for two hours. From the position of the extrema, which usually appear on the constructed graph of the dependence "pH_{susp} = f (τ)" during the first two minutes of contact with the liquid phase, an instantaneous surface reaction is estimated, which indicates the type of aprotic ACA (Lewis centers), which prevail at the surface of the dispersed material. That is, it characterizes the acidity of the strongest ACA surface and is expressed by the measured value of pH^{eq}_{susp}. When the contact time increases, the dependence graph shows longer hydration and hydrolysis processes followed by the establishment of acid-base equilibrium in the system, which is characterized by the achievement of a constant value of pH_{susp} = const = pH_{PZC}. Taking into account that in practice it takes a long time to establish equilibrium, the value of pH_{PZC} can be calculated by the formula:

$$pH_{PZC} = pH_0 + (pH^{eq}_{susp} - pH_0) \cdot (pH_0 - 6) \quad (1)$$

For a rough approximation of the spectrum width of ACA based on the acid-base characteristic, the value of ΔpH is calculated according to the formula:

$$\Delta pH = pH_{PZC} - pH^{eq}_{susp} \quad (2)$$

The value of ΔpH characterizes the width of the range of ACA with different acid-base properties on the surface. An increase in the value of ΔpH shows the broadening of the ACA spectrum on the surface of the dispersed material. For an approximate quantitative assessment of the ACA of the surface based on the data of potentiometric studies, the time of establishment of the equilibrium state in the suspension is fixed. The duration of the period of establishment of the equilibrium state in the suspension can characterize the total number of ACAs that participate in interactions with the liquid phase.

The Parks-Bobyrenko method with the use of potentiometric titration expands the understanding of the acid-base properties of the solid surface of a dispersed material during potentiometric studies of suspensions. The value of pH_{PZC} is estimated by the point of intersection of the curves of potentiometric titration of the electrolyte solution (blank experiment) and the suspension of dispersed material in this electrolyte (working titration). Taking into account the fact that dispersed materials can be characterized by an overall acidic or alkaline surface, an alkaline or acidic KCl solution is selected as the background electrolyte, respectively, and an HCl or NaOH solution is used as the titrant. First, a blank experiment is conducted. In a potentiometric cell with glass and silver chloride electrodes, 25 cm^3 of the original electrolyte is added (for example, a 0.1M aqueous KCl solution with a $pH_0 \approx 10$, the value of which is regulated by adding a 0.1M NaOH solution or a 0.1M aqueous solution of KCl with a $pH_0 \approx 2$, the value which is adjusted by adding 0.1M HCl solution). After stabilization of the potential of the glass electrode (after 2–3 minutes with continuous stirring with a magnetic stirrer), the solution is titrated with 0.1M HCl or NaOH solution until the end point of the titration is reached. At the same time, the titrant is added in small portions of 2 cm^3 every 2-3 minutes after stabilization of the pH value. After that, working titration is carried out. 25 cm^3 of 0.1M KCl solution and a weight of the investigated dispersed material (0.10, 0.25, 0.50 g) are added to the potentiometric cell. The suspension is stirred with a magnetic stirrer until the pH_{susp} stabilizes and fixes. After that, the suspension is titrated as in the blank experiment.

According to the titration results, the amount of excessively adsorbed OH^- ions (titrant – HCl solution) or H^+ ions (titrant NaOH solution) on the surface of the dispersed material (ΔX, mol/m^2) is calculated by the formula:

$$\Delta X = \frac{\Delta pH \cdot \Delta V \cdot C}{m \cdot S}, \tag{3}$$

where: $\Delta pH = pH_0 - pH^{eq}_{susp}$ – change in the pH of the suspension as a result of hydrolytic adsorption; ΔV – volume of added titrant, dm3; C – concentration of HCl or NaOH solution (titrant), mol/dm^3; m – dispersed material weight, g; S – specific surface of the investigated dispersed material, m^2/g; the multiplier that was added to take into account the concentration of functional groups per unit surface area of the dispersed material.

According to the constructed graphs of the dependence of "$pH_{susp} = f(V)$" and "$\Delta X = f(pH_0)$" the following characteristics and values are defined:

1) according to the nature of the dependence graph "$\Delta X = f(pH_0)$", the chemical nature of surface is evaluated according to the classification: polyfunctional solid (practically straight line of the graph), monofunctional strong alkali or acid (curve with a sharp drop and establishment of a constant value of ΔX), bifunctional surface with strong and weak acid and base ACAs (curve with two peaks); a solid with a weakly acidic or weakly alkaline surface (curve with minor weakly pronounced peaks);

2) pH_{PZC} – the pH value of the suspension at which adsorption of the same amount of H^+ and OH^- ions occurs on the surface of the dispersed material; is defined as the point of intersection of the curves of the potentiometric titration of the electrolyte solution (blank test) and the suspension (working titration) on the graph $pH_{susp} = f(V)$;

3) pH_{IAT} – the value of the pH of the suspension at the isoadsorption point, which indicates the preference of ACA with a certain acid-base characteristic; is defined as the point of intersection of three graphs $pH_{susp} = f(V)$ for different concentrations, and for a more precise value, as the point of intersection of the graph $\Delta X = f(pH_0)$ with the abscissa axis, i.e. at $\Delta X = 0$; the value of pH_{IAT} indicates the preference of ACA with pKa, i.e. $pH_{IAT} \approx pKa$;

4) the value of the exchange capacity of ACA (characteristic of the speed of hydrolytic processes at the interphase boundary), defined as the tangent of the angle of inclination of the straight line $\Delta X = f(pH_0)$, i.e. the value of the multiplier k in the equation $\Delta X = k \cdot pH_0 \pm b$.

Conclusions

An overview of the nature of the surface of dispersed materials of different chemical nature was conducted. It is shown that the surface of the solid body has a hydroxyl-hydrate layer with a wide range of active adsorption centers (ACA) of Brønsted and Lewis, which is formed as a result of chemical and physical adsorption of water molecules. Acid-base characteristics of ACA vary in a wide range, because they have a very diverse chemical structure. The analysis made it possible to establish that potentiometric (pH-metric) methods are the most acceptable, informative and accessible for researching the acid-base properties of the surface of dispersed materials. The Nechyporenko method (direct potentiometry) and the Parks-Bobirenko method (potentiometric titration) deserve special attention. The proposed methods make it possible to conduct simple experimental studies in suspensions and obtain sufficiently complete information about the acid-base properties of the surface of dispersed materials.

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