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The contemporary theories dealing with the adsorption of polar organic compounds from polar solvent on polar wide-gap adsorbents are reviewed. It is proposed to approximate the energies of adsorption and solvation interactions by means of the magnitude of the highest effective charges of the atoms which constitute the adsorbate and the solvent. The adsorption energies of a number of heterocyclic nitrogen-containing compounds and aromatic amine on Si, Al, Mg, Zr oxides and calcium hydroxyapatite are calculated based on adsorption measurements. It is shown that the adsorption energies of organic compounds linearly correlate with the effective charge of their nitrogen atoms. An explanation of these correlations is proposed based on the concept of the dominant nature of electrostatic interactions. It is shown that the difference in adsorption properties of wide-gap polar adsorbents can be explained by the difference in effective charges of hydrogen atoms in surface OH-groups being adsorption centers of nitrogen-containing molecules. It is concluded that the effective charges of hydrogen surface atoms in OH-groups of adsorbents involved decrease in the following series:  $\equiv\text{SiOH}$ ,  $\equiv\text{P(O)OH}$ ,  $\equiv\text{AlOH}$ ,  $-\text{MgOH}$ , and  $\equiv\text{ZrOH}$ .

**Keywords:** adsorption, oxides, hydroxyapatite, polar organic compounds, electrostatic interaction.

**Introduction**

It is generally accepted that the main factor which determines the adsorption of polar compounds in aqueous solutions is the ability of water molecules to form hydrogen bonds both with the molecules themselves, and with the surface of the adsorbent [1–10]. Therefore, according to Koganovskiy's works [1], the adsorption of polar organic molecules on hydrophilic surfaces of oxides, hydroxides or aluminosilicates is possible due to the specific chemical interactions which could yield the considerable amount of energy required to ensure the accumulation of several water molecules into one formation, with the number of water molecules in such a cluster depending on the size of the landing area of the adsorbed molecules.

According to Tarasevich [2,3], the adsorption nature of organic compounds is determined by the nature of an active centre of the adsorbent surface. For example, depending on the type of the exchange cation of the layered silicate, the organic molecules can enter directly into the first coordination sphere of cations displacing water from it. Also, the organic molecules can interact with exchangeable cations

through bridged water molecule to form outer-sphere complexes.

Chuiko [4] described the adsorption of small electron-donating molecules on the silica surface as their interaction with hydroxylated silicon atoms. Based on the analysis of profiles of electron density and electrostatic potential, it was concluded that the silicon surface atoms possess the electron-withdrawing properties. Due to these properties, these atoms can coordinate small «elongated» molecule with electron-donating atoms. The possibility of the formation of silicon complexes with coordination numbers 5 and 6 was studied in detail in work [5], where the reactions of nucleophilic substitution of its functional groups were considered. It was shown that the deformation energy of the tetrahedral surrounding of silicon atoms is very important for the activation barrier of such reactions. Therefore, the reactions on the silica surface are possible under stringent conditions (at increased temperature, pressure, and reactant concentrations) [6,7]. In the case of the adsorption on silica, the formation of a coordination bonds between the organic molecules and hydroxylated surface atoms of silicon in aqueous

solutions is quite unlikely. It was argued that the migration channels of the adsorbate molecules into the subsurface layer of the silica are hexagonal cavity of surface sites with (111)  $\beta$ -cristobalite structure [8]. The concentration of such adsorption centres is by one order of magnitude lower than the content of the  $\equiv\text{SiOH}$  groups. In solutions such cavities are occupied by water molecules, which creates a potential barrier for a coordinating binding of organic molecules.

The ability to predict the adsorption properties of a given adsorbent from knowledge of the physicochemical properties of the adsorbate is an important objective in adsorbent-adsorbate interaction studies. Up to now, various parameters for predicting adsorption of organic compounds were proposed [9]. In our opinion, the best approach to forecast adsorption activity could be based on a comparison between the electronic structures of the adsorbate and adsorbent. In this regard, their electronic properties are of paramount importance since it is the orbital symmetry, the degree of orbital overlapping, the energies of the molecular orbital and the electronic density which are the general parameters determining the result of chemical interaction. The quantum chemical and molecular mechanics methods as well as correlative approach based on the combination of adsorption equilibrium with electronic properties of adsorbate can be used for estimation of the adsorbability. If the system is simple enough, the result of chemical interaction can be estimated from SCF MO calculations. For a complicated system, in particular a solid surface, the perturbation MO theory, which is capable to visualize many factors responsible for chemical bonding phenomena, can be used.

In the second order of the perturbation theory, the energy of chemical interaction can be estimated as the total of the contributions arising from pair interactions between the orbitals of the adsorbate and adsorbent as follows:

$$\Delta E = \sum \frac{H_{ij}^2}{\varepsilon_i - \varepsilon_j},$$

where  $H_{ij}$  is the matrix of the interaction functions of orbitals,  $\varepsilon_i$  and  $\varepsilon_j$  are the energies of the Mos.

According to this equation, chemical reactivity follows essentially from a consideration of the difference in the MO energy between the highest occupied orbital (HOMO) of the donor and the lowest unoccupied orbital (LUMO) of the acceptor,

i.e. the frontier orbitals. As was noted for the first time by Klopman, two approaches can be distinguished: (i) for large enough differences in energy,  $\varepsilon_i - \varepsilon_j$ , the quantity  $\Delta E$  is mainly determined by the value  $H_{ij}$ ; (ii) for rather small energy differences, interaction between the HOMO and LUMO becomes predominant. By analogy, two approaches can be followed when chemisorption is considered [10–13]: charge-controlled adsorption, when the interaction is determined by the atom charges of the adsorbate and adsorbent; and frontier-controlled adsorption, when the frontier orbital energies of the adsorbate and adsorbent are close to each other.

At present, it is reliably known that charge-controlled adsorption is characteristic of wide-zone polar adsorbents. Adsorption of polar organic compounds on these adsorbents is caused by the steric accessibility and by the values of the greatest effective charges of atoms taking part in forming surface hydrogen or coordination bonds [14].

It is known that in the case of the adsorption of small polar organic molecules on the hydrophilic surfaces from aqueous solutions, consequent elementary stages can be distinguished:

1. removal of the solvent molecules from the surface of the adsorbent (i.e. desolvation of parts of the surface which match the «landing site» of the adsorbed molecules);
2. desolvation of the «reaction centre» of the adsorbate molecules (i.e. desolvation of those atoms of molecule which are directly involved in the binding with the surface);
3. the formation of the adsorption bond between the adsorbate molecules and the surface of the adsorbent.

Then, the experimentally observed free energy of adsorption ( $\Delta G_{\text{exp}}$ ) can be determined by the ratio of the adsorption and the solvation interactions:

$$\Delta G_{\text{exp}} = \Delta G_{12} - \Delta G_{13} - \Delta G_{23}, \quad (1)$$

where the subscripts 1, 2 and 3 indicate the adsorbent, the adsorbate and the solvent, respectively;  $\Delta G_{12}$  is the Gibbs' free energy of an interaction between the adsorbate and the adsorbent,  $\Delta G_{13}$  and  $\Delta G_{23}$  are the solvation energies of the adsorbent and the adsorbate, respectively.

If the condition  $|\Delta G_{12}| > |\Delta G_{13} + \Delta G_{23}|$  is met, then the adsorption of the adsorbent becomes thermodynamically available. To analyze situations when such a condition can occur, it is convenient to present intermolecular interactions as the sum of the individual components which have a clear

physical meaning:

$$E_{\text{int}} = E_{\text{es}} + E_{\text{ex}} + E_{\text{pol}} + E_{\text{ct}} + E_{\text{disp}}, \quad (2)$$

where  $E_{\text{es}}$  is the energy of the electrostatic interaction,  $E_{\text{ex}}$  is the repulsion exchange energy of filled electron shells of molecules,  $E_{\text{pol}}$  is the polarization energy,  $E_{\text{ct}}$  is the interaction energy of the frontier orbitals with the charge transfer, and  $E_{\text{disp}}$  is the energy of dispersive interactions.

The theoretical calculation of each component of this expansion requires knowledge of the composition and geometry of the adsorption complex and its local surroundings both from the side of adsorbent, and from the side of the solution. It is clear that such research is very time-consuming.

However, if the dominant terms in Eq. (2) for  $\Delta G_{12}$ ,  $\Delta G_{13}$  and  $\Delta G_{23}$  are determined, then it becomes possible to identify those physical and chemical properties of the adsorbate and adsorbent with which the total energy of interaction can correlate well.

The adsorption and spectroscopic studies [10] have shown that aromatic amines, alcohols, aldehydes, ketones and acids are adsorbed from aqueous solutions on the surfaces of the silica and alumina via hydrogen bonds. It is generally known that the polar functional groups of molecules are involved in the formation of such bonds. Also, these polar functional groups of molecules are connected with water molecules by hydrogen bonding in the solution. Therefore, the adsorption of organic molecules must be accompanied by a restructuring of their solvation shells or by desolvation of their «reactionary» centres: the atoms of oxygen, nitrogen, and associated hydrogen atoms. Thus, the magnitude of terms  $\Delta G_{12}$ ,  $\Delta G_{13}$  and  $\Delta G_{23}$  in Eq. (1) for the adsorbed polar compounds from the aqueous solution on hydrophilic adsorbents can be approximated by energies of the hydrogen bonding.

According to Eq. (1), a necessary condition for such adsorption is that the energy of surface hydrogen binding should exceed the energy of hydrogen bonds of «reaction-capable» centres of the adsorbent and adsorbate particles. As is known, the hydrogen bond is one of the types of intermolecular interactions which can occur through the interaction of hydrogen atoms. This type of interaction is considered unique and was considered in many studies as a highly specific property of molecules which possess in the structure an electronegative atom bonded with hydrogen atoms. Also, from the standpoint of determination of the chemical bond as an interaction accompanied by rearrangement of the electron shells of molecules, hydrogen bond

should be considered as a type of covalent bond. The formation of the hydrogen bonds is also accompanied by a redistribution of the electron density and can lead to qualitative changes of the structure of the interacting molecules. The understanding of the nature of the hydrogen bond requires a combination of four concepts: the electrostatic interaction, the polarization effects, the exchange forces of repulsion and van der Waals forces. Clearly, the division of the interaction into four components is artificial; other schemes of decomposition of total interaction energy could be considered. Non-empirical quantum chemical calculations of recent years have clearly demonstrated that the electrostatic interaction forces yield the main contribution to the energy of hydrogen bonds. These forces determine the relative stability and equilibrium configuration of complexes. It has been shown that for many of the molecular complexes with hydrogen bonding, the energy of the electrostatic component at distances more than  $\sim 0.3$  nm almost completely coincides with the value of the total interaction energy. The mutual polarization and charge transfer, i.e.  $E_{\text{pol}}$  and  $E_{\text{ct}}$  in Eq. (2), make a relatively small contribution to the energy and play a significant role only in the effects of increasing the dipole moment of the complex, increasing the intensity of the bands of valence bonds in IR spectrum, and others.

In the perturbation MO theory the value of the  $E_{\text{es}}$  is actually classical electrostatic interaction energy of the unperturbed molecule. Its value is calculated as the Coulomb interaction of a discrete set of point charges or dipoles. For example, the electrostatic interaction between two molecules of water at relatively large distances is considered as the Coulomb interaction of two dipoles, and in the course of approach of the molecules to each other the interaction of the four lone electron pairs of the oxygen atoms with a negative charge and four positively charged hydrogen atoms should be taken into account.

Currently, it is generally assumed that the electrostatic and covalent components of the total interaction energy contribute to the interaction between oxygen and hydrogen atoms during the hydrogen bonding. Therefore, it should be concluded that the formation of hydrogen bonds between the water molecules can be considered as a reaction to the charge control. The best correlation parameter of the total energy of interaction with the electronic structure of water molecules must be the value of the electron density on the interacting atoms. In the literature, these correlations been considered. For example, the authors of work [15] had shown that

the lengths of the hydrogen bonds X-H...Y (where X=NH<sub>2</sub>, OH, or F and Y=NH<sub>3</sub>, H<sub>2</sub>O, or HF) are the functions of the value of positive charge of the hydrogen atom.

This article presents the study of the adsorption isotherms of series of heterocyclic nitrogen-bearing compounds and aromatic amines from water solutions on oxides of Si, Al, Mg, Zr and calcium hydroxyapatite, aimed at the experimental confirmation of the fact that possible correlation exists between adsorption of polar organic compounds and effective charges 'reaction' centres of its molecules and atoms of the surface. The free energy of adsorption was calculated based on experimental values of the adsorption constants. The adsorption model employed here is based on the assumption of additivity of the interaction energy of the dissolved molecule with the electric field of the solvent and the solid surface.

#### Experimental

An adsorption was studied by the static method. Weighed amounts of adsorbent (0.100 g powdered activated carbon and 1.000 g oxides) were added to precisely measured volumes (10.00 cm<sup>3</sup>) of the solution containing (0.1÷1.0)·10<sup>-2</sup> M organic compounds. A background electrolyte (0.1 M KCl) was added to the solutions to maintain constant ionic strength. The suspensions were allowed to stand for 24 h with periodic stirring and then were centrifuged. The concentrations of the solutions were determined spectrophotometrically by SF-46 with corrections for the evaporation of highly volatile compounds being made via blank experiments. Values of adsorption were calculated as (C<sub>0</sub>-C)V/m, where C<sub>0</sub> and C are the initial and equilibrium concentrations of organic compounds in solution, respectively. All measurements were performed at 18±2°C.

The studied organic compounds before using were purified by distillation or recrystallization. The silica gel, α-alumina, magnesium oxide, zirconium oxides and calcium hydroxyapatite were used as the adsorbents. The BET specific surface areas were 16.9, 7.1, 28.0 and 12.8 m<sup>2</sup>/g for SiO<sub>2</sub>, α-Al<sub>2</sub>O<sub>3</sub>, MgO and ZrO<sub>2</sub>, respectively. Calcium hydroxyapatite HAP was synthesised by precipitation from aqueous solution Ca(NO<sub>3</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> at pH>12. Impurity ions NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were removed by calcination at the temperature of 240°C. HAP structure was verified by X-ray diffraction analysis. The specific surface area of HAP powder as determined by benzoic acid adsorption from water was equal to 5.2 m<sup>2</sup>/g, while as determined by aniline adsorption from water was equal to 5.9 m<sup>2</sup>/g.

Repeatability of adsorption measurements was verified by means of parallel experiments. It was found that the limiting relative uncertainty of determining the values of the adsorption did not exceed 12%; it did not exceed 26% and 3% for the adsorption constants of the Langmuir isotherm equation and for the free energy of adsorption, respectively. The highest possible relative standard deviations in three parallel measurements did not exceed the following values: 14.5% for the values of adsorption, 31.5% for the adsorption constants and 3.5% for the free energies of adsorption.

The values of atom effective charges (as a difference between charge of nuclei and effective number of electrons in atom) were calculated by the iterative extended Huckel method, which differs from the usual RHM by the procedure of self-consistent for charges atoms of the molecule. The results of calculations for aromatic and heterocyclic amines under study are listed in Table.

**Effective charges of nitrogen atoms in aromatic and heterocyclic amines**

Organic compound	-Q(N), e
benzamide	0.128
indole	0.136
2-aminopyridine	0.179
α-naphthylamine	0.187
diphenylamine	0.190
m-toluidine	0.199
aniline	0.207
pyridine	0.234
α-picoline	0.240
γ-picoline	0.240
quinoline	0.205
2,8-dimethylquinoline	0.210

#### Results and discussion

To compare the absorbability of organic compounds on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>, and Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> under the same conditions, we studied their adsorption. The aromatic amines and the heterocyclic nitrogen-bearing compounds were used in the experiments. The aromatic and heterocyclic compounds were chosen because of their rapid quantitative determination in aqueous solution by spectrophotometry. The studies were conducted at the pH values of their aqueous solutions.

It was shown that the adsorption isotherms of the studied compounds conform to classic Langmuir curves and are rather well describable by a linear

dependence between the reciprocal value of the adsorption  $1/\Gamma$ , and the reciprocal concentration  $1/c$ . From obtained adsorption isotherms the adsorption constants (B) and adsorption free energy ( $\Delta G$ ) of organic compounds can be calculated ( $\Delta G = -RT \ln(55.6B)$ ).

When comparing obtained adsorption constants of organic bases with their effective charges of nitrogen atoms, symbate correlations were found: the greater an effective charge of their nitrogen atoms is, the greater is their adsorbability. As an example, Fig. 1 shows the comparison of the adsorption constants of aromatic and heterocyclic amines adsorbed on silica gel and calcium hydroxyapatite with the effective charges of their nitrogen atoms. Fig. 2 illustrates the comparison of the adsorption energy of organic bases with the effective charges of their nitrogen atoms for silica gel, calcium hydroxyapatite, aluminium  $\alpha$ -oxide, magnesium oxide and zirconium oxide. It follows from these

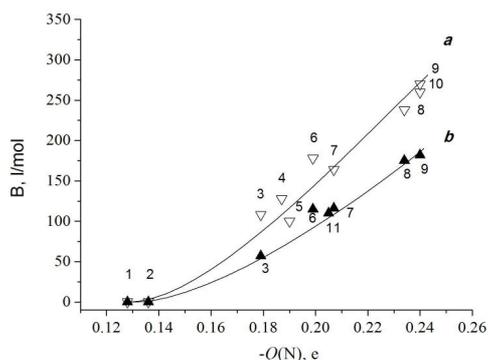


Fig. 1. Comparison of aromatic and heterocyclic amines adsorption constants for silica gel (a) and calcium hydroxyapatite (b) with effective charges of their nitrogen atom: benzamide (1), indole (2), 2-aminopyridine (3),  $\alpha$ -naphthylamine (4), diphenylamine (5), m-toluidine (6), aniline (7), pyridine (8),  $\alpha$ -picoline (9),  $\gamma$ -picoline (10), quinoline (11)

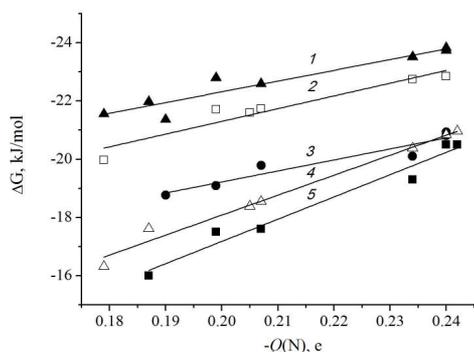


Fig. 2. Comparison of aromatic and heterocyclic amines adsorption energy for silica gel (1), calcium hydroxyapatite (2), aluminium  $\delta$ -oxide (3), magnesium oxide (4) and zirconium oxide (5) with effective charges of their nitrogen atom

data that observed adsorption energy is linearly correlated with the effective charges of nitrogen atoms of studied aromatic and heterocyclic amines.

In our opinion, such correlations can be explained if the adsorption of polar molecules in the polar adsorbent is considered to be the result of intermolecular interactions, predominantly through hydrogen bonds. As stated above, the total energy of molecular hydrogen-bonded complexes for the equilibrium interatomic distances often coincides with the electrostatic component of the interaction. Electrostatic interaction energy (E) of the adsorbate particles with an electrostatic field of adsorbent is generally determined by the following integral value:

$$E = \int \rho(\vec{r})V(\vec{r})d\tau, \quad (3)$$

where the integration is performed through the entire volume of molecule,  $\rho(r)$  is the density of the molecular charge,  $V(r)$  is the potential of the electrostatic field of the solvation complex.

The density of molecular charge  $\rho(\vec{r})$  can be presented as the sum M of effective charges  $Q_i$ ; then replacing the integration by summation to simplify the equation (4) one obtains:

$$E = \sum_i^M Q_i V_i(\vec{r}_i), \quad (4)$$

where  $V_i(\vec{r}_i)$  is the potential created by all the charges of the system except for the charge  $Q_i$ .

Isolating in the sum (4) the dominant member which is determined by the largest effective charge of adsorbate  $Q_N$  and the smallest distance between the point of this charge and the surface of the adsorbent, one obtains:

$$E = \sum_i^{M-1} Q_i V_i(\vec{r}_i) + Q_N V(\vec{r}), \quad (5)$$

where  $V(\vec{r})$  is the potential which is produced by all the charges of the system, excluding the charge  $Q_N$ .

When analysing the interrelation between adsorption energy and magnitude  $Q_N$ , one should consider that magnitude  $\Delta G$  (which is experimentally determined) is related to the sum of desolvation processes of «reaction» centres of the adsorbent and adsorbate, and their direct interaction as follows:

$$\Delta G = \Delta G_{\text{ads}} - \Delta G_{\text{solv}}, \quad (6)$$

The equation (5) can be used to approximate  $\Delta G_{\text{ads}}$  и  $\Delta G_{\text{solv}}$ ; then we obtain:

$$\Delta G_{\text{ads}} = \sum_1^{M-1} Q_i V_i(\vec{r}_i) + Q_N V(\vec{r}), \quad (7)$$

$$\Delta G_{\text{solv}} = \sum_1^{L-1} Q_i V_i^*(\vec{r}_i) + Q_N V^*(\vec{r}), \quad (8)$$

where  $V_i(\vec{r}_i)$  и  $V_i^*(\vec{r}_i)$  are the potentials of the fields for adsorption complex and solvation complex, respectively;  $L$  is the number of effective charges in solvation complex (in the general case  $L \neq M$ ).

The first terms of Eqs. (7) and (8) are necessarily dependent on charge  $Q_N$ , while the last terms depend on potentials  $V_i(r_i)$  and  $V_i^*(r_i)$ . However, their difference for the same  $Q_N$  exhibits much weaker dependence on its magnitude, i.e.:

$$\sum_1^{M-1} Q_i V_i(\vec{r}_i) - \sum_1^{L-1} Q_i V_i^*(\vec{r}_i) \approx \text{const.}$$

The combination of Eqs. (6), (7) and (8) yields:

$$\Delta G \approx \text{const} + Q_N \Delta V, \quad (9)$$

where  $\Delta V = V(\vec{r}) - V^*(\vec{r})$ .

Also, the potential difference  $\Delta V$  in Eq. (9) is independent of  $Q_N$ , while is determined by geometry of solvation and adsorption complexes. The magnitude of  $\Delta V$  is almost constant for a number of compounds which possess close composition and structure. Therefore, according to Eq. (9), a linear dependence could be expected to exist between the adsorption energy  $\Delta G$  and the largest effective charge of adsorbate  $Q_N$ .

Thus, the observed symbate relation between adsorption constants and  $Q_N$  agrees with the model of charged-controlled adsorption of polar organic compounds which implies that the energies of polar atoms interaction are directly proportional to their effective charges values [10]:

$$\Delta G_{\text{EXP}} = \Delta G_{12} - \Delta G_{13} - \Delta G_{23} \approx E_{12} - E_{13} - E_{23} \approx Q_1 Q_2 / r_{12} - Q_1 Q_3 / r_{13} - Q_2 Q_3^* / r_{23}, \quad (10)$$

where the subscripts 1, 2 and 3 denote adsorbent, adsorbate and solvent, correspondingly;  $\Delta G_{\text{EXP}}$  is the experimentally determined adsorption energy;  $\Delta G_{12}$  is the free energy of interaction between adsorbate

and adsorbent when no solvation exists;  $\Delta G_{13}$  and  $\Delta G_{23}$  are the solvation energies of adsorbent and adsorbate;  $E_{ij}$  is the Columbic energy;  $Q_i$  are the effective charges of atoms in «reaction» centres of adsorbent, adsorbate and solvent<sup>1</sup>, correspondingly; and  $r_{ij}$  is the interatomic spacing in adsorption and solvation complexes.

Equation (10) is very simplified and based on considering the process of the adsorption of polar organic compounds from aqueous solution onto polar surfaces as a result of substitution of a part of molecular solvation shell for adsorbent hydroxyl group. Since interaction of two atoms located near to each other and having the greatest charges predominates over all other possible interactions between charges and multipole moments, electrostatic interaction was approximated by columbic interaction of two point charges.

According to Eq. (10), the difference in adsorption properties of calcium hydroxyapatite, silica gel, aluminium, magnesium and zirconium oxides can be explained by the difference in effective charges of hydrogen atoms in surface OH-groups being essentially the adsorption centres for nitrogen containing molecules. As far as adsorption constants of organic bases are the largest for  $\text{SiO}_2$  and the smallest for zirconium oxide, we can conclude that effective charges of hydrogen atoms in OH-groups for adsorbents involved changes in series:



When comparing electronegativity values of atoms (P 2.1; Si 1.74; Al 1.47; Mg 1.23; Zr 1.22), it should be expected that in  $\equiv\text{POH}$  groups effective charge on hydrogen atom should be greater than that in  $\equiv\text{SiOH}$  groups. The point is that more electronegative atom of phosphorus should pull back electron density from neighbouring atoms to a greater extent than atoms of silicium in similar compounds. Disturbance of a given relationship is likely to be caused by influence of negatively charged  $\text{H}_2\text{PO}_4^-$  ions on calcium hydroxyapatite surface to form surface P-OH groups. To verify this presumption, quantum chemical modelling of  $\text{H}_3\text{PO}_4$  molecule and  $\text{H}_2\text{PO}_4^-$  anion was performed. The results of calculations by MNDO method showed that in comparison with acid molecule excess negative charge in anion reduces effective charge values of hydrogen atoms in  $\equiv\text{POH}$  groups from +0.246 to +0.182 [14].

<sup>1</sup> Aqueous solution is described by two effective charges  $Q_3$  and  $Q_3^*$ , which correspond to charges of oxygen and hydrogen atoms of  $\text{H}_2\text{O}$  molecule. Aromatic and heterocyclic amines can be adsorbed on oxides by means of hydrogen bonds from aqueous solutions because there is an excess of the charge on nitrogen atoms over a half of oxygen atoms charge in water molecules [12].

It is interesting to note that the model of charged-controlled adsorption allows explaining why surface OH-groups, and not calcium ions, take part in adsorption of organic bases on calcium hydroxyapatite. The effective charge of calcium atoms in calcium hydroxyapatite is certainly greater than that of hydrogen atoms in OH-groups. In the approximation of charged-controlled model this means that calcium ions must rather strongly interact with electronegative atoms of both water molecules and organic compounds ones. Since effective charge of oxygen atoms in water molecule is greater than that of nitrogen atoms in studied aromatic amines we should make a conclusion that molecules of nitrogen-containing organic bases are unable to expel water molecules from hydrated shells of calcium ions, and therefore are not absorbed. It should be also taken into account that interaction of calcium ions with water molecules has predominantly electrostatic character and therefore two O2p(n)-orbitals of oxygen atom in water molecule take part in interaction. In contrast, when hydrogen bonds are formed with the OH-groups of the adsorbent, such interaction predominantly involves one O2p(n)-orbital of the oxygen atom.

As the charge of nitrogen atom is larger in its absolute values than a half of charge value of oxygen atom in water molecule, nitrogen containing molecules can compete with water molecules and can be selectively absorbed on hydroxyl groups of calcium hydroxyapatite. These conclusions are consistently explained by a number of experimental data and the conclusion made about the fact that nitrogen-containing organic compounds adsorbed on calcium hydroxyapatite predominantly due to forming of hydrogen bonds with surface  $\equiv\text{POH}$  groups.

It is necessary to note that the conclusion about the possibility of a linear correlation  $\Delta G(Q_N)$  is true primarily in those cases where the adsorbate molecule has only one atom with a sufficiently large charge and we can ignore the influence of the electric multipole moments. A more rigorous description of the relationship  $\Delta G(Q_N)$  requires consideration of the charge redistribution in the molecule under the influence of the electric field of the adsorbent [8]. In addition to this fact, also we must take into account the statistical nature of adsorption and solvation processes: the probability of required orientation adsorbate particle is determined by its size, inertial properties, etc. It became clear that precise theoretical calculation of the adsorption energy is a rather time-consuming task and cannot be viewed as a method of prediction of the surface

properties of substances. In our opinion, for practical purposes it is more convenient to use the correlations  $\Delta G(Q_N)$ .

### Conclusions

The selective adsorption of polar organic compounds on polar adsorbents is caused by weak chemical interactions via hydrogen bonds with adsorbents and water molecules. The most promising way to predict the surface activity of a substance is through a comparison of the electronic structures of the adsorbate and adsorbent. From this viewpoint, the orbital symmetry, effective charges on the atoms and molecular orbital energies are the general parameters which determine the result of surface interaction. It is proposed and experimentally confirmed that chemisorption can be considered in the approximation of two models: adsorption controlled by quantities of effective charges of adsorbate, solvent and adsorbent atoms, and adsorption controlled by orbital interactions of their frontier orbitals.

Our studies indicate that adsorption of the compounds with polar functional groups onto wide-gap polar adsorbents is charge-controlled. It was shown that the adsorption of organic compounds onto wide-gap polar adsorbents is controlled by the values of the greatest effective charges on the atoms which take part in the formation of surface hydrogen bonds.

The difference in adsorption properties of calcium hydroxyapatite, silica gel, aluminium, magnesium and zirconium oxides can be explained by the difference in effective charges of hydrogen atoms in surface OH-groups being essentially adsorption centres for nitrogen containing molecules. As far as adsorption constants of organic bases are the greatest for silica gel and the smallest for zirconium oxide, we can conclude that effective charges of hydrogen atoms in OH-groups for adsorbents involved decrease in the following series:  $\equiv\text{SiOH}$ ,  $\equiv\text{P(O)OH}$ ,  $\equiv\text{AlOH}$ ,  $-\text{MgOH}$ , and  $\equiv\text{ZrOH}$ .

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## ЗАРЯДОВО-КОНТРОЛЬОВАНА АДСОРБЦІЯ НА ШИРОКОЗОННИХ АДСОРБЕНТАХ

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*Розглянуто сучасні уявлення про адсорбцію полярних органічних сполук на полярних широкозонних адсорбентах з полярного розчинника. Запропоновано апроксимувати енергії адсорбційних і сольватаційних взаємодій через величини найбільших ефективних зарядів атомів молекул адсорбенту і розчинника. На підставі адсорбційних вимірів розраховані енергії адсорбції ряду гетероциклічних нітрогеновмісних сполук і ароматичних амінів на оксидах Si, Al, Mg, Zr і кальцій гідроксоапатиту. Показано, що енергії адсорбції органічних сполук лінійно корелюють із ефективними зарядами їх атомів нітрогену. Запропоновано пояснення таких кореляцій на підставі уявлень про домінуючий характер електростатичних взаємодій. Показано, що різниця в адсорбційних властивостях широкозонних полярних адсорбентів може бути пояснена різницею у ефективних зарядах атомів гідрогену в поверхневих OH-групах, які являються центрами адсорбції для нітрогеновмісних молекул. Зроблено висновок, що ефективні заряди атомів гідрогену у OH-групах досліджених адсорбентів зменшуються в ряду:  $\approx \text{SiOH}$ ,  $\approx \text{P(O)OH}$ ,  $\approx \text{AlOH}$ ,  $\approx \text{MgOH}$ ,  $\approx \text{ZrOH}$ .*

**Ключові слова:** адсорбція, оксиди, гідроксоапатит, полярні органічні сполуки, електростатична взаємодія.

## CHARGE-CONTROLLED ADSORPTION ON WIDE-GAP POLAR ADSORBENTS

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*The contemporary theories dealing with the adsorption of polar organic compounds from polar solvent on polar wide-gap adsorbents are reviewed. It is proposed to approximate the energies of adsorption and solvation interactions by means of the magnitude of the highest effective charges of the atoms which constitute the adsorbate and the solvent. The adsorption energies of a number of heterocyclic nitrogen-containing compounds and aromatic amine on Si, Al, Mg, Zr oxides and calcium hydroxyapatite are calculated based on adsorption measurements. It is shown that the adsorption energies of organic compounds linearly correlate with the effective charge of their nitrogen atoms. An explanation of these correlations is proposed based on the concept of the dominant nature of electrostatic interactions. It is shown that the difference in adsorption properties of wide-gap polar adsorbents can be explained by the difference in effective charges of hydrogen atoms in surface OH-groups being adsorption centers of nitrogen-containing molecules. It is concluded that the effective charges of hydrogen surface atoms in OH-groups of adsorbents involved decrease in the following series:  $\approx \text{SiOH}$ ,  $\approx \text{P(O)OH}$ ,  $\approx \text{AlOH}$ ,  $\approx \text{MgOH}$ , and  $\approx \text{ZrOH}$ .*

**Keywords:** adsorption; oxides; hydroxyapatite; polar organic compounds; electrostatic interaction.

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