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ADSORPTION PROPERTIES OF LOW-BANDGAP SOLIDS

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Abstract. Adsorption of aromatic and heterocyclic compounds from aqueous solutions on Mn(III), Pb(IV), V(V) oxides and activated carbon under static conditions has been studied. The energies of occupied and unoccupied orbitals have been used as correlation parameters between the electronic and adsorptive properties of organic molecules. Frontier-controlled adsorptive mechanism is postulated for interpretation of the observed correlations for the specific adsorption of organic compounds on low-bandgap adsorbents.

Keywords: adsorption, Mn(III), Pb(IV) and V(V) oxides, activated carbon, organic compounds, frontier orbitals.

1. Introduction

The ability to predict the adsorption properties of a given adsorbent on the basis of the physicochemical properties of the adsorbate is an important objective in adsorbent-adsorbate interaction studies. At present various parameters for predicting non-specific and specific adsorption of organic compounds were proposed [1]. In our opinion, the forecasting of specific adsorption activity is best approached from a comparison between the electronic structures of the adsorbate and adsorbent. In this respect, their electronic properties are of paramount importance since they are: 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 of visualizing many of the 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:

$$\Delta E = \sum H_{ij}^2/(e_i - e_j) \qquad (1)$$

where H_{ij} is the matrix of the interaction functions of orbitals, e_i and e_j are the energies of the MOs.

According to Eq. (1), the 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 [2]. As it was noted for the first time by G. Klopman [3], two approaches can be distinguished: (i) for rather large differences in energy, $e_i - e_j$, the quantity ΔE is mainly determined by the value H_{ij}; (ii) for rather small energy differences, the interaction between the HOMO and LUMO becomes predominant. By analogy, two approaches can be followed when specific adsorption is considered [4, 5]: the charge-controlled adsorption, when the interaction is determined by the atom charges of the adsorbate and adsorbent; and the frontier-controlled adsorption, when the frontier orbital energies of the adsorbate and adsorbent are close to each other. A large number of examples in which a perturbation theory has been applied to the description of specific adsorption on a solid surface were considered in a number of studies (cf. [6, 7]).

At present it is reliably known that the 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 [8]. Frontier-controlled adsorption is a characteristic feature of low-bandgap adsorbents.

In this study, the highest oxides of manganese, vanadium, lead and activated carbon were selected as subjects of research. Despite of clear-cut distinction in electronic constitution they have rather close properties. They are characterized by the relatively large conductance and they intensively absorb light in the visible region of a spectrum, which indicates that the energies of their occupied and unoccupied levels are close enough to each other. It could be supposed that aromatic compounds with appropriate orbitals can be adsorbed both on oxides and activated carbon due to chemical interaction. For example, a possibility of selective chemical adsorption of some chlorophenols on manganese oxide was proved by H. Ulrich and A. Stone [9]. Similar conclusions about the possibility of specific adsorption of aromatic compounds on activated carbon were made by J. Mattson *et al.* [10], E. Wright and A. Powell [11], H. Tamon and M. Okazaki [12, 13]. In the studies of the relationships between the adsorbability and such parameters as solute solubility, molecular refraction or molar volume I. Abe *et al.* [14] found that the adsorbability of aromatic compounds on the activated carbon is generally higher than that of other organic compounds. This phenomenon was explained by the electronic and resonance effects resulting from the strong interaction of aromatics with *p*-electrons in the graphitic structure of activated carbon. Apparently the organic compounds with appropriate orbital can be adsorbed by carbon not only due to the dispersion attraction, but also as a result of a chemical interaction. To verify this hypothesis, it is necessary to compare data on the adsorption of organic compounds with energies of their frontier orbitals [4, 5]. In the present study, the adsorption of a number of aromatic and heterocyclic nitrogen- and oxygen-containing hydrocarbons from their aqueous solutions on oxides and activated carbon under static conditions has been studied. The UV electronic spectra of the adsorbed compounds have been employed to identify adsorption interactions.

2. Experimental

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^3) of the solution containing $1 \cdot 10^{-3}$ M of the organic compounds. A background electrolyte (0.1 M KCl) was added to the solutions to maintain a constant ionic strength. The suspensions were allowed to stand for 24 h with a periodic stirring and were then centrifuged. The concentrations of the solutions were determined spectrophotometrically with corrections for evaporation of highly volatile compounds and the solubility of vanadium pentaoxide being made *via* blank experiments. Values of adsorption were calculated as $(C_0 - C)/C_0 \cdot 100$ %, where C_0 and C – initial and equilibrium concentrations of organic compounds in the solution. Reproducibility of adsorption measurements was verified by means of parallel experiments. The standard deviation for adsorption measurements did not exceed 0.25 μmol/g. All measurements were performed at 291 ± 2 K.

The organic compounds studied were purified before use either by distillation or recrystallisation. As the adsorbents, the birch activated carbon "BAU" ("Sorbent", Russia), synthetic *g*-MnO(OH) (manganite), V_2O_5 and PbO_2 were used. The specific surface area of adsorbents powder as determined by BET methods based on the low-temperature adsorption of nitrogen was (in m^2/g) 18.2 for *g*-MnO(OH), 1.5 for PbO_2, 14.2 for V_2O_5 and 740 for activated carbon.

The UV reflection spectra of the adsorbed compounds were measured *via* a standard procedure employing Specord M-40 spectrophotometer. The organic compounds were deposited onto adsorbent surface in a state of aqueous or alcohol solutions. The oxides and activated carbon were not subjected to additional dehydration by evacuation or heating. Values of ionization potentials and electronic transition energies of the organic molecules were taken from the reference data.

3. Results and Discussion

3.1. Approximating of Molecular Orbital Energies

The values e_i and e_j in Eq. (1) are known to have the meaning of the theoretical values of the MO energies expressed by the Hartree-Fock single-electron approximation. However, for practical purposes, it is easier to use the experimental characteristics of the electron levels rather than their theoretical values. These characteristics may be obtained by a photoelectron spectroscopy and absorption spectroscopic method. In this case, the values of e_i and e_j are linked to the ionization potentials and the electron transition energies *via* the following expressions:

$$I_{V,i} = -(e_I + E_{rel}) \quad (2)$$

$$\Delta E_{ij} = e_j - e_i + E'_{rel} \quad (3)$$

where $I_{V,i}$ is the vertical ionization potential, ΔE_{ij} is the vertical electron transition energy between the HOMO and LUMO, E_{rel} and E'_{rel} are the relaxation energies of the given orbitals.

From Eqs. (2) and (3) it follows that:

$$e_{HOMO} = -(I_V + E_{rel})$$

$$e_{LUMO} = -(I_V - \Delta E_{ij} + E_{rel} + E'_{rel}) =$$

$$= e^*_{LUMO} - (E_{rel} + E'_{rel})$$

where e^*_{LUMO} is the "conditional" energy of LUMO without correction by relaxation energies:

$$e^*_{LUMO} = -(I_V - \Delta E_{ij})$$

It should be mentioned that the values of I_V and ΔE_{ij}, which are measured under vacuum conditions are changed significantly when a solvent is present in the system. However, these changes are caused not by changes in the values of e_i but result from additional relaxation processes. Apparently, any comparison of the I_V or ΔE_{ij} values for different molecules can only be carried out within the accuracy of their ΔE_{rel} and $\Delta E'_{rel}$ values. For this reason, we have used I_V and e^*_{LUMO} as the simplest parameters characterizing HOMO and LUMO molecules [4, 5].

3.2. Adsorption Properties of Manganese(III), Lead(IV) and Vanadium(V) Oxides

Studies of the adsorption of organic compounds on the highest oxides of manganese, lead and vanadium are complicated by their possible oxidizing. The products of oxidation can remain on a surface of oxide or can be desorbed in the solution. If optically activated compound is desorbed, then one can observe the change of electronic absorption spectra of the solution. We observed similar phenomena in the studies of adsorption of some organic compounds on examined oxides. It was found that most aromatic amines and alcohols are rather rapidly oxidized by manganese, lead and vanadium oxides. The electronic absorption spectra of their solutions quickly undergo considerable qualitative changes. For 1-naphthylamine and 1-naphthol, a complete extraction from the solution was observed. Besides, the decrease of a portion of oxides in ten times and the increase in concentrations of 1-naphthylamine and 1-naphthol does not influence an extent of their extraction, indicating that their chemical transformations take place. The carboxylic acids and compounds with NO_2-groups are rather strongly adsorbed by manganese and vanadium oxides and do not change their absorption spectra. An exception was found for nitromethane and 2-nitro-2-methylpropane adsorption. Their electronic absorption spectra are changed after the contact with oxides of manganese(III) and vanadium(V), because the nitrozo-group appears in the solution. It was detected that $p \rightarrow p*$ absorption band is displaced to 220 nm and a maximum $n \rightarrow p*$ band at 260 nm had also disappeared.

It is seen that no correlation exists between the chemical composition and adsorption of organic compounds. This fact is that one should expect from the viewpoint of perturbation MO theory: the chemical reactivity follows essentially from the difference in the MO energy of frontier orbitals. By comparison of ionization potentials of compounds which change their absorption spectra after the addition to oxides it was shown that, in general, the compounds with ionization potential smaller than 8 eV are oxidized. The exceptions are some compounds with relatively large ionization potentials, for example: acrylonitrile (10.92 eV), nitromethane (11.29 eV), picric acid (10.27 eV). As their LUMO energies are the highest among the compounds studied, we supposed that the extent of their destruction should correlate not with the ionization potential, but with energies of the vacant orbital.

In Figs. 1-3 the results of graphic comparison of adsorption of the organic compounds with the energies of their LUMO and HOMO are shown. Compounds changing the absorption spectra are indicated by marks. To compare the adsorbability of compounds, the magnitudes of their adsorption under identical conditions at equal initial concentration of solutions ($1 \cdot 10^{-3}$ mol/l) were used. The examination of the adsorption isotherms was found to be less informative because the oxidation of organic compounds can take place with the increase of their concentrations.

When constructing Figs. 1-3, we assumed that the adsorption depends monotonically on the changes of LUMO and HOMO energies of adsorbed compounds. In this case epy data set could be interpreted in the framework of the molecular orbitals perturbation theory: the nearer are the energies of frontier orbitals of an adsorbent and adsorbate, the more gain is in energy of their interaction.

It was found that correlations between adsorption and energies of frontier orbitals for *g*-MnO(OH) and V_2O_5 are similar (Figs. 1 and 2). However, certain distinctions in adsorption of pyridine, picolines and lutidines were observed. These compounds with first ionization potentials of *ca.* 9 eV are adsorbed on *g*-MnO(OH) but are not adsorbed on V_2O_5. This behavior could possibly be attributed to lower values of HOMO energy of Mn(III) oxide which is also supported by the photoelectron spectroscopy data for manganese and vanadium oxides [15-17]. According to these data, HOMO of V_2O_5 formed by 3*p*-levels of vanadium(V) cation is located by ~0.5 eV higher than HOMO of Mn_2O_3 formed by e_g^*-levels of Mn(III) cation.

According to data in Fig.3, compounds with $I_V < 8.2$ eV are quickly oxidized by PbO_2. The compounds with $I_V > 8.2$ eV are adsorbed on lead dioxide antisymbately to values of their ionization potentials: magnitudes of adsorption are decreased and are equal to zero value at 9 eV. Compounds with low values of energies LUMO (2,4-dinitrotoluene, *p*-nitrobenzaldehyde, nitromethane, acrylonitrile, 2-nitro-2-methylpropane, picric acid) are not adsorbed on PbO_2.

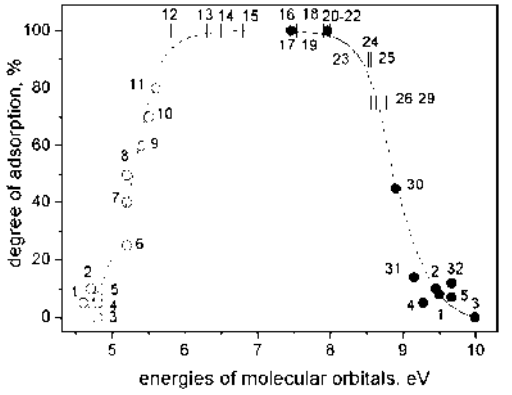

Fig. 1. The comparison of the organic compounds adsorption on *g*-MnO(OH) with energies of their unoccupied (blank points) and occupied orbitals (filled points): 4-picoline (1); benzamide (2); nitrobenzene (3); furfurol (4); pyridine (5); 2,4-dinitrotoluene (6); cyanobenzene (7); benzene carboxylic acid (8); *p*-nitrobenzaldehyde (9); *p*-nitrobenzoic acid (10); 3,5-dinitrobenzoic acid (11); acrylonitrile (12); 2-nitro-2-methylpropane (13); picric acid (14); nitromethane (15); *N*,*N*-diethylaniline (16); 1-naphthylamine (17); diphenylamine (18); *m*–toluidine (19); indole (20); 1-naphthol (21); aniline (22); *p*-methylphenol (23); phloroglucinol (24); pyrocatechin (25); resorcin (26); quinoline (27); phenol (28); pyrogallol (29); 2,6- lutidine (30); 2-picoline (31) and benzaldehyde (32)

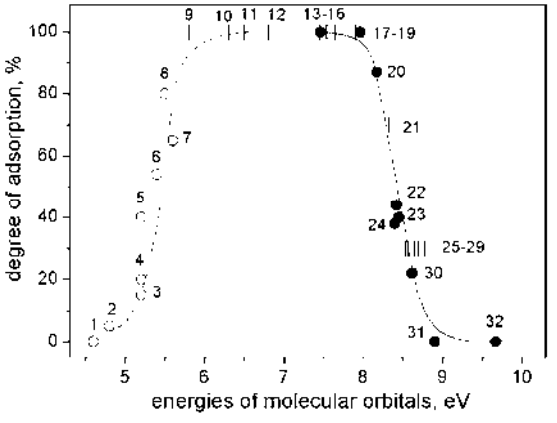

Fig. 2. The comparison of the organic compounds adsorption on V_2O_5 with energies of their unoccupied (blank points) and occupied orbitals (filled points): 4-picoline (1); nitrobenzene (2); 2,4-dinitrotoluene (3); cyanobenzene (4); benzene carboxylic acid (5); *p*-nitrobenzaldehyde (6); 3,5-dinitrobenzoic acid (7); *p*-nitrobenzoic acid (8); acrylonitrile (9); 2-nitro-2-methylpropane (10); picric acid (11); nitromethane (12); *N*,*N*-diethylaniline (13); 1-naphthylamine (14); diphenylamine (15); *m*–toluidine (16); indole (17); 1-naphthol (18); aniline (19); 2,8-dimethylquinoline (20); *p*-methylphenol (21); anisole (22); 2-aminopyridine (23); dibenzofuran (24); pyrogallol (25); resorcin (26); phenol (27); phloroglucinol (28); pyrocatechin (29); quinoline (30); 2,6- lutidine (31) and pyridine (32)

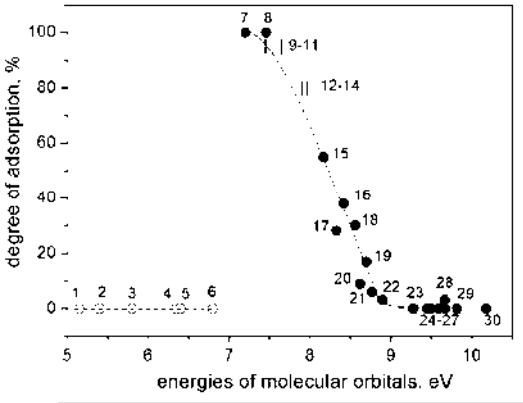

Fig. 3. The comparison of the organic compounds adsorption on PbO_2 with energies of their unoccupied (blank points) and occupied orbitals (filled points): 2,4-dinitrotoluene (1); *p*-nitrobenzaldehyde (2); nitromethane (3); acrylonitrile (4); 2-nitro-2-methylpropane (5); picric acid (6); 1-naphthylamine (7); 1-naphthol (8); *N*,*N*-dimethylaniline (9); diphenylamine (10); *m*-toluidine (11); indole (12); 1-naphthol (13); aniline (14); 2,8-dimethylquinoline (15); anisole (16); *p*-methylphenol (17); resorcin (18); quinoline (19); phenols (20); pyrogallol (21); 2,6-lutidine (22); furfurol (23); benzamide (24); γ-picoline (25); pyridine (26); benzene carboxylic acid (27); benzaldehyde (28); cyanobenzene (29) and *p*-nitrobenzoic acid (30)

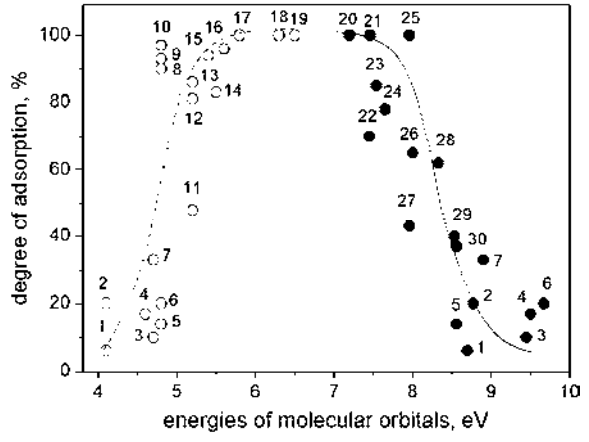

Fig. 4. The comparison of the organic compounds adsorption on the active carbon with energies of their unoccupied (blank points) and occupied orbitals (filled points): phenol (1); pyrogallol (2); benzamide (3); 4-picoline (4); phloroglucinol (5); pyridine (6); 2,6-lutidine (7); furfurol (8); nitrobenzene (9); quinoline (10); benzonitrile (11); 1,3-dinitrobenzene (12); 2,4-dinitrotoluene (13); *p*-nitrobenzoic acid (14); *p*-nitrobenzaldehyde (15); 3,5-dinitrobenzoic acid (16); acrylonitrile (17); 2-nitro-2-methylpropane (18); 2,4,6-trinitrophenol (19); benzidine (20); *a*-naphthylamine (21); *N*,*N*-dimethylaniline (22); diphenylamine (23); *m*-toluidine (24); 1-naphthol (25); aniline (26); 1-methylnaphthalene (27); *p*-cresol (28); pyrocatechol (29) and resorcin (30)

Distinctions in adsorption of organic compounds with $e^*_{LUMO} > 5$ eV on lead, manganese and vanadium oxides could possibly be attributed to lower values of both LUMO and HOMO energies of PbO_2 which is also supported by the spectroscopy data. According to photoelectron spectroscopic data [18], in a valence region of a spectrum PbO_2 two separate bands of electrons emissions with average energies 3 and 9 eV below than the Fermi level of oxide are observed. The first band has the well-expressed shoulder at ~4.5 eV. According to calculations, the peaks at 3 and 4.5 eV are conditioned by the removal of electrons, accordingly, with Pb6*p*+O2*p* and O2*p*(*n*)-levels. Relatively to vacuum level binding energies of these levels are equal to, accordingly, 9 and 10.5 eV. The threshold wavelength of absorption band in UV spectrum of PbO_2 is equal to 15000 cm^{-1} (~1,9 eV). Therefore, LUMO of PbO_2 formed by σ*-orbitals of Pb6*p*+O2*p* level is located only by ~1.9 eV higher than HOMO of oxide and is equal to ~7 eV relatively to the vacuum level. Thus, compounds with low values of LUMO energies could not be adsorbed on PbO_2 surface, whereas, on the contrary, compounds with low values of ionization potentials can be adsorbed and irreversible oxidized by PbO_2.

To explain the regularity of oxidation of organic compounds with the ionization potential smaller than 9 eV by examined oxides we had to suppose that the probability of complete transfer of an electron from adsorbed molecules to the metal cations should be higher, the closer are their orbital energies. It can be supposed that at $I_V > 9$ eV only the partial transfer of electronic density from the adsorbate MO to the adsorbent orbital takes place. This is sufficient enough for the formation of donor-acceptor bond, but is insufficient for reorganization of chemical bonds. The adsorption of compounds with $e^*_{LUMO} > 5$ eV due to the strong donor-acceptor interactions should take place with the transfer of electronic density from the oxide to the unoccupied orbital of organic molecules. It is probable that the increase of the electronic density in the antibonding orbital leads to the destruction of the chemical bond and molecules as a whole.

From the thermodynamic point of view the energy of adsorption from the solution can be expressed as the sum of several components:

$$\Delta G_{EXP} = \Delta G_T - \Delta G_R$$

where ΔG_{EXP} is the experimentally observed adsorption energy gain; ΔG_T is the "true" free energy of the interaction between the adsorbent and adsorbate; ΔG_R is the energy of reorganization of electronic structure of the adsorbed molecule and adsorption site.

The magnitude ΔG_T is determined by the orbital interaction between the adsorbent and adsorbate and can correlate with energies of their frontier orbitals. Energy of reorganization ΔG_R is determined by the particular structure of an adsorbed molecule and also by the reaction centres of the adsorbent surface. Therefore oxidative ability of compounds will correlate with the energies of their highest occupied orbital only in the case when their reorganization energies are approximately the same. Apparently, such structurally similar compounds as aromatic amines, alcohols and acids have approximately equal reorganization energies.

The proposed model of adsorption can explain the chemical instability of the nitromethane and 2-nitro-2-methylpropane, where the transformation of the nitro-group to the nitrozo-group takes place after the contact with oxides of manganese(III) and vanadium(V). The LUMO of the nitromethane is the three-centric p^*-orbital of NO_2-group with the energy equal to 6.8 eV. Due to the strong donor-acceptor interaction, the electronic density in p^*-orbital of nitromethane is increased and the bond between nitrogen and oxygen atoms is broken.

3.3. Adsorption Properties of Activated Carbon

The result of comparison of the adsorption data for activated carbon with LUMO and HOMO energies of organic compounds is shown in Fig. 4. It is found that adsorption values for all aromatic amines and polyatomic alcohols steadily correlate with the first vertical ionization potentials of their molecules. The adsorption of these compounds is decreased with the reduction of the HOMO energy of their molecules. This correlation can be explained by the interactions between HOMO of adsorbate and LUMO of carbon (see filled points in Fig. 4).

The data for heterocyclic compounds, carboxylic acids and nitro-containing aromatic compounds, with ionization potentials higher than 8.5 eV, do not obey this correlation. Apparently, the interactions between HOMO of carbon and LUMO of adsorbates are more preferable for their molecules. Therefore adsorption data for such compounds are shown in Fig. 4 with their LUMO energies (see blank points).

For the first time conclusions about the possibility of adsorption of nitro-substituted aromatic compounds on activated carbon by means of their low-lying acceptor orbitals were made by J. Mattson *et al.* [10]. Based on the data of internal reflectance in infrared spectra of adsorbed phenol and nitrophenols, the authors concluded that hydrogen bonding with carbon polar groups is small and cannot be regarded as the primary cause for their adsorption. The charge-transfer interaction of their aromatic ring with the surface of activated carbon was considered to play the major role in these processes. It was concluded that nitrophenols are adsorbed on activated

carbon by a donor-acceptor complex mechanism involving carbonyl oxygen of the carbon surface acting as the electron donor and the aromatic ring of the solute acting as an acceptor.

Similar conclusions about the possibility of specific adsorption of aromatic compounds substituted by electron-donating groups on the activated carbon were also made by H. Tamon and M. Okazaki [12, 13]. It was found that the adsorption of such compounds on the activated carbon can be related to the energy difference between their HOMO and LUMO of the adsorbent. For chloro- and nitrophenols A. Oskouie *et al.* [19] established the relationship between their electron density and adsorption capacity on the activated carbon. It was concluded that HOMO electron densities of both the adsorbate and the adsorbent are also the major factors which determine the value of the Freundlich exponent for the phenolic adsorbate – carbonaceous adsorbent systems.

According to the data of J. Mattson *et al.* [10], the infrared spectra clearly reveal that nitro- and hydroxyl-groups of phenolic compounds are not involved directly in the solute-carbon interaction. In the present study, the role of *p*-electronic interactions was investigated by the methods of the reflectance electron spectroscopy. It is found that the adsorption of aromatic amines and polyatomic alcohols on the activated carbon is accompanied by non-proportional blue or red shifts of $n \rightarrow p^*$ and $p \rightarrow p^*$ absorption bands, as compared with their spectra in water solutions and on the surface of silica, alumina or magnesium oxide. For such compounds as phenol, pyrogallol, phloroglucinol, benzamide, 4-picoline and pyridine that are adsorbed on the activated carbon from aqueous solutions comparatively weakly we found no fundamental changes in their electronic spectra.

As an example in Fig. 5 UV spectra of adsorbed 1-naphthylamine, resorcin and quinoline on the activated carbon and MgO are shown. It is known that polar organic compounds are adsorbed on MgO *via* weak hydrogen bonding. Therefore spectra of organic compounds on the surface of MgO are useful for comparative analysis.

It is found that position and intensities of absorption bands in the spectrum of 1-aphthylamine and resorcin after adsorbtion on carbon fundamentally change. Their molecules have rather highly located HOMO which can be involved in the interactions with unoccupied carbon orbitals. The transfer of electron density from adsorbed molecules to carbon leads to the displacement of their $p \rightarrow p^*$ absorption bands. In addition, the electric dipole moments of molecules, associated with the electron transfer, change in such a way that the intensities of the associated absorption bands also undergo appreciable changes (see curves a-d in Fig. 5).

In contrast to spectra of 1-aphthylamine and resorcin, the position of short-wave absorption band at 45000 cm^{-1} of adsorbed quinoline does not change (curves e, f in Fig.5). Therefore the spectra of quinoline on carbon and magnesia were normalized in comparison with its short-wave absorption band. It is found that the intensity of long-wavelength absorption band of quinoline adsorbed on carbon becomes lower. As quinoline is characterized by rather lowly located LUMO, we conclude that its molecules are adsorbed *via* unoccupied p^*-orbitals. Reduction of intensities of the $n \rightarrow p^*$ and $p \rightarrow p^*$ absorption bands of the adsorbed quinoline testifies that its lowly located unoccupied orbital is involved to the interactions with occupied carbon orbitals.

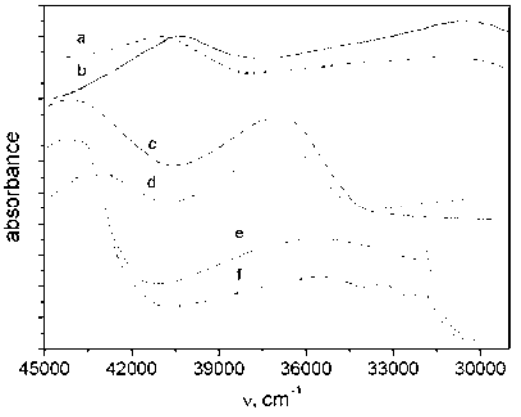

Fig. 5. UV spectra of 1-naphthylamine (a, b), resorcin (c, d) and quinoline (e, f) adsorbed on MgO (a, c, e) and the activated carbon (b, d, f)

Thus, spectroscopic data give evidence of the fact that *p*-electrons of aromatic molecules can participate in the formation of the chemical bond with the activated carbon. As the effect of the shift of $p \rightarrow p^*$ absorption bands was observed not for all studied compounds, it could be assumed that this interaction is rather selective and is determined by the values of HOMO and LUMO of the adsorbed molecules.

It is also necessary to mention that the adsorbability of polar compounds from aqueous solutions depends on energies of their aquation. It is rather problematic to determine the magnitudes of aquation energies as it requires taking into consideration the structure of formed adsorptive complexes. In fact, if the adsorption of, for example, aniline or phenol by means of their *p*-electrons of benzene rings takes place without change of their hydrated shells around polar OH– and NH_2–groups, then for the calculation of the proper adsorption energy it is necessary to take into account only the part of the hydration energy which corresponds to *p*-electrons of their molecules. Such estimations are possible only on the theoretical basis. For the practical

prediction of surface properties of a substance it would be of interest to detect correlations directly for experimental values of adsorption, which should certainly be measured in some identical conditions.

4. Conclusions

Thus, the most aromatic compounds are rather selectively adsorbed on the activated carbon and manganese(III), lead(IV) and vanadium(V) oxides. Though metal oxides and carbon have clear-cut distinction in the electronic constitution, these solids have rather narrow width of a band-gap and therefore aromatic compounds can be adsorbed on their surfaces not only due to a dispersion attraction or hydrogen bonding but also due to specific chemical interaction. From the comparison of the adsorption data and frontier orbital energies it is found that adsorption values for all aromatic amines and polyatomic alcohols steadily correlate with the first vertical ionization potentials of their molecules. The adsorption of these compounds decreases with the reduction of the highest occupied molecular orbital energy of their molecules. This correlation can be explained by the overlapping between HOMO of the adsorbate and LUMO of the oxide surface. The data for heterocyclic compounds, carboxylic acids and nitro-containing aromatic compounds, with ionization potentials higher than 9 eV, do not obey this correlation. Apparently the overlapping between HOMO of oxides or the activated carbon and LUMO of such adsorbates is more preferable for their molecules. Adsorption values for such compounds correlate with their LUMO energies. The observed regularities allow everyone to predict the adsorption properties of the highest oxides of manganese, lead, vanadium and activated carbon as well as any other low-bandgap solids.

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АДСОРБЦІЙНІ ВЛАСТИВОСТІ ВУЗЬКОЗОННИХ ТВЕРДИХ ФАЗ

Анотація. *Вивчена адсорбція ароматичних і гетероциклічних сполук з водних розчинів на оксидах Mn(III), Pb(IV), V(V) та активованому вугіллі за статичних умов. Енергії зайнятих і вільних орбіталей використані як параметри кореляції між електронними і адсорбційними властивостями органічних молекул. На основі моделі орбітально-контрольованої адсорбції надано пояснення спостережуваним кореляціям для специфічної адсорбції органічних сполук на вузькозонних адсорбентах.*

Ключові слова: *адсорбція, оксиди Mn(III), Pb(IV) і V(V), активоване вугілля, органічні сполуки, граничні орбіталі.*