Specific Adsorption of Aspartic Acid on Iron (III) and Nickel (II) Oxides

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Abstract

The dependences of zeta – potential and adsorption of aspartic acid on NiO and Fe_2O_3 oxides were investigated as a function of aspartic acid concentration, pH and adsorption time using microelectrophoresis and potentiometric titration methods. Shifting of pH_{IEP} (the isoelectric point or IEP) towards the acid zone for Fe_2O_3 and towards the base zone for NiO in the solutions of aspartic acid in comparison with HCl shows the presence of specific adsorption of aspartic acid anion and cation forms on the surfaces of Fe_2O_3 and NiO oxides, respectively. The complexation process of Fe(Ⅲ) ions with aspartic acid in the bulk solution and on the oxide surface was examined by spectrophotometer. It was determined that Fe(Ⅲ) ions form complexes with aspartic acid in the bulk solution.

Introduction

Currently, a lot of investigations have been devoted to the study of colloid-chemical mechanisms of the process run in the dispersion systems containing biologically active substances (BAS). It is caused by the significant role which such systems play in the vital activity of plant and animal organisms. BAS are widely used in such spheres as medicine, pharmacology, agriculture and food industry. Study of interactions in the given systems contributes greatly to the development of the theory of the BAS specific adsorption on the solid surfaces [1-4]. One of the most important BAS are proteins. Proteins are complex natural polymers containing different aminoacids, which determine the character of proteins interactions with a surface. Therefore, the study of the specific adsorption mechanism of the primary aminoacids on the model systems depending on their character and acid-base properties is of vital interest.

Metal oxides can be used as model systems because their electrosurface properties within the aqueous solutions of simple electrolytes are well known.

The main interest has Fe_2O_3 oxide as iron is a part of blood cells therefore it is called "life metal". Another major problem arises due to removing toxic compounds from the organisms, such as nickel and its oxides. For example interaction of nickel with aminoacids leads to severe allergic reactions in the humane organism.

The aim of the given study is the experimental investigation of the specific adsorption of the primary BAS: aspartic acid, glycine, asparagines on the surface of nickel (II) and iron (III) oxides depending on the composition of the aqueous phase (concentration of aminoacids, pH) and a time of adsorption.

Despite many works studying disperse systems containing BAS its mechanism of interactions with a solid surface is still not clarified. In this work electrokinetic and adsorptive properties of iron (III) and nickel (II) oxides in aspartic acid aqueous solutions are studied. Also complexation processes in the system aspartic acid (AA) + Fe^{3+} are under investigation.

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Experimental

All the chemicals and other reagents used during the study were of analytical grade. For preparation of solutions and experiments deionized water was used. Powders of NiO, Fe_2O_3 oxides and aqueous solutions of aminoacids: glycine, and L - aspartic acid and simple electrolytes (HCl, KOH, KCl) were used as the objects. L - aspartic acid concentrations were used such as $1 \cdot 10^{-2}$, $5 \cdot 10^{-3}$, $1 \cdot 10^{-3}$, $5 \cdot 10^{-4}$, $1 \cdot 10^{-4}$, $5 \cdot 10^{-5}$, $1 \cdot 10^{-5}$ mol/l. Concentrated L-aspartic acid solutions were prepared using the exact weight and more diluted solutions were made by the progressive dilution method. pH was changed by adding HCl or KOH, respectively. The following pH values in aqueous L - aspartic acid solutions were used 3,0; 3,5; 4,0; 4,5; 5,0; 5,5; 6,0. Concentrations prepared were checked using electroconductivity meter and titration methods.

Adsorption of the aminoacids was determined according to change of their concentrations before and after adsorption. Concentration of aminoacids was measured using titration with alkali in the presence of phenolphthalein indicator; for the study of complexation – method of isomolecular series and spectrophotometry were used. Investigation of the oxide adsorption properties was carried out using powders with the particles 0.5-10.0 micrometers. Specific surfaces were determined using BET method and were 3.3 m^2/g and 2.8 m^2/g for NiO and Fe_2O_3, respectively.

NiO and Fe_2O_3 are crystal polydispersed powders with particle size from 0.1 μm till 40.0 μm. In order to avoid surface contaminants the oxides were rinsed by plenty of distilled water till electroconductivity and pH of the rinsing water remained constant and then the oxides were dried in an oven at 105°C.

Electrokinetic potential, zeta-potential (ζ) was measured using method of microelectrophoresis. The radius of the used particles were ranging from 0.5 μm till 1.0 μm obtained by fractional sedimentation. Zeta-potential values were calculated according to Helmholtz-Smoluchowski equation with boundary condition such as æ×a>>1, where æ is an inverse thickness of the double electric layer (DEL), a is a radius of particles.

Adsorptive and electrokinetic properties of NiO and Fe_2O_3 were studied as function of concentration and pH of aminoacids solutions and adsorption time. To show a role of aspartic acid, electrokinetic experiments were carried out for NiO and Fe_2O_3 in solutions of simple electrolytes such as HCl, KOH, KCl.

The complexation processes of Fe^{3+} ions with aspartic acid were investigated using spectrophotometry. Spectrophotometric investigations were carried out using spectrophotometer CF-26 produced by LOMO. Dependences of optical density on the length of transmitted light wave within the range λ = 200-600 nm were measured in the quartz cuvettes with thickness 10 mm for aspartic acid pure solutions, solutions of $FeCl_3$ and compositions of AA+$FeCl_3$ at different concentrations of AA and electrolytes. Spectra of the systems under investigations were compared with initial ones. Shifting of spectral peaks indicated the presence of complexation.

Results and Discussions

Presence in the aminoacids two different groups such as acid (carboxyl, $- COO^-$) and base (amino, $- NH_2^+$) groups leads to their acid-base properties and their ability of anion or cation forms sorption. That is why above mentioned aminoacids were selected for the present work.

In aqueous solutions of aminoacids different physical (aggregation) and chemical (chemical condensation) processes take place. These processes can influence on the adsorption equilibrium. Because of that the electrokinetic potential of Fe_2O_3 (NiO) in the aqueous solutions of AA was measured as a function of an adsorption time (t_c). On the basis of the obtained results time t_c = 24 hours which corresponds ζ = f(t_c) is constant was selected. In Fig. 1 zeta-potential of Fe_2O_3 versus pH at different AA concentrations is shown. Shift of pH_{iep} towards the acid zone in the presence of the aminoacid (Fig. 1, curve 2, 3) compare with pH_{iep} in the aqueous solutions of HCl (Fig. 1, curve 4) is presented. This fact tells about a specific sorption of AA anion form. Aspartic acid is a weaker acid than HCl (Table 1), the concentration of H^+ ions is less, consequently H^+ ions adsorption is less and zeta-potential is less.
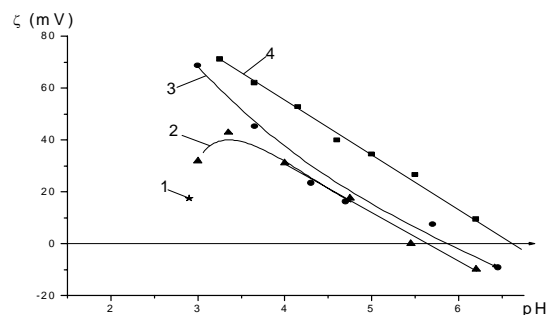

Fig. 1. Dependences of zeta-potential of Fe_2O_3 particles versus pH in the aqueous solutions: 1 – 10^{-2} mol/l AA, 2 – 10^{-3} mol/l AA, 3 – 10^{-4} mol/l AA, 4 – HCl.
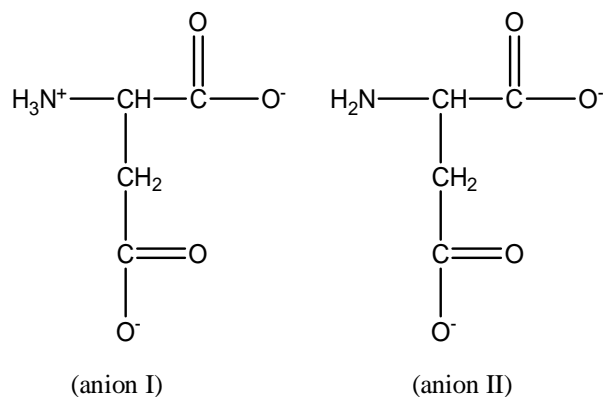
Table 1

pH values in the aqueous solutions of HCl
and aspartic acid

C (mol/l)	10^{-2}	10^{-3}	$5 \cdot 10^{-4}$	10^{-4}
pH (HCl)	2.0	3.0	3.3	4.0
pH (AA)	2.85	3.4	4.25	5.8

AA – aspartic acid

Zeta-potential value for Fe_2O_3 can decrease because of the domination of specific adsorptionwith a positive charged surface and due to specific interactions with a formation of surface complexes. Specific adsorption of aminoacids is possible due to donor-acceptor bonds formation between a metal atom on the oxide surface and ligand groups of the aminoacid molecules. The ligand groups are such as: $-NH_2$, $-COOH$, $-COO^-$ (Table 2). Accordinganion forms of AA. Anion forms of AA can be adsorbed

on Fe_2O_3 due to electrostatic interactions to the literature [5, 6] -NH_2 is a stronger ligand than $-COOH$ and $-COO^-$ groups. Analysing dependences Fig. 1 we take into account AA ion composition in aqueous solutions at working pH. The data are presented in Table 2. It is know from the literature that aspartic acid can exist in two anion forms:

(anion I)   (anion II)

Table 2

Ion forms in the aspartic acid solutions

Aspartic acid							
pH	C (%)	pH	C (%)	pH	C (%)	pH	C (%)
3	9.76	3	79.30	3	10.95	3	$1.7 \cdot 10^{-6}$
4	0.51	4	41.79	4	57.69	4	$8.7 \cdot 10^{-5}$
5	$8.3 \cdot 10^{-3}$	5	6.76	5	93.24	5	$1.3 \cdot 10^{-3}$
6	$8.8 \cdot 10^{-5}$	6	0.72	6	99.27	6	0.015

Both anions can be adsorbed specifically due to donor-acceptor bonds formation with iron crystal net. The anion I can form a donor-acceptor bond using the oxygen atom of the carboxyl group while the anion II can do this using the nitrogen atom of the amino group and the oxygen atom of the carboxyl group. It should be noted that in the anion II nitrogen bonds of $-NH_3^+$ group are completely saturated and the amino group can not be a ligand. Despite that the probability of *AA* cation specific adsorption on the carboxyl group should be estimated. The role of this cation on adsorption can not be significant as it is a counter ion and if this cation was adsorbed specifically zeta-potential values of *Fe₂O₃* would have been higher in the *AA* solutions than in

HCl solutions. This fact was not proved by the experiments.

According Table 2 anion I concentration increases from 11% till 99%. at different *pH* (3 ÷ 6). In case of specific adsorption of the anion I, zeta-potential values should increase towards the base zone in Fig. 1. At such high concentrations of specifically adsorbed anion I at *pH>4* the oxide surface should be charged negatively. However from Fig. 1 values of zeta-potential do not change accordingly above estimations. In addition according to the experimental data obtained and above estimations of the ligands no the cation nor the zwitter ion can not adsorb specifically. In conclusion interactions of the anion I with the positive charge iron

oxide surface are due to Coulomb forces and the anion I is an opposite charge ion.

According to the above conclusions that an anion is adsorbed and from both anions the behaviour of the anion I can not explain the fact of specific adsorption we can conclude that the anion II is responsible for the specific character of *AA* adsorption on the surface of iron oxide. The donor acceptor bond can be fixed on the amino group. Increase of ΔpH_{IEP} with increase of the aminoacid concentration is in good agreement with the above conception.

Fig. 2 shows that in all cases zeta-potential values of Fe_2O_3 in *AA* solutions (curve 1) are positive and less than in the *HCl* solutions (curve 2). Influence of H^+ ions adsorption on zeta-potential at different *AA* concentrations is presented in curve 3. Values of zeta-potential at *AA* concentrations $C_{AA}=1\cdot10^{-2}\div5\cdot10^{-4}$ mol/l in the curve 1 are less than in the curve 3, which can be explained by the leading role of *AA* anions in the specific adsorption with increase of *AA* concentrations. In Fig. 3 dependences $\zeta = f(pH)$ for the system *NiO* – aqueous *AA* solutions are shown. Shift of pH_{IEP} in the presence of the aminoacid compare with pH_{IEP} in *HCl* solutions has a direction from acid zone towards base zone. It is necessary to point out that for *NiO* shift of pH_{IEP} compare with Fe_2O_3 is in an opposite direction. It testifies a specific adsorption of *AA* cation form on the surface of *NiO*.
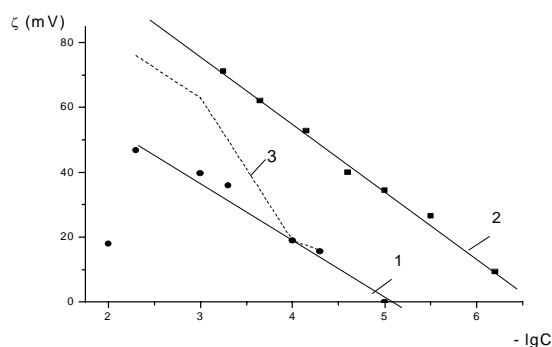

Fig. 2. Dependences of zeta-potential of Fe_2O_3 particles versus – lgC in the aqueous solutions: 1– AA, 2 – HCl.

Indication of *AA* cation specific adsorption is proved by the direction of zeta-potential values shift and relatively high zeta-potential values for *AA* curves and *HCl* curves in the region of positive zeta –potential values at any fixed *pH* values. According to Table 2 these is only one cation that is why these is no a question about a nature of the specifically adsorbed cation, however these is a

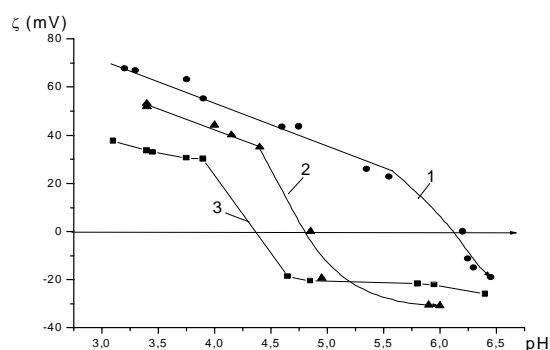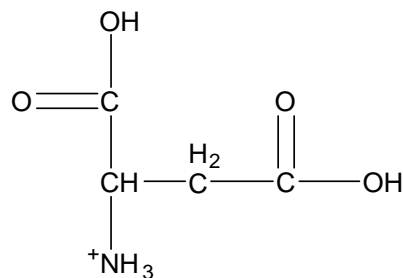question about a localisation place of the donor-acceptor bond.

Fig. 3. Dependences of zeta-potential of NiO particles versus pH in the aqueous solutions: $1 – 10^{-4}$ mol/l AA, $2 – 10^{-3}$ mol/l AA, 3 – HCl.

As noticed above the amino group can not be a ligand. Consequently in this case a coordination bond formed using the carboxyl group has a leading role.

During the analysis of the obtained data on *NiO* it is interesting to notice that $|\Delta pH_{IEP}|$ is higher for the solution with less *AA* concentration than for the more concentrated *AA*. This fact can be explained by the adsorption of *AA* cation form. In general cation and anion forms of *AA* can adsorb on the studied oxides specifically. Shift of pH_{IEP} toward acid or base zone shows a specific adsorption of an anion or a cation. An increase of *AA* concentration gives an increase of an anion form in the solution. According to the experimental data influence of an anion form increases with an increase of *AA* concentration.

In Fig. 4 dependences $\zeta = f(-lgC_{AA})$ for *NiO* – *AA* aqueous solutions are presented. To show the role of *AA* ions the curve 3 in Fig. 3 is plotted the same way as in Fig. 1. From Fig. 4 it is obvious the specific character of *AA* cations adsorption (the curve 3 is below the curve 1) and the additional influence of the anion II specific adsorption is confirmed to the rapprochement of the curves 3 and 1 at high *AA* concentrations.
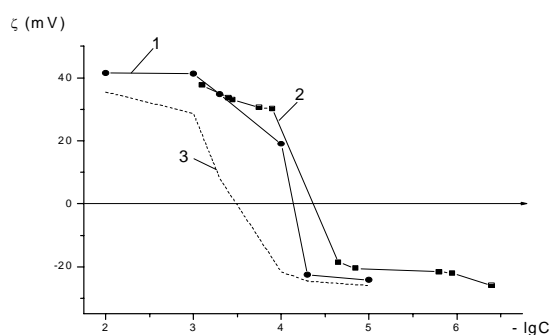
Fig. 4. Dependences of zeta-potential of NiO particles versus – lgC in the aqueous solutions: 1 – AA, 2 – HCl.

Experimental results on *AA* adsorption on Fe_2O_3 surface are shown in Fig. 5. From Fig. 5 it is obvious that in the system $Fe_2O_3 – AA$ aqueous solutions Γ value is:

– monotonically increase in the region where t_c changes from 0 to 60 minutes and stays constant at $60 < t_c < 3000$ minutes;

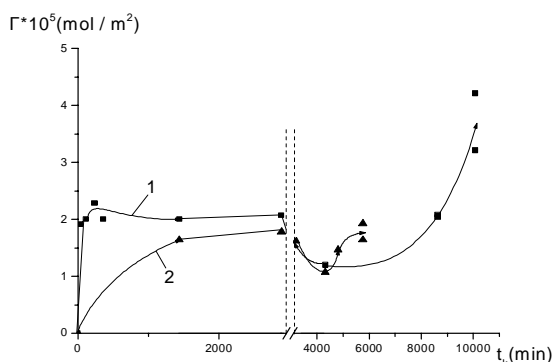– further these is a region of a non monotonical complex change of $\Gamma = f(t_c)$.

Fig. 5. Dependences $\Gamma – t_c$ for the system of AA aqueous solutions – Fe_2O_3: 1 – 10^{-2} mol/l; 2 – $5 \cdot 10^{-3}$ mol/l.

We assume that the non monotonical way of dependences $\Gamma = f(t_c)$ at $t_c > 3000$ minutes is due to long processes of *Fe (III)* cation hydrolyses on the iron oxide surface, which leads to changes of the cation and anion forms of *AA* in the solution. The *Fe (III)* hydrolysis is proved by the monotonical dependence $\Gamma = f(t_c)$ for the system *NiO – AA* aqueous solutions shown in Fig. 6 as *Ni (II)* cation does not hydrolyse at *pH<7* [7]. Analysing the obtained data we concluded that the time t_c (0-3000 minutes) corresponds the adsorption of monomolecular forms from the true *AA* solutions and reaching a local equilibrium. At the time $t_c > 3000$ minutes the complex molecular formations (associations) and colloid particles (aggregates) form in the bulk solution.
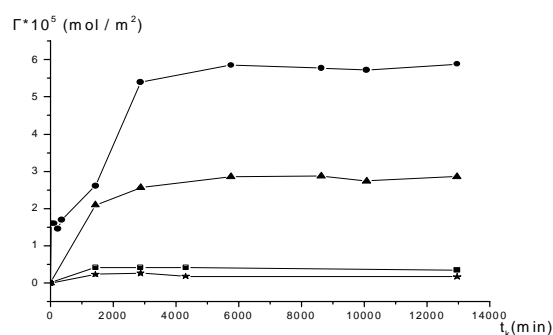

Fig. 6. Dependences $\Gamma – t_c$ for the system AA – NiO: 1 – 10^{-2} mol/l; 2 – $5 \cdot 10^{-3}$ mol/l; 3 – 10^{-3} mol/l; 4 – $5 \cdot 10^{-4}$ mol/l.

Since aminoacids aggregates formation the adsorption is transferred into the adagulation. The adagulation is a process governed by other roles than adsorption. The fact of associates and aggregates formation is found in the literature [8]. The investigation of AC adsorption isotherm presented in Fig. 7 for Fe_2O_3 and *NiO* at $t_c = 24$ hours showed that *NiO* adsorbs aspartic acid in large quantities compare with *NiO* at all concentrations. This connects with *Fe (III)* cation hydrolysis. Experimental curves at $t_c = 24$ hours have a character similar for Langmuir adsorption isotherm. At this consideration in the studied region of *AA* concentrations a monolayer formation of *AA* takes place on the oxide surfaces. From Langmuir equation of adsorption the average surface oxide area of *AA* molecule (S_0) was calculated (for Fe_2O_3, $S_0 = 8,3 \cdot 10^{-20}$ m^2 and for *NiO*, $S_0 = 6,4 \cdot 10^{-20}$ m^2). A small value of S_0 for *AA* (close to the geometric dimensions of the molecule [9]) proves the fact that *AA* molecules are dehydrated and adsorbed specifically on the oxide surfaces.
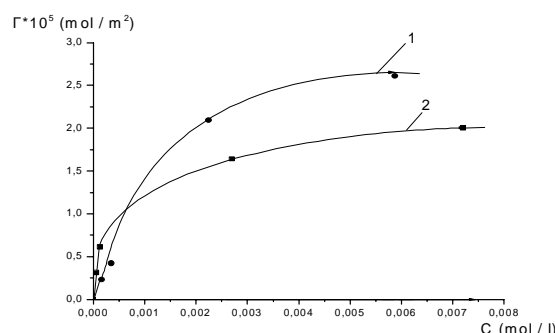

Fig.7. Dependences $\Gamma – lgC$ for the system AA – Fe_2O_3 (NiO): NiO – curve 1, Fe_2O_3 – curve 2.

Spectrophotometric study of the complex formation processes in the system $AA + FeCl_3$ was performed at different *pH*. Maximum of the electron

spectra adsorption in the solution of *FeCl₃* (C = 0.1 mol/l) at *pH* = 2.0 is at λ = 402 nm, but in the presence of *AA* it is shifted towards λ = 390 nm. It is important that at *pH = 2* these is only non hydrolysed cation Fe^{3+} in the solution. This shift proves the complex formation of *Fe (III)* ions with AA in the solution. At increase pH up to 5.1 the picks become broader and their maximum are shifted into long wave part of the spectra as for *FeCl₃* solution, as for *FeCl₃+AA*. This connects with hydrocomplex formation of *Fe (III)* in *FeCl₃* solution with increase of *pH* and formation of complex complexes of *Fe (III)* carrying hydroxide groups as ligands and *AA* for the system *FeCl₃ +AA*. Change of electron spectra at different *pH* confirms the fact of the ligand exchange.

Conclusions

Experimental results showed that aspartic acid adsorbs specifically. An anion plays a leading role in the specific adsorption on the surface of *Fe₂O₃* but a cation is on *NiO*. The obtained data were analysed according to the coordination theory. According to the obtained results and data from the literature about an amino acid state in a bulk volume, specific adsorption a counter anion forms due to a donor-acceptor bond formation on the amino group and a counter cation on the carboxyl group. Complex formation of *Fe (III)* with aspartic acid in the aqueous solutions is confirmed by spectrophotometry. The analyse of these spectres showed the presence of maximum shifts for the appropriate cations in the presence of aspartic acid, which confirm the fact of complex formation between *Fe (III)* cation and aspartic acid. It should note that a possibility of

a ligand exchange of *AA* and *OH⁻* for these systems is important for studying specific adsorption of *AA* on the metal oxides, as the oxide surfaces are in a significant degree hydrolysed.

Acknowledgements

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