

## Estimation of the specific content and nature of sorption sites of iron(III) and zirconium(IV) oxyhydroxides

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The sorption of anions  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ , and  $[\text{Fe}(\text{CN})_6]^{4-}$  from aqueous solutions on the surface of  $\text{Fe}^{\text{III}}$  and  $\text{Zr}^{\text{IV}}$  oxyhydroxide hydrogels freshly precipitated at pH 4–13 was studied. The region of sorbate concentrations was from 0.00025 to 0.06 mol L<sup>-1</sup>. The plots of the anion uptakes vs. their equilibrium concentrations are represented by isotherms of the first type, which are well described by the Langmuir equation if the quantity of the amount adsorbed is expressed as mol-site g<sup>-1</sup>. The maximum uptakes and constants of the Langmuir equation were calculated. The phosphate anions occupy the same number of sorption sites on the sorbents precipitated at different pH. The average specific content of sorption sites for the ferro- and zirconogels in the metastability period is independent of the pH of their precipitation, being  $3.1 \cdot 10^{-3}$  and  $3.2 \cdot 10^{-3}$  mol-site g<sup>-1</sup>, respectively. The  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  anions are sorbed only on the positively charged sites of the hydrogels and occupy not more than  $2 \cdot 10$  mol-site g<sup>-1</sup> in the studied interval of pH of precipitation.

**Key words:** oxyhydroxide, iron(III), zirconium(IV), hydrogel, sorption, phosphate anions, complex anions, isotherms, sorption sites.

Freshly precipitated gels of metal oxyhydroxides, in particular, of  $\text{Fe}^{\text{III}}$  and  $\text{Zr}^{\text{IV}}$ , prepared by the fast alkaline hydrolysis of salt solutions, being washed-off from the mother liquor and stored in water, exist as metastable phases. Their composition and acid-base and sorption properties remain virtually unchanged for a time period from several days to several weeks.<sup>1–5</sup> Some published data<sup>5</sup> suggest that the specific surfaces of the hydrogels obtained by the alkaline hydrolysis of aqueous solutions of metal salts, such as  $\text{Fe}^{\text{III}}$ ,  $\text{Zr}^{\text{IV}}$ ,  $\text{Ti}^{\text{IV}}$ ,  $\text{Cr}^{\text{III}}$ , and  $\text{In}^{\text{III}}$  salts, are independent of the pH of precipitation. Therefore, the interaction with protons, hydroxyl groups, and sorbate ions during the metastability period can be reduced to the recharge of the surface.

In several cases, the sorption isotherms of hydrophosphate anions by the ferrogels precipitated at a constant pH of precipitation ( $\text{pH}_{\text{pr}}$ ) are dome-shaped.<sup>6</sup> The sorption of phosphate anions on the ferrogels does not increase with an increase in the anion concentration, unlike the sorption on goethite,<sup>7</sup> but somewhat decreases, and the initial regions deviate from the ordinate more strongly than those in the Langmuir isotherms.<sup>8</sup> This character of the isotherms can be explained<sup>8,9</sup> by different forms in which the sorbate exists in solutions.

When the positive charge of the surface decreases, the uptake of several anions (sulfate, chromate, oxalate) on

goethite and other crystalline oxyhydroxide sorbents<sup>7,10</sup> in the region of the negatively charged surface decreases to zero. For the sorption of hydrophosphate anions on the ferrogels, a change in the surface charge does not noticeably change the uptake value.

It was supposed<sup>8,9,11–13</sup> that the character of sorption processes is also affected by the heterogeneous nature of sites on the oxyhydroxide surface.

In this work, we attempted to reveal the regularities of sorption on the oxyhydroxide hydrogels and to determine the content of sorption sites of different nature for the hydrogels of metal oxyhydroxides in the metastability period.

Freshly precipitated hydrogels of  $\text{Fe}^{\text{III}}$  and  $\text{Zr}^{\text{IV}}$  oxyhydroxides with almost the same pH values of the zero-charge point ( $\text{pH}_{\text{zcp}}$ ) and specific surface and similar metastability periods were chosen as objects for the study.<sup>4,5</sup> Phosphate, ferrocyanide, and ferricyanide anions were used as sorbates. Phosphate anions were chosen as sorbates due to their important biological role. In addition, data on the sorption of phosphate anions on the oxyhydroxide hydrogels are virtually lacking. Complex iron cyanides were chosen, because they are, on the one hand, anions of strong complex acids<sup>14</sup> and are not prone to extract protons from solution and, on the other hand, do not undergo heterogeneous hydrolysis due to their

stability ( $K_{st}$  for  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  is<sup>14,15</sup>  $10^{37}$  and  $10^{44}$ , respectively).

### Experimental

Ferrogels were prepared from an aqueous solution of  $\text{FeCl}_3$  (analytical grade) with the concentration  $111.4 \text{ g Fe L}^{-1}$  ( $1.995 \text{ mol L}^{-1}$ ). To prepare each sample of the ferrogel, the initial solution (5 mL) was diluted before precipitation to 50 mL, *i.e.*, 0.01 moles of the oxyhydroxide ( $1.06 \text{ g of Fe}(\text{OH})_3$ ). Zirconogels ( $7 \cdot 10^{-3}$ – $8 \cdot 10^{-3} \text{ mol}$ ) were synthesized by the dissolution of  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (2.19 g) in water (50 mL) followed by neutralization with a 2 *M* solution of NaOH. To prepare sorbate solutions, we used 0.1 *M* solutions of  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{Na}_3\text{PO}_4$  with the content of  $3.1 \text{ g P L}^{-1}$  and 0.1 *M* solutions of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  (reagent grade), whose aliquots were diluted to needed concentrations. A solution of  $\text{NH}_4\text{VO}_3$  (1.25 g) and concentrated  $\text{HNO}_3$  (reagent grade, 10 mL) in water (0.5 L), a solution of  $(\text{NH}_4)_2\text{MoO}_4$  (30.26 g) in 2.5 *M*  $\text{H}_2\text{SO}_4$  (0.5 L), and a solution of 6 *M*  $\text{HNO}_3$  were used for the spectrophotometric determination of the phosphorus content in solution.<sup>16</sup> The contents of the complex ions in solutions were measured spectrophotometrically from the intensities of absorption bands at  $\lambda = 323$  and  $325 \text{ nm}$  ( $\epsilon = 840$  and  $330$ ) for  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , respectively. A 2 *M* solution of NaOH (reagent grade) was used for gel precipitation.

Hydrogels were precipitated at a specified pH value. For this purpose, a solution of NaOH was added (for ~5 min) to an aliquot of a 4–5-fold diluted salt solution to a constant pH value of precipitation ( $\text{pH}_{\text{pr}}$ ). Then the gel was separated from the mother liquor and washed with distilled water ( $3 \times 5 \text{ min}$ ) by decantation using a centrifuge with  $n = 2000 \text{ rpm}$  (angular rotor of an OPn-8 centrifuge, minimum acceleration  $1400 \text{ m s}^{-2}$ , maximum acceleration  $4000 \text{ m s}^{-2}$ ), and precipitation was carried out at pH 4–13. The washed-off gel was repulped in water, diluted in a volumetric flask to 100 mL, and added to a solution containing an aliquot of the initial solution of the sorbate diluted to 150 mL. The total volume of the suspension was 250 mL.

Ten values of the concentration of the phosphate anions in an interval of  $0.94 \cdot 10^{-3}$ – $5.8 \cdot 10^{-2} \text{ mol L}^{-1}$  and ten values of the concentration of the iron cyanide complex in an interval of  $0.25 \cdot 10^{-3}$ – $0.01 \text{ mol L}^{-1}$  were used.

It was found in preliminary experiments that the sorption process was equilibrated within a period shorter than 10 min. Sorption was carried out for 1 h with continuous magnetic stirring at room ( $18$ – $20^\circ\text{C}$ ) temperature. The suspension from the system was sampled three times at an interval of 20 min to avoid an error associated with the incorrect measurement of the equilibration time  $\tau_{\text{eq}}$ . The samples were filtered through the "blue strip" filter, and the residual sorbate content was determined in the filtrate spectrophotometrically on an SF-26LOMO spectrophotometer. This content was taken as the equilibrium concentration.

In all cases, the pH of the initial solution of the sorbate and suspension were monitored. All pH measurements were carried out on an I.130.2M.1 ionometer with an ESL-63-07 glass electrode and an EVL-1M3.1 auxiliary electrode. Both electrodes were immersed into the reaction mixture during measurements.

The uptake value was calculated using the formula

$$A (\text{mol g}^{-1}) = [0.25(C_{\text{in}} - C_{\text{eq}})]/m, \quad (1)$$

where  $C_{\text{in}}$  is the sorbate concentration in the initial solution,  $\text{mol L}^{-1}$ ;  $C_{\text{eq}}$  is the equilibrium sorbate concentration,  $\text{mol L}^{-1}$ ;  $m$  is the sorbent weight, g.

The relative error of adsorption determination is 20%. The results are presented in Tables 1–5 and Figs 1 and 2.

Anions of orthophosphoric acid are very easily transformed into each other due to dissociation and hydrolysis in an aqueous solution. In the interval  $\text{pH}_{\text{pr}} = 4$ – $13$ , orthophosphoric acid forms anions  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ . The dissociation constants of orthophosphoric acid<sup>17</sup> and experimental pH values of the suspension were used for the processing of sorption data. The content of each of the forms that can exist at this pH was calculated for each experimental point (see Table 1). The example of the calculation is given further. If the pH of the suspension is 5, the  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  anions coexist at

**Table 1.** Sorption of anions from a solution of  $\text{NaH}_2\text{PO}_4$  on the surface of the freshly precipitated zirconogel with  $\text{pH}_{\text{pr}} = 13$  and the concentration  $0.032 \text{ mol L}^{-1}$  without a ionic background

$C_{\text{in}} \cdot 10^3$ /mol L <sup>-1</sup>	$\text{pH}_{\text{susp}}$	$C_{\text{eq}} \cdot 10^3$ /mol L <sup>-1</sup>	$A \cdot 10^3$ /mol g <sup>-1</sup>	$-Z^*$	Content of predominant form (%)	$A_r \cdot 10^3$ /mol-site g <sup>-1</sup>	$C_{\text{eq}}/A_r$
0.94	11.60	0	0.18	3	61	0.47	0
4.13	11.36	0.50	0.69	3	51	1.73	0.32
6.00	10.92	1.30	0.90	2	69	2.08	0.63
9.30	10.62	3.00	1.21	2	80	2.68	1.13
15.10	8.46	6.30	1.70	2	100	3.40	1.85
25.5	7.34	12.2	2.56	2	65	4.26	2.86
28.0	7.16	14.9	2.52	1	45	3.92	3.81
39.0	6.79	22.8	3.13	1	55	4.54	5.03
44.0	6.64	27.5	3.19	1	63	4.37	6.30
48.0	6.41	31.1	3.25	1	71	4.26	7.40

\* Charge of the predominant form.

**Table 2.** Parameters of the sorption isotherms of phosphate anions on the ferro- and zirconogels (in parentheses) at the sorbent concentration 0.037 (0.032) mol L<sup>-1</sup> estimated from the Langmuir equation at different pH<sub>pr</sub>

pH <sub>pr</sub>	$A_{\max} \cdot 10^3/\text{mol-site g}^{-1}$			$K/\text{L mol}^{-1}$		
	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>
4	2.56 (4.15)	3.44 (2.98)	2.46 (3.00)	1262 (1500)	916 (3160)	2820 (3740)
9	3.28 (3.73)	3.03	2.24 (2.68)	1076 (2130)	390	1030 (2270)
13	2.99 (4.48)	3.48 (2.84)	2.60 (1.89)	632 (830)	135 (420)	380 (2150)

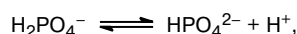
**Table 3.** Parameters of the sorption isotherms of anions HPO<sub>4</sub><sup>2-</sup> on the ferrogels at different pH<sub>pr</sub> and sorbent concentrations 4 (I), 10 (II), and 20 g L<sup>-1</sup> (III) estimated from the Langmuir equation

pH <sub>pr</sub>	$A_{\max} \cdot 10^3/\text{mol-site g}^{-1}$			$K/\text{L mol}^{-1}$		
	I	II	III	I	II	III
4	3.44	3.61	—	916	4500	—
5	3.20	—	—	800	—	—
7	2.82	—	3.74	810	—	1420
9	3.03	2.82	—	390	270	—
10	3.03	—	3.20	360	—	357
11	3.23	—	—	230	—	—
12	3.26	—	—	150	—	—
13	3.22	4.29	3.15	200	100	133

**Table 4.** Parameters of the sorption isotherms of the Fe<sup>II</sup> and Fe<sup>III</sup> cyanide complexes on the ferro- and zirconogels (in parentheses) at the sorbent concentration 4 g L<sup>-1</sup> estimated from the Langmuir equation

pH <sub>pr</sub>	$A_{\max} \cdot 10^3/\text{mol-site g}^{-1}$		$K \cdot 10^{-3}/\text{L mol}^{-1}$	
	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	[Fe(CN) <sub>6</sub> ] <sup>4-</sup>
4	1.62 (1.76)	1.93 (1.86)	16.39 (15.04)	19.51 (22.01)
5	1.19 (1.14)	1.59 (1.56)	12.89 (8.70)	10.10 (18.95)
6	0.72 (1.08)	1.22 (0.99)	9.96 (7.01)	8.77
7	0.33 (0.80)	1.00 (0.67)	6.02 (6.15)	2.60 (6.59)
8	0.15 (0.47)	0.70 (0.51)	2.50	1.06 (1.66)
9	0 (0)	0 (0)	0 (0)	0 (0)

equilibration. Substituting the activities by concentrations, we have



and the dissociation constant is  $K_{\text{dII}} = [\text{HPO}_4^{2-}][\text{H}^+]/[\text{H}_2\text{PO}_4^-]$ . From this  $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = K_{\text{dII}}/[\text{H}^+] = 10^{-7}/10^{-5} = 0.01 = 1 : 100$ . Therefore, at pH = 5 the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anion predominates, whose content is 99%. At pH = 6  $K_{\text{dII}}/[\text{H}^+] = 10^{-7}/10^{-6} = 0.1$ , etc. Thus, we calculated that at pH < 5 the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anions are present in the solution, in the region 5 < pH < 8.5 the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> anions coexist, in the region 8.5 < pH < 10.1 the HPO<sub>4</sub><sup>2-</sup> anions exist, at 10.1 < pH < 12.5 the HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> anions coexist, and at pH > 12.5 only the PO<sub>4</sub><sup>3-</sup> anions

**Table 5.** Anion uptakes  $A$  and  $A_r$  from solutions of Na<sub>2</sub>HPO<sub>4</sub> on the surface of the freshly precipitated ferrogel as functions of its pH<sub>pr</sub> at different sorbent and sorbate concentrations without a ionic background

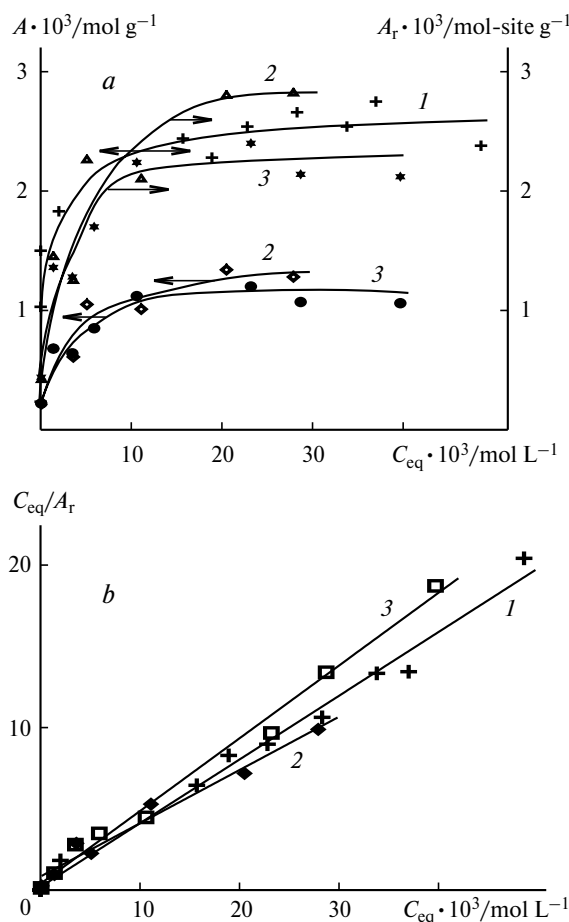
$C_{\text{in}}/\text{mol L}^{-1}$	pH <sub>pr</sub>	$(A/A_r) \cdot 10^3$ * at $C_{\text{Fe}(\text{OH})_3}/\text{g L}^{-1}$			
		4.0	6.66	10	20
0.006	4	0.93/1.62	0.90/0.90	0.60/0.60	0.30/0.30
	5	1.14/1.94	0.90/1.53	0.60/1.02	0.30/0.51
	7	0.88/1.76	0.77/1.54	0.60/1.20	0.30/0.60
	9	0.61/1.43	0.76/1.77	0.54/1.27	0.30/0.70
	10	0.57/1.45	0.54/1.38	0.54/1.38	0.29/0.74
	11	0.50/1.40	0.48/1.34	0.42/1.18	0.29/0.81
	12	0.40/1.37	0.48/1.37	0.42/1.20	0.27/0.77
	13	0.40/1.16	0.42/1.22	0.39/1.13	0.24/0.70
	4	1.77/3.54	1.89/3.21	1.71/2.91	1.25/2.13
	5	2.51/5.02	1.89/3.78	1.71/3.42	1.25/2.50
	7	1.35/2.70	1.66/3.32	1.40/2.80	1.17/2.34
	9	1.35/2.70	1.66/3.32	0.85/1.70	1.00/2.00
	10	1.35/2.90	1.31/2.81	0.85/1.83	0.78/1.66
0.025	11	1.35/3.48	1.31/3.00	0.69/1.59	0.72/1.66
	12	1.35/3.17	1.31/3.08	0.69/1.62	0.62/1.46
	13	1.35/3.28	1.14/3.02	0.45/1.19	0.56/1.32
0.058	4	—	—	1.80/3.60	1.92/3.84
	5	—	—	1.80/3.60	—
	7	—	—	1.40/2.80	1.67/3.34
	9	—	—	1.24/2.60	—
	10	—	—	1.17/2.57	1.24/2.73
	11	—	—	1.09/2.51	1.16/2.67
	12	—	—	1.09/2.56	0.97/2.28
	13	—	—	0.89/2.18	0.97/2.38

\* Mol (mol-site)<sup>-1</sup>.

are observed. Since the mutual transformations of the phosphate anions occur very easily, all the three varieties were used as the initial sorbates.

## Results and Discussion

The experimental sorption isotherms of the phosphate anions  $A = f(C_{\text{eq}})$  on the ferro- and zirconogels cannot be described by the Langmuir equation. Perhaps, this is explained by the fact that with an increase in the initial sorbate concentration the pH value of the suspension

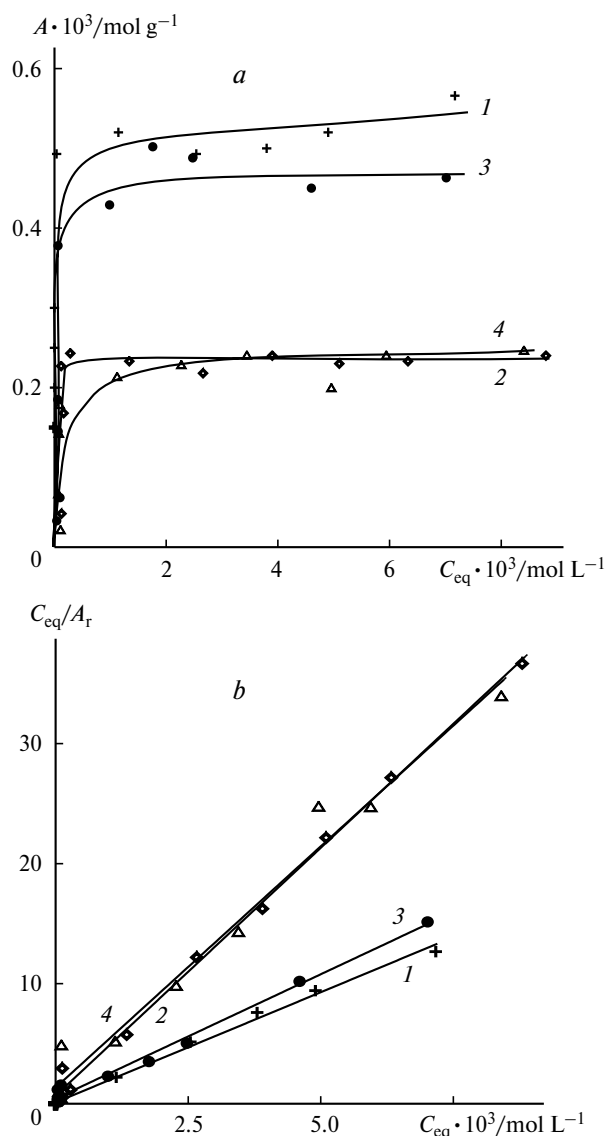


**Fig. 1.** Sorption isotherms of phosphate anions on the ferrogels in the coordinates  $A = f(C_{\text{eq}})$  and  $A_r = f(C_{\text{eq}})$  (a) and in the coordinates of the linear Langmuir equation (b); sorbate form:  $\text{H}_2\text{PO}_4^-$  (1),  $\text{HPO}_4^{2-}$  (2), and  $\text{PO}_4^{3-}$  (3);  $\text{pH}_{\text{pr}} = 4$  (1) and 9 (2 and 3);  $C_{\text{eq}}$  is the equilibrium sorbate concentration.

changes more strongly due to the interaction of a sorbate solution with the sorbent. As a result, the ratio between bare sorption sites of different nature changes.

We assumed that a singly charged ion occupies one sorption site, a doubly charged ion occupies two sites, etc. The method of data processing for heterogeneous hydrolysis<sup>1</sup> was based on the assumption that two surface OH groups are used for the formation of one  $\text{E}(\text{OH})_2$  molecule from the sorbate on the oxyhydroxide surface, while the formation of  $\text{E}(\text{OH})_3$  needs three OH groups. The following approach can be used in this work for convenience of comparison of the uptakes of the anions bearing different charges under study.

Let us express the amount adsorbed not in  $\text{mol g}^{-1}$  but in  $\text{mol-site g}^{-1}$  as proposed earlier.<sup>18</sup> The amount adsorbed  $A$  should be multiplied by the ion charge in order to express the experimental values of the amount adsorbed in  $\text{mol-site g}^{-1}$ . Then we accept that the ion composition of the sorbate in the sorbent phase corresponds to the ion



**Fig. 2.** Sorption isotherms of ferro- and ferricyanide anions on the ferro- and zirconogels in the form  $A = f(C_{\text{eq}})$  (a) and in the coordinates of the linear Langmuir equation (b); sorbents: ferrogel (1, 2) and zirconogel (3, 4); sorbate form:  $[\text{Fe}(\text{CN})_6]^{3-}$  (1, 2) and  $[\text{Fe}(\text{CN})_6]^{4-}$  (3, 4);  $\text{pH}_{\text{pr}} = 4$  (1, 3) and 6 (2, 4).

composition of the sorbate in the equilibrium solution. Based on these assumptions and using the calculated contents of the coexisting forms of the phosphate anions, we calculated the uptake values reduced to  $\text{mol-site g}^{-1}$ , which were designated as  $A_r$ . The results of this calculation and experimental  $A$  values are given in Table 1.

If  $A_r$  values are used instead of  $A$ , the data obtained in the  $C_{\text{eq}}$  interval from 0 to 0.04–0.05  $\text{mol L}^{-1}$  in the systems without a foreign ionic background satisfy the Langmuir equation in the following form:

$$C_{\text{eq}}/A_r = 1/(A_r^{\text{max}}K) + C_{\text{eq}}/A_r^{\text{max}}. \quad (2)$$

Similar examples are presented in Fig. 1. The maximum uptakes and sorption constants were calculated by Eq. (2) and are given in Tables 2 and 3.

Since  $K_3[Fe(CN)_6]$  and  $K_4[Fe(CN)_6]$  are salts of strong complex acids<sup>14</sup> with the radius of the hydrated anion not less than 2.5 Å, they are not prone to hydrolysis and their anions are not involved in protolytic reactions. Therefore, these complex anions are sorbed in the form of  $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_6]^{4-}$  ions, and each anion occupies simultaneously three or four sorption sites, respectively, on the sorbent surface.

For the sorption of the ferro- and ferricyanide anions, the experimental isotherms are well described by the Langmuir equation, and their slope is much larger than that typical of the adsorption of the phosphate anions (see Fig. 2). In this case, the uptake is described by the Langmuir equation whether the amount adsorbed is expressed by  $A$  or  $A_r$ . At low concentrations of the ferro- and ferricyanide anions ( $<0.001$  mol L<sup>-1</sup>), they are sorbed almost completely regardless of the  $pH_{pr}$  of the sorbent. At higher sorbate concentrations, the dependence of the uptake on  $pH_{pr}$  becomes more pronounced. With an increase in the  $pH_{pr}$ , the  $A$  value decreases successively and becomes zero at  $pH_{pr}$  9. At  $pH_{pr}$  8, the  $A$  values are very low for the both complexes. Therefore, the accuracy of determination of  $A$  decreases strongly. The maximum uptakes  $A_{max}$  and sorption constants for the sorption of the complex anions are given in Table 4.

An analysis of the data in Tables 2 and 3 shows that the anions capable of protolytic transformations are sorbed in the whole interval of  $pH_{pr}$ . This agrees with published data.<sup>7,19</sup> The sorbed phosphate anions occupy almost the same number of sorption sites:  $(3.10 \pm 0.30) \cdot 10^{-3}$  and  $(3.20 \pm 0.8) \cdot 10^{-3}$  mol-site g<sup>-1</sup> for adsorption on the ferro- and zirconogels, respectively. These values are averaged of all  $A_r$  obtained by the processing of the sorption isotherms (see Tables 2 and 3).

On the contrary, for the complex sorbate anions, the maximum uptake decreases regularly with an increase in the  $pH_{pr}$  and does not exceed  $2 \cdot 10^{-3}$  mol-site g<sup>-1</sup> even at the minimum  $pH_{pr}$  4. Their sorption ceases completely when the charge of the sorbent surface changes to negative values (at  $pH_1 > 8.2$ ).<sup>2</sup> The sorption constants for the complex anions decrease with an increase in the  $pH_{pr}$ . Somewhat higher  $A_{max}$  are observed for the  $[Fe(CN)_6]^{4-}$  anion.

As follows from the dependence of  $A_r$  on the  $pH_{pr}$  for the phosphate anions (see Table 5), the sorption is completed at low initial concentrations of the sorbate and (or) high concentrations of the sorbent. In addition, the number of occupied sites increases with an increase in the  $pH_{pr}$ , i.e., with an increase in the  $pH_{susp}$ . This increase occurs with an increase in the contribution of doubly charged and three-charge ions among the sorbate ions. The uptake somewhat decreases only at  $pH_{pr} = 12-13$ . For high

sorbate concentrations and low sorbent concentrations, the uptake of the phosphate anions reaches maximum values and remains virtually constant in the whole  $pH_{pr}$  interval. If the initial sorbate concentration is high and the sorbent concentration is low, the plot of  $A_r$  vs.  $pH_{pr}$  passes through a minimum value. Finally, when the concentrations of the sorbate and sorbent are simultaneously high or low, the  $A_r$  value somewhat decreases with an increase in the  $pH_{pr}$ . This is likely a result of an enhancement of the electrostatic repulsion of the  $PO_4^{3-}$  ions from the surface with a high negative charge.

The data obtained provide some insight into the mechanism of anion sorption and nature of sorption sites and helps to make approximate estimations of the specific content of these sites. Evidently, the mechanism of sorption of the  $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_6]^{4-}$  anions is the simplest one. The sorption of these anions is controlled by the surface charge, because they are sorbed only on the positively charged surface. The sorbed ions can be considered to retain on the sorbent almost exclusively due to attraction between opposite charges. The electrostatic nature of the sorption process is also confirmed by the character of the dependence of the sorption constants on the pH. These constants decrease as the attraction force between the ions and surface weakens. The maximum uptake of the both complex anions is much lower than the uptake of the phosphate anions. Therefore, they occupy only a part of the available sorption sites. These large hydrated anions can hardly penetrate the double electric layer (DEL). Therefore, it can be assumed that the sorbed anions  $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_6]^{4-}$  are localized at the positively charged surface dividing the compact and diffuse parts of the DEL. When reaching this interface, the sorbed ions displace some counterions from the diffuse layer. Thus, the sorption sites are likely to be adsorbed excessive protons and exist outside the physical surface of the sorbent. The boundary surface between the compact and diffuse parts of the DEL can be considered homogeneous and, on account of this, the sorption isotherms are well described by the Langmuir equation.

The sorption of the phosphate anions is characterized by a quite different mechanism, which is indicated by a weak dependence of the uptake on the surface charge. The phosphate anions are sorbed on the surface bearing both the positive and negative charges and on the neutral surface as well. The anions with the highest negative charge ( $PO_4^{3-}$ ) are well sorbed on the negatively charged surface. In addition, the number of sites is rather rigidly restricted and almost independent of the  $pH_{pr}$ . It cannot be excluded that the adsorption of the phosphate anions is a chemisorption process.

The dome-shaped experimental sorption isotherms of the phosphate anions on the hydrogels of iron(III) and zirconium(IV) oxyhydroxides are explained by the change in the  $pH_{susp}$  values with a change in the equilibrium

concentration of the sorbate and  $\text{pH}_{\text{pr}}$ . This facilitates the mutual transformations of the phosphate anions with different degrees of protonation, which occupy during adsorption the number of sorption sites equal to their charge. Then the number of the occupied sites remains unchanged, and the amount of sorbed phosphorus decreases on going from  $\text{H}_2\text{PO}_4^-$  to  $\text{PO}_4^{3-}$ .

If we assume that the phosphate anions can be sorbed on the stable sorption sites, whose existence is pH-independent, we can accept that the total content of the sorption sites for the ferrogels is  $\sim(3-4) \cdot 10^{-3}$  mol-site  $\text{g}^{-1}$ . This enhanced considerably the sorption capacity of the hydrogels over the capacity of the crystalline oxyhydroxides.<sup>7,10-13,20</sup> Up to 10% of these sites fall on the strongly bound OH groups, which are active in heterogeneous hydrolysis. The content of positively charged, most likely, protonated sites achieved the maximum value ( $2 \cdot 10^{-3}$  mol-site  $\text{g}^{-1}$ ) at  $\text{pH}_{\text{pr}}$  4 and decreases to zero at  $\text{pH}_{\text{pr}}$  9. A very similar quantitative distribution of the sorption sites is observed for the zirconogels and explains the similarity of the sorption properties of the both oxyhydroxide sorbents.<sup>2</sup>

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