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Estimation of oxyhydroxide specific surface area using the amounts of OH groups adsorbed

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A procedure for pH-metric determination of the limiting adsorption of OH groups (A_{OH}) by Fe^{III}, Zr^{IV}, Cr^{III}, and In^{III} oxyhydroxide hydrogels from 0.1 and 1.0 *M* solutions of NaCl is described. Data on the molecular area occupied by a single OH group on the hydrogel surface (S_{OH}) and the S_{spec} values, which were calculated from A_{OH} and S_{OH}, are presented. The S_{spec} value does not depend on the pH of hydrogel precipitation; the true S_{spec} value can be determined only from sorption of the OH groups at the actual point of zero charge of the hydrogel. The A_{OH} values for hydrogels were found to change only slightly during aging of hydrogels in electrolyte solutions.

Key words: hydrogel, oxyhydroxide, limiting adsorption, hydroxy group, specific surface area, zero-charge point, aging, ionic medium.

Estimation of the specific surface area (S_{spec}) of amorphous hydrogels of metal oxyhydroxides is a relatively difficult task. Most of the known methods of determination of S_{spec} are based on the adsorption of various substances from solutions or from the gas phase. Prior to measuring the adsorption of gases and vapors, samples are pre-treated to remove sorbed water,[1] and this can considerably decrease the S_{spec} value. The results obtained by traditional methods of measuring S_{spec} in the analysis of amorphous metal oxyhydroxides depend on the way of treatment of the colloid suspension and the particular procedure.[2] Measurements of adsorption from solutions give more reliable data on S_{spec} in these systems. Drying of the sample prior to BET measurements of S_{spec} causes degreadation of the fine structure existing in the aqueous medium.[3] The estimation of S_{spec} from the size of gel particles[1] is faced with experimental difficulties and is not sufficiently precise because it does not take into account the internal surface of particles.

Obviously, the most reliable results could be gained by a method based on adsorption of small-size particles having a simple composition and a stable structure whose concentration in solution can be easily, precisely and quickly determined. In the case of metal oxyhydroxide hydrogels, OH groups can serve as this type of particle.

Previously,[4,5] we found that oxyhydroxides of Fe^{III}, Cr^{III}, Zr^{IV}, Ti^{IV}, In^{III}, Zn^{II}, Al^{III}, and other metals are capable of adsorbing substantial amounts of OH groups on the surface. This can take place both in the processes of hydrolytic precipitation of oxyhydroxides from solutions of salts and upon contacting dry oxides or gel-like oxyhydroxides with electrolyte solutions, especially solutions of alkali. In order to use the OH adsorption values to estimate S_{spec}, it is necessary to study first the pattern of the adsorption isotherm, *i.e.*, the dependence of the equilibrium (for crystalline oxides) or pseudo-equilibrium (for gels) adsorption of OH groups on their equilibrium concentration in solution. In addition, the molecular area for a OH group on the oxyhydroxide surface should be determined.

Published data[6—17] concerning the molecular area of an OH group are contradictory; surface concentrations ranging from 1 to 15 OH groups per 1 nm^2 have been reported for various oxyhydroxides.

In this work, we determined the limiting adsorption values of OH groups for samples of Fe^{III}, Cr^{III}, Zr^{IV}, and In^{III} oxyhydroxide hydrogels prepared by precipitation at different pH (pH_{pr}) and washed from the mother liquor and also for samples of calcined oxides with known S_{spec}, namely, γ-Al_2O_3, Cr_2O_3, Y_2O_3, Sm_2O_3, and In_2O_3. The results were used to calculate the molecular area of a single OH group on the hydrogel surface.

Experimental

The samples of oxyhydroxide hydrogels were prepared by previously described procedures.[7,18—20] Reagent and analytical grade initial chemicals were used. Solutions were prepared using double-distilled water and recrystallized salts. Ferro-, indio-, chromo-, and zirconogels in amounts of 0.007—0.008 moles each were prepared by alkaline hydrolysis of aqueous solutions of $Fe(ClO_4)_3$ (81.75 g of Fe/L), $In(NO_3)_3$ (100 g of In/L), and $CrCl_3$ (38.93 g of Cr/L), respectively, to pH up to 7,

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Table 1. Example of calculation of the amount of OH groups adsorbed in the check experiment

V_m/mL	V_{susp} /L	$[OH]_0$* /g-ion L^{-1}	pH of filtrate	$(a_{OH})_{eq}$ /g-ion L^{-1}	V_{HCl} /mL mL^{-1}	$[OH]_{eq}$ /g-ion L^{-1}	A_{OH} /g-ion g^{-1}
0	0.2	0	4.89	$<10^{-7}$	0	0	0
5	0.205	0.00506	5.82	$<10^{-7}$	0	$<10^{-7}$	0.00086
17	0.217	0.01625	11.30	0.00199	0.0206	0.00206	0.00242
30	0.23	0.02705	12.03	0.01071	0.113	0.0113	0.00285
40	0.24	0.03457	12.10	0.01259	0.191	0.0191	0.00292
50	0.25	0.04148	12.35	0.02239	0.261	0.0261	0.00303

Note. Experimental conditions: $Zr(OH)_4$, $pH_{pr} = 5.5$, 0.1 *M* NaCl.

* The value calculated with allowance for the concentration of the alkali added (0.104 *N*).

9, and 11; and by dissolution of 2.19 g of $ZrO(NO_3)_2 \cdot H_2O$ in 50 ml of water followed by neutralization with 2 *M* NaOH up to pH 5.5, 7, and 10. The precipitation was carried out with permanent pH-metric monitoring until a specified pH_{pr} (pH_1) value invariable for ~5 min was attained in ~50 ml of the suspension. The precipitates were separated from the mother liquor by centrifuging, washed three times with decantation of water, and centrifuged at $n = 2000$ rpm for 5 min.

The amounts of OH groups adsorbed were determined by titration of hydrogel suspensions with aqueous NaOH. The titration was conducted on a pH-121 pH-meter under Ar in a quartz half-open cell with an ESL-43-07 glass electrode and a EVL-1M1 auxiliary electrode immersed in the suspension. Prior to titration, argon was passed for 1.5 h through the gel suspension and through a solution of the blank electrolyte (NaCl) in order to remove the dissolved CO_2; then 100 mL of the suspension was added to 100 mL of the electrolyte solution prepared in such a way that the concentration of NaCl in the final volume of the suspension adjusted to a value of 1.0 or 0.1 mol L^{-1}. The pH value of the suspension at this instant was taken as the initial point of the titration curve. Then, a 0.2 *N* solution of NaOH was added in portions, the system being kept for 5 min after the addition of each portion for the pH to settle. The same volume of the blank electrolyte solution was titrated in a similar way. The concentration of adsorbed hydroxyl ions A_{OH} (g ion g^{-1}) was calculated from the formula

$$A_{OH} = ([OH]_0 - [OH]_{eq})V_{susp}, \qquad (1)$$

where $[OH]_0$ is the concentration of the OH groups in the blank solution (g-ion g^{-1}) and $[OH]_{eq}$ is the equilibrium concentration of the OH groups in the suspension (g-ion g^{-1}).

The experiments showed that titration was reversible;* hence, the samples virtually did not change during the titration.

The pH measurements produce the activity values a_{OH} rather than the true OH^- concentrations; hence, the activity coefficients of the OH groups should be taken into account. Besides, for pH > 12, the addition of new small portions of the alkali induced very slight changes in the pH, which deteriorates the accuracy of measurements in this pH region. It is also necessary to check the readouts of a glass electrode kept in an alkaline solution for a long period.

To determine the activity coefficients (γ_{OH}) and to check the readouts of the glass electrode, we determined the true pseudo-equilibrium* concentrations of the OH groups by titration of the alkali with an acid.

Let us consider the check experiment taking Table 1 as an example. Five portions of the alkali were added to a hydrogel sample (200 mL) in the same cell under argon. After the addition of the first portion (5 mL), one-fifth of the suspension volume (41 mL) was taken and filtered through a fine paper filter. Then pH of the the filtrate was measured and the filtrate was titrated with 0.1 *N* HCl. This gave the equilibrium concentration $[OH]_{eq}$ corresponding to the given titrant volume $V_T = 5$ mL on the titration curve. It can be seen that at this point of the curve, all the alkali added was absorbed by the gel. The next portion of the alkali was added to the remaining 80% of the suspension, the alkali amount being 80% of that needed for 200 mL of the suspension ($(17 - 5) \cdot 0.8 = 9.6$ mL). One-fourth of the remaining suspension was withdrawn ($(205 - 41 + 9.6)/4 = 43.4$ mL) and treated as described above. The residual concentration of the OH groups was 0.00206 *N*. The amount adsorbed A_{OH} calculated using Eq. (1) was $\{(0.01625 - 0.00206) \cdot 0.173.6 \text{ L}\}/1.27 \text{ g } Zr(OH)_4 \cdot 0.8 = 0.002424$ g-ion OH/g. The next portion of the alkali was added to the remaining 60% of the suspension, one-third of the remaining suspension volume was taken, and so on. Finally, we got five values of equilibrium concentration $[OH]_{eq}$ corresponding to five points on the pH-metric titration curve. For convenience and clearness of calculations, the titrant volume was normalized to 100% of the suspension volume.

Based on the a_{OH} and $[OH]_{eq}$ values obtained in the check experiments, the activity coefficients (γ_{OH}) were calculated; they are given in Table 2. The coefficients were used to construct a calibration plot suitable for determination of γ_{OH} for any a_{OH} value within the pH range studied. Examples of calculations for the correction of the pH-metric titration curves to obtain the adsorption isotherm** are given in Tables 3 and 4. Figures 1 and 2 show examples of the resulting isotherms of adsorption of the OH groups by various oxyhydroxide samples.

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* The reversibility of titration means that upon the back titration of the alkali by an acid, *i.e.*, upon the addition of acid in amounts equivalent to the amount of the alkali added during ditect titration results in the same pH, and the titration curves for the direct and back titrations thus coincide. This implies that titration with an alkali does not cause any irreversible changes in the sample.

* An equilibrium concentration of OH groups is called pseudo-equilibrium merely because the phases of amorphous hydrogels are thermodynamically in a nonequilibrium state. Thus, the system as a whole is in a nonequilibrium state, and the equilibrium established between the amorphous gel and an alkali solution is apparent (*i.e.*, it is a pseudo-equilibrium), although this state is retained for long periods.

** Titration was conducted at a temperature of 22±4°C; since the ionic product of water K_w changes insignificantly over this temperature range, the dependence obtained can be considered to be an isotherm.

Table 2. Activity coefficients of the OH groups in the region of adsorption measurements (1 to 50 mL of alkali added) in 0.1 *M* NaCl

$[OH^-]$* /g-ion L^{-1}	pOH	a_{OH} /g-ion L^{-1}	γ_{OH}**
0.001075	2.95	0.00112	1.0
0.00206	2.70	0.00200	0.97
0.00235	2.63	0.00234	0.99
0.00319	2.51	0.00309	0.97
0.00527	2.30	0.00501	0.95
0.00831	2.13	0.00741	0.89
0.00905	2.10	0.00794	0.88
0.0113	1.97	0.01072	0.94
0.0126	2.03	0.00933	0.83
0.0141	1.95	0.0112	0.79
0.0169	1.88	0.0132	0.78
0.0182	1.86	0.0138	0.76
0.0191	1.90	0.0126	0.66
0.0196	1.83	0.0148	0.75
0.02228	1.79	0.0162	0.73
0.02485	1.76	0.0174	0.70
0.0261	1.65	0.0224	0.86
0.02817	1.73	0.0186	0.66
0.0316	1.67	0.0214	0.68
0.03217	1.68	0.0209	0.65
0.0392	1.61	0.0245	0.63
0.03967	1.63	0.0234	0.59
0.0432	1.62	0.0240	0.55

* Calculation.

** Experiment.

Table 5 presents the limiting adsorption values A_{OH} for hydrogels freshly precipitated at various pH_{pr}.

To find the molecular area of an OH group S_{OH}, we attempted to use calcined crystalline samples of oxides with constant S_{spec} values which were assumed to remain unchanged on contact with a solution. The samples used in these experiments are listed and described in Table 6, which also gives the amounts of OH groups adsorbed by these samples.

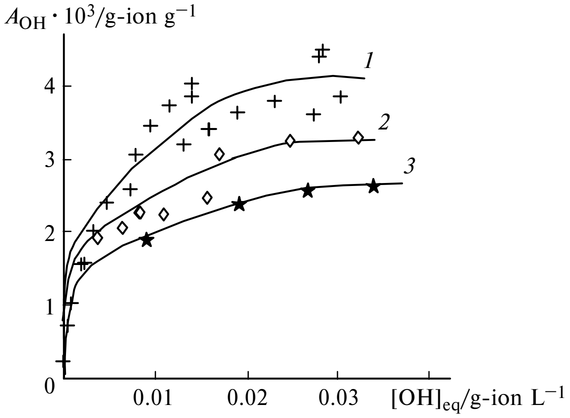

Fig. 1. Adsorption isotherms of OH groups (A_{OH}) on the surface of freshly precipitated Cr^{III} oxyhydroxides with precipitation pH of 7 (*1*); 8 (*2*); 9 (*3*). $[OH]_{eq}$ is the equilibrium concentration of OH groups in the suspension.

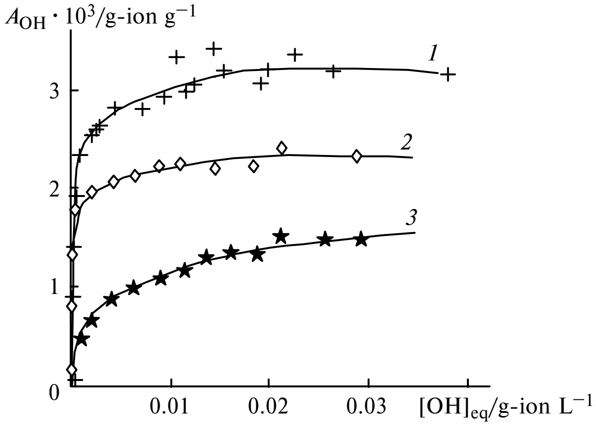

Fig. 2. Adsorption isotherms of OH groups (A_{OH}) on the surface of freshly precipitated Zr^{IV} oxyhydroxides with precipitation pH of 5.5 (*1*); 7 (*2*); 10 (*3*). $[OH]_{eq}$ is the equilibrium concentration of OH groups in the suspension.

Table 3. Calculation of the amounts of OH groups adsorbed on the freshly precipitated ferrogel with pH_{pr} 8 using the data of pH-metric titration of a suspension in 0.1 *M* NaCl

V_{titr} /mL	$[OH]_0$ /g-ion L^{-1}	pOH_{susp}	$(a_{OH})_{eq}$ /g-ion L^{-1}	γ_{OH}	$[OH]_{eq}$ /g-ion L^{-1}	A_{OH} /g-ion g^{-1}
0	0	7.44	$3.63 \cdot 10^{-8}$	1.0	$3.63 \cdot 10^{-8}$	0
1	0.001075	4.85	$1.41 \cdot 10^{-5}$	1.0	$1.41 \cdot 10^{-5}$	0.000213
3	0.003190	3.40	0.000398	1.0	0.000398	0.000567
5	0.005270	2.80	0.001585	0.98	0.001617	0.000749
8	0.008310	2.50	0.003162	0.97	0.003260	0.001050
11	0.011260	2.33	0.004677	0.94	0.004976	0.001326
14	0.01410	2.18	0.006607	0.90	0.00734	0.001446
17	0.01690	2.06	0.00871	0.87	0.01001	0.001497
20	0.01960	1.99	0.01023	0.84	0.01218	0.001632
23	0.02228	1.95	0.01122	0.82	0.01368	0.001918
26	0.02485	1.90	0.01259	0.79	0.01594	0.002014
30	0.02817	1.85	0.01412	0.77	0.01834	0.002261
35	0.03217	1.77	0.0170	0.72	0.02358	0.002018
40	0.03600	1.74	0.01820	0.69	0.02638	0.002309
45	0.03967	1.69	0.02042	0.65	0.03141	0.002024
50	0.04320	1.66	0.02188	0.63	0.03473	0.002117

Table 4. Calculation of the amounts of OH groups adsorbed on the freshly precipitated chromogel with pH_{pr} 8 using the data of pH-metric titration of the suspension in 0.1 *M* NaCl

V_{titr} /mL	$[OH]_0$ /g-ion L^{-1}	pOH_{susp}	$(a_{OH})_{eq}$ /g-ion L^{-1}	γ_{OH}	$[OH]_{eq}$ /g-ion L^{-1}	A_{OH} /g-ion g^{-1}
0	0	6.89	$1.29 \cdot 10^{-8}$	1.0	$1.29 \cdot 10^{-8}$	0
1	0.001075	5.79	$1.62 \cdot 10^{-6}$	1.0	$1.62 \cdot 10^{-6}$	0.000253
3	0.003190	3.95	0.000112	1.0	0.000112	0.000753
5	0.005270	3.00	0.001	1.0	0.001	0.001055
8	0.008310	2.70	0.001995	0.98	0.002036	0.001572
11	0.011260	2.45	0.003548	0.96	0.003696	0.001923
14	0.01410	2.25	0.005623	0.92	0.006112	0.002059
17	0.01690	2.13	0.007413	0.89	0.008058	0.002312
20	0.01960	2.04	0.00912	0.85	0.01099	0.002844
23	0.02228	1.95	0.01122	0.82	0.01368	0.002310
26	0.02485	1.91	0.01230	0.80	0.01537	0.002581
30	0.02817	1.88	0.01318	0.78	0.01690	0.003123
40	0.03600	1.78	0.0170	0.71	0.02394	0.003487
50	0.04320	1.69	0.02042	0.65	0.03141	0.003552

The S_{spec} values were measured using the nitrogen thermodesorption method on a Flowsorb-II 2300 laboratory electron surface analyzer (for Al and Cr oxides) or using the low-temperature nitrogen desorption method on a Carlo Erba Strumentazione Microstructure Lab. Sorptomatic 1900 instrument (for Y, Sm, and In oxides).

Results and Discussion

The shape of the isotherms is associated with so-called "high-affinity" or H-type isotherms.[21] The limiting adsorption A_{OH} value corresponds to the plateau on the curve of the specific amount of sorbed hydroxyl ions *vs.* pH of the equilibrium solution. This value was used to calculate S_{spec}.

Table 5. Pseudo-equilibrium values of the amounts of OH groups sorbed on freshly precipitated hydrogels in 0.1 *M* NaCl

pH_{pr}	Zr	Cr	Fe	In
5.5	0.0033	—	—	—
7	0.0024	0.0041	0.0024	0.00135
8	—	0.0033	0.0021	—
9	—	0.0025	0.0015	0.00115
9.5	0.0015	—	—	—
10	—	—	—	0.0008

Table 6. The results of determination of S_{OH} for dry oxides

Oxide	Pretreatment	S_{spec} /m^2 g^{-1}	A_{OH} / g-ion g^{-1}	S_{OH} /Å^2
γ-Al_2O_3	Calcined for 2 h at 1000 °C	73.6	0.0002	60
Cr_2O_3	Obtained by decomposition of $(NH_4)_2Cr_2O_7$ and calcined for 2 h at 1000 °C	3.9	$1.4 \cdot 10^{-5}$	46
Y_2O_3	Air-dry, reactive	12.6	$2.6 \cdot 10^{-5}$	80
Sm_2O_3	Air-dry, reactive	3.6	$5.2 \cdot 10^{-5}$	38
In_2O_3	Air-dry, reactive	3.25	$1.2 \cdot 10^{-5}$	45

It can be seen that the amounts of OH^- groups adsorbed at saturation decrease with an increase in pH_{pr} for all the hydrogels studied. Meanwhile, we found previously[5] that oxyhydroxide hydrogels possess a true point of surface zero charge, which corresponds to a definite precipitation pH (pH_{PZC}), does not depend on electrolyte concentration in the suspension, and is a constant for a given initial compound and a given ionic medium. Evidently, hydrogels obtained at pH_{pr} values lower than that corresponding to the true point of zero charge (pH_{PZC}) have a positive surface charge, and some of the OH groups are consumed for neutralizing this charge. As a result, the A_{OH} and S_{spec} values obtained are overestimated. On the contrary, when pH_{pr} is higher than that of the true point of surface zero charge (pH_{PZC}), the hydrogel surface is already partly occupied by sorbed OH groups, and the determined A_{OH} and S_{spec} values are underestimated. Thus, the actual A_{OH} and S_{spec} values are found when pH_{pr} corresponds to the true pH_{PZC} of hydrogels in the given electrolyte.

The published data on the sorption capacity of oxyhydroxides toward OH groups are rather contradictory. Thus it has been reported[6] that a ferrogel sample precipitated from a solution of $Fe(NO_3)_3$ by the addition of aqueous NaOH up to pH 8 had a surface density of sorption sites C_s of 7—8 sites nm^{-2}. This Figure involves all the surface sites, which can be occupied either by OH groups or by protons, depending on the conditions. Obviously, not all of these sites can be occupied by OH groups. We found[4] that freshly precipitated ferrogels $Fe(OH)_3$ have a pseudo-equilibrium capacity for OH groups of $(1.0—1.5) \cdot 10^{-3}$ g-ion g^{-1}. If we assume that S_{spec} for these samples is equal to 600—800 m^2 g^{-1}, the molecular area for an OH group

(S_{OH}) would be 66—133 Å^2, which corresponds to C_s of 1 or 2 OH groups per nm^2. Having measured the values of pseudo-equilibrium sorption of chlorine-containing complexes of rhodium and iridium,[7] we found the C_s value for freshly precipitated ferrogels to be 2 or 3 OH groups per nm^2. Other works[8,9] give the following C_s values for goethite: 2.7 OH groups per nm^2 and 3 or 4 sorption sites per nm^2. The published data for Fe^{III} oxyhydroxides are also diverse,[10—15] namely, 5, 2, 7, and 15 OH groups per nm^2 (for akaganeite). The highest amount of OH groups sorbed on a neutral γ-Al_2O_3 surface can be estimated as 2 OH groups per nm^2; the values for the Zr^{IV} oxyhydroxide surface are 8 [15] and 5[16], and that for anatase[17] is 1 OH group per nm^2. The data for other oxyhydroxides are scarce. The scatter of the published data on the sorption capacity of oxyhydroxides toward OH groups can be explained by the fact that the researchers cited used hydrogels with a nonzero charge of the surface.

After plotting the dependence of A_{OH} on pH$_{pr}$ (Fig. 3) using the data of Table 5, we can find the A_{OH} values corresponding to the noncharged surface:

	Zr	Cr	Fe	In
pH$_{PZC}$ [5]	9.4	8.4	8.1	10
$A_{OH} \cdot 10^4$/g-ion g^{-1}	14	31	19.5	9

Figure 3 indicates that the dependences of A_{OH} and pH$_{PZC}$ on the gel pH$_{pr}$[4] are linear. This proves that the variation of A_{OH} is governed by the surface charge but not by the surface area.

Apparently, the S_{spec} of a hydrogel is dependent on the nature of initial salt, the swamping electrolyte ions, the precipitating agent, and the temperature of precipitation but not on the pH$_{pr}$, while the pH$_{pr}$ influences only the surface charge. This, apparently, accounts for all the specific features of the behavior of hydrogels in the determination of their pH$_{PZC}$.

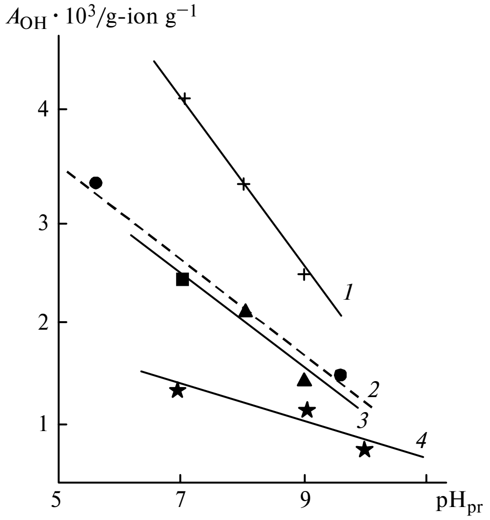

Fig. 3. Dependence of the limiting adsorption of OH groups (A_{OH}) by oxyhydroxide hydrogels on the precipitation pH: (*1*) chromogels, (*2*) zirconogels, (*3*) ferrogels, (*4*) indiogels.

According to the data obtained, of the four hydrogels studied, the highest capacity toward OH groups was shown by chromogel, while the lowest one was noted for indiogel. Previously, we showed that in the pH$_{pr}$ range of 7—11, indiogels have the composition $In(OH)_3 \cdot 0.5H_2O \cdot 0.21NaOH$. Sodium hydroxide is strongly bound to indium hydroxide and is not washed out by water. In the case of indiogel, A_{OH} = $9 \cdot 10^{-4}$ g-ions g^{-1} corresponds to a molar ratio of 0.15, hence, one mole of $In(OH)_3$ binds 0.36 OH groups and 3 moles of $In(OH)_3$ bind up to one OH group.

Ferrogels and zirconogels are characterized by very close A_{OH} values near the pH$_{PZC}$ point; these hydrogels also exhibit similar sorption and acid-base properties at almost equal ionic potentials.[5] Accordingly, similar S_{spec} values can be expected of the hydrogels. However, the differences between A_{OH} and, correspondingly, S_{spec} values of chromogels and ferrogels are very great over the whole range of pH$_{pr}$. This explains why sorption activities of these oxyhydroxides are sharply different, despite close acid-base properties and equal ionic potentials of Fe^{III} and Cr^{III} cations.[5] Hence, the difference between the properties of chromogels and ferrogels is due to different mechanisms of their hydrolytic polymerization during alkaline hydrolysis.

Let us consider the S_{spec} values and the surface charge of hydrogels in order to analyze data on the kinetics of heterogeneous hydrolysis.[4] Weakly basic indiogel has a positively charged surface up to pH$_{pr}$ 10, the surface charge being dependent on the pH$_{pr}$ only slightly, and the surface area is much lower than that of other hydrogels studied. These properties can be responsible for the lower sorption activity of indiogel as compared to other hydrogels, this activity being influenced only slightly by the pH$_{pr}$.[4,5] It is more difficult to explain why the large surface area of chromogel does not provide the corresponding increase in the sorption activity. Taking account of our previous study on the sorption of negatively charged complex ions,[4] we can suggest that an increase in the sorption activity is counterbalanced by the high concentration of the surface negative charge on chromogels with pH$_{pr}$ > 8. In addition, the amphoteric character of Cr^{III} hydroxide implies its higher affinity to OH groups*.

The variation of A_{OH} for hydrogels on aging in electrolyte solutions are presented in Table 7. It can be seen that the A_{OH} values for gels aged for 2 h and for 20 h at temperatures near the water boiling point differ little from each other and from values for freshly prepared samples. This agrees with observations indicating that the sorption activity[22] changes only slightly during aging under the same conditions. Contrary to the common opinion that the composition and properties of

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* The ability of $Cr(OH)_3$ to form anionic hydroxo complexes $[Cr(OH)_4]^-$ or $[Cr(OH)_6]^{-3}$, which is not typical of iron(III) hydroxide.

Table 7. Amounts of OH groups adsorbed at limiting sorption on the surfaces of hydrogels precipitated at pH_{pr} 7 and 8 and aged by heating in electrolyte solutions

Aging conditions	Gel (pH_{pr})			
	Zr (7)	Fe (8)	Cr (8)	In (7)
NaCl, *1* M, 2 h, 80 °C	0.0025	0.0012	0.0030	0.00115
Na_2SO_4, 0.5 *M*, 2 h, 80 °C	0.0024	0.0015	0.0030	0.0011
NaCl, 1 *M*, 20 h, 96 °C	0.0020	0.0015	0.0026	—
Na_2SO_4, 0.5 *M*, 20 h, 96 °C	0.0024	0.0017	0.0031	0.0012

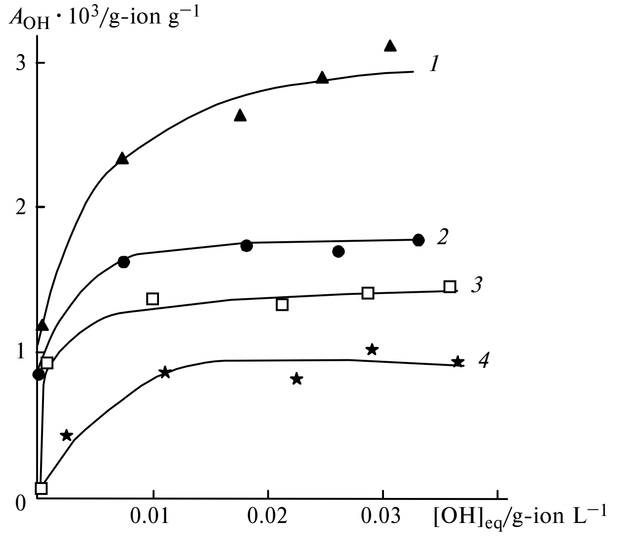

Fig. 4. Adsorption isotherms of OH groups (A_{OH}) on the surface of the oxyhydroxide hydrogels freshly precipitated from a 1 *M* solution of NaCl: (*1*) chromogel, pH_{pr} 9.5; (*2*) zirconogel, pH_{pr} 9.5; (*3*) ferrogel, pH_{pr} 8; (*4*) indiogel, pH_{pr} 10.

amorphous oxyhydroxides change very rapidly, these data demonstrate that Fe^{III}, Cr^{III}, In^{III}, and Zr^{IV} oxyhydroxides are stable (or metastable) systems, the surface charge being the only parameter that can be easily changed.

As noted above, the specific surface area can be calculated from the limiting sorption values A_{OH} if the value of molecular area of an OH group on the oxyhydroxide surface is known; we denote this value by S_{OH}.

The S_{OH} value (in Å^2) was calculated from the A_{OH} values for crystalline samples with known S_{spec} (see Table 6) or using published data. The S_{OH}, A_{OH}, and S_{spec} values are related to each other by the expression:

$$S_{spec} = S_{OH}A_{OH}N_A/10^{20} \text{ m}^2 \text{ g}^{-1}, \qquad (2)$$

where N_A is the Avogadro constant and 1 m^2 = 10^{20} Å^2.

Thus, from known S_{spec}, we can get

$$S_{OH} = S_{spec} \cdot 10^{20}/A_{OH}N_A. \qquad (3)$$

It follows from Table 6 that the S_{OH} values for crystalline dry samples are highly scattered. It is known[23] that, on contacting oxides with water or aqueous solutions of electrolytes, gel layers of oxyhydroxides are formed on their surfaces, although it is unclear to what extent this affects the S_{spec} value. It is also known[24] that oxides of rare earth elements (here, Y and Sm)[24] rapidly absorb water molecules from air or aqueous solutions to give $Ln(OH)_3$ hydroxides. The hydration of the Sm_2O_3 oxide to give $Sm(OH)_3$ should proceed to a much higher extent than that of Y_2O_3.[24] It can be suggested that this induces an at least twofold increase in its surface area, resulting in $S_{OH} \approx 45–50$ Å^2. The pseudo-equilibrium in the hydration of these air-dry oxides at ~20°C is established over a period of 10 to 15 min[4]; hence, under the conditions of our experiments, attainment of such a pseudo-equilibrium is quite likely.

Apparently, the surfaces of polymeric oxyhydroxides do not possess a close packing of atoms, typical of surfaces of nonhydrated crystalline oxides. The ion radii of the central atoms of the oxyhydroxides studied differ from each other by a factor of not more than 1.5.[5] Therefore, the hydrogel surfaces should be uniform networks of polymeric chains. A plausible assumption is that *the molecular area of a OH group at a given ionic strength is the same for all the oxyhydroxides and is about 50 Å^2. This is the main assumption we made in calculations.* A C_s value equal to 2 OH groups per nm^2 is often reported for hydrogels. Using the value S_{OH} = 50 Å^2 and the above data for hydrogels, we derive the following S_{spec} values:

	Zr	Cr	Fe	I
S_{spec} /m$^2 \cdot$g^{-1} E(OH)$_n$	420	930	585	240

The resulting values are at the same level as those usually reported for amorphous oxyhydroxides. Obviously, these values are closer to actual S_{spec} than the data for surface areas found by the BET method for pre-dried amorphous samples. For example, the S_{spec} value obtained by the BET method for the Fe^{III} oxyhydroxide precipitated[25] from a solution of Fe^{III} nitrate on treatment with ammonia at pH 7.5 and dried over phosphoric anhydride at ~20°C is ~300 m^2 g^{-1}. For the oxyhydroxide precipitated from a solution of Fe^{III} perchlorate at pH 7, the pH-metric titration method gives ~600 m^2 g^{-1}. The $Fe(NO_3)_3$/NaOH ferrogel[6] with pH_{pr} = 8 aged in the mother liquor for 4 h and dried had S_{spec} of ~300 according to the BET method, or ~350 from the of negative adsorption* of Na^+, or ~700 m^2 g^{-1} from the negative adsorption* of Mg^{2+}.

Thus, the data we obtained with some assumptions give reasonable S_{spec} values.

The size of the molecular area and the specific surface area of a hydrogel can depend on the ionic strength of the swaming electrolyte. In order to verify this assumption, a number of experiments were carried out in which sorption isotherms of OH groups were measured using a 1 *M* solution of NaCl. The results

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* A method of measuring the specific surface area.[6]

Table 8. Activity coefficients of the OH groups in the region of adsorption measurements (from 1 to 50 mL of alkali added) in 1 *M* NaCl

$[OH^-]$* /g-ion L^{-1}	pOH	a_{OH} /g-ion L^{-1}	γ_{OH}
0.00023	3.89	0.000129	0.56
0.00053	3.54	0.000288	0.54
0.00206	2.92	0.00120	0.58
0.00724	2.32	0.00478	0.66
0.00724	2.35	0.00447	0.62
0.0099	2.26	0.00549	0.55
0.01741	2.01	0.00977	0.56
0.01788	1.99	0.01023	0.57
0.02071	1.89	0.01288	0.62
0.0212	1.98	0.01047	0.49
0.02447	1.86	0.01380	0.56
0.02606	1.85	0.01412	0.54
0.02865	1.79	0.01622	0.57
0.0287	1.86	0.01380	0.48
0.03094	1.72	0.01906	0.62
0.03294	1.75	0.01778	0.54
0.03565	1.74	0.01820	0.51
0.03618	1.67	0.02138	0.59

* From the results of titration.

obtained are presented in Fig. 4. Table 8 gives the results of calculation of γ_{OH} in a 1 *M* solution of NaCl using the data of titration and pH measurements by a glass electrode. It can be seen that the activity coefficient in a 1 *M* solution, unlike that in 0.1 *M* solutions, is virtually constant (0.56±0.023). Due to a higher ionic strength of the inert electrolyte, the changes in a_{OH} are offset by its own OH groups. Meanwhile, the A_{OH} values obtained by titration in a 1 *M* solution of NaCl virtually coincide with those obtained for a 0.1 *M* solution. Therefore, the molecular area of a OH group does not depend on the ionic strength of the solution. It may be recommended to perform the measurements at an ionic strength equal to 1 using NaCl because in this medium, the γ_{OH} values are constant and the glass electrode is protected from the action of alkali by the sodium ions present in the solution at high concentrations.

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