Sorption properties of indium oxohydroxides

S. I. Pechenyuk,* S. I. Matveenko, E. V. Kalinkina, and N. L. Mikhailova

Institute of Chemistry, Kola Science Center of the Russian Academy of Sciences,
14 ul. Fersmana, 184200 Apatity, Russian Federation.
Fax: +7 (815 5) 53 0925. E-mail: root@ksc-ic.murmansk.su

The influence of the pH of precipitation and of the ionic medium on the sorption properties (the surface charge and the kinetic characteristics of sorption) of indium oxohydroxides obtained by alkaline hydrolysis of indium nitrate was investigated. It was found by the method of zero charge point, by the indicator reactions of heterogeneous hydrolysis, by drop titration, and by thermography that $In(OH)_3 \cdot 0.5\, H_2O \cdot (0.2-0.3)\, NaOH$ with a very small degree of crystallinity is formed at $pH > 6$. The basic properties of the oxohydroxide increase with increasing pH of precipitation up to 9—10 and then remain constant. The rates of the indicator reactions depend slightly on the pH of precipitation. The sorption properties of indium oxohydroxides differ markedly from those of ferrogels obtained under similar conditions. The results obtained can be explained by the formation of quasi-stable microstructures during the precipitation of indium oxohydroxide.

Key words: sorption properties; zero charge point; indium oxohydroxide; indicator reaction rate.

Oxohydroxide-based sorbents are of great interest for both chemical and environmental technologies.[1,2] It has been shown previously[3] that as-prepared gelatinous oxohydroxide sorbents have significant advantages as compared to dry granulated oxide sorbents. Nevertheless, the sorption properties of gelatinous oxohydroxides are poorly studied. Previuosly, a comparative study of the sorption properties of gels of metal oxohydroxides in various ionic media has been carried out in order to create a theoretical model for prediction of the conditions of extracting complex-forming metals from complex-forming media by inorganic oxohydroxide sorbents.[4—8] The behavior of as-prepared oxohydroxides at the initial period was of special interest.

In this work, indium oxohydroxides that were not subjected to drying and known as *indiogels* were studied. It was of interest to compare the behavior of indium(III) oxohydroxides with that of iron(III)[4—6] and chromium(III) oxohydroxides, since they have the equally charged central atoms but different ionic radii and electronic structures.

The sorption properties of indium oxohydroxides are practically unknown except work[9] in which the effects of the pH of precipitation and the temperatures of drying and calcination on the specific surface area and pore structure of $In(OH)_3$ were studied by the adsorption method (sorption of benzene vapor). The samples obtained at pH 8 and 10 and dried at temperatures not higher than 120 °C have S_{sp} = 169 and 124 $m^2\ g^{-1}$, respectively. Calcination results in a decrease in S_{sp} to 25—30 $m^2\ g^{-1}$.

In this work, a series of samples of indium oxohydroxide was obtained and their sorption properties were studied by the method of zero charge point (ZCP)[10] and by the indicator reactions of heterogeneous hydrolysis of complex anions ($IrCl_6^{2-}$ and $PtCl_4^{2-}$).[1,4—8] The sorption properties mean the capability of an oxohydroxide (a dispersed phase) to extract a sorbate from the bulk of a solution (a dispersion medium) rapidly and to a high degree (close to 100%). Since a sorbent is a highly dispersed phase that is far from equilibrium, the kinetic parameters (the rate constants of indicator reactions) are more suitable as characteristics. The sorption of the H_3O^+ and OH^- ions being studied by the ZCP method has a pseudo-equilibrium nature; it is used for the estimation of the sign and value of the charge of the surface of a sorbent. The interrelation between the charge of the surface and the rate of heterogeneous hydrolysis was of special interest.

Experimental

For preparing the indiogels, a solution of $In(NO_3)_3$ obtained by dissolution of a weighed portion of In_2O_3 (analytical grade) in excess nitric acid (chemically pure grade) was used; the concentration of the solution was 0.10 g In per mL, 1 mol L^{-1} with respect to HNO_3. The aliquot of a solution corresponding to 1.2 g $In(OH)_3$ (0.007 mol) was diluted with distilled water, and a solution of NaOH (chemically pure grade) was added under stirring and pH-metric control till the establishment of the specified pH of precipitation (pH_1) in a ~50 mL suspension which is constant during ~5 min. The precipitate was separated by centrifuging, triply washed by

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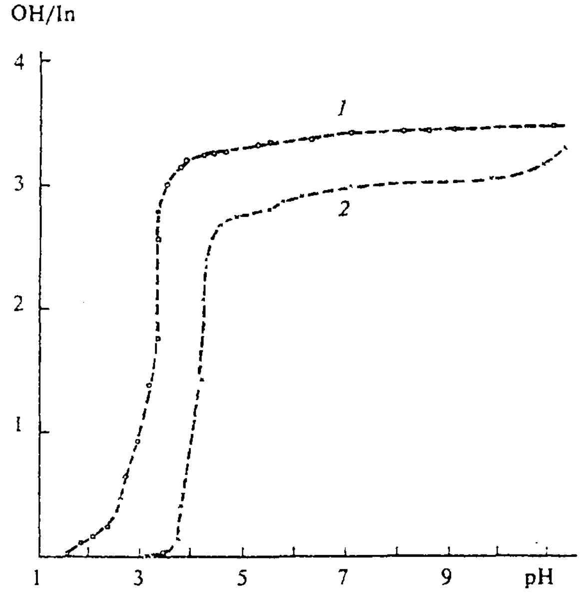

Fig. 1. Drop titration of solutions of In^{III} salts: *1*, titration of a 0.1566 *M* solution of $In(NO_3)_3$ (the data of this work); *2*, titration of a 0.0154 *M* solution of $InCl_3$ (the literature data, Ref. 13).

decantation with H_2O, and centrifuged again. The samples obtained were slurried in 50 mL of water and used for experiments.

Composition of indiogels. The compositions of the samples obtained at different pH_1 were determined by drop titration with NaOH (see Refs. 4—8) (Fig. 1). The samples of $In(OH)_3$ (0.007 mol) corresponding to pH_1 7, 9, and 11, were washed with water as described above and introduced in 200 mL of 0.5 *M* KNO_3. The precipitate was filtered off, and the pH values of the washing liquor (pH_2), the suspension in 0.5 *M* KNO_3 (pH_s), and the filtrate (pH_3) were measured. To calculate the OH/In ratio in the samples, the amounts of the alkali washed off and displaced by the electrolyte were determined (Table 1).

After washing, the samples were dried in a vacuum desiccator over concentrated H_2SO_4 at ~20 °C for 6—7 days and then studied by the DTA—TG and X-ray diffraction methods. The thermal analysis was carried out with the ~0.2 g sample at a heating rate of 10 deg min^{-1} on an NTR-70 instrument combined with PRT-1000 and a Pt—PtRh thermocouple and PP-63 instrument combined with a VT-1000 torsion balance. X-ray diffraction study was performed on a DRON-2 diffractometer with the use of Cu-Kα-radiation (graphite as monochromator).

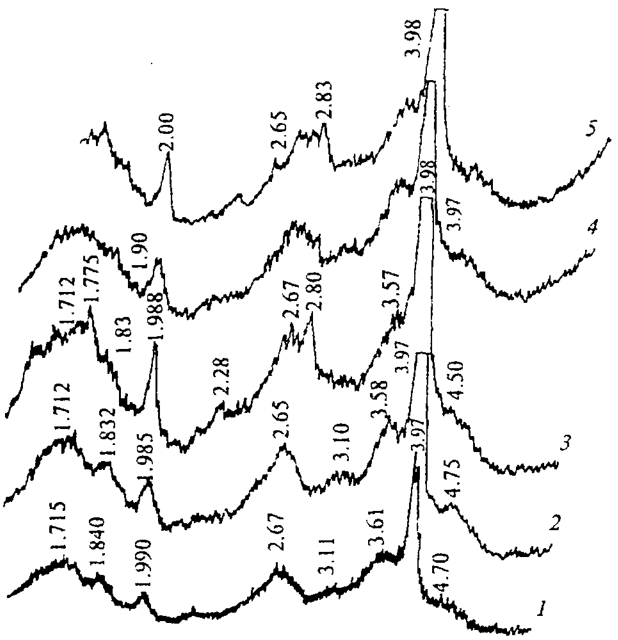

Fig. 2. Diffractograms of dried samples of In^{III} oxohydroxides with the pH of precipitation: 7 (*1*), 9 (*2*), 11 (*3*); of samples with pH_1 9 washed and stored under water for 11 days (*4*) and under mother liquor (*5*).

The DTA curves obtained are practically identical: they have one endo-effect corresponding to the removal of total water from the sample. They differ only by the fact that the maximum of endo-effect for the sample with pH_1 7 corresponds to 204 °C and the maxima for two other pH values correspond to 262—264 °C (the latter is close to the value available in the literature, Ref. 9). No effects of crystallization of the product of dehydration are observed on the DTA curves. The compositions of the samples are calculated based on the TG data (see below).

It is seen from the diffractograms presented in Fig. 2 (the age of the samples from the moment of precipitation is equal to 10—15 days) that all the samples are slightly crystallized.

Determination of the pH of the zero point was performed by the Parks method[10] modified by us for gels[1] and by the potentiometric titration of samples on a pH-121 pH-meter in an argon atmosphere in a half-open type quartz cell with an ESL-43-07 glass electrode and an EVL-1M1 accessory elec-

Table 1. The OH/In ratios determined by drop titration of $In(NO_3)_3$ with a solution of NaOH

pH_1	pH_2	V_2/mL	pH_3	V_3/mL	OH^a /eq (g-at. In)$^{-1}$	OH^b or H /g-eq (g-at. In)$^{-1}$	OH^c /eq (g-at. In)$^{-1}$
7.0	6.3	368	5.7	200	3.19	0	3.19
8.96	8.3	310	6.4	200	3.24	0	3.24
11.	10.6	330	10.	200	3.323	0.006 OH	3.32

[a] The amount of OH introduced. [b] The amount of washed off OH or attached H during washing. [c] OH in the precipitate.

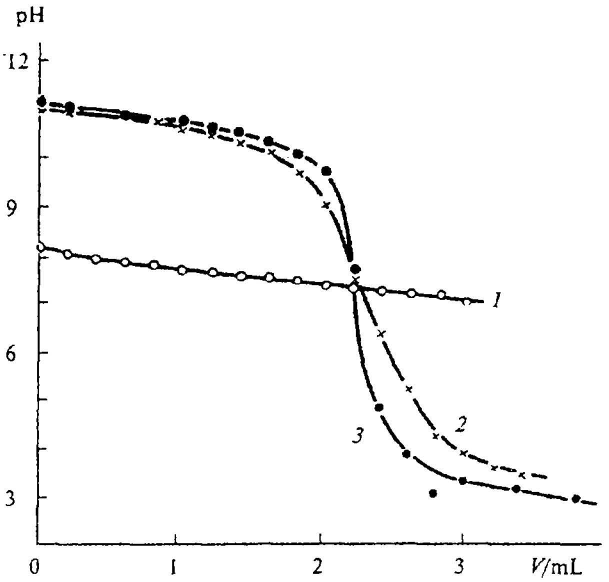

Fig. 3. Potentiometric titration of In oxohydroxides in a 0.1 *M* solution of NaCl: *1*, the starting In_2O_3; *2*, indiogel with pH_1 9; *3*, the blank experiment.

Table 2. Values of pH_{ZCP} of indiogels and In_2O_3 in solutions of NaCl and Na_2SO_4 at pH 7—11

C/N	pH_{ZCP}					
	In_2O_3	7	8	9	10	11
			NaCl			
0.01	5.7	5.1	6.8	8.1	9.9	—
0.1	6.3	5.9	7.6	8.8	10.2	10.4
1.0	7.3	6.7	7.9	9.1	9.7	10.6
			Na_2SO_4			
0.01	—	—	7.7	8.6	10.1	—
0.1	—	7.4	8.2	9.3	9.9	—
1.0	—	—	8.4	9.3	10.0	—

trode immersed in a slurry of indiogel (pH_s) or in a reference solution (pH_0). Prior to titration, argon was purged for ~1.5 h through the slurry of the gel washed as described above and a solution of an electrolyte to remove dissolved CO_2. Then the slurry (50 mL) was introduced to 150 mL of a solution of the electrolyte prepared in such a way that the concentration of the electrolyte was 1.0, 0.1, or 0.01 mol L^{-1} in the final volume of the slurry. To estimate the initial pH or the pH_0 values, a 0.123 mol L^{-1} solution of carbonate-free NaOH (5 mL) was added, then the slurry was titrated by a solution of the acid (0.1 *M*, fixanal) whose anion corresponds to the anion of the electrolyte at the rate of 0.4 mL min^{-1}. Recrystallized NaCl, Na_2SO_4, and $NaClO_4$ were used as supporting electrolytes. The amount of excess OH^- (H_3O^+) ions sorbed was determined by comparing pH_s and pH_0 during the blank experiment at the specified volume of the titrant. The pH_{ZCP} can be found graphically as the intersection point of the titration curve for the gel sample gel and the curve from the blank experiment (Fig. 3). The results of the determination of pH_{ZCP} are presented in Table 2.

Indicator reactions of heterogeneous hydrolysis. As in the other works,[4—8] the reaction rates of heterogeneous hydrolysis of $IrCl_6^{2-}$ and $PtCl_4^{2-}$ were used to characterize the surface properties. K_2IrCl_6 and K_2PtCl_4 obtained according to the known procedures[11] and characterized by elemental microanalysis and X-ray diffraction data were used. The initial concentrations of the Ir and Pt complexes were (2—3) · 10^{-4} mol L^{-1}, the volume of the reaction mixture was 200 mL, and the measurement and calculation procedures are similar to those described previously in Ref. 1. The contents of Ir and Pt were determined according to the known procedures.[12] The results are presented in Tables 3—5. Some data for the starting dry crystalline In_2O_3 were obtained for comparison (see Tables 2 and 5).

Results and Discussion

Drop titration of a solution of $In(NO_3)_3$ (see Fig. 1 and Table 1) with alkali and thermal analysis showed that $In(OH)_3$ was formed at the pH_1 > 4 region. The shape of the titration curve is typical and resembles those published previously.[13,14] The results of calculation of the OH/In ratio from the titration curve (see Table 1) practically coincide with the results of TG, which distinguishes In^{III} oxohydoxides from Fe^{III} oxohydroxides obtained under similar conditions.[4,15] Based on the thermal analysis, the compositions of the samples are the following:

pH_1	Composition
7	$In(OH)_3 \cdot 0.5\ H_2O \cdot 0.21\ NaOH$
9	$In(OH)_3 \cdot 0.57\ H_2O \cdot 0.21\ NaOH$
11	$In(OH)_3 \cdot 0.45\ H_2O \cdot 0.21\ NaOH$

Table 3. The rate constants (k_{obs}) of the heterogeneous hydrolysis of $PtCl_4^{2-}$ on the surface of indiogels in a 0.1 *M* solution of NaCl at pH 7—11

T/°C	$k_{obs} \cdot 10^4/s^{-1}$ [E_a/kJ mol^{-1}]							
	7	8	8.5	8.75	9	9.5	10	11
40	Plateau	3.5	4.0	4.7	2.70	2.59	2.26	2.30
50	—	7 (8.7)	9.60	12.8	8.2	8.0	6.2	7.2
60	—	22	~35[a]	~35[b]	22.6	21.9	15.6	20.0
		[79.2]	[92.5]	[84.5[b]]	[89.5]	[92.1]	[81.9]	[89.5]

[a] Extrapolation with the use of the temperature coefficient gives 2.3 · 10^{-3} s^{-1}. [b] Extrapolation with the use of the temperature coefficient.

Table 4. The rate constants (k_{obs}) of the heterogeneous hydrolysis of $IrCl_6^{2-}$ on the surface of indiogels in solutions of NaCl at pH_l 6—11

T/°C	$k_{obs} \cdot 10^4/s^{-1}$ [E_a/kJ mol^{-1}]					
	6	7	8	9	10	11
	C_{NaCl} = 0.5 mol L^{-1}					
80	6.9	13.5	15.8	18.6	—	—
70	1.5	4.0	5.3	7.4	11.0	11.0
60	—	—	1.4	2.6	2.9	2.9
50	—	—	—	—	0.7	0.9
		[114]	[114]	[100]	[119]	[119]
	C_{NaCl} = 0.1 mol L^{-1}					
70	—	—	—	15.3	18.3	—
60	—	—	—	6.2	7.1	—
50	—	—	—	1.6	2.2	—
		—	—	[103]	[100]	—

Table 5. The effect of the nature and concentration of the ionic background (C/N) on the rate of heterogeneous hydrolysis (k_{obs}) on the washed samples of indiogels and In_2O_3

T/°C	pH_l indiogel	Electrolyte	$k_{obs} \cdot 10^4/s^{-1}$				
			0.01	0.1	0.25	0.5	1.0
			$PtCl_4^{2-}$				
50	9	NaCl	—	8.2	6.4	2.4	1.6
50	9	Na_2SO_4	7.1	5.5	—	2.2	—[b]
50	9	$NaClO_4$	—	—	—	33.4	—
50	[a]	NaCl	—	1.0	—	—	—
			$IrCl_6^{2-}$				
80	[a]	NaCl	1.7	0.6	—	—	→0
60	9	NaCl	—	6.2	3.1	2.6	—
60	10	NaCl	—	7.1	—	2.9	—
60	9	$NaClO_4$	—	—	—	10.0	—
60	9	Na_2SO_4	—	—	→0	→0	→0

[a] For the concentration of electrolyte from 0.01 to 1.0 mol L^{-1}. [b] In_2O_3. [c] In 0.5 M Na_2SO_4 the precipitates of indiogel are strongly peptized and very difficultly filtered.

It has previously been reported[13] that the acid residues are resplaced completely with OH groups when the stoichiometric amount of alkali is added to a solution of $InCl_3$, (see Fig. 1, curve *2*). According to the reported data,[16] hydroxide dried at 120 °C is crystalline and has the composition of $In(OH)_3$. It is known[17] that $In(OH)_3$ loses structural water without formation of intermediates on heating in the temperature range of 200—350 °C. This explains the simple shape of the DTA curves obtained by us.

The titration curve (see Fig. 1) shows that pH_l 7, 9, and 11 correspond to the range of the OH/In ratios which significantly exceed 3. It is seen that $In(OH)_3$ sorbs up to 0.3 g-eq mol^{-1} of OH groups, some portion of which is hardly removed during washing off (see Table 1). Based on the composition, indium hydroxide is not polymerized during precipitation and drying as does Fe^{III} hydroxide (as well as titanium and zirconium hydroxides),[4—8] although it could be expected on the basis of the hydrolytic polymerization of the In^{3+} cations in solutions.[14,18,19] Even dried, the samples of indium hydroxides have a very small degree of crystallinity, because $In(OH)_3$ crystallizes slowly at room temperature. Therefore, it is reasonable to suggest that we are dealing mainly with the amorphous phase when carrying out the pH_{ZCP} and kinetic measurements; hence, the term "indiogel" is quite proper.

The acid-base titration curves of indiogels (see Fig. 3) are typical of poorly soluble amphoteric and weakly basic hydroxides and oxohydroxides.[1] As in all previous cases,[4—8] the titration is reversible. It follows from the data of Table 2 that the dependence of pH_{ZCP} on the concentration of an electrolyte is typical of gels; this confirms once more the gelatinous nature of the samples under study. The curves of the dependence of pH_{ZCP} on pH_l in a NaCl medium intersect at pH_l 10.0 and pH_{ZCP} 9.9 and almost at the same point in a Na_2SO_4 medium. Hence, the surface of indiogels has a more basic nature than that of ferrogels for which pH_l of the corresponding intersection point in the medium of NaCl is equal to 8.1. However, the samples studied contain the strongly bound 0.2 mol of NaOH per mole of $In(OH)_3$. This seems to explain the coincidence of the intersection points for chloride and nitrate media which is a difference between indiogels and other gels.[8] The data presented in Table 2 show that at $pH_l < 10$ indiogels with the added alkali sorb extra OH groups from a solution in addition to those strongly bound 0.2 mol mol^{-1}.

The results of studies of indiogels by the method of indicator reactions of the heterogeneous hydrolysis of $PtCl_4^{2-}$ (see Table 3) and $IrCl_6^{2-}$ (see Table 4) show that the rates of decrease in the concentrations of Ir and Pt in the solution contacting the indiogel obey the first-order law, as in the works reported previously.[1,4—8] The dependences of the observed reaction rate constants k_{obs} on pH_l for these complexes are quite different. For $IrCl_6^{2-}$ a pattern is observed which is similar to that obtained by us for ferrogels[4]: k_{obs} increases smoothly with increasing pH_l and comes to a plateau at $pH_l >$ 9—10. For $PtCl_4^{2-}$ the k_{obs} value is practically independent of pH_l; we did not observed such a phenomenon previously. This difference cannot be explained on the basis of the data available. As known,[1] the behavior of planar-square complexes in the reactions of heterogeneous hydrolysis is characterized by some characteristics.

The temperature dependences of the rate and activation energy E_a of the indicator reactions on indiogels are typical of the heterogeneous hydrolysis of these complexes. The E_a values are on the average equal to 110±4* and 87±4.4* kJ mol^{-1} for $IrCl_6^{2-}$ and $PtCl_4^{2-}$, respectively. A strong dependence of k_{obs} on the concentration of the ionic background of NaCl and Na_2SO_4 was observed (see Table 5). It is known[1] that the effect of

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* The average arithmetic error.

NaCl on the rate of heterogeneous hydrolysis is due to excess ligand in the course of the aquation of complexes, and the effect of sulfate ions is due to the interaction between the background electrolyte and the oxohydroxide sorbent.

A comparison of the starting In_2O_3 and the aged indiogel samples shows (see Table 2) that the oxide behaves as a gel during titration.[1] This can be explained by the formation of a gel film on the oxide surface during hydration.[20] The k_{obs} values for the heterogeneous hydrolysis of the starting In_2O_3 (see Table 5) were determined, and they proved to be significantly less than those for indiogels (see Tables 3 and 4).

The samples washed off from the mother liquor immediately after preparation and stored for 11 days under a water layer do not exhibit a decrease in the rate of heterogeneous hydrolysis of $IrCl_6^{2-}$. Thus, for the sample with pH_I 9 aged under water, $k_{obs} = 7.0 \cdot 10^{-4}\ s^{-1}$ at 70 °C in a 0.5 *M* solution of NaCl. For the sample with pH_I 7, $k_{obs} = 3.3 \cdot 10^{-4}\ s^{-1}$ under the same conditions, and this coincides with the k_{obs} values for the corresponding as-prepared samples. For the samples which were not washed off but stored under the mother liquor under the same conditions, $k_{obs} = 2.4 \cdot 10^{-4}\ s^{-1}$ and $1.3 \cdot 10^{-4}\ s^{-1}$, respectively. Thus, the sorption activity of the practically washed off samples does not decrease in the course of aging for the time mentioned, but this effect is quite noticeable for the unwashed samples. When the as-prepared indiogel samples are used without removal and washing off the mother liquor, their sorption activity decreases sharply: for $IrCl_6^{2-}$ in a 0.5 *M* solution of NaCl, $k_{obs} = 0.5 \cdot 10^{-4}\ s^{-1}$ (pH_I 9, 60 °C) and $3.6 \cdot 10^{-4}\ s^{-1}$ (pH_I 8, 70 °C), whereas for the washed off samples, $k_{obs} = 2.6 \cdot 10^{-4}\ s^{-1}$ and $5.3 \cdot 10^{-4}\ s^{-1}$, respectively.

For the xerogels with pH_I 8 and 10 dried in a vacuum desiccator over concentrated H_2SO_4 for 10 days, the following values of k_{obs} of the heterogeneous hydrolysis of $IrCl_6^{2-}$ at 60 °C in 0.5 *M* NaCl were obtained: $1.7 \cdot 10^{-4}\ s^{-1}$ and $3.1 \cdot 10^{-4}\ s^{-1}$, respectively; these practically coincide with those for the as-prepared samples. According to the data reported previously,[9] S_{sp} of the sample with pH_I 8 is higher by a factor of ~1.5 than that of the sample with pH_I 10; however, the rate of the indicator reaction for the second sample is about twice higher. This confirms the suggestion made by us[1] that the specific surface area of the gel does not determine the rate of heterogeneous hydrolysis.

A comparison with Fe^{III} oxohydroxides shows that heterogeneous hydrolysis on indiogels always occurs on the positively charged surface of the gel (*i.e.*, at $pH > pH_{ZCP}$), whereas on ferrogels, unlike this, the process in most cases occurs on the negatively charged surface ($pH > pH_{ZCP}$). The Fe^{III} oxohydroxide that posesses the less basic nature and consists of the macromolecules of hydrolytic polymers[21] exhibits significantly higher sorption activity than $In(OH)_3$.

Thus, a typical process of heterogeneous hydrolysis of complex anions occurs on indiogels; for indium, as for other transition and p-metals, gels with specified sorption properties can be obtained. The sorption properties of indiogels are rather stable. This is likely due to the formation of the quasi-stable microstructure of the gel which does not change under mild conditions of washing and drying. The data obtained concern precisely $In(OH)_3 \cdot 0.2\ NaOH$ rather than $In(OH)_3$. We failed to remove excess alkali by washing. It behaves as if it is strongly adsorbed, as it follows from the shape of the indiogel titration curves which are similar to the corresponding curves for ferro-, titano-, and zirconogels. The decrease in the sorption activity of the samples stored under the mother liquor or used together with it is most likely explained by the fact that the anions of the mother liquor gradually displace a portion of the excess OH groups.

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