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Determination of particle size in aqueous suspensions of hydrogels of iron(III), indium(III), aluminum, chromium(III), titanium(IV), and zirconium(IV) oxohydroxides

S. I. Pechenyuk,★ D. P. Domonov, and V. N. Nakonechnyi

I. V. Tananaev Institute of Rare Element and Mineral Chemistry and Technology,
Kola Research Center, Russian Academy of Sciences,
26a ul. Fersmana, 184209 Apatity, Murmansk Region, Russian Federation.
Fax: +7 (815 5) 57 6425. E-mail: pechenyuk@chemy.kolasc.net.ru

Dispersion of hydrogels of Fe^{III}, In^{III}, Al^{III}, Cr^{III}, Ti^{IV}, and Zr^{IV} oxohydroxides in an aqueous medium was studied by sedimentation analysis. The hydrogel dispersion depends on the metal nature, pH of precipitation, and suspension concentration. The systems are predominantly polydisperse, and the gel particle size ranges from 2 to 140 μm. The data obtained suggest that the gel particles are formed by three-dimensional networks consisting of polymeric chains metal—oxygen and contain cavities filled with water.

Key words: sedimentation analysis, oxyhydroxides, equivalent radius of particle, density, dispersion.

The role of nanoparticles in the genesis of gel systems has intensely been studied.[1] Hydrogels of tri- and tetravalent metal oxohydroxides (MOH) are interesting representatives of these systems.[2—6] The study of the rheological properties of freshly prepared monolith gels,[7—10] whose three-dimensional framework retained, suggests that the MOH hydrogels possess noticeable shear strength. They are continuous polymeric matrices in which liquid-crystalline phases consisting of fragments with unstable structure can be formed. It remains unclear how far these conclusions can be extended to suspensions of gels obtained by the fast alkali hydrolysis of aqueous solutions of the corresponding metal salts with continuous stirring in a vortex mode followed by washing from a mother liquor by multiple centrifuging and repulping.[3]

In this work, we attempted to reveal the state of the MOH gels in suspensions using sedimentation analysis, which is widely used to determine the fractional composition of microheterogeneous systems. There are many variants of apparatus equipment and mathematical methods for processing results of sedimentation analysis,[11—15] which is poorly used for studying hydrogels.[13,14]

We have previously found that the properties of objects called MOH hydrogels change remarkably due to the interaction with electrolyte solutions. This concerns acid-base and sorption characteristics,[5,6] consistency, and even color of the hydrogels. Due to partial crystallization, the concentrations of impurity ions and intramicellar water[4] and sedimentation rate change. We succeeded to develop a method for determination of the specific surface S_{sp} of the oxohydroxide hydrogels from the limiting amount adsorbed of the OH groups[16] and showed that the S_{sp} values for the freshly prepared MOH are independent of the pH of their precipitation. The S_{sp} values of Fe^{III}, Cr^{III}, Zr^{IV}, and In^{III} oxohydroxides are equal to 585, 930, 420, and 240 $m^2 g^{-1}$, respectively.

In this work, we studied the freshly precipitated at different pH and washed Fe^{III}, In^{III}, Al^{III}, Cr^{III}, Ti^{IV}, and Zr^{IV} oxohydroxides. The dispersion of their suspensions was studied by the sedimentation method in a gravitation field at different suspension concentrations in water and in an electrolyte (NaCl and Na_2SO_4) solution. We attempted to determine how the S_{sp} values of the MOH hydrogels depend on dispersion.

Experimental

The method of fast alkali hydrolysis of metal salt solutions was used to obtain MOH hydrogels.[17] All reagents were reagent and analytical pure grades. The stock solutions for preparation of the ferro- alumo-, and chromogels were aqueous solutions of $FeCl_3$ (53.3 g L^{-1} of Fe), $Al(NO_3)_3$ (48.75 g L^{-1} of Al), and $CrCl_3$ (38.93 g L^{-1} of Cr). A crystalline sample of $ZrO(NO_3)_2 \cdot 2.3H_2O$ served for the preparation of the zirconogel, and titanogel preparation used $TiCl_4$ (Merck—Schuchardt) with a density of 1.728 g cm^{-3}. Aliquots or weighed samples of the starting substances corresponding to 0.01 mole were diluted with water to ~50 mL. Then the solution was neutralized with a 2 *M* solution of NaOH with continuous stirring and pH-metric monitoring until a specified pH value was established and remained stable for ~5 min. Gels of Me^{III} were precipitated at pH_{pr} = 7, 9, and 11, and those of Me^{IV} were precipitated at pH_{pr} = 6, 8, and 10. The MOH precipitates were separated from a mother liquor and three times washed with H_2O by decantation using

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centrifuging, each time for 5 min at n = 2000 rpm. The washed precipitates were suspended in water to a volume of 250 mL to obtain a suspension with a concentration of 0.04 mol L^{-1}; this suspension was diluted two- and fourfold to obtain suspensions with concentrations of 0.02 and 0.01 mol L^{-1}, respectively. A solution of sodium chloride with a concentration of 1.0 mol L^{-1} was used as a dispersion medium containing a supporting electrolyte. To study the influence of the electrolyte on the sedimentation rate of MOH, the washed samples were suspended in an electrolyte solution and the corresponding correction for a volume change was introduced. After vigorous stirring, the suspension was poured into a sedimentometer.

To determine particle sizes in a dispersed phase (DP), the density of the MOH hydrogels was found by a bottle method. For this purpose, a portion of the hydrogel (10 mmol) was placed into a picnometer with a known volume, water was poured to a mark, and the picnometer was weighed. Knowing the number of hydrogel moles determined by the weight of the starting salt, we calculated the density of the gel ρ with and without account for the contents of intramicellar water and impurity ions[4] (Tables 1 and 2).

Sedimentation rates were measured at room temperature (20±5 °C) in calibrated tubular glass sedimentometers with a height of the suspension (liquid) column of 665±10 mm. The sedimentation rate was determined either from the velocity of movement of the boundary between a suspension and a pure liquid u (for the fast sedimentation of particles) or the velocity of increasing the sediment column u' (for slow rate of settling).[15] A known procedure[11,15] was used for mathematical processing of sedimentation curves. The whole DP weight in the sedimentometer (Q) was divided into the height of the suspension column H. For the rate of particle sedimentation u during time τ, a substance was settled from the column with the length $u\tau$, and the weight of the settled substance was expressed by the equation

$$m = Q\,u\tau/H, \quad (1)$$

where Q is the DP weight in the sedimentometer, kg; H is the height of the suspension column; u is the sedimentation rate of

Table 1. Molecular formulas of the metal oxohydroxide hydrogels[4] precipitated at pH 6—10

M	Molecular formula (number of intermicellar water molecules)			
	6*	7**	9	10***
Al^{III} [20]	$Al(OH)_3 \cdot 0.1NaNO_3$ $(125H_2O)$	$Al(OH)_3 \cdot 0.1NaNO_3$ $(125H_2O)$	$Al(OH)_3 \cdot 0.1NaNO_3$ $(125H_2O)$	—
Fe^{III}	—	$Fe(OH)_{2.5}Cl_{0.5}$ $(106H_2O)$	$Fe(OH)_{2.6}Cl_{0.4}$ $(78H_2O)$	$Fe(OH)_3$ $(67H_2O)$
In^{III}	—	$In(OH)_{2.7}(NO_3)_{0.3}$ $(117\ H_2O)$	$In(OH)_{2.9}(NO_3)_{0.1}$ $(115H_2O)$	$In(OH)_3$ $(112H_2O)$
Cr^{III}	—	$Cr(OH)_{2.5}Cl_{0.5}$ $(88H_2O)$	$Cr(OH)_{2.75}Cl_{0.25}$ $(63H_2O)$	$Cr(OH)_3$ $(74H_2O)$
Ti^{IV}	$TiO(OH)_2 \cdot 0.23NaCl$ $(83H_2O)$	$TiO(OH)_2 \cdot 0.26NaCl$ $(81H_2O)$	—	$TiO(OH)_2 \cdot 0.3NaCl$ $(77H_2O)$
Zr^{IV}	$Zr(OH)_{3.8} \cdot (NO_3)_{0.2}$ $(103H_2O)$	$Zr(OH)_{3.8} \cdot (NO_3)_{0.2}$ $(128H_2O)$	—	$Zr(OH)_{3.9} \cdot (NO_3)_{0.1}$ $(135H_2O)$

* For aluminum oxohydroxide, pH = 5.

** For Ti^{IV} and Zr^{IV} oxohydroxides, pH = 8.

*** For Fe^{III}, In^{III}, and Cr^{III} oxohydroxides, pH = 11.

Table 2. Densities ($cm^3\ g^{-1}$) of the dispersed phase of the metal oxohydroxide hydrogels*

M	Medium	Densities at precipitation pH 6—11											
		6**		7		8		9		10		11	
		ρ	ρ'	ρ	ρ'	ρ	ρ'	ρ	ρ'	ρ	ρ'	ρ	ρ'
Al^{III}	H_2O	1.90	1.02	2.44	1.02	—	—	2.39	1.02	—	—	—	—
	NaCl	—	1.04	1.47	1.05	—	—	2.39	1.05	—	—	—	—
Fe^{III}	H_2O	—	—	2.85	1.04	—	—	3.10	1.05	—	—	3.76	1.06
	NaCl	—	—	1.60	1.06	—	—	1.72	1.06	—	—	2.36	1.09
In^{III}	H_2O	—	—	3.43	1.06	—	—	3.98	1.06	—	—	4.06	1.06
	NaCl	—	—	2.57	1.09	—	—	2.52	1.09	—	—	3.06	1.10
Cr^{III}	H_2O	—	—	2.21	1.04	—	—	4.43	1.07	—	—	3.50	1.06
Zr^{IV}	H_2O	3.52	1.06	—	—	3.21	1.05	—	—	3.04	1.04	—	—
Ti^{IV}	H_2O	3.03	1.05	—	—	2.94	1.05	—	—	3.22	1.06	—	—

* ρ and ρ' are the densities ignoring and taking into account intramicellar water, respectively.

** For aluminum oxohydroxide, pH = 5.

particles, m s^{-1}; τ is the time of substance sedimentation, s. Assuming a spherical shape of the particles that obeys Stokes law, one can obtain for a monodipersed system

$$m = [2Qg(\rho - \rho_0)r^2\tau]/9\eta H, \qquad (2)$$

where r is the equivalent radius of a DP particle; ρ and ρ_0 are the densities of the DP and dispersion medium, respectively, kg m^{-3}; η is the dynamic viscosity, poise. The dispersion analysis of polydisperse systems is based on the concept that a system consists of several fractions, which can be considered as individual monodisperse systems (Fig. 1). A sedimentation curve, being a dependence of the sediment weight on the sedimentation time, is divided into several regions, and tangent lines to the curve are drawn at the boundary points. These tangent lines cut regions in the ordinate corresponding to the weights of the fractions with $r \geq r_1$, $r \geq r_2$, *etc.* Then the equivalent radii r_1, r_2, *etc.* are calculated using Eq. (2). The Q/H value is accepted constant. The resulting sedimentation curves for suspensions of different MOH with a concentration of 0.04 mol L^{-1} are presented in Fig. 2.

Similar curves for the ferrogels, under different conditions, are shown in Fig. 3. The results of an analysis of the sedimentation curves are given in Tables 3 and 4. When processing the experimental curves, we divided a curve into two—six regions and, correspondingly, determined the equivalent radii for two—six gel fractions. Only the equivalent radii calculated with account for intramicellar water are given in Tables 3 and 4. In calculations ignoring intramicellar water, the equivalent radii values decrease by 6—7 times.

Taking into account the measurement accuracy of all equivalent radii of gel particles used for calculation, the width of the confidence interval was estimated as ±35%. The temperature influence on the dynamic viscosity of the DP was taken into account in calculations.

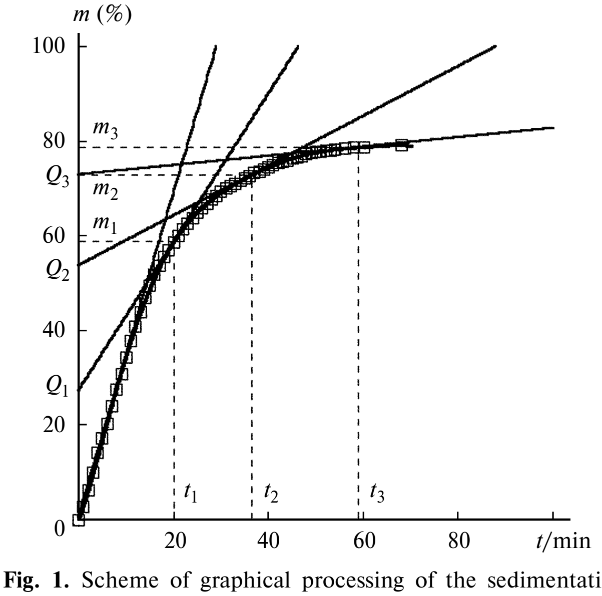

Fig. 1. Scheme of graphical processing of the sedimentation curve; Q_1 is the weight of the largest fraction (% of m); $Q_2 - Q_1$ is the weight of the second (by particle size) fraction; $Q_3 - Q_2 - Q_1$ is the weight of the third (by particle size) fraction, *etc.* The number of fractions isolated for the polydisperse system is determined by the number of tangent lines, if the curve contains no linear regions.

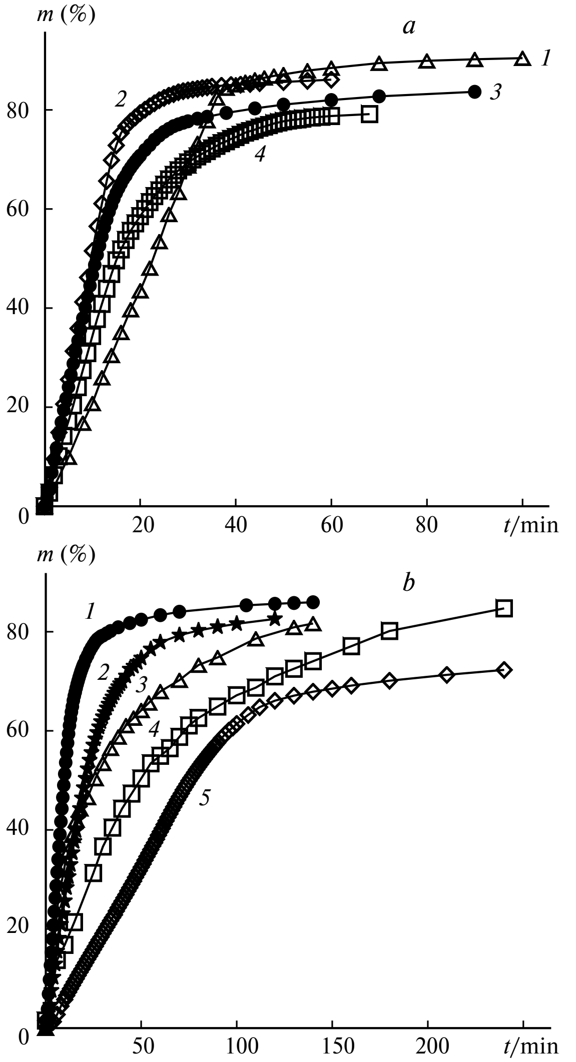

Fig. 2. Sedimentation curves for the titanium and indium (*a*) and zirconium and chromium (*b*) hydrogels with a suspension concentration of 0.04 mol L^{-1}; precipitation pH for Ti^{IV}, 10 (*1*), 8 (*2*), and 6 (*3*); for In^{III}, 11 (*4*); for Zr^{IV}, 10 (*1*), 8 (*2*), and 6 (*3*); for Cr^{III}, 10 (*4*) and 9 (*5*); *m* is the gel weight; *t* is time. Water is the dispersion medium.

Results and Discussion

Our earlier data[4] on the content of impurity ions and intramicellar water were used to calculate the densities of the hydrogels (see Tables 1 and 2). When intramicellar water is ignored the data in Table 2 show that the zirconogels have the highest density, the alumogels are characterized by the lowest density, while the densities of other gels are close. In addition, the densities calculated for different hydrogels and different precipitation pH val-

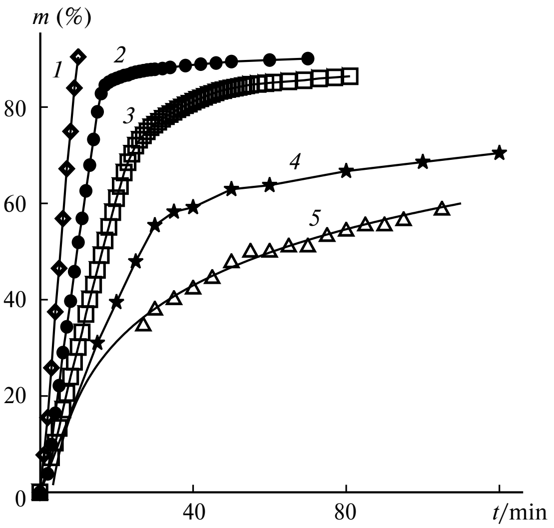

Fig. 3. Sedimentation curves for the ferrogels with a suspension concentration of 0.01 (*1*), 0.02 (*2*), and 0.04 mol L^{-1} (*3—5*) precipitated at pH = 7 (*4*), 9 (*1—3*), and 11 (*5*); *m* is the gel weight; *t* is time. Water is the dispersion medium.

ues, with allowance for intramicellar water, differ slightly from the DP (water) density. To calculate the size of DP particles in the cases under study, it is more correct to use the DP density values taking into account intramicellar water.

Some of the obtained sedimentation curves of the type $m = f(\tau)$ (*m* is the sediment weight, and τ is time) for suspensions with a concentration of 0.04 mol L^{-1} DP have a shape characteristic of bi- and tridisperse systems (see Figs 2 and 3). They consist of two or three linear regions. Other curves are convex, which is characteristic of systems with marked polydispersion (see Fig. 3). This is well seen in Table 3 containing the data on the number and specific content of the fractions. Oxohydroxide of Cr^{III} with pH_{pr} 7 and 11 settles most slowly and, therefore, the sedimentation rate was measured only for fractions with insignificant volumes (see Table 3). This agrees with the earlier obtained data on the unusual properties of Cr^{III} oxohydroxide, especially on its abnormally high specific surface.[16] The sizes of hydrogel particles calculated taking into account intramicellar water agree well with the results of visual observations. Since these coarse particles differ slightly in density from water, they can be only strongly hydrated hydrogels.

Comparing the time intervals τ necessary for the precipitation of at least 60—70% weight of the DP (Table 3), one can see that the precipitation rate of the gel particles in an aqueous medium at the same DP concentration (0.04 mol L^{-1}) at different central ions of oxohydroxide change in the following order: Ti^{IV}, $In^{III} \geq Fe^{III} > Zr^{IV} > Al^{III} \gg Cr^{III}$.

The precipitation rate depends on the pH_{pr} of the gels (see Table 3). This dependence can be explained by differences in surface charge of the gels. Let us compare the true pH values in the zero-charge point (pH_{zcp}) for the freshly precipitated oxohydroxides with the corresponding pH_{pr} values.[3]

pH	Fe^{III}	Cr^{III}	Zr^{IV}	Ti^{IV}	In^{III}	Al^{III}
pH_{zcp}	8.1	7.9	9.2	4.7	10.2	8.3
pH_{pr}	8.1	8.4	9.4	4.5	10.0	9.4

Evidently, except for Ti^{IV} oxohydroxide, all gels precipitated at pH = 6 or 7 and the indiogel precipitated at

Table 3. Influence of the central ion nature and pH of precipitation (pH_{pr}) of the MOH hydrogels on the granulometric composition of their aqueous suspensions with a concentration of 0.04 mol L^{-1}*

M	pH_{pr}	*t*/s	*m* (%)	$[Q_x$ (%)]/(*r*/μm) for fractions *1—6*					
				1	*2*	*3*	*4*	*5*	*6*
Al^{III}	7	7980	48	27/95	17.5/48	—	—	—	—
	9	8100	55	20.5/74	22.5/47	—	—	—	—
Fe^{III}	7	3450	51	24.5/65	16.5/47	—	—	—	—
	9	3450	85	27.5/66	28/56	15/48	10/41	—	—
	11	3600	66	47/55	14/37	—	—	—	—
In^{III}	9	3480	78	20/74	11/62	23/48	8/42	12/37	—
	11	1980	84.5	28/75	37/63	17/49	—	—	—
Cr^{III}	7	$2 \cdot 10^7$	14	14/2	—	—	—	—	—
	9	9600	69	28/29	35/23	—	—	—	—
	11	$8.6 \cdot 10^5$	11	1/3.5	2/2.5	—	—	—	—
Zr^{IV}	6	7800	75	12/121	5/92	11/58	13/45	11/34	11/28
	8	5400	83	48/71	25/55	9/34	—	—	—
	10	4200	84	48/83	7/72	18/59	9/39	—	—
Ti^{IV}	6	4200	81	6/73	23/58	13/52	12/44	10/40	11/32
	8	5400	81	9/60	7/52	16/38	17/29	10/24	—
	10	4200	90	76/46	6/40	6/35	—	—	—

* Intramicellar water was taken into account in the calculation of the equivalent radius *r*.

Table 4. Influence of the medium nature and concentration (*C*) of the MOH hydrogels on the granulometric composition of their suspensions

M	pH_{pr}	Medium	C/mol L^{-1}	t/s	m (%)	$[Q_x$ (%)$]/(r/\mu m)$ for fractions *1—4*			
						1	*2*	*3*	*4*
Fe^{III}	7	NaCl	0.04	6000	78	23/107	19/79	24/60	—
	9	NaCl	0.04	3000	81	27/92	36/68	—	—
	9	H_2O	0.01	600	90	90/129	—	—	—
	9	H_2O	0.02	4200	90	86/77	4/50	—	—
In^{III}	7	NaCl	0.04	3600	71	15/64	17/54	25/45	—
	9	NaCl	0.04	3000	79	17/75	30/58	20/48	—
	11	NaCl	0.04	3000	81	42/57	22/45	—	—
	11	H_2O	0.02	780	90	90/108	—	—	—
	11	H_2O	0.01	600	90	90/101	—	—	—
Zr^{IV}	10	H_2O	0.02	3600	89	80/87	7/64	—	—
	10	H_2O	0.01	480	100	4/147	24/138	32/131	40/126

pH 9 have positively charged surfaces, whereas the surfaces of all gels precipitated at pH = 10 or 11 are negative. All titanogels have the negatively charged surfaces. The ferro-, indio-, and chromogels precipitated at pH = 8 or 9, and their surfaces have weak positive charges, while the surfaces of the alumo- and zirconogels are weakly negative. The surfaces of the Al^{III} and Zr^{III} gels are close to neutral and, as follows from Table 3, these gels precipitate with the highest rate and most completely. For the Cr^{III} oxohydroxide hydrogel obtained at $pH_{pr} = 9$, *i.e.*, near pH_{zcp}, the precipitation rate is higher and the particle size is larger than those for the chromogels precipitated at pH = 7 or 11 and having high positive and, correspondingly, negative surface charges.

Therefore, suspensions of the gels with uncharged surface should be least stable to precipitation. The coagulation threshold values were studied from the sedimentation stability of the anatase obtained by $TiCl_4$ hydrolysis on heating.[18] The parallel determination of the electrokinetic potential and isoelectric point (IEP) showed that the pH of the IEP of the anatase was 5.7, and this is precisely the pH region where the suspension is least stable. With an increase in the pH of the suspension, stability of the anatase suspension increases in the region of the negative surface charge.

An analysis of the data in Tables 2 and 3 suggests that the particle sizes for different MOH differ slightly, except for Cr^{III} oxohydroxide.

At lower (0.02 and 0.01 mol L^{-1}) concentrations of suspensions, the sedimentation curves gain properties characteristic of a monodisperse system (two linear regions) or of a system where one fraction prevails. The precipitation rate and equivalent radii increase, which is especially noticeable for Fe^{III} and Zr^{IV} oxohydroxides (see Table 4). These changes in the curve shape have been described previously.[12] As shown[14] for suspensions of silica and polystyrene latex, when the volume DP concentration exceeds 6—10%, the interaction between suspension particles affects the sedimentation rate. Since concentrations of 0.04 *M* in the suspensions used in this work correspond to volume concentrations of 6—10%, a similar interaction should manifests itself for the precipitation of the oxohydroxide hydrogels. An increase in the equivalent radii of particles for dilute suspensions (*cf.* Tables 3 and 4) can be considered[12,14] as a result of higher freedom of motion for the particles and a decrease in the number of collisions between the particles due to a decrease in the suspension concentration.

The replacement of water as a DM with a solution of NaCl induced no substantial changes in the sedimentation rate in the systems under study (*cf.* Tables 3 and 4).

It is of interest to compare the results obtained with the data on the stability of concentrated suspensions of Al^{III} oxohydroxides (3.7 mol L^{-1} or 10—15 wt.% oxohydroxide) in a strongly alkaline solution. This solution was stabilized by carboxymethylcellulose, which enhances the viscosity of the DP.[13] Although suspension concentrations, in this case, exceed by two orders of magnitude the maximum concentration of the suspensions used by us (0.04 mol L^{-1}), the sedimentation curves presented in both works are similar. Therefore, the mutual influence of DP particles can be observed for concentrations of MOH suspensions of 0.04 mol L^{-1}. Lower values of equivalent radii of gel particles for the suspensions with a concentration of 0.04 mol L^{-1} (see Table 3), as compared to particle sizes for the suspensions with concentrations of 0.02 and 0.01 mol L^{-1} (see Table 4), also can be explained, most likely, by the mutual influence of the DP particles.

Thus, we found that the MOH produced by fast alkali hydrolysis in the convex mode form gel particles with the diameter from 2—3 to 140 μm. Vigorous continuous stirring during precipitation of the oxohydroxide gels from solutions and during their washing breaks the monolith body of the gel into dispersed particles. The structure of these particles cannot be studied by rheological methods or the "cross diffusion" method.[10]

Layered spiral-like fragments and a plate-like texture were found in the monolith gels of MOH by electron microscopy.[9] Aggregates in which oxohydroxide gel molecules are coiled represent a set of spirals enclosed into each other. It can be assumed that the gel particles in the suspensions are fragments of the spiral agglomerates discussed in the previous works.[7—10]

Let us try to estimate the spatial characteristics of the MOH hydrogels using the data of picnometry and sedimentation analysis. As an example, we consider the indiogel with pH_{pr} 11 of composition $In(OH)_3$ or $In(OH)_3 \cdot 112H_2O$ [4] (molecular weight 2187) with a picnometric density of 1.06 g cm^{-3} and water as a DP.

The volume of 0.01 mole of the gel is 20.63 cm^3. Accepting that the crystallochemical radius of In^{3+} is 0.092 nm and the radius of the OH group is 0.15 nm,[19] we find that ~98% of this volume are occupied by intramicellar water.

Then, let us assume that the gel consists of polymeric MOH chains and these polymeric chains are broken into individual particles when the gel is crushed. For instance, consider an indiogel fraction with the mean equivalent radius r = 55 μm, which contains 22.8% of the gel substance (see Table 3). The average number of particles in the fraction is $6.74 \cdot 10^{-6}$. If we believe that a dispersion particle consists of a continuous polymeric chain, then this chain should have a length of $0.46 \cdot 2 \cdot 10^{14} \cdot 10^{-9} = 9.3 \cdot 10^4$ m. The diameter of this polymeric chain is tentatively 0.78 nm, and its surface area is $2.28 \cdot 10^{-4}$ m^2. In this case, the surface area of all particles in the fraction is $2.28 \cdot 10^{-4} \cdot 6.74 \cdot 10^6 = 1540$ m^2. The specific surface of the hydrogel, taking into account intramicellar water, is 309 m^2 g^{-1}, and that, ignoring intramicellar water, is 4071 m^2 g^{-1} of dry $In(OH)_3$. This value more than 16-fold exceeds the S_{sp} value found[16] by us in the study of the sorption capacity of OH groups. Similar calculations for other MOH hydrogels studied give values of the same order.

Therefore, dispersion particles of the hydrogels cannot contain a continuous polymeric chain, even when coiled as a spiral. Evidently, they possess a three-dimensional network structure. Special experiments showed that an increase in the number of centrifuge rotations during hydrogel washing from 2000 to 8000 rpm can decrease the amount of intramicellar water by 20—30%. The behavior of the hydrogels during squashing can also be due to the presence of three-dimensional cavities in the particle structure.

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