

STRUCTURE FORMATION OF THE MIXED GELS OF ZIRCONIUM OXYHYDRATE AND SILICIC ACID PRODUCED WITH DIFFERENT SEQUENCING OF REAGENTS

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The physicochemical characteristics of single and mixed zirconia and silica gels produced by the sol-gel technique at different synthesis pH and sequence of introducing the reagents in the mother liquid are presented. As a result of comparing the data obtained by different research methods, it is found that in the mixed gels, irrespective of the synthesis technique, Si–O–Zr bonds are present. The introduction of a zirconium salt in the mother liquid containing a silicate salt leads to the preferred formation of zirconia gel granules of 20-30 nm in diameter enclosed in the matrix of silica gel. The inverse sequence of introducing the gel-forming components in the reaction mixture promotes the formation of large gel aggregates containing the particles of less than 10 nm and having a high degree of polymerization. Mixed gels of zirconium oxyhydrate and silicic acid have an order higher sorptive capacity for yttrium (III) and calcium cations, as compared to single silica gels and zirconia gels.

Keywords: zirconia gel, silica gel, mixed gels, sol-gel technique, inorganic polymers, structure formation processes, Si–O–Zr bonds.

INTRODUCTION

Compounds based on hydrated silica have found an extensive use both in industry and household. However, the drawbacks of these sorption materials include low sorptive capacity and moderate selectivity towards the metal cations. This caused the need to modify sorbents based on silica gel. In the recent several years, mixed gels of silicic acid with oxyhydrates (and oxides) of rare and rare-earth elements have been intensively studied. Unlike single gels, these materials possess an increased thermal and chemical stability, mechanical strength, catalytic activity, and sorption selectivity. Mixed gels find an extensive use in manufacturing heat-resistant ceramics, alkali-resistant glasses, and heterogeneous catalysis [1, 2]. Mixed gels of silicic acid and zirconium oxyhydrate are produced using techniques such as mechanical dispersion of the components [3], silicate deposition on zirconia gel, zirconium impregnation in silicate matrix [4]. The most promising is the sol-gel technique providing successful control of the product properties [5].

The hydrolysis rate is known to considerably affect the structure formation in sols and subsequent gel properties. The higher the degree of oversaturation of the mother liquid, the lesser the size of particles of the emerging nuclei and the higher the dispersiveness and surface area and, hence, the number of available sorption centers of forming gel particles. High degrees of oversaturation of the mother liquid occur at high hydrolysis rates, therefore, fast hydrolysis is the most common conventional method to synthesize oxyhydrate sorbents [6]. At the same time, the number of available sorption centers is

determined not only by the surface area of sorbent granules, but also their structure. Quantum chemical calculations show that granules with an ordered structure have more available sorption centers than the unordered particles. The most suitable ways to slow down the rate of hydrolysis is to decrease the mixing rate of the components and to use low concentrations of gel-forming substances [7]. This work studies the physicochemical characteristics of single and mixed gels of silicic acid and zirconium oxyhydrates produced by slow hydrolysis (sol-gel technique; the mixing time of all reagents is 60 min) with minimum concentrations of gel-forming reagents. Mixed gels were synthesized with a different sequence of introducing gel-forming substances in the mother liquid.

EXPERIMENTAL

Gels were synthesized by the hydrolysis of aqueous solutions of sodium metasilicate and zirconium oxychloride. Final concentrations of gel-forming substances in the reaction mixture (after mixing all components) were 0.05 mol/l. Single silica gels (denoted in Fig. 1 and Table 1 as S) were synthesized by the introduction of hydrochloric acid (0.2 M) in the solution of sodium metasilicate at pH of 6.0 and 7.0. Outside the pH range of 6-7, silicic acid at this concentration does not form a gel. Single zirconia gels (denoted in Fig. 1 and Table 1 as Z) were synthesized by the introduction of an aqueous ammonia solution (0.2 M) in the zirconium oxychloride solution at pH of 4.0, 6.0, 8.0, and 10.0.

Mixed gels were produced by two methods: 1) the introduction of zirconium oxychloride in the mother liquid containing sodium metasilicate (denoted in Fig. 1 and Table 1 as SZ) and 2) the introduction of sodium metasilicate in the mother liquid containing zirconium oxychloride (denoted in Fig. 1 and Table 1 as ZS). The Si/Zr molar ratio in the reaction mixture was 1/1. Mixed gels were synthesized at pH from 4 to 11 with a step of 1 pH unit. The pH of the mother liquid was adjusted after introducing zirconium and silicon salts by NaOH and HCl solutions with a concentration of 0.2 mol/l. Syntheses were performed at room temperature ($20\pm 2^\circ\text{C}$). All reagents used were of at least chemically pure grade.

After the synthesis, all gels were left in the mother liquid for aging for 24 h, then they were filtered out and eight times washed with water until negative reaction on the counterion of occluded salts, which was checked by the standard techniques [8]. The samples were dried in a desiccator over molten calcium chloride to a constant weight (about 5 months). In addition to silica gels produced under the described conditions, for comparison, the properties of KSMG and KSKG commercial silica gels were studied, which were brought to a constant weight under the same conditions. Gels were not heat treated.

The specific surface area was determined using the BET method by nitrogen sorption on a SORBI-MS device. Sorption properties towards Ca^{2+} and Y^{3+} ions were studied by the batch method. Yttrium nitrate and calcium chloride were used as sorbates, to which potassium nitrate and chloride respectively were added for a constant ionic strength. Sorbate concentrations were determined trilonometrically with xylenol orange (for yttrium nitrate) and murexide (for calcium chloride) indicators.

The pH was controlled with an I-120.2 ionomer. Morphologic properties were studied using a Jeol JSM-7001F scanning electron microscope. The thermolytic curves were recorded on a MoM Paulik–Paulik–Erdey 3434-C derivatograph in corundum crucibles with a heating rate of $10^\circ\text{C}/\text{min}$ under the own vapor atmosphere; temperature ranged from room to 900°C . For each sample, at least 4 thermograms for 70-72 mg portions were recorded. The thermogravimetry (TG) and differential thermal analysis (DTA) curves were normalized to a portion weight of 75 mg and averaged. The differential thermogravimetry (DTG) curves were obtained by the differentiation of the averaged TG curve.

The density was measured by a pycnometric method in water. The gross composition (number of moles of total water k per mole of oxide: $\text{ZrO}_2 \cdot k\text{H}_2\text{O}$, $\text{SiO}_2 \cdot k\text{H}_2\text{O}$, $\text{ZrO}_2 \cdot \text{SiO}_2 \cdot k\text{H}_2\text{O}$) was calculated based on the thermogravimetric data. The ^1H NMR spectra were recorded on a BS-467A Tesla NMR spectrometer modified to measure broad lines and the first-order derivative of NMR absorption lines in solids in a temperature range from -155°C to 30°C . The IR spectra were recorded on a Vertex 80 (Bruker) IR Fourier spectrometer in a range of $4000\text{-}400\text{ cm}^{-1}$ with a step of 0.48 cm^{-1} from powdered samples prepared in the form of pellets with cesium iodide.

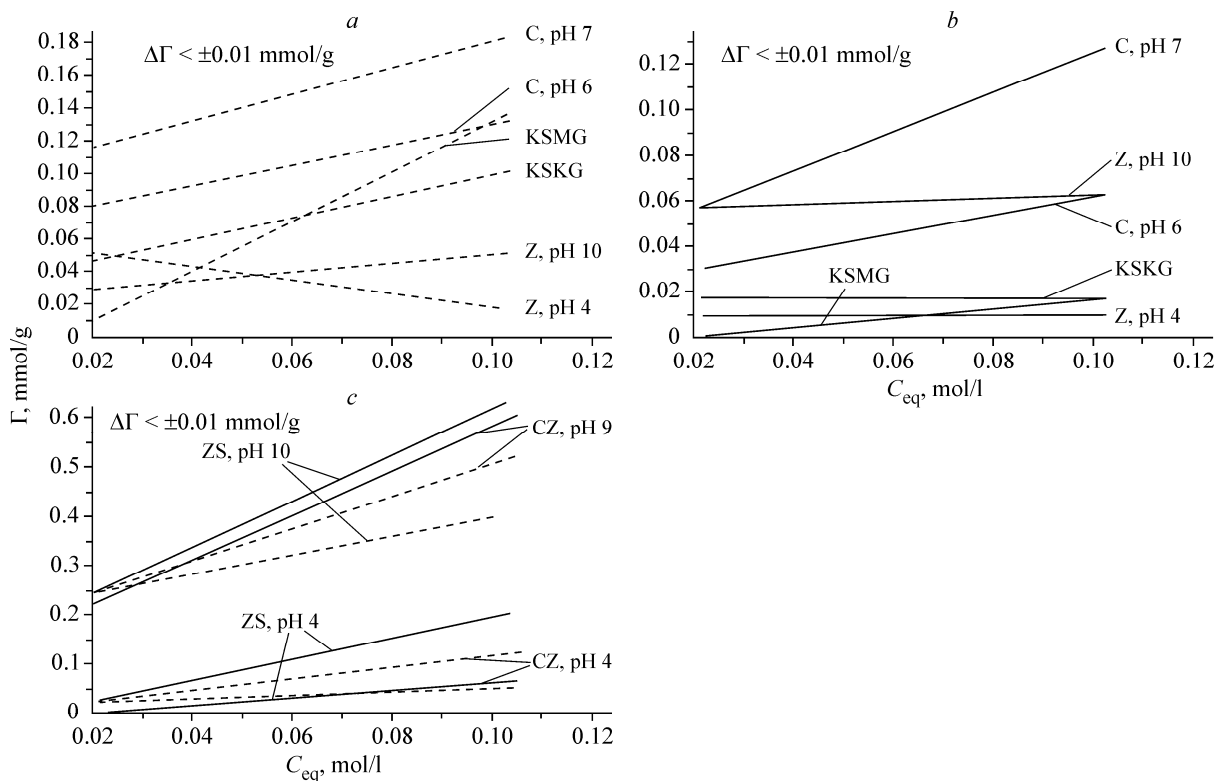


Fig. 1. Sorption isotherms of calcium (solid line) and yttrium (dotted line) ions for the samples with the maximum and minimum sorptive capacity: (a, b) single gels, (c) mixed gels.

Out of the series of gels synthesized under the same conditions, at least three samples were selected for the investigation, in which the discrepancy in sorptive capacity towards calcium ions was below 0.005 mmol/g. Such a selection was based on the results of the previous studies [7].

RESULTS AND DISCUSSION

Fig. 1 depicts the sorption isotherms of the samples with the maximum and minimum sorption properties towards calcium and yttrium ions. Single silica gels sorb approximately 1.5 times more ions of yttrium than calcium. Zirconia gels sorb both ions studied in roughly the same amounts. Commercial KSMG and KSKG silica gels sorb calcium and yttrium ions as the worst samples studied. Mixed gels, as opposed to single ones, sorb approximately 1.5 times more ions of calcium than yttrium. Overall, the sorptive capacity of mixed gels is almost an order higher as compared with single ones.

The patterns of change in sorption properties with varying pH are in general the same for both ions. Among single gels, the best sorption properties have the samples produced at maximum pH (pH of 7 for silica gels and pH of 10 for zirconia gels). For mixed gels, it is typical that there is the maximum pH above which sorption properties decrease. For SZ samples, this pH is 9; for ZS gels it is 10.

Enhancement of the sorption properties towards cations occurring with an increase in pH is quite regular. As it is known from the literature [9], the sorption properties largely depend on a surface charge of the sorbing agent forming during the synthesis. For zirconia gel, it is known [10] that if pH of the mother liquid is lower than the point of zero charge (pH_{PZS}), then the surface charge of gel particles is positive, and if it is higher than this point, then the charge is negative. According to the data of [10], pH_{PZS} of air-dry zirconia gels is below 6.5. When the surface is positively charged, zirconia gel exhibits anion-exchange properties, and when it is negatively charged, it exhibits cation-exchange properties. Such a transition is not observed for silica gel: it possesses only cation-exchange properties [9]. The elemental analysis of the samples, performed using scanning electron microscopy, shows that in the composition of mixed gels produced at $pH < pH_{PZS}$ of zirconia gel, a

small amount of chlorides is present, and in the composition of samples synthesized at $\text{pH} > \text{pH}_{\text{PZS}}$ of zirconia gel, the trace sodium ion impurity is observed. In single gels as well as in the samples obtained at pH of about pH_{PZS} of zirconia gel, foreign ion impurities were not found. The gels were washed with distilled water, therefore chlorine and sodium ions are likely to remain in the form of counterions on the ion-exchange centers. Thus, the pH of the mother liquid being higher than pH_{PZS} of zirconia gel enhances the sorption properties of mixed gels towards cations.

As is known [9], in oxyhydrate materials, ion absorption proceeds not only by the ion-exchange mechanism, but also sorption, when ions form bridging bonds with the gel matrix via the OH groups. According to Kepert's data [11], in a pH range of 9-10, zirconium compounds are represented mainly by hydroxo complexes. According to the studies of Baes and Mesmer [12], in a pH range of 9.0-11.0, silicon oxyhydrate is most rich with $\text{Si}_4\text{O}_8(\text{OH})_6^{2-}$ and $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$ moieties containing the maximum number of available OH groups. Therefore, the sorption maxima of both cations on the mixed gels obtained at pH of 9.0 and 10.0 are related to the largest number of available OH groups.

The determination of the density and specific surface area shows that gels sorbing metal cations well typically are characterized by the minimum values of these measures. Thus, single silica gels with high sorption properties have a density of about 1.9 g/cm^3 ; those with low sorption properties of about 2.1 g/cm^3 ; for zirconia gels and ZS samples these values are 2.1 g/cm^3 and 2.2 g/cm^3 ; for SZ samples 2.2 g/cm^3 and 2.4 g/cm^3 . The specific surface area differs much more. The ZS samples with the minimum sorptive capacity towards yttrium and calcium ions have an inappreciable surface of about $1 \text{ m}^2/\text{g}$, which is by 2 orders of magnitude less than that of SZ samples ($170\text{-}190 \text{ m}^2/\text{g}$), which, in turn, 3 times less compared with commercial silica gels ($500\text{-}600 \text{ m}^2/\text{g}$). Consequently, the sorption of metal cations depends on the structure of inorganic polymeric chains rather than on the macrostructure.

When SZ samples are synthesized, in the beginning of the process, drops of the zirconium oxychloride solution fall into the mother liquid with a pH of about 12. Under these conditions, the intensive hydrolysis of the zirconyl ion proceeds with the formation of zirconium oxyhydrate nuclei. Since the zirconium oxychloride solution has a pH of about 1, its introduction gradually decreases the pH of the mother liquid. Therewith, the formation rate of new zirconium oxyhydrate nuclei gradually decreases and their growth rate increases. Simultaneously with a decrease in the pH the solubility of silica decreases, and the polymerization of silicic acid occurs above the already formed nuclei of zirconia gel, which hinders the aggregation of zirconium oxyhydrate nuclei. Therefore, in the mixed ZS gel, the grains of zirconia gel are enclosed in the silica gel matrix. When ZS samples are synthesized, sodium silicate drops fall into the mother liquid with a low pH (less than 2). According to Iler [13], at this pH the formation of nuclei of polysilicic acid occurs very slowly. Negatively charged silicate ions are likely to interact with positively charged zirconyl ions and form copolymer structures. The possibility of copolymerization of zirconium oxyhydrate and silicic acid is supported by both calculated [14] and experimental data. In [15-17], using IR spectroscopy the presence of Si-O-Zr bonds in mixed silicon and zirconium oxyhydrates produced by the sol-gel technique was detected. A TD-DFT calculation of the absorption frequencies in the IR spectrum, performed for $[\text{SiO}_2\cdot\text{ZrO}_2\cdot k\text{H}_2\text{O}]_n$ particles (to the degree of polymerization $n = 10$ and the degree of hydration $k = 5$), whose structure calculation is presented in [14], showed that in low-molecular particles, Si-O-Zr bonds can have the absorption maxima in the ranges of $970\text{-}990 \text{ cm}^{-1}$ and $650\text{-}670 \text{ cm}^{-1}$.

Fig. 2 depicts the IR spectra of the samples of single and mixed gels with the maximum (max) and minimum (min) sorption properties towards the metal cations. Frequencies corresponding to the vibrations of adsorbed water of bound and free OH groups, which are typical of zirconium and silicon oxyhydrates [15-17], are present also in the mixed gels. However, the spectra of the mixed gels feature a wide variety. They contain the absorption maxima at the frequencies of $987\text{-}984 \text{ cm}^{-1}$ and $668\text{-}662 \text{ cm}^{-1}$, which are typical of the stretching and bending vibrations of Si-O-Zr bonds [15-17] present in the spectra of both SZ and ZS samples. It should be noted that the IR spectra of mixed SZ and ZS gels produced at a pH of 4 are highly similar in both frequencies and intensities of the absorption maxima.

Fig. 3 depicts the micrographs of the mixed gels obtained in electron elastic scattering mode. It is seen that the samples of the mixed gels produced at different reagent sequencing have no visible segregation. The Si/Zr molar ratio

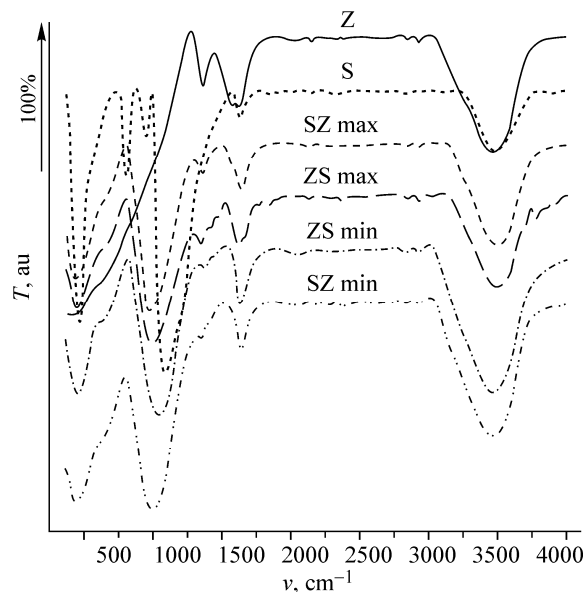


Fig. 2. Infrared spectra of single and mixed gels.

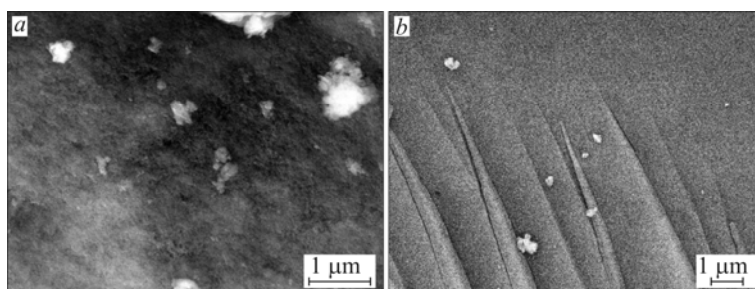


Fig. 3. Micrographs of mixed gels obtained in electron elastic scattering mode: SZ (a), ZS (b).

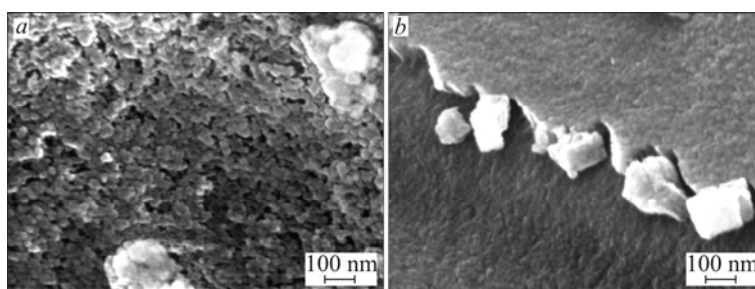


Fig. 4. Micrographs of mixed gels obtained in secondary electron mode: SZ (a), ZS (b).

determined in this mode for both gel types was 1/1. Fig. 4 depicts the micrographs of the mixed gels obtained in secondary electron mode. The SZ samples consist of the grains with a diameter of 20-30 nm; in ZS gels, the grain size is about 10 nm. When zirconium oxychloride is introduced in the sodium silicate solution, the size of composite gel grains is the sum of the sizes of zirconia gel particles and the polysilicic acid shell formed on their surface. When the reagent sequencing changes, due to the slow hydrolysis of silicate ions the composite gel particles interact with each other and form high polymeric structures, which explains small values of the specific surface area of these samples.

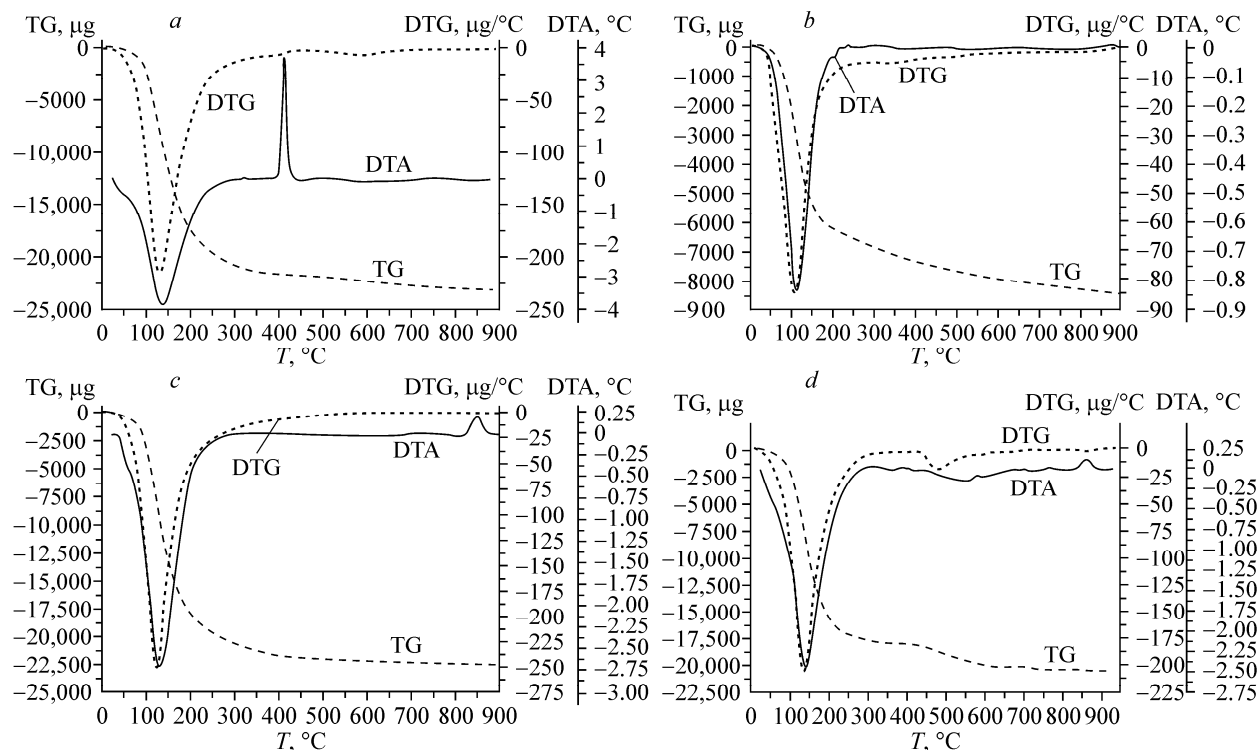


Fig. 5. Thermograms of single and mixed gels: Z (a), S (b), SZ (c), ZS (d).

The analysis of thermograms of mixed gels shows that the distribution of the types of bound water substantially depends on the reagent sequencing in the mother liquid. Fig. 5 depicts the typical thermograms of single and mixed gels (with the maximum sorption properties). In the thermograms of mixed ZS gels, the same features are observed as in the thermograms of single gels: dehydration generally ends at a temperature of about 350°C; at higher temperatures dehydration occurs without a noticeable endothermic effect of the DTA curve; the amount of removable water is not too large. According to Iler [13], above 350°C water is removed from the terminal OH groups located at a considerable distance from each other. The exothermic effect in the DTA curve corresponding to the transition of zirconia from the amorphous to crystalline state is shifted to a high temperature region, which is explained by difficulties in the crystallization of zirconia microgranules that are enclosed in the silica gel framework. In the thermograms of mixed ZS gels, the weight loss, which is absent in the case of single gels, is observed at a temperature of 450–600°C, to which a noticeable endothermic effect in the DTA curve corresponds. This seems to be water removed from the OH groups in high polymer structures. The exothermic effect of zirconia crystallization in the thermograms of samples of both types of composite gels is shifted to the high temperature region.

The calculation of the NMR spectra is given in Table 1. β is the parameter indicating the broadening of the curve corresponding to these types of protons. An increase in this parameter corresponds to an increase in the binding of the groups to which these protons belong. R_{H-H} is the distance between protons in the respective groups. Individual protons apparently correspond to the protons of terminal OH groups. As is seen from Table 1, the ZS samples almost do not contain protons belonging to loosely bound OH groups. All OH groups of these gels seem to be involved in the formation of polymeric chains. The minimum distance between the nearest protons in these gels (column H_2 in Table 1) suggests that these protons belong to the nearest OH groups or adsorbed water molecules. An increase in the percentage of these protons in the SZ and S samples with a simultaneous increase in the H–H distance gives grounds to expect that SZ and, particularly, S samples have the maximum fraction of adsorbed water and the minimum fraction of “ol” bridges, which matches the literature data [9]. The concentration of three-proton moieties (column H_3 in Table 1) can be due to the presence of protonated water molecules in the gel structure or the existence of developed polymeric structures. In the case of ZS gels possessing a considerable amount

TABLE 1. Interpretation of the ^1H NMR Spectra of Broad Lines and Gross Compositions of Single and Mixed Gels

Sample	Gross composition	H		H		H ₂			H ₃		
		%	β_1	%	β_2	%	$R_{\text{H-H}}$	β	%	$R_{\text{H-H}}$	β
S	$\text{SiO}_2 \cdot 0.42\text{H}_2\text{O}$	1.1	0.6	11.0	1.5	73.7	1.70	2.3	14.2	1.62	1.6
SZ max	$\text{SiO}_2 \cdot \text{ZrO}_2 \cdot 4.35\text{H}_2\text{O}$	0.4	1.0	7.6	2.0	73.6	1.59	2.4	18.4	1.60	1.6
SZ min	$\text{SiO}_2 \cdot \text{ZrO}_2 \cdot 3.98\text{H}_2\text{O}$	0.8	1.1	11.7	2.2	61.5	1.60	2.1	26.0	1.66	2.1
ZS max	$\text{SiO}_2 \cdot \text{ZrO}_2 \cdot 4.90\text{H}_2\text{O}$	0.1	0.4	0.7	1.6	55.5	1.57	2.4	43.8	1.60	2.0
ZS min	$\text{SiO}_2 \cdot \text{ZrO}_2 \cdot 5.24\text{H}_2\text{O}$	0	0	0	0	50.6	1.57	2.2	49.4	1.60	2.0
Z	$\text{ZrO}_2 \cdot 2.87\text{H}_2\text{O}$	0.1	0.6	0	0	52.6	1.60	2.3	47.3	1.60	2.0

of total water, both variants of the structural fragments appear to be present. In the case of ZS gels with the maximum sorption properties and Z gels, the three-proton moieties seem to correspond to the developed polymeric structures.

CONCLUSIONS

The formation of mixed gels based on zirconium oxyhydrate and silicic acid is determined by the sequence of reagent introduction in the mother liquid. The introduction of zirconium oxychloride in the mother liquid containing sodium silicate promotes the formation of zirconia gel particles with subsequent polymerization of silica gel above it; the final grain size is 20–30 nm. The introduction of sodium silicate in the zirconium oxychloride solution leads to the formation of mixed gel particles of about 10 nm with a high degree of polymerization. In the composition of samples with a high degree of polymerization, a large amount of total water is present, which mainly enters in the composition of the polymeric structures.

The sorption properties of single and mixed zirconia and silica gels towards metal cations are essentially determined by the structural features rather than the specific surface area. Mixed gels synthesized from solutions with the minimum concentrations of gel-forming reagents have an order higher sorptive capacity towards calcium and yttrium (III) ions, as compared to single silica and zirconia gels.

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