



## Gelation of Aluminosilicate Systems Under Different Chemical Conditions

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**Abstract.** Optically clear aluminosilicate gels of different chemical compositions (0–0.9 mole ratios of total Al/(Si + Al)) were prepared directly from solutions of inorganic aluminum salts, tetraethoxysilane, water and alcohol without the time-consuming sol forming. However, in these gels only 0–75% of total Al content was incorporated by chemical bonding into the gel network depending on the compositions of gels and the preparation conditions. The incorporation of aluminum atoms into the gel framework and the structure of wet gels were investigated by chemical analysis,  $^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance, and small angle X-ray scattering. The present method may be most favourable for the preparation of aluminosilicate gels with 0.30–0.70 mole ratios of total Al/(Si + Al). At lower Al content acidic catalysis is required. Above 0.70 mole ratio homogeneous gels cannot be obtained by this method. The highest aluminum incorporation in homogeneous gel structures of various mole ratios of total Al/(Si + Al) was 0.53 mole ratio of bonded Al/(Si + Al) in contradiction to 0.1 mole ratio of Al/(Si + Al) achieved by traditional melting process of glass.

**Keywords:** sol-gel, aluminosilicate gel, hydrolysis,  $\text{Al}(\text{NO}_3)_3$

### 1. Introduction

The main purpose of this work was to prepare aluminosilicate gels as intermediate products in the sol-gel procedure of ceramic or glass materials with high aluminum content. Special attention has been denoted to significantly exceed the Al content that can be achieved by traditional high-temperature melting methods (about 0.1 mole ratio of Al/(Si + Al) in glass [1–3]). In order to develop a low energy consuming sol-gel procedure for aluminosilicate ceramics with high Al content, considerable effort has been expended to form Al–O–Si bonds even in the solution or gel state.

The effect of preparation conditions on the gelation and on the incorporation of Al atoms into the gel networks by chemical bonds was reported in a previous paper [4]. The aim of the present work was to study the Al incorporation under different chemical conditions varying the chemical composition, using different Al-containing precursors and solvents. In the present work we established the chemical processes resulting in homogeneous gel network with high aluminum content.

In the sol-gel preparation of aluminosilicate gels, the aluminum precursor used has generally been aluminum alkoxides [5–10]. These materials are quite difficult to handle owing to their rapid hydrolysis and low solubility in water and alcohol. Due to the rapid hydrolysis of Al alkoxides, which may lead to phase

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separation, they are difficult to use for preparing multi-component systems. The other type of compound generally used is an inorganic Al salt. Inorganic salts of aluminum are inexpensive, their hydrolysis can be controlled, resulting in an acidic solution. However, it is necessary to remove the anions of the salts from gels. For the use of aluminum sulphate [11–13] and aluminum chloride [9, 11, 14, 15] in the sol-gel method, there are only few examples. Aluminum nitrate is often used as precursor in preparing mullite, however, in these processes the bonding between silicon and aluminum forms rather at high temperature ( $\approx 1000^\circ\text{C}$ ) than in gel phase [12, 16–22]. The published sol-gel method using solutions containing inorganic aluminum salts generally involves a time-consuming sol formation step [8].

In most sol-gel syntheses reported, ethanol was used as the solvent [5, 7, 10, 17, 19, 21]. There are also examples for the usage of methanol [5, 18, 23], 1-propanol [5], 2-propanol [24], 1-butanol [5, 24], and ethylene glycol [5] etc.

## 2. Experimental

### 2.1. Preparation of Gels

The gels were prepared by a rapid sol-gel method, in one step without sol formation. Tetraethoxysilane (TEOS) and an aluminum salt ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , or  $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2$ ) were dissolved in an organic solvent (1-propanol, 2-propanol, ethanol, 1-butanol, or ethylene glycol). For these experiments the composition used most frequently was: 1 mol of TEOS, 1 mol of Al salt, 6 mol of alcohol. The chemical compositions of the systems with different Al/(Si + Al) mole ratios are listed in Table 1. The gelation was performed by refluxing at about  $80^\circ\text{C}$  for 10–11 h. In a closed system this same process at  $80^\circ\text{C}$  required 20–22 h.

### 2.2. Characterisation Methods

The gel time was determined by measuring the viscosity as a function of time in a Hoppler rolling ball microviscosimeter. The gel time was defined, as the time required reaching infinitely high viscosity. These results were compared with visual observations based on the tilting test tube method.

In the present work the bonded Al content in the network was determined by washing the gels with

Table 1. Chemical compositions of solutions containing different Al/(Si + Al) mole ratios.

Series	TEOS (mol)	Al nitrate (mol)	1-propanol (mol)	Excess water (mol)	Al/(Si + Al) mole ratio
Series I.	1.9–0.2	0.1–1.8	6	40	0.05–0.9
Series II.	1.9–0.2	0.1–1.8	6	5	0.05–0.9
Series III.	1.9–0.8	0.1–1.2	11.4–4.8	27.6–1.2	0.05–0.6
Series IV.	1.9–0.4	0.1–1.6	6	14.1–0.6	0.05–0.8

The mole ratios of total water/(Si + Al) were  $>20$  (20.5–28.1) in the Series I. and  $\geq 3$  (3.0–10.6) in the Series II., respectively. In the Series III. the mole ratio of total water/Si (15.0) and the mole ratio of total water/propanol (2.5) were constant. The Series IV. was characterised by constant mole ratio of total water/(Si + Al) (7.5) and constant mole ratio of total water/propanol (2.5).

pure water during intensive stirring. Mass ratio of water/samples was 100 and the washing time 1 h. Water soluble Al was determined by complexometry and inductively coupled plasma spectroscopy (ICP) (Plasmalab 8440, Labtam), respectively. The error of determination, including the washing procedure, was within 5%. The bonded Al content of gels is given in percentage of the total initial value. The amount of nitrate ions removed by washing was measured by UV spectroscopy (301 nm) using a Perkin-Elmer  $\lambda$ -15 UV-VIS spectrophotometer. The remaining nitrogen content in the gels (after washing) was determined by elemental analysis.

$^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance ( $^{27}\text{Al}$  MAS NMR) measurements were performed at room temperature, using a BRUKER AVANCE DRX-500 NMR spectrometer (11.70 Tesla) at 130.3182 MHz. A 52 mm BB{1H}CP/MAS probehead was employed with a 7 mm  $\text{ZrO}_2/\text{Kel-F}$  rotor. After a  $1 \mu\text{s}$  X pulse (flip angle was ca. 10 degrees to care about the major contribution of the  $(1/2, -1/2)$  transition in the observed centerband and the well determined signal response to the rf pulse.) 4096 data points were acquired during 31 ms, followed by 1 s relaxation delay. 28 FID were accumulated. The typical spectral width was 65360 Hz (501 ppm), the line broadening parameter was 30 Hz, and each spectrum comprised 2 K data points. All NMR spectra were recorded at MAS conditions to reduce the nuclear quadrupolar interactions to second-order quadrupole shift level. The spinning speed of 4000 Hz caused spinning sidebands with periodicity of 30 ppm in the spectra. This spinning rate increased the spectral resolution but could not resolve completely the centerbands of the components.

The analysis of the overlapping signals with computer simulated powder pattern fit was not possible because of the featureless overlapping Gaussian shape of the centerband signals. In the absence of this characteristic second-order quadrupole powder pattern we could not estimate  $C_q$  (the quadrupole coupling constant),  $\eta_q$  (the asymmetry parameter) and second-order quadrupole shift values. The observed overlapping signals (except of the spinning sidebands) were decomposed to Lorentz curves by BRUKER WINFIT software on the basis of typical chemical shifts known from the literature. The obtained fitting parameters were the chemical shift, the half peak width, and the integral ratio of the components. The  $^{27}\text{Al}$  chemical shifts were recorded with respect to  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  as an external reference.

For the small-angle X-ray scattering (SAXS) measurements, we used a 12 kW X-ray generator and a pinhole X-ray camera with variable distances from the sample to the two-dimensional detector (20.5–98.5 cm). The gels were covered in vacuum tight foil to prevent drying during the measurements. The two dimensional spectra were corrected for parasitic pinhole scattering, as well as for the foil scattering, and then radially averaged to obtain the scattered intensity,  $I(q)$ , as a function of the scattering vector,

$$q = 4\pi \sin \theta / \lambda \quad (1)$$

where  $\lambda$  is the incident X-ray wavelength (1.54 Å) and  $2\theta$  the scattering angle between the incident and diffracted beam. The curves are interpreted on the basis of the Guinier law and the fractal theory [5].

Atmospheric pressure chemical ionisation (APCI) MS spectra were recorded on a VG QUATTRO instrument. The soluble material of aluminosilicate gel was washed out by water and the solution obtained was analysed. In APCI, the sample solution was sprayed at high temperature by a hot gas flux, followed by (crown) discharge ionisation. The structure of the positively charged ions, formed by the ionisation process, was determined after a second collision induced fragmentation (CID).

### 3. Results

#### 3.1. Effect of Different Aluminum Salts on Gelation

It was not possible to prepare a homogeneous gel from aluminum acetate by the present direct gel preparation method even in the presence of a catalyst. Gel

samples could not be prepared from TEOS and Al chloride or sulphate in 1-propanol without the addition of excess water, only amorphous precipitation was obtained by this way. Optically clear gels were prepared from inorganic Al salts (sulphate, chloride, and nitrate) with the following compositions: 40 mol of water/Al salt, 1 mole ratio of TEOS/Al salt, and 6 mole ratio of propanol/Al salt. This chemical composition was based on the solubility of the Al sulphate in the mixture of water and 1-propanol. (Solubility in 1-propanol: Al nitrate 5.6 g, chloride 1.5 g, sulphate 0.05 g eq.  $\text{Al}_2\text{O}_3/100 \text{ cm}^3$  [11].) Comparison of these optically clear gels showed no difference among the samples in Al incorporation. About 100% of the Al content of gels were washed out by water. Thus the incorporation of Al ions into the silica gel frameworks was negligible in this series containing high water content.

Aluminosilicate gels with lower water content were prepared (7.0 mol of water/Al salt) using the more soluble Al salts (nitrate and chloride) than Al sulphate in order to increase the Al incorporation in the gel structures. Comparing the Al incorporation the amount of bonded Al atoms was considerably lower in the chloride-containing gel than in the nitrate-containing system (Table 2). Most of the nitrate ions escaped as nitrous gases during gelation and heat treatment, although almost the total amount of chloride remained in the gels (Table 2). This result was also supported by  $^{27}\text{Al}$  MAS NMR (Fig. 1). In the NMR spectrum of gel prepared from Al chloride (Fig. 1, curve B), only one sharp peak can be observed at  $-1.2 \pm 0.2$  ppm, which arises from non-bonded but partly hydrolysed, octahedral Al ions [8, 16, 26]. By analogy to the research and results in the literature [27, 28], the negative chemical shift of the peak occurs due to the chloride ions. In the NMR curve of gel containing nitrate (Fig. 1, curve A), two peaks at around 0 ppm ( $0.5 \pm 0.06$  ppm) and at  $58 \pm 1$  ppm are. As is well known, the peak of 58 ppm belongs to the tetrahedrally co-ordinated Al, which is bonded by Al–O–Si connections in the gel network as  $\text{AlO}_4$  units [8, 29–32]. The peak at

Table 2. Effect of aluminum salt on gels.

Aluminum salts	$t_g$ (minute)	Bonded Al (%)	Anion content (%)
Al nitrate	$120 \pm 10$	$35 \pm 5$	$52 \pm 5$
Al chloride	$170 \pm 20$	$16 \pm 2$	$90 \pm 10$

Chemical composition of samples: 0.1 mol TEOS, 0.1 mol  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  or  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.6 mol 1-propanol, and 0.5 or 0.8 mol water, respectively. The time of heat treatment: 22 h at  $80^\circ\text{C}$ .

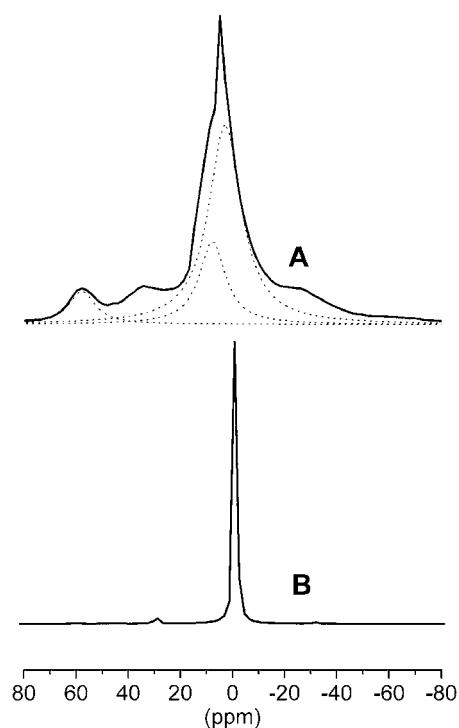


Figure 1.  $^{27}\text{Al}$  MAS NMR spectra for wet nitrate-containing (A) and chloride-containing aluminosilicate gels (B).

0 ppm might be resolved to components. One of these at 0 ppm could be attributed to the hydrated  $\text{Al}^{3+}$ ; the other peak at about 4 ppm is generally identified as corresponding to the Al atoms octahedrally bonded in the gel structure. According to the literature Al resonance of  $\approx 4$  ppm could be observed in the spectra of Al dimers [33, 34], of polymeric Al species [8, 29, 34–39], of clay minerals [40, 41], and of mullite [24, 42]. Some authors reported six co-ordinated Al atoms in glassy aluminosilicate [29–31, 43]. In aluminosilicate gels with composition of mullite, the octahedrally co-ordinated Al atoms are dominant as reported by Jaymes et al. [16].

On the basis of NMR data obtained by deconvolution and integration of the NMR signal to determine area under the peaks, 98–99% of the Al content resonates at  $-1.2 \pm 0.1$  ppm in wet chloride-containing gels. Thus, only 1–2% of Al content is bonded in the gel structures. Under the same conditions, with the use of Al nitrate, 67.5% of the Al content may be assigned to the peak around 0 ppm (non-bonded Al ions), 25.5% of the Al content to the peak around 4 ppm (Al atoms bonded octahedrally), and 7% of the Al content to the peak of 58 ppm (Al atoms bonded tetrahedrally). These results

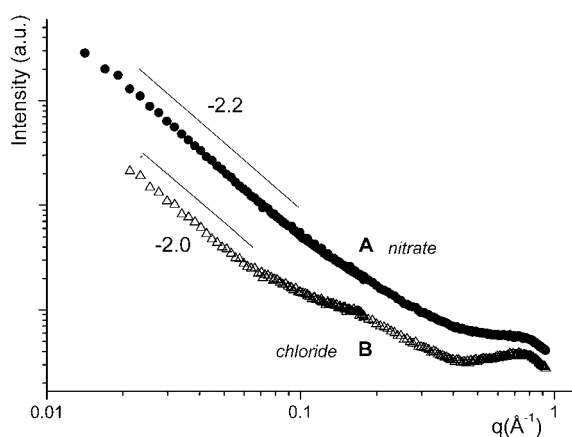


Figure 2. SAXS curves for aluminosilicate gels prepared from Al nitrate (A) and Al chloride (B).

correspond to the data obtained by chemical measurements (Table 2). By a washing step with water, 84% and 65% of total Al content could be removed from the chloride- and the nitrate-containing gels, respectively.

On the basis of SAXS measurements, both nitrate- and chloride-containing gels can be characterised by fractal-like networks (Fig. 2). On the log-log plot of scattering curves, a linear region can be observed with a slope of  $-2.2$  (A curve) and  $-2.0$  (B curve) indicating mass fractals [8, 25]. Considering the  $q$ -range of linear regions, the structure of chloride-containing gels is considerably less homogeneous than that of the nitrate-containing gels. The  $q$ -range of the linear region extended over  $0.02$ – $0.06 \text{\AA}^{-1}$  at the use of chloride (Fig. 2, curve B) and  $0.02$ – $0.1 \text{\AA}^{-1}$  with the use of nitrate (Fig. 2, curve A). The strong and broad distortion of scattering curve B (chloride) at about  $0.17 \text{\AA}^{-1}$  is due to the non-bonded Al content, which shows some arrangements in the gel indicating probably the beginning of phase separation. Scattering curve A (nitrate) is slightly distorted because of the lower number of the non-bonded Al ions. Curve A shows no phase separation.

### 3.2. Solvent Effect on Gelation

According to the results reported in Table 3, 1-propanol is the most suitable for gelation and Al incorporation. However, the data for Al incorporation and nitrate content in the samples prepared in 1-propanol and 2-propanol are very similar, 1-propanol was proved to be better than 2-propanol because of its higher boiling-point

Table 3. Effect of solvent on gels.

Solvent	Dielectric constant (25°C) [44]	$t_g$ (minute)	Bonded Al (%)	$\text{NO}_3^-$ content (%)	Slope of scattering curves at the range of 0.02–0.06 $\text{\AA}^{-1}$
Ethylene glycol <sup>a</sup>	37.0	85 ± 25	36 ± 10	52 ± 15	2.2 ± 0.2
Methanol	32.6	80 ± 15	30 ± 10	52 ± 15	1.9 ± 0.2
Ethanol	24.3	65 ± 10	37 ± 4	50 ± 5	1.9 ± 0.2
1-propanol	20.1	60 ± 10	52 ± 5	41 ± 4	2.1 ± 0.1
2-propanol	18.3	55 ± 10	52 ± 7	42 ± 6	1.7 ± 0.2
1-butanol <sup>a</sup>	17.1	50 ± 15	49 ± 12	42 ± 10	2.2 ± 0.2

<sup>a</sup>Not homogeneous gel samples. Bonded Al and  $\text{NO}_3^-$  content of gels are given in the percent of total initial value. Chemical composition of samples: 0.05 mol TEOS, 0.05 mol  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 0.3 mol alcohol. The time of heat treatment: 22 h at 80°C.

(97°C > 82°C). Thus, the hydrolysis of Al(III) could be speed up by raising the temperature above 80°C to avoid the intense boiling. In the samples formed in ethanol or in methanol, the number of incorporated Al atoms was lower, the nitrate content was higher than in the samples with propanol due to the higher polarity of ethanol or of methanol solution. The gel samples formed in 1-butanol and ethylene glycol were not homogeneous, some amorphous precipitation could be observed in both samples.

The SAXS curves for aluminosilicate gels prepared in various kinds of alcohol and pure silica gel show very similar fractal structures after a washing step to remove the precipitation from the gels with 1-butanol or with ethylene glycol. The similar mass fractal dimensions (the average  $\mu = 2.2 \pm 0.2$ ) of the aluminosilicate and pure silica gels prepared under the same acidic conditions prove the gel frameworks to be dominated by silica network (see Table 3 and Fig. 3) [8, 25]. The silica gel structure is slightly modified by the incorporation of Al atoms [25]. The SAXS curve for gel prepared in 1-propanol is the best similar curve to that of pure silica gel indicating the best homogeneous gel structure for 1-propanol-containing gel.

The organic compounds present in the gels made in 1-propanol were investigated by the GC-MS, TG-MS, and APCI-MS-MS techniques. In the samples with low solvent content, 1–5% of the initial nitrogen content (nitrate ions and their decomposed products) reacted with alcohol, resulting in some oxidised products. The gels prepared in 1-propanol were found to contain the largest amount of 1-propanol and a decreasing amount of ethanol, diethyl-oxalate, propyl-2-OH-propanoate, 2-OH-propyl acetate, 2-OH-propanoic acid, and their esters detected by MS techniques. Under heat treatment

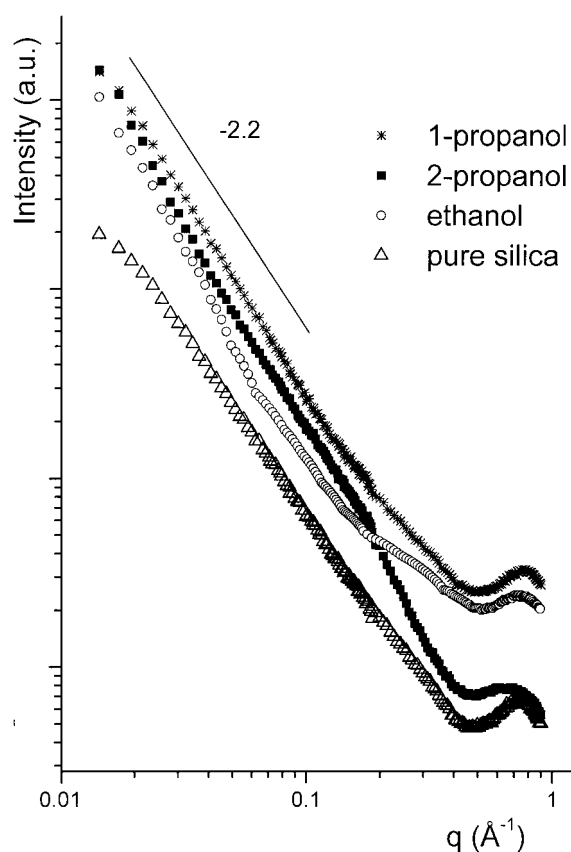


Figure 3. SAXS curves for aluminosilicate gels prepared with different solvents and for pure silica gel.

the majority of oxidised products remained in the gels up to 400°C according to the TG-MS investigation. The increasing solvent content greatly reduced the degree of oxidation.

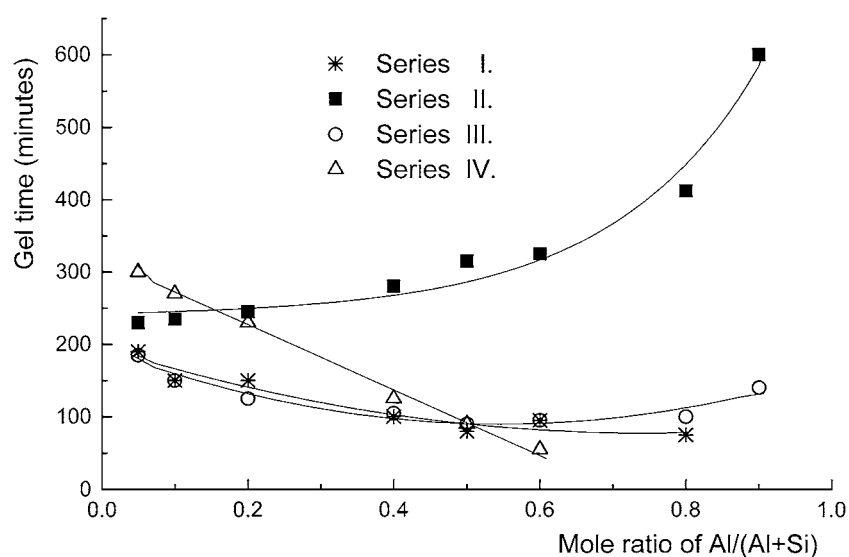


Figure 4. Gel time measured by microviscosimeter at 80°C vs. the chemical composition. Lines are drawn as guide for the eye.

### 3.3. Effect of Chemical Composition on Gelation

In order to obtain as much information as possible on the effect of chemical composition, present work includes measurements with various mole ratios of Al/Si at different solvent content. (The chemical composition of gel samples can be see in Table 1.)

In Series I. (samples with high water content) gel time as a function of Al/(Si + Al) mole ratio showed a nearly exponential increase similar to that of water content (Fig. 4). In the gel time of Series II. (samples with low water content), some changes may be observed mainly below 0.20 and above 0.80 mole ratios of Al/(Si + Al). In the case of 0.20 mole ratio, the gel time remained practically unchanged when water was replaced by 0.2 and 2.0 M HNO<sub>3</sub> aqueous solutions. The gel time of samples in Series III. (constant mole ratios of total water/Si and of total water/propanol) decreased fairly linearly with growing Al content due to the diminishing water/Al ratios (Fig. 4). The gel time in Series IV. changed in a similar way to Series II. in spite of the constant mole ratio (7.5) of total water/(Si + Al) of gels (Fig. 4).

In all gel samples obtained in Series I., the incorporation of Al atoms and the escape of nitrate ions were negligible. In the gel samples in Series II., III., and IV., the incorporated Al content in the percentage of the initial (total) Al content as well as nitrate escape shows very similar changes as a function of mole

ratio of Al/(Si + Al) (Fig. 5). At about 0.20 mole ratio of Al/(Si + Al), there is minimum Al incorporation in this representation of every series, the best results were measured between 0.40–0.60 mole ratios. However, considering the mole ratio of Al/Si bonded in the gel network, a monotone increase can be observed as a function of mole ratio of Al/(Si + Al) (Fig. 6). Nitrate ions escaped in a considerable degree also above 0.20 mole ratio but no maximum could be observed as a function of Al mole ratio. In the initial solution of gel preparation (gelling solution) with 0.20 mole ratio of Al/(Si + Al), the percentage of bonded Al content of the initial amount changed from 27% to 36, 39% when water was replaced by 0.2 and 2.0 M HNO<sub>3</sub> aqueous solutions, respectively. By this acidic catalysis the nitrate content of gels decreased by 15–20%.

SAXS curves in Fig. 7 for gels obtained with 0.20, 0.40, and 0.60 mole ratios of Al/(Si + Al) show good correspondence, indicating similar mass fractal structures. The slope of the linear regions in the log-log representation over q-range of 0.02–0.3 Å<sup>-1</sup> varies between -1.9 and -2.2 ± 0.1. The slope slightly increases with growing Al content. In the case of pure silica gel, the slope is -1.9. The curve of the sample with 0.70 mole ratio of Al/(Si + Al) differs from the others. Only a short linear region can be observed over q-range of 0.02–0.07 Å<sup>-1</sup> having a slope of -2.3 ± 0.1. In the q-range of 0.1–1.1 Å<sup>-1</sup>, broad reflections appear due to a quasi-ordered structure.

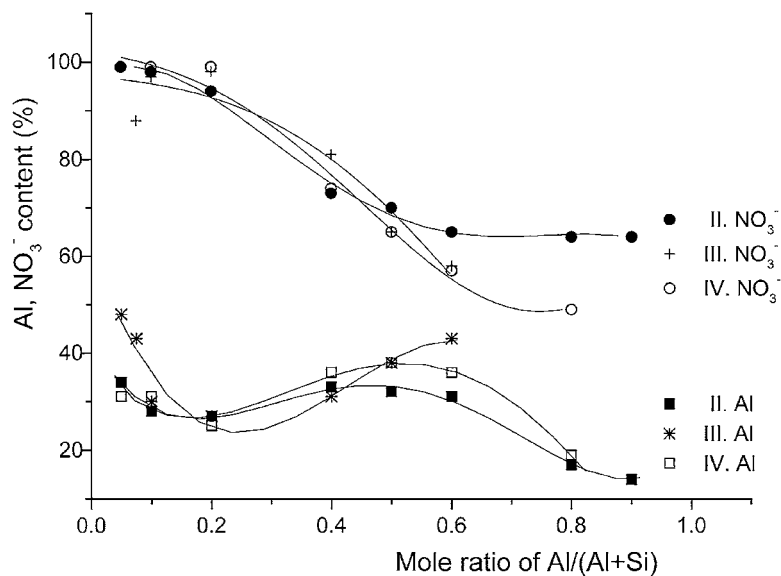


Figure 5. Dependence of the bonded Al and NO<sub>3</sub><sup>-</sup> content on the chemical composition (Series II, III, IV). Lines are drawn as guides for the eye.

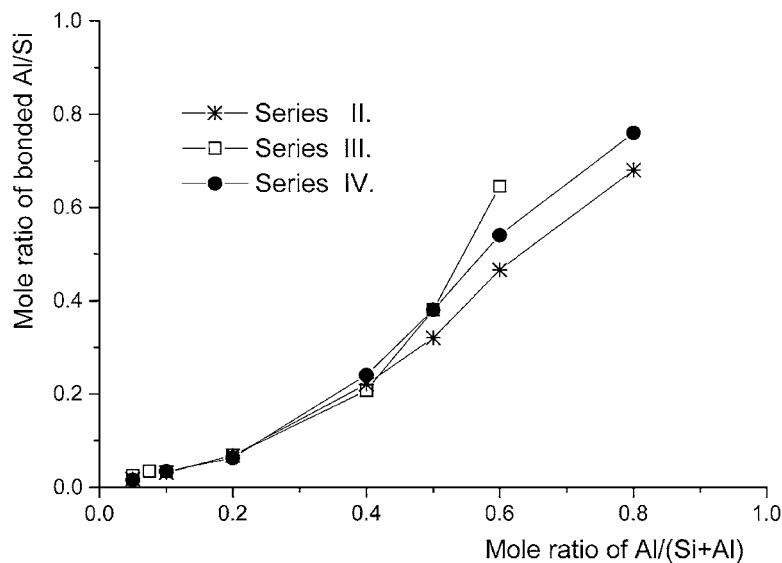


Figure 6. Mole ratio of Al/Si bonded in the gel network in the function of mole ratio of Al/(Si + Al) in the initial solutions of gelation. Lines are drawn as guides for the eye.

#### 4. Discussion

The fundamental processes of the gelation are the hydrolysis and the condensation of TEOS and Al<sup>III</sup> salt. During these processes, OH ions replace one or more water molecules in the co-ordination sphere of Al<sup>III</sup>, followed by condensation resulting in Al–O(H)–Si

bonds, besides formation of Si–O–Si bonds from TEOS [25]. The Al incorporation, i.e. the formation of Al–O(H)–Si bonds, depend strongly on the chemical materials and compositions used in the preparation.

Aluminum sulphate and acetate cannot be used for the present direct gel preparation because of their very low solubility in alcohol and water. With the

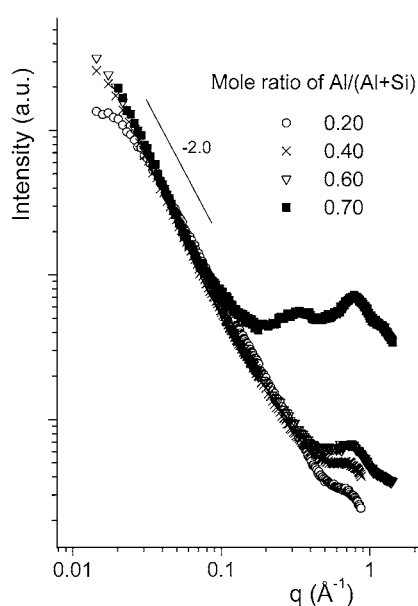


Figure 7. SAXS curves for aluminosilicate gels prepared with different mole ratio of Al/(Si + Al).

use of these materials, an amorphous precipitation was formed. Thus Al-containing sol preparation has to be applied as the initial step of the sol-gel process. In spite of that optically clear gels can be obtained from both Al chloride and nitrate with TEOS,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is less suitable for sol-gel processes than  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The extent of Al incorporation into the gel network was much lower in the chloride-containing gels than in the nitrate-containing gels. The gel structure obtained with Al chloride is not homogeneous, it is dominated by the silica network having fractal-like structure strongly deformed by the non-bonded Al content. The non-bonded Al content forms associates of hydrated Al(III) ions connected by weak hydrogen bonds which may result in phase separation. In addition, in the case of Al chloride, a washing step is needed to remove the anions.

Al nitrate proved to be the best Al precursor for the direct gel preparation of homogeneous, optically clear aluminosilicate gels. Al nitrate shows quite good solubility in water and alcohol, it hydrolyses strongly to produce an acidic solution, which is required for gelation. Thus, catalysis is not needed in this process. The hydrolysis speed of Al nitrate is closer to that of TEOS compared to the Al alkoxides generally used for sol-gel methods [8, 45, 46]. The less difference between hydrolysis speeds promotes the formation of a homogeneous gel structure and the Al incorporation. According to the TG-MS measurements, the nitrate content

escapes as nitrous gases during the gelation (about 50% at 80°C) and heat treatment (about 50% between 80 and 400°C), contributing to hydrolysis and incorporation of Al atoms into the gel network. Due to the spontaneous decomposition of nitrate content, the washing step is unnecessary.

As a result of measurements carried out with various kinds of alcohol, it may be established that the incorporation of Al atoms decreases as a function of growing solvent polarity (Table 3). However, the more polar the solvent, the better the dissolution of Al nitrate is. The best solvent for this sol-gel method is 1-propanol, owing to its polarity required for the dissolution of Al nitrate but it can dissolve TEOS as well. In addition, 1-propanol decreases the polarity of the system of gelation. In the less polar medium,  $\text{HNO}_3$  molecules form from the nitrate ions and they may escape as nitrous gases. The decomposition of  $\text{HNO}_3$  molecules results in the decrease of acidity which causes the hydrolysis of Al ions. The minority of  $\text{HNO}_3$  molecules (1–5%) decomposes in a reaction with 1-propanol resulting in some oxidised products, which remain in gel up to 400°C. The most oxidised products can connect to the  $\text{Al}^{\text{III}}$  ions and occupy the co-ordination sites around the aluminum ions to hinder the precipitation of Al content during the gelation [47]. The solvents of high polarity (e.g. ethylene glycol or methanol result in some precipitation in gel.

The amount of 1-propanol in the gelling solutions depends on the water content and preparation conditions [4]. The water content strongly effects the incorporation of Al atoms into the gel framework. The higher the amount of water, the lower the number of incorporated Al atoms is. The advantageous effect of the lowering amount of solvent is due to the consequent increase of Al and Si concentration, which favours the condensation reactions. In addition, at small amount of water the decrease of the polarity is more enhanced during the addition of propanol. On the basis of present measurements with different mole ratios of Al/Is and solvent/metal ions, high water content (>10 mole ratios of water/(Si + Al)) cannot be advised at any mole ratio of Al/Si for this sol-gel method. In summary, 3.4–5.4 mole ratios of total water/(Si + Al) and 2–10 mole ratios of 1-propanol/(Si + Al) proved to be favourable mole ratios for gelation and Al incorporation.

The mole ratio of Al/Si bonded in the gel networks increased continuously with the growth of Al/(Si + Al) mole ratios in the initial gelling solutions (Fig. 6). However, the efficiency of Al incorporation, that is the ratio



of the incorporated and the initial amount of Al, did not change continuously as a function of the initial Al/(Si + Al) mole ratios (Fig. 5). Due to the increasing acidity required for the gelation, Al incorporation became more and more effective in the range of 0.10–0.40 mole ratios of Al/(Si + Al). (The mole ratios of total water/Al greatly decreased in this range, resulting in more intensive acidity in the solutions.) The above result has been verified experimentally by acidic catalysis, when the efficiency of the incorporation considerably improved approaching the maximum value of these measurements series. Thus, acidic catalysis is needed to prepare gels of low Al/(Al + Si) mole ratio. In the range of 0.40–0.70 mole ratio, the change is small. At lower than 0.60–0.70 mole ratio the gelling procedure is dominated by hydrolysis and the condensation of TEOS. The silica networks are only modified by the incorporated Al atoms. It can also be proved by SAXS measurements. The SAXS curves for pure silica gel and aluminosilicate gels with different solvents or with 0.20, 0.40, 0.60 mole ratios of Al/(Si + Al) are similar (Figs. 3 and 7, respectively). Above 0.60 mole ratio the efficiency of Al incorporation gradually decreased because the formation of gel networks became more and more difficult owing to the reduced amount of TEOS. The main part of Al content, which cannot be built up in the small extent of silica framework, hinders the formation of continuous gel network. Above 0.70 mole ratio the gelling procedure comprises two steps, one of which is the formation of the silica network modified by bonded Al atoms. The other one is the formation of a pure Al-containing phase due to the hydrolysis and the condensation of Al nitrate. The SAXS curve for gel sample of 0.70 mole ratio is completely different from the others, proving present preparation method cannot be used to form a homogeneous gel structure with higher than 0.70 mole ratio of aluminum content.

## 5. Conclusions

Beside TEOS, Al nitrate and 1-propanol proved to be the best materials for the direct gel preparation of homogeneous, optically clear aluminosilicate gels. As favourable chemical compositions for this process, 0.40–0.60 mole ratios of total Al/(Si + Al), 3.4–5.4 mole ratios of total water/(Si + Al), and 2–10 mole ratios of 1-propanol/(Si + Al) can be applied. At lower than 0.30–0.40 mole ratios of total Al/(Si + Al), the use of an acidic catalysis is required to obtain a homo-

geneous gel with the desired Al content in the gel networks. At higher than 0.60–0.70 mole ratios homogeneous gel cannot be prepared by this way. In contradiction to the traditional melting process of glass, our method enables us to increase the amount of Al content 5 fold larger, considering the fact that a homogeneous gel structure is required.

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