

# “Spontaneous” growth of fibrous products on the surface of silicic acid gels

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Received: 8 December 2006 / Accepted: 16 January 2007 / Published online: 13 April 2007  
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**Abstract** We have observed occurrence of fibrous products on gel surface in four-component system of KK (silicic acid sol)–H<sub>2</sub>O–HCl–NH<sub>3</sub>, KK–H<sub>2</sub>O–HCl–NaOH and KK–H<sub>2</sub>O–HCl–TEA (triethanolamine). Bundles of fibres occur in the system with NH<sub>3</sub>, sticks and needles in system with NaOH, and finally in the system with TEA we can mostly observe the occurrence of crystalline products. Dependency of product morphology on initial sol composition is occurring in observed systems. In the case of system with NH<sub>3</sub>, mostly the length of nascent fibres is influenced by the composition, and in the systems with NaOH and TEA it is also final shape of nascent products. Morphology of nascent products in systems with NH<sub>3</sub> and NaOH is controlled by quantity of added HCl, but in the system with TEA it is quantity of added TEA. It is characteristic for all observed systems that “spontaneously” occurring products consist of crystalline phase, that is chloride of respective alkali, and amorphous phase, that is SiO<sub>2</sub>. Beginning of respective chloride crystallization in observed systems probably initializes occurrence of products on gel surface. Further growth of crystals is influenced by present colloid of SiO<sub>2</sub> that interacts with surface of

growing crystal leading to anisotropy of its growth and therefore to “spontaneous” occurrence of fibrous products.

**Keywords** Chemical gardens · Sol-gel · Silicic acid · Fibres · Spontaneous growth

## 1 Introduction

Sol-gel methods based on the use and control of solution-sol-gel-product transition allow preparation of various materials often with unanticipated characteristics [1–3]. Interesting phenomenon of sol-gel-product transition is “spontaneous” occurrence of various and often fibrous formations. These “spontaneously” occurred fibrous formations are measured in dimensions from nanometers to centimeters [4–9]. Best-known systems, in which “spontaneous” growth of fibres and fibrous structures occurs, are not only called chemical gardens but also silicate gardens, colloidal gardens and crystal gardens, mostly because of the similarity to the growth of plants [10]. They occur after addition of grain of soluble salt of metal into solutions containing anions such as silicates, aluminates, borates, carbonates, phosphates, ferricyanides and many others [11]. Mechanism of their occurrence is explained by the occurrence of amorphous gel precipitate that creates semipermeable membrane on the boundary line between added grain of soluble salt of metal and solution of used anion. Water diffuses into the space between crystal and membrane, because concentration of dissolved salt is higher there than in the surrounding solution. Osmotic pressure rises, membrane is stretching and breaks. Solution of salt that is in the space between crystal and membrane blows through this hole. When it comes into contact with solution of anion, gel precipitate is created and it

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immediately wraps blown stream of liquid with semipermeable membrane and stops its further spreading. The whole process repeats in consequence of continuing dissolving of added crystal and oscillatory growth occurs [12]. In this manner, tubes are created with walls of respective amorphous or crystalline silicate [9, 11].

Nascent crystalline material is in few cases decisive for final shape. This is how anorganic materials are “spontaneously” created with morphogenesis similar to biological systems in water solution of silicates in the presence of water-soluble baric salts [13]. Driving force of “spontaneous” growth in this case is crystallization of respective salt that is affected and controlled by present colloid. Interaction of colloidal particles and surface of growing crystal becomes control mechanism and under certain specific circumstances leads to the occurrence of various products different from expected shape of crystallizing material [13].

Occurrence, growth rate and shape of these products are complicated function of individual components concentration in observed system, their proportion, response time and conditions of preparation (temperature, mixing, water evaporation rate, etc.).

There is interest in processes of “spontaneous” occurrence of products [9, 10, 12], their structure [14] or possibilities of their preparation in classical [11] or modified [15] way.

Processes parallel to described “spontaneous” processes are used for creation of sticks, fibres or eventually tubes out of  $\text{SiO}_2$  on nanolevel. In these processes,  $\text{SiO}_2$  sol prepared by sol-gel method is applied to the surface of crystal created directly in the solution [5, 6], or to the structure of organic gel [7, 8].

Process of “spontaneous” growth of fibrous formations similar to that of “silicate garden” was observed during drying of some  $\text{SiO}_2$  gels, but this process took place on the boundary of solid matter and air. This phenomenon was observed for the first time during drying of sonogels prepared in  $\text{TEOS-H}_2\text{O-HCl-NH}_3$  system [16].

It was found out that these fibrous formations consist of crystalline  $\text{NH}_4\text{Cl}$  wrapped in flimsy layer of  $\text{SiO}_2$ . Mechanism of fibre growth depends on presence of  $\text{SiO}_2$  sol. Similar to that of “silicate gardens”, it creates semipermeable membrane allowing diffusion of water from gel, and so osmotic pressure is created in the case, that causes rupture of membrane and consequential oscillatory growth [16]. Similar fibre growth was also observed in the  $\text{KK-H}_2\text{O-HCl-ALKALI}$  system (ALKALI =  $\text{NH}_3$ ,  $\text{NaOH}$ , TEA) [17, 18]. According to our knowledge, not a great attention has been paid to these systems, even though they are the potential source of processes for preparation of  $\text{SiO}_2$  fibres, respectively, nanotubes or  $\text{SiO}_2$  nanofibres.

In this work, we are dealing with systematic observation of fibre creation in  $\text{KK-H}_2\text{O-HCl-ALKALI}$  system.

## 2 Experimental

### 2.1 Preparation of silicic acid sol

We have used freshly prepared solution of sodium silicates in water for preparation of silicic acid. Solution of sodium silicates has been prepared by dissolving of porous  $\text{SiO}_2$  (Silica from DEGUSSA company) in calculated quantity of  $\text{NaOH}$  solution. Solution of sodium silicates had concentration of  $\text{SiO}_2 \sim 1.5 \text{ mol dm}^{-3}$  and molar rate of  $\text{Na}_2\text{O}:\text{SiO}_2$  was 1:3. Silicic acid sol has been prepared by ionic exchange of  $\text{Na}^+$  for  $\text{H}^+$  using Amberlite IR cation exchanger— $120\text{H}^+$  form 0.3–1.2. Created sol had concentration of  $\text{SiO}_2 \sim 1.25 \text{ mol dm}^{-3}$  and  $\text{pH} \sim 2.4$ .

### 2.2 Preparation of samples

Samples for observation of fibre occurrence areas in  $\text{KK-H}_2\text{O-HCl-NH}_3$ ,  $\text{KK-H}_2\text{O-HCl-NaOH}$  and  $\text{KK-H}_2\text{O-HCl-TEA}$  systems have been prepared by use of hydrochloric acid solution with concentration of  $10 \text{ mol dm}^{-3}$ , solution of ammonia, sodium hydroxide and triethanolamine with concentration of  $7.5 \text{ mol dm}^{-3}$ . Individual sol samples have been mixed in undermentioned way, to get sol samples with molar rate of  $\text{SiO}_2:\text{HCl}:\text{ALKALI}$  according to the Table 1. Prepared samples had concentration of  $\text{SiO}_2 \sim 0.75 \text{ mol dm}^{-3}$ .

While mixing, we have added required quantity of water and acid solution to required quantity of freshly prepared silicic acid sol into polyethylene bowl. Finally, we have added alkali solution while intense mixing. We have placed samples after gelling at laboratory temperature on the watch glass. The gel has retracted during waiting and fibres occurred on the samples usually 3 days later.

### 2.3 Fibre characterization

Observations with raster electron microscope have been performed on Aquasem machine of TESCAN Brno manufacturer and Vega machine of the same producer. Measurements of infra-red spectra in area of  $4000$  to  $700 \text{ cm}^{-1}$  have been realized with the help of FT-IR spectrophotometer Spectrum One of Perkin-Elmer company. X-ray diffraction analysis has been done on Philips PW 1730/10 machine with  $\text{CuK}_\alpha$  radiation. Optical microscopy has been used for observation of shape and length of occurred fibrous products.

**Table 1** Molar rates of SiO<sub>2</sub>:HCl:ALKALI for prepared samples

Sample	SiO <sub>2</sub>	HCl	Alkali
1	1.00	5.34	0.00
2	1.00	4.45	0.67
3	1.00	3.56	1.34
4	1.00	2.67	2.00
5	1.00	1.78	2.67
6	1.00	0.89	3.34
7	1.00	0.00	4.01
8	1.00	4.45	0.00
9	1.00	3.56	0.67
10	1.00	2.67	1.34
11	1.00	1.78	2.00
12	1.00	0.89	2.67
13	1.00	0.00	3.34
14	1.00	3.56	0.00
15	1.00	2.67	0.67
16	1.00	1.78	1.34
17	1.00	0.89	2.00
18	1.00	0.00	2.67
19	1.00	2.67	0.00
20	1.00	1.78	0.67
21	1.00	0.89	1.34
22	1.00	0.00	2.00
23	1.00	1.78	0.00
24	1.00	0.89	0.67
25	1.00	0.00	1.34
26	1.00	0.89	0.00
27	1.00	0.00	0.67
28	1.00	0.00	0.00

### 3 Results and discussion

#### 3.1 Observation of fibre occurrence areas

We have projected composition in KK–H<sub>2</sub>O–HCl–NH<sub>3</sub>, KK–H<sub>2</sub>O–HCl–NaOH and KK–H<sub>2</sub>O–HCl–TEA four-component systems so as the concentration of particular components changes according to the scheme of three-component diagram with H<sub>2</sub>O, HCl and respective ALKALI peak points. Concentration of KK has been the same in all samples. We have observed fibre occurrence areas, their morphology and for some samples from particular systems also their chemical composition.

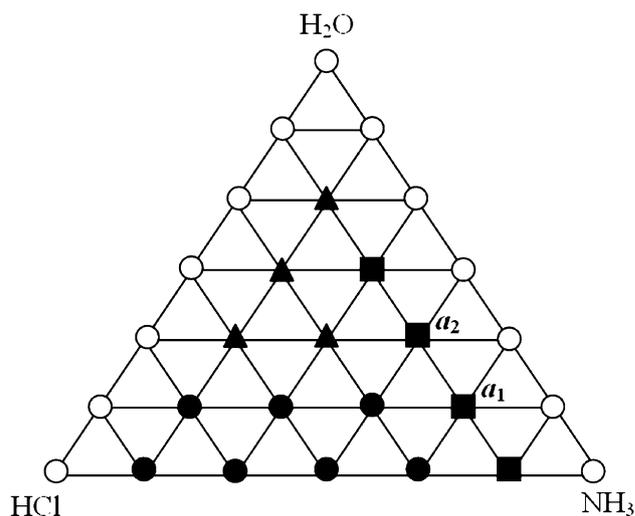
##### 3.1.1 System KK–H<sub>2</sub>O–HCl–NH<sub>3</sub>

Products with the shape of fibres occurred in this system. Their quantity, length of fibres and morphology depend on initial sol composition. We have identified three types of products in this system. Compositions allowing occurrence

of short fibres (to 2 mm) covering only small areas of gel surface are marked on Fig. 1 with symbol ●. Compositions allowing occurrence of long fibres (to 6 mm) on whole gel surface are marked with symbol ■. Symbol ▲ marks compositions allowing occurrence of short fibres (to 2 mm) covered with small grains on small limited areas of gel surface. No fibres (○) occur on gel surface at peak joint lines of H<sub>2</sub>O–HCl and H<sub>2</sub>O–NH<sub>3</sub>. Figure 1 shows, that long fibres (■) occur when quantity of hydrochloric acid added to the solution is small and NH<sub>3</sub> is excessive. These solutions are alkalic and they have constant concentration of NH<sub>4</sub>Cl. Increase in quantity of added HCl results in shortening of nascent fibres and also in decrease of their quantity. Smooth short fibres (●) occur at higher HCl concentrations and lower H<sub>2</sub>O concentrations. Small grains (▲) begin to occur on surface of fibres at lower and medium HCl concentrations and low NH<sub>3</sub> concentration.

For further characterization have been selected fibres from the area where long fibres have been occurring on gels of composition that is marked on Fig. 1 as *a*<sub>1</sub> and *a*<sub>2</sub>. Fibres that have occurred at *a*<sub>1</sub> composition and have been observed with electron raster microscope are shown on Fig. 2. Figure 3 shows fibres that have occurred at *a*<sub>2</sub> composition. Relatively long fibres aligned into bundles occur on gels of either composition.

X-ray diffraction analysis has proved ammonium chloride as dominant crystalline phase at both samples. Infrared spectra of samples of *a*<sub>1</sub> and *a*<sub>2</sub> composition are shown at Fig. 4. Maximum of wide band, equivalent to O–H stretching vibration of water, is in the range of 3400 up to 3500 cm<sup>-1</sup>. This band partially covers the band of N–H stretching vibration, in our case it is of the ion [NH<sub>4</sub>]<sup>+</sup>. Bands around 1400 cm<sup>-1</sup> belong to various deformation



**Fig. 1** Occurrence areas of particular product types for KK–H<sub>2</sub>O–HCl–NH<sub>3</sub> system

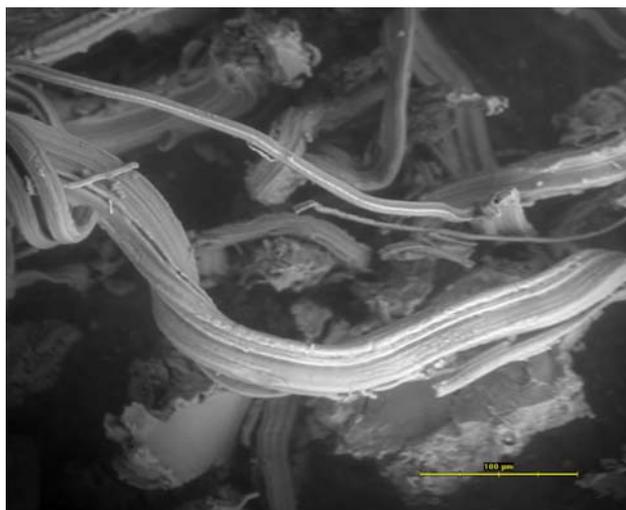


Fig. 2 Products occurred at  $a_1$  composition

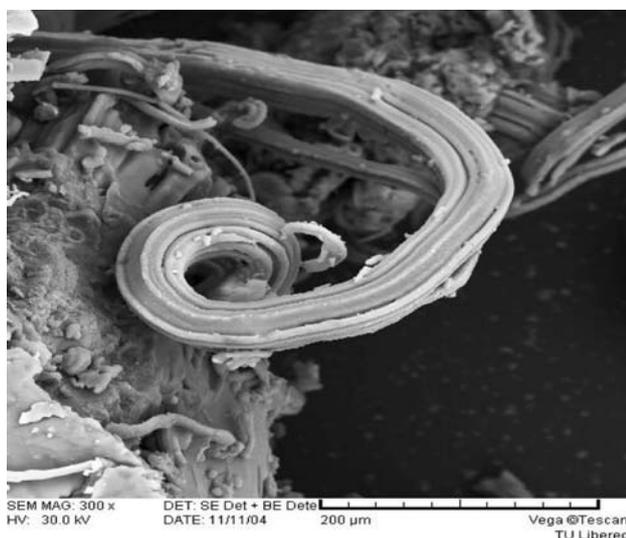


Fig. 3 Products occurred at  $a_2$  composition

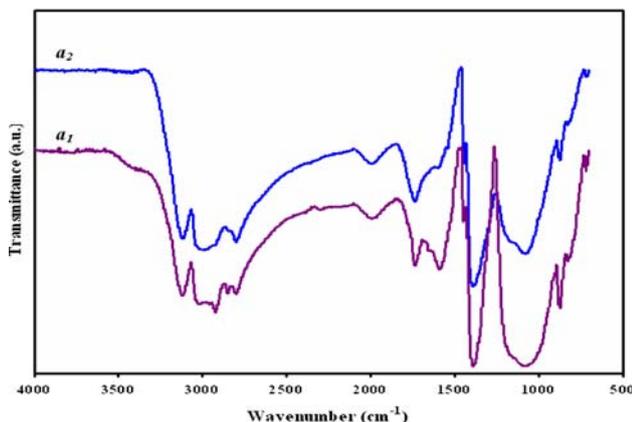


Fig. 4 Infrared spectra of  $a_1$  and  $a_2$  samples in KK–H<sub>2</sub>O–HCl–NH<sub>3</sub> system

vibrations [NH<sub>4</sub>]<sup>+</sup>. Band in the range of 1200 up to 1000 cm<sup>-1</sup> is characteristic for its asymmetric Si–O–Si stretching vibration. Band nearing 800 cm<sup>-1</sup> can be assigned to symmetric Si–O–Si stretching vibration [19–21]. Based on these facts we can state, that crystalline NH<sub>4</sub>Cl and amorphous SiO<sub>2</sub> is present in observed fibres.

3.1.2 KK–H<sub>2</sub>O–HCl–NaOH system

In this system, (Fig. 5) products occurring on the surface of gels are long from 0.5 to 3 mm and have the shape of sticks with rectangular cross section (■) and needles (●), eventually, sticks and needles (◐) occur together. Products in the shape of sticks with grainy surface (▲) also occur. No fibres (○) occur on gel surface at peak joint lines of H<sub>2</sub>O–HCl and H<sub>2</sub>O–NaOH. Morphology of nascent products is significantly dependent on concentration of nascent NaCl and pH of initial solution. If NaCl is not present, products on the gel surface do not occur. Baccilar products occur at low HCl concentration and at surplus of NaOH. pH value is decreasing along with gradual increase of HCl and not only sticks but also needles are occurring.

Further increase of HCl concentration results in morphology change of nascent products to sticks with grainy surface. For further characterization have been selected products from the area where the longest products (to 3 mm) have been occurring on gels of composition that is marked on Fig. 5 as  $b_1$  and  $b_2$ . Fibres that have occurred at  $b_1$  composition and have been observed with electron raster microscope are shown on Fig. 6 and those at  $b_2$  composition are shown on Fig. 7.

Figures 6 and 7 show that occurring are products with the baccilar shape of rectangular or square cross-section.

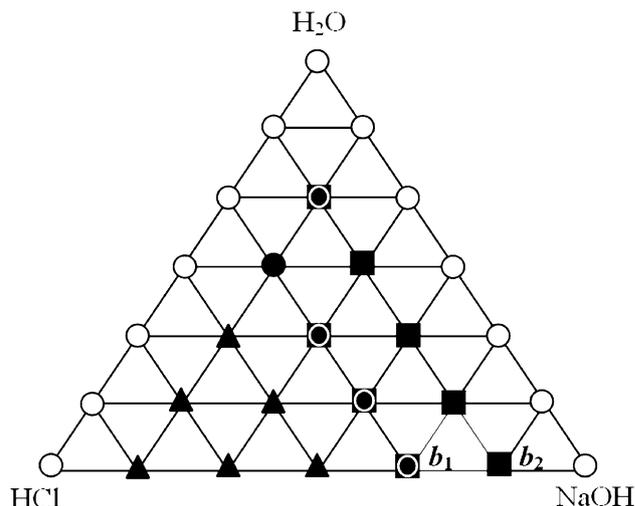


Fig. 5 Occurrence areas of particular product types for KK–H<sub>2</sub>O–HCl–NaOH system

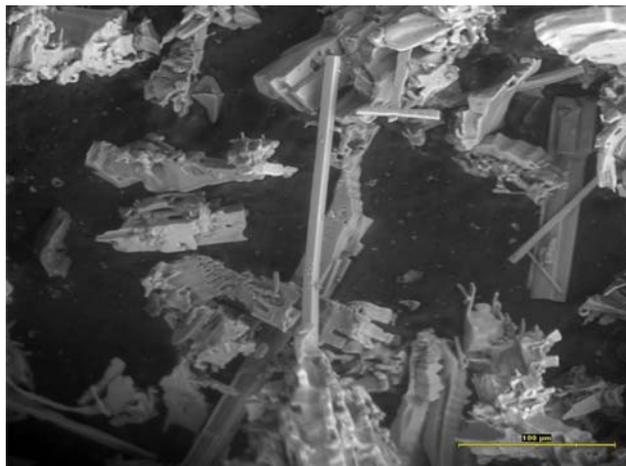


Fig. 6 Products occurred at  $b_1$  composition

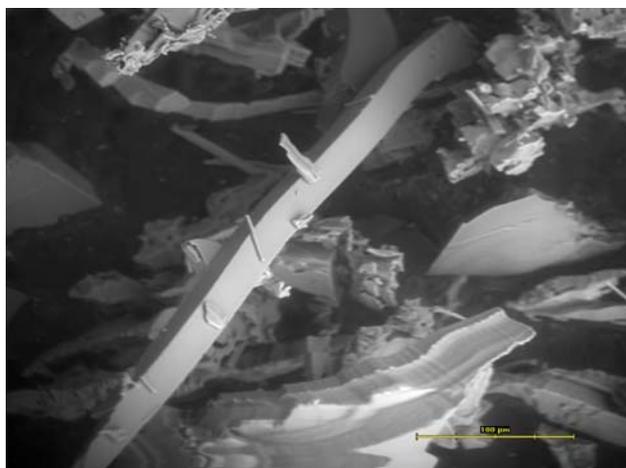


Fig. 7 Products occurred at  $b_2$  composition

These products have morphology equivalent to crystalline shapes. X-ray diffraction analysis has proved sodium chloride as dominant crystalline phase at both samples. Infrared spectra of the samples of  $b_1$  and  $b_2$  composition (Fig. 8) show, that, as in previous case, there are distinct bands of Si–O–Si vibrations in the area of 1200–1000  $\text{cm}^{-1}$  and around 800  $\text{cm}^{-1}$  proving the presence of  $\text{SiO}_2$  in the samples [19–21]. Based on these measurements we can state, that amorphous  $\text{SiO}_2$  is also present in these samples as it was in the previous case. But crystalline sodium chloride is present in this system as well.

### 3.1.3 KK–HCl–TEA–H<sub>2</sub>O system

As we can see in Fig. 9, this system differs from two previous systems from the view of nascent products. First significant difference is, that products also occur on the joint line of TEA–H<sub>2</sub>O. These are dendritic crystalline products ( $\blacktriangle$ ). Another difference is well observable

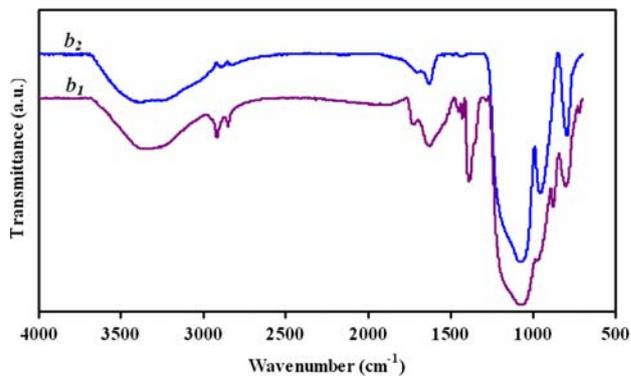


Fig. 8 Infrared spectra of  $b_1$  and  $b_2$  samples in KK–H<sub>2</sub>O–HCl–NaOH system

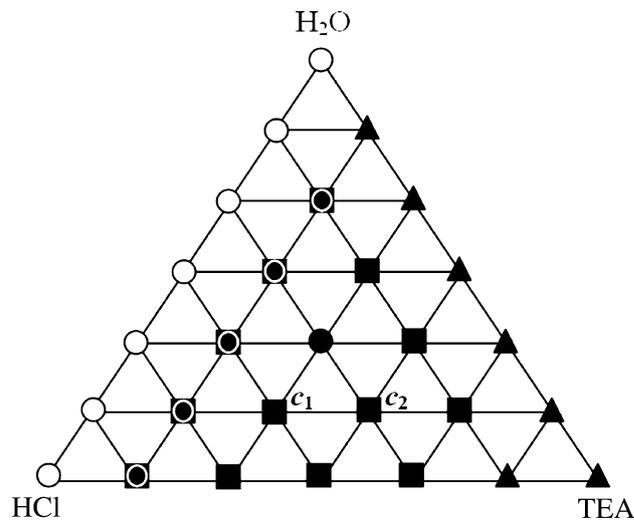
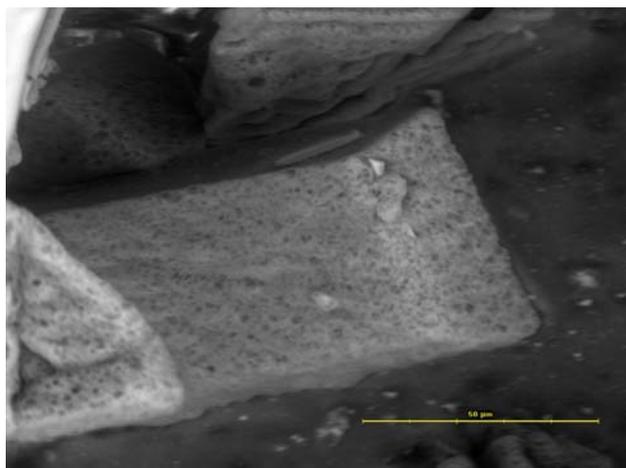


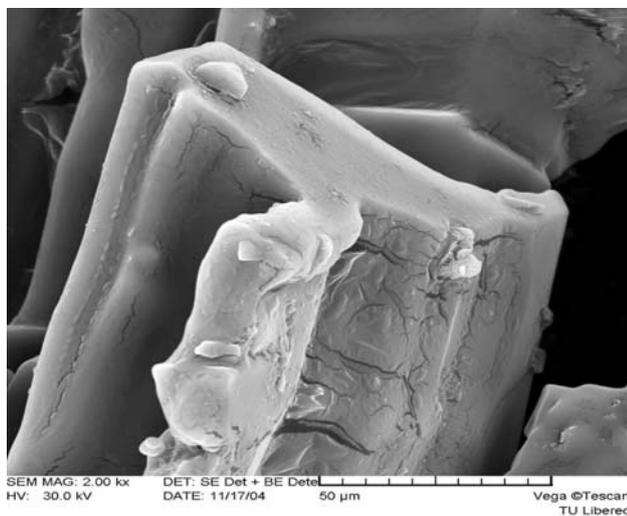
Fig. 9 Occurrence areas of particular product types for KK–HCl–TEA–H<sub>2</sub>O system

dependency of nascent products morphology on concentration of added TEA. Crystalline products ( $\circ$ ) occur at the smallest added quantity of TEA along with bacillar products. Increase in quantity of added TEA results in occurrence of irregular crystalline shapes ( $\blacksquare$ ) on gel surface and in one case also the product with regular crystalline shape ( $\bullet$ ). Nascent products are long to 25 mm.

For further characterization have been selected fibres from the area where the longest products have been occurring on gels of composition that is marked on Fig. 9 as  $c_1$  and  $c_2$ . Fibres that have occurred at  $c_1$  and  $c_2$  composition and have been observed with electron raster microscope are shown on Figs. 10 and 11. Also products of bacillar shape occur at sample of  $c_1$  composition in addition to compact products, but only compact products with complicated morphology are present at sample of  $c_2$  composition.



**Fig. 10** Products occurred at  $c_1$  composition

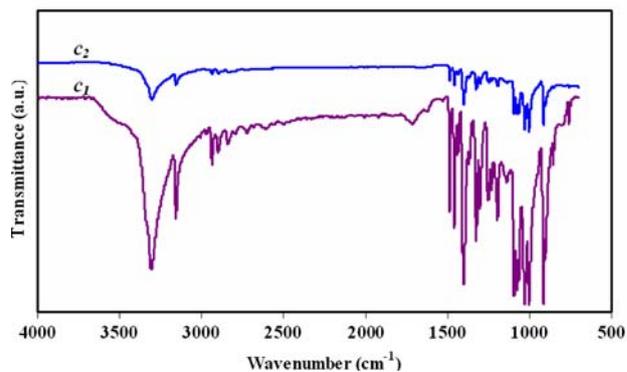


**Fig. 11** Products occurred at  $c_2$  composition

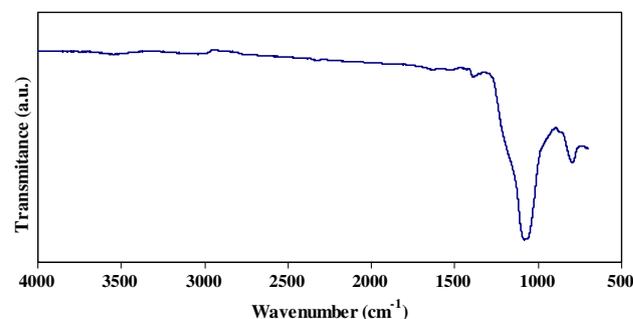
X-ray diffraction analysis has proved TEA chloride as dominant crystalline phase at both samples. Infrared spectra of the samples of  $c_1$  and  $c_2$  composition (Fig. 12) show, that areas of  $1200\text{--}1000\text{ cm}^{-1}$  and around  $800\text{ cm}^{-1}$  with distinct bands of Si–O–Si vibrations are overlapped with absorption bands of TEA chloride [19–21]. To confirm presence of  $\text{SiO}_2$ , sample of  $c_2$  composition was heat-treated at  $600\text{ }^\circ\text{C}$ . Infrared spectrum of acquired product is on Fig. 13 and it is evident, that the product is  $\text{SiO}_2$ . We can state, that, as in two previous systems, there is amorphous  $\text{SiO}_2$  present along with crystalline phase, in this case it is TEA chloride.

### 3.2 Mechanism of product occurrence

Based on discovered facts we can presume, that crystallization of relevant chloride is control process of product

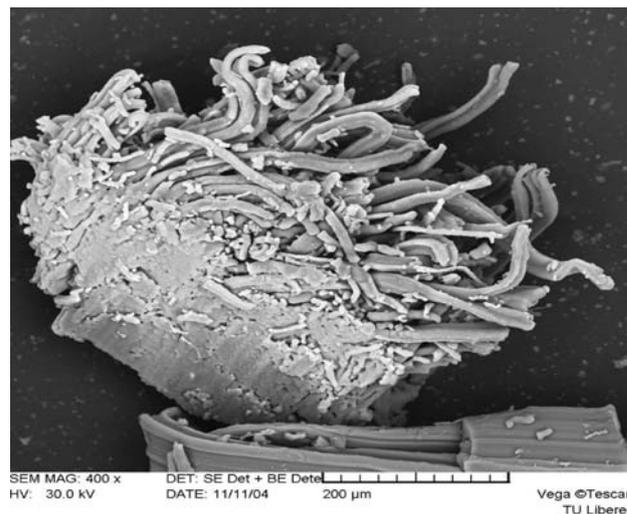


**Fig. 12** Infrared spectra of  $c_1$  and  $c_2$  samples in KK–HCl–TEA– $\text{H}_2\text{O}$  system



**Fig. 13** Infrared spectrum of  $c_2$  sample after firing ( $600\text{ }^\circ\text{C}$ ;  $0.5\text{ }^\circ\text{C min}^{-1}$ )

occurrence on gel surface in observed systems. But further growth of crystals does not occur in homogenous environment. It is influenced by present colloid of  $\text{SiO}_2$  interacting with surface of growing crystal, what leads to anisotropy of its further growth [22, 23].



**Fig. 14** Growth of products on gel surface in KK–HCl– $\text{NH}_3$ – $\text{H}_2\text{O}$  system

Result is the occurrence of long fibrous products to 6 mm at  $\text{NH}_4\text{Cl}$  crystallization (Fig. 14), long bacillar crystals to 3 mm at  $\text{NaCl}$  crystallization and long sticks to 25 mm with almost round cross-section at TEA chloride crystallization. At the same time, it also explains the fact, why chloride of respective alkali and also amorphous  $\text{SiO}_2$  are identified in products occurring on gel surface in all observed systems.

#### 4 Conclusions

Above-mentioned facts make it clear, that shape of nascent fibrous products is function of used alkali in the first place, but also of sol composition and consequently of gel allowing occurrence of fibrous products. So, bundles of fibres occur in the system with  $\text{NH}_3$ , sticks and needles in system with  $\text{NaOH}$ , and finally in the system with TEA we can mostly observe the occurrence of crystalline products. In the case of system with  $\text{NH}_3$ , mostly the length of nascent fibres is influenced by the composition, and in the systems with  $\text{NaOH}$  and TEA it is also the final shape. Morphology of nascent products in systems with  $\text{NH}_3$  and  $\text{NaOH}$  is controlled by quantity of added  $\text{HCl}$ . In systems with TEA, it is the quantity of added TEA. It is characteristic for all observed systems that “spontaneously” occurring products consist of crystalline phase, that is chloride of respective alkali, and amorphous phase, that is  $\text{SiO}_2$ . The occurrence of fibrous products in observed systems can be used for preparation of sticks or tubes from pure  $\text{SiO}_2$ .

#### References

1. Sakka S (1982) In: Tomozawa M, Doremus RH (eds) Treatise on materials science and technology. Academic Press, London, p 129

2. Brinker CJ, Scherer GW (1990) Sol-gel science: the physics and chemistry of sol-gel processing. Academic Press, Boston
3. Rahaman MN (2003) Ceramic processing and sintering. Marcel Dekker, New York
4. Rao CNR, Müller A, Cheetham AK (2004) The chemistry of nanomaterials—synthesis, properties and applications, vols. 1 and 2. WILEY-VCH Verlag GmbH & Co.KGAA, Weinheim
5. Miyaji F, Watanabe Y, Suyama Y (2003) Mater Res Bull 38:1669
6. Mokoena EM, Datye AK, Coville NJ (2003) J Sol-Gel Sci Technol 28:307
7. Bied C, Moreau JJE, Vellutini L, Man MWC (2003) J Sol-Gel Sci Technol 26:583
8. Vergnes A, Nobili M, Delord P, Cipelletti L, Corriu RJP, Boury B (2003) J Sol-Gel Sci Technol 26:621
9. Thouvenel-Romans S, Van Saarloos W, Steinbock O (2004) Europhys Lett 67:48
10. Cartwright JHE, García-Ruiz JM, Novella ML, Otálora F (2002) J Colloid Interf Sci 256:351
11. Balköse D, Özkan F, Köktürk U, Ulutan S, Ülkü S, Nişli G (2002) J Sol-Gel Sci Technol 23:253
12. Thouvenel-Romans S, Steinbock O (2003) J Am Chem Soc 125:4338
13. Gaecía-Ruiz JM, Hyde ST, Carnerup AM, Christy AG, Van Kranendonk MJ, Welham NJ (2003) Science 302:1194
14. Collins C, Zhou W, Mackay AL, Klinowski J (1998) Chem Phys Lett 286:88
15. Bormashenko E, Bormasenko Y, Stanevsky O, Pogreb R (2006) Chem Phys Lett 417:341
16. Atik M, Zarzycki J (1989) J Mater Sci Lett 8:32
17. Pagáčová J, Plško A, Staňová I, Lukáč A (2004) In: Dusza J (ed) Nanoved. Slovak Academy of Sciences, Košice, pp 40
18. Lukáč A, Plško A, Pagáčová J, Staňová I, Exnar P, Kovačič V (2005) In: Plešingerová B, Kuffa T (eds) Proceeding of VIth conference preparation of ceramic materials, Faculty of Metallurgy Technical University, Košice, p 95
19. Innocenzi P (2003) J Non-Crystal Solids 316:309
20. Fidalgo A, Ilharco LM (2001) J Non-Crystal Solids 283:144
21. Socrates G (2001) Infrared and Raman characteristic group frequencies. Chichester, John Wiley
22. Hall N (2004) Chemical Communications 1–4 (focus article)
23. Qi L, Cölfen H, Antonietti M, Li M, Hopwood JD, Asley AJ, Mann S (2001) Chem A Euro J 7:3526