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Investigation of hydrolysis and condensation of methyltriethoxysilane in aqueous systems

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ABSTRACT

An effective synthesis of methylethoxysilanes and emulsification of methyltriethoxysilane is described. Hydrolysis and condensation products of methyltriethoxysilane were identified and studied using ^{29}Si NMR, mass spectrometry and infrared spectroscopy. The presented analyses are important from practical point of view, as the emulsion in question is used for hydrophobization of building materials and soil. The most striking finding is high stability of the low molecular products of hydrolysis - methylsilanetriol [$MeSi(OH)_3$] and its dimer [$(OH)_2(Me)SiOSi(Me)(OH)_2$]. All of which were still present in the aqueous medium, after 40 days of storage at ambient conditions. This finding suggests that condensation processes leading to the formation of polymer network are slow in the emulsion and a large number of reactive hydroxyl groups are present in the system allowing for the effective hydrophobization of mineral material.

1. Introduction

Alkoxysilanes are widely used as substrates for manufacturing silicones and silicone-based materials. They are commonly prepared by alcoholysis of corresponding chlorosilanes (Scheme 1). The side product, hydrochloric acid is typically removed by addition of tertiary amines [1,2]. Alternative processes involve reaction of organochlorosilanes with alkali metal alcoholates [3,4] or alkyl orthoformates (Scheme 2) [5,6].

$$RSiCl_3 + 3\ R'OH \longrightarrow RSi(OR')_3 + 3\ HCl$$

Scheme 1

$$R_3SiCl + HC(OR')_3 \longrightarrow R_3SiOR' + R'Cl + HCOOR'$$

Scheme 2

Alkoxysilanes can be also obtained by alcoholysis of organosilanes, bearing silyl hydride functionality (Scheme 3) [7,8]. This process requires a presence of the catalyst such as strong base.

$$R_{4-n}SiH_n + n\ R'OH \xrightarrow{Catalyst} R_{4-n}Si(OR')_n + nH_2$$

Scheme 3

Recently Stryker's reagent ($[Ph_3PCuH]_6$) [8] and *tris*(pentafluorphenyl) borane ($B[C_6F_5]_3$) [9-11] were reported as effective catalysts of the alcoholysis of hydrosilanes. Solutions of alkoxysilanes in organic solvents are commonly used for impregnation of wood [12,13] and modification of inorganic surfaces [14]. Today, environmental regulations limit an employment of the organic solvents in these applications and force their replacement by aqueous silicone emulsions [15-17].

Krichmayer and co-workers [18,19] described the aqueous emulsions containing alkoxycarbosilanes or siloxanes and polyacrylate resins for a protection of porous building materials and construction areas. He has also patented grafted polymers of acrylic and methacrylic acid derivatives with silicone resins bearing large number of alkoxy groups for a waterproofing, and in particular for the protection of buildings [19]. Aqueous emulsions containing alkoxysilanes and vinyl polymers have been also described [20]. Aqueous solutions of sodium silicate or potassium methylsilanolate were often used for the treatment of soil. Environmental considerations restrict their application due to the formation of strong alkaline by-products, being extremely harmful for environment. In the past, Sztromajer *et al.* [21] reported a direct use of organochloro silanes for soil modification, but the formed hydrogen chloride restricts their use in an open space (Scheme 4).

$$Me_nSiCl_{4-n} + H_2O \longrightarrow (MenSiO_{4-n})_x + (4-n)\ HCl$$

Scheme 4

Recently, we have presented a very effective method of hydrophobization of mineral building materials using aqueous emulsions of ethoxysilanes. This process allows for total elimination of water capillary action at the methyltriethoxy silane concentration of 0.08 wt. % in a building material or soil [22]. The developed process is environmentally friendly as the only volatile by-products of hydrolysis and condensation are an ethanol and water. The other aspect dealt with, in this work, is the analysis of the polymer resin formation process in order to understand the aging of emulsion under contact with moisture that also occurs on treatment of building materials and soil..

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2. Experimental

Methyltrichlorosilane (Aldrich), ethanol, sodium hydrogen carbonate, methylene chloride and methanol (POCH) were used without purification. Poly(vinyl alcohol), Moviol® 8-88 (Aldrich), $M_w = 6.7 \times 10^4$ g/mol reagent grade was used without purification. Sulfarokanol L-327 was kindly supplied by Zakład Chemiczny "Silikony Polskie" Nowa Sarzyna.

2.1. Instrumentation

Gas chromatography analyses were performed using a Hewlett-Packard HP 6890 chromatograph equipped with thermal conductivity detector and HP 1 capillary column l = 30 m, d = 0.53 mm. Typical conditions were as follows: helium carrier gas at the flow rate 5 mL/min; detector temperature 250^0 C and column temperature was programmed: 3 min at 60 °C isoth., ramp from 60 to 240 °C at rate 10 °C/min. and 15 min at 240 °C isothermal.

^{29}Si NMR spectra were recorded on a Bruker DRX 500 operating system at 99.6 MHz in the inverse gate pulse sequence mode with a relaxation delay of 3 s, scan number 10 K, time domain 65 K and 90 deg pulse 15.00. D_2O or $CDCl_3$ were used as solvent.

Solid state ^{29}Si NMR spectra were run with a DSX 400 Bruker spectrometer. Spectra were acquired with cross-polarization, at 59.627 MHz applying 90-μs pulses, 6 s pulse delay, and 3 ms contact time, with samples in 4.0 mm zirconia rotors spinning at 8 kHz. Chemical shifts were referenced to Q_8M_8. The proportional parts of T^0_2 and T^0_3 units were estimated by deconvolution of the two broad peaks in the region of -55 up to -72 ppm.

Chemical Ionization (CI) mass spectra were recorded on a Finnigan MAT 95 double focusing (BE geometry) mass spectrometer (Finnigan MAT, Bremen, Germany). Standard CI mass spectra were obtained using isobutene as a reagent gas and the operating conditions were as follows: electron energy of 20 eV, accelerating voltage of 4.6 kV; ion source temperature of 200 °C. Samples were introduced via a direct insertion probe heated from 30 to 300 °C.

Mass spectra were recorded with a GC-MS Finningan MAT 95 instrument using chemical ionization technique. The reactive gas (H^+ carrier) was isobutane at 10^{-4} Torr. The mass-spectrometer worked in tandem with the gas chromatograph that was fitted with a standard capillary column DB-1 l = 30 m. The temperature was programmed to fit to the corresponding chromatogram recorded earlier on the HP-6890 instrument. Since ionization occurred under mild conditions, a fragmentation of analyzed species was limited. Siloxane monomers and oligomers gave a strong M+1 peaks and/or its simple fragmentation product, which dominate over other fragmentation products.

IR spectra were taken with the Nicolet 6700 Series FTIR apparatus working with Omnic program, at resolution of 2 cm^{-1}.

2.2. Synthesis

2.2.1. Synthesis of alkoxysilanes

Typical synthesis of alkoxysilanes was performed in the round-bottomed 500 mL flask (1) equipped with a dropping funnel (3), capillary tube (2), reflux condenser (4), separator of organic compounds (cold trap) (5), and HCl absorber (6) (Figure 1). A flask was charged with 46 g (1 mol) of ethanol. It was vigorously stirred at room temperature, while 149.5 g (1 mol) of methyltrichlorosilane was added drop wise. Samples were withdrawn at various time intervals and subjected to GC analysis. Alcoholysis was carried out with a nitrogen spurge at constant gas flow. Hydrogen chloride was removed from nitrogen stream (50 mL/min) by absorption in water. After the reaction was completed the mixture was heated up and was kept at reflux for 3 hours. The crude product (methyltriethoxysilane) was neutralized by addition of sodium hydrogen carbonate (50 g, 0.6 mol) and was further used as such. GC analysis has shown that it contained 91% of methyltriethoxysilane (Figure 2) (162 g), ^{29}Si NMR, δ: -44.27 ppm. The product structure was confirmed by GC-MS analysis.

Synthesis of trimethylethoxysilane and dimethyldiethoxy silane were performed in an analogous way to the process described above. The yield of trimethylethoxysilane was 91.5% (^{29}Si NMR, δ: -17.6 ppm) and the yield of dimethyldiethoxy silane was 91% (^{29}Si NMR, δ: -3.54 ppm). The total yield of $MeSi(OCH_2CH_3)_3$, $Me_2Si(OCH_2CH_3)_2$, $Me_3SiOCH_2CH_3$ and their siloxane oligomers was 99.73%, 99.96% and 98.21%, respectively. Obtained alkoxysilanes were converted to emulsions without further purification.

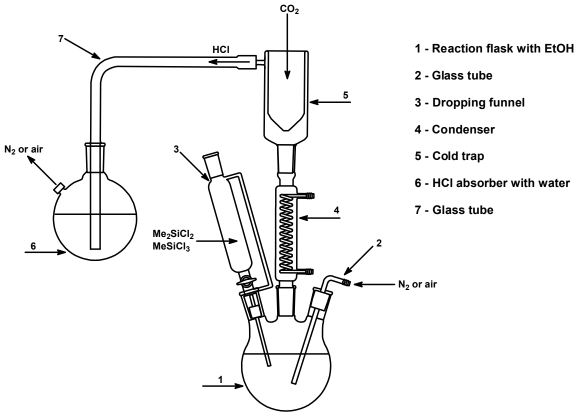


Figure 1. Reactor for synthesis of alkoxysilanes.

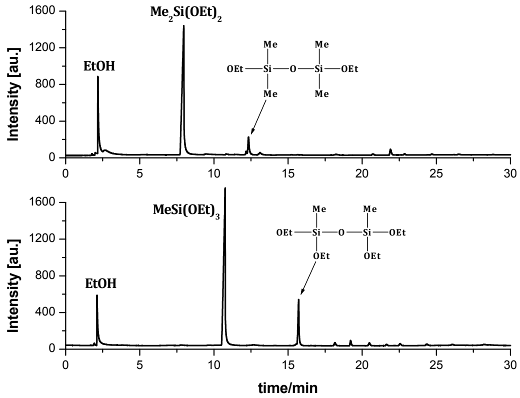


Figure 2. Exemplary gas chromatograms of the reaction mixture after alcoholysis of dimethyldichlorosilane (Me_2SiCl_2) – (A) and methyltrichloro silane ($MeSiCl_3$) – (B).

2.2.2. Preparation of the water emulsion of methyltriethoxysilane

Stock solution of 10 % (weight) aqueous solution of Moviol 8-88 and 2 weight % solution of sulforokanol L-327 in demineralized water were prepared separately. Twelve parts, by weight, of the stock solution of Moviol 8-88 was diluted with 18 parts by weight of demineralized water. The mixture was homogenized for 5 min using a high-speed MPW-120 homogenizer set to 4,000 rpm. 50 parts by weight of $CH_3Si(OCH_2CH_3)_3$ was introduced with vigorous mixing to yield an emulsion. The mixture was stirred for 4 minutes.

Subsequently, 20 parts by weight of the stock solution of sulforokanol L-327 were added to it and homogenized for 5 min at 3,000 rpm. The resulting final emulsion was stable and did not separate after 15 minutes of centrifuging at 3,000 rpm and is considered as an excellent product for hydrophobization of building material and soil [22]. The obtained aqueous emulsion was subjected to ^{29}Si MAS NMR studies (Figure 3 and 4) during three months in order to assess the rate of condensation and the structure of condensation products.

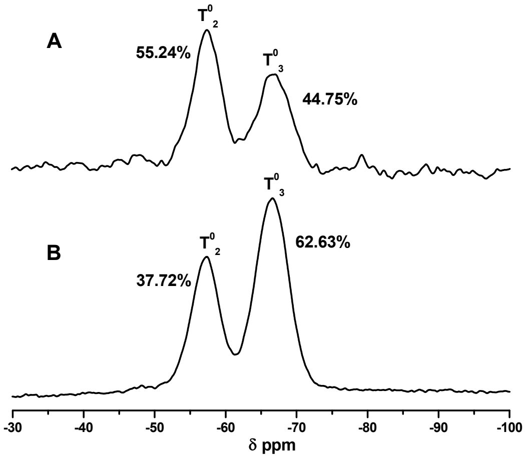


Figure 3. ^{29}Si MAS NMR spectra of the aqueous emulsion of $MeSi(OEt)_3$ after 45 days (A) and 90 days (B) of aging at room under atmospheric conditions, temperature.

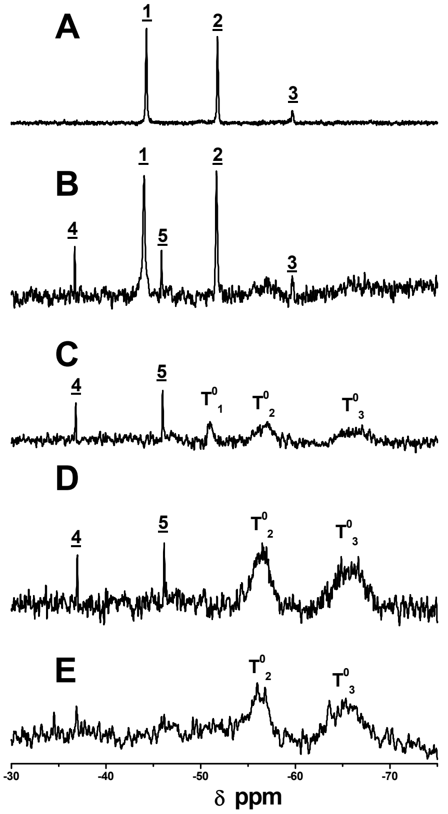


Figure 4. Solution ^{29}Si NMR spectra (in $CDCl_3$) of the aqueous emulsion of $MeSi(OEt)_3$. Spectra were taken after: (A) 8 hours, (B) 12 days, (C) 24 days, (D) 40 days, (E) 50 days.

2.2.3. Reaction of methyltriethoxysilane with H_2O ($MeSi(OEt)_3/H_2O$ = 0.1 mol/mol)

A separate study of hydrolysis and condensation of $MeSi(OEt)_3$ were performed in a 50 mL Schlenk flask equipped with magnetic stirrer and suba-seal. Molar ratio of silane to the demineralized water ($MeSi(OEt)_3/H_2O$) was 0.1. The originally two phase system homogenized after 18 hours. Samples were withdrawn periodically using Hamilton syringe with a long needle and directly analyzed by gas-liquid chromatography (organic layer), ^{29}Si NMR (Figure 5) and CI-MS (Figure 6). The following molecular ions were identified in the system *m/z*: 95 $[CH_3Si(OH)_3]H^+$; 123 $[CH_3Si(OH)_2(OCH_2CH_3)]H^+$; 151 $[CH_3Si(OH)(OCH_2CH_3)_2]H^+$; 171 $\{[CH_3Si(OH)_2]_2O\}H^+$; 199 $[CH_3Si(OH)_2Osi(OH)(OCH_2CH_3)CH_3]H^+$; 227 $[CH_3Si(OH)_2OSi(OCH_2CH_3)_2CH_3]H^+$; 255 $[CH_3Si(OH)(OCH_2CH_3)OSi(OCH_2CH_3)_2CH_3]H^+$; 283 $[CH_3Si(OCH_2CH_3)_2OSi(OCH_2CH_3)_2CH_3]H^+$.

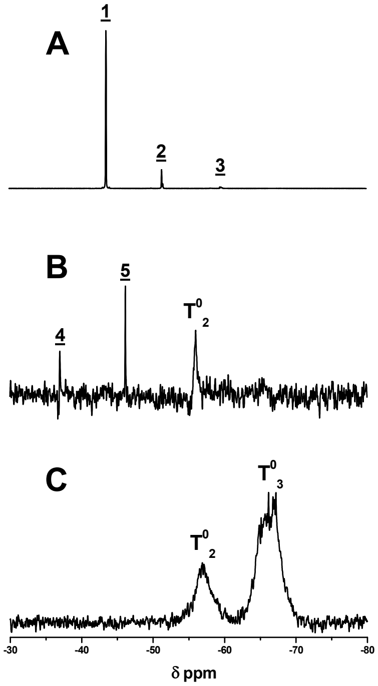


Figure 5. Solution ^{29}Si NMR spectra in $CDCl_3$ at inverse gated decoupling of the model hydrolysis and condensation of $MeSi(OEt)_3$. Molar ratio $MeSi(OEt)_3/H_2O$ = 0.1 taken after 5 hours (A), 18 hours (B), and after washing separation and concentrating of organic phase at 60 °C (C). (see Section 2.2.3).

3. Results and discussion

3.1. Ethanolysis of chlorosilanes

We have developed the environmentally friendly synthetic methodology that allows for preparation of alkoxysilanes, from the respective chlorosilanes, with high yields (in the range of 91-92%) *via* "reverse addition" Silane to alcohol, that is contrary to a typical procedure, e.g. [23]. The remaining ethanolated products are partly condensed dimers and trimmers. However, as illustrated in Figure 2, the increase of the number of methyl groups at silicon limits the content of dimers in the final product. The simple synthetic process of ethoxysilanes preparation involves addition of appropriate chlorosilane under the surface of alcohol (Figure 1). Additionally the reaction mixture is purged with dry nitrogen. The method limits the contact of chlorosilanes and alkoxysilanes with an atmospheric moisture, and hydrochloric acid, which catalyzes side reactions and lowers the yield of alkoxysilanes. The only side product (HCl) is removed from the reaction mixture in a stream of nitrogen and is further absorbed by water, yielding a technical grade hydrochloric acid. Thus, the whole alcoholysis process becomes an environmentally friendly. Addition of chlorosilanes to EtOH results in a rapid reaction and formation of an appropriate alkoxysilane accompanied by the evolution of HCl (Scheme 5).

$$Me_nSiCl_{(4-n)} \quad + \quad (4-n)\ EtOH \longrightarrow Me_nSi(OEt)_{(4-n)} \quad + \quad (4-n)\ HCl$$

Scheme 5

The synthetic process is much more effective, when compared to the substitution of chlorine by alkoxy moieties at silicon atom, using organometallics that is typically used in laboratories, but is not economic on industrial scale. Alcoholysis was carried out at room temperature, at a constant rate of nitrogen flow through the reaction mixture. The additional cold trap allows for an effective separation of organic vapours from gas stream leading to an additional purification of HCl (Figure 1). The course of the reaction was monitored by gas chromatography analyses of samples withdrawn from the reaction mixture. After the addition was completed residual HCl was removed from the product by addition of sodium hydrogen carbonate.

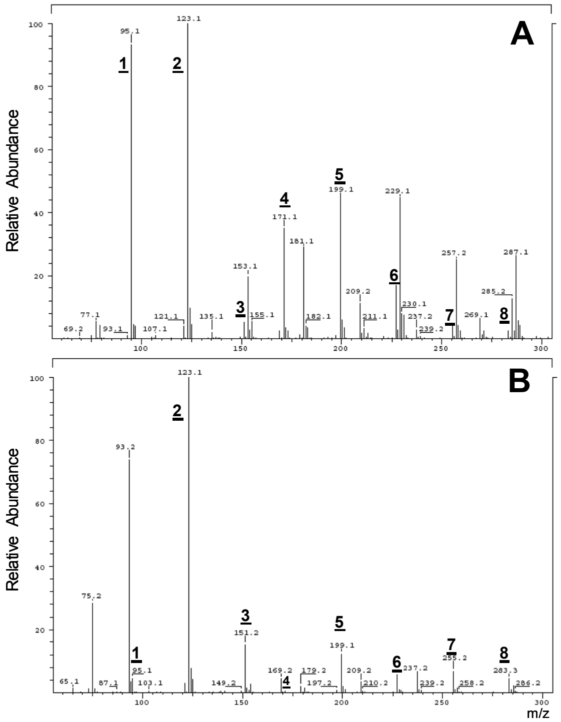
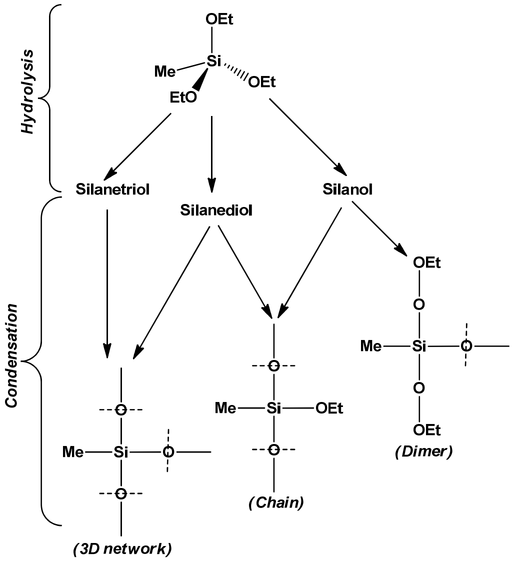


Figure 6. MS (chemical ionization) of hydrolysis and condensation products of methyltriethoxysilane, by direct ionization. Molar ratio $MeSi(OEt)_3/H_2O$ = 0.1, room temperature, reaction time 18 hours. (A) Spectra taken at 35 °C, (B) Spectra taken at 95 °C.

3.2. Studies of the hydrolysis of methyltrimethoxysilane and its condensation products

Some hydrolysis products of organoalkoxysilanes were analyzed and characterized in the past [24,25] by such techniques as IR [26], gas chromatography-mass spectroscopy and ^{29}Si NMR [27-29].

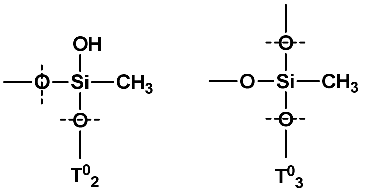
Alkoxy groups at the central silicon atom undergo step-wise hydrolysis when methyltriethoxysilane is mixed with water yielding silanols, silanediols and silanetriols. Silanols are in general regarded as species of low stability and are prone to condensation and formation of thermodynamically stable siloxanes, by elimination of water. Partially condensed siloxanes bearing OH moieties condense further, generating oligomer and polymer products (Scheme 6).



Scheme 6

^{29}Si NMR is an extremely useful technique applied to study hydrolysis and polycondensation of alkoxysilanes [28-33]. Thus we have employed a high-resolution ^{29}Si NMR in our investigation of hydrolysis methyltriethoxysilane and subsequent condensation processes taking place in aqueous emulsion of methyltriethoxysilane, in order to understand a composition of the emulsion and the final process of hydrophobization.

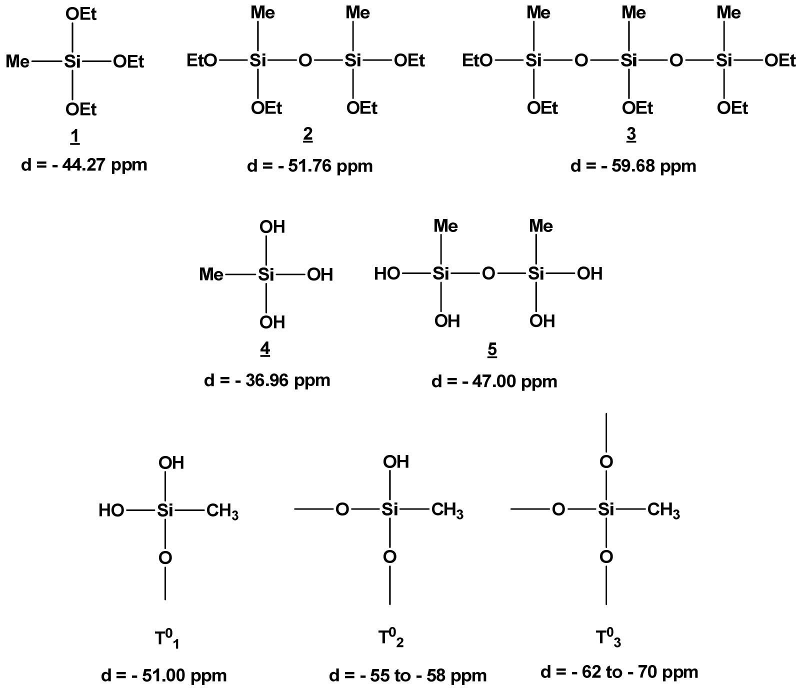
The analysis proved that oligomeric resin formed on aging of the emulsion is composed of two types of siloxane units (Scheme 7).



Scheme 7

The analysis of the ^{29}Si MAS NMR spectra (Figure 3) confirms that the prepared polymers are highly branched with two broad resonances centred at -56 ppm and -66 ppm, which correspond to T^0_2 and T^0_3 environments [33]. The data obtained for aged emulsion after 45 days (A) and 90 days (B) show clearly that the condensation of Si-OH occurs slowly on exposure of the emulsion to atmosphere (water evaporation from open system), leading to the increase in branched and crosslinked units present in condensed resin.

The content of T^0_3 units increases to 62.6% after 90 days of aging under atmospheric conditions. The content of T^0_2 units decreases at the same time by 18%. In order to better understand transformation of the $MeSi(OEt)_3$ emulsion a model reaction of $MeSi(OEt)_3$ with water was investigated by ^{29}Si NMR. The results indicate that at the initial stage of condensation low molecular weight products dominate. After 8 hours, only monomer, dimer and trimer could be observed (Figure 4a).



Scheme 8

After twelve days the same low molecular weight species were still present, however, some new hydrolysis products were also detected at -47 ppm and -36.96 ppm (Figure 4b) (Scheme 8).

The observed ^{29}Si NMR signals were assigned to silanetriol (4) and its condensed dimer (5) based on the literature [29,31]. These two species (4) and (5) are still present after 24 and 40 days. In addition, condensation products containing T^0_1, T^0_2 and T^0_3 units (resonances centred at -51, -57 and -66 ppm respectively, Figure 4c, d) started to appear after 24 days. ^{29}Si-NMR spectra taken after 50 days shows almost total disappearance of the low molecular weight hydrolysis products and T^0_1 units (Figure 4e). This spectrum shows only two broad signals corresponding to T^0_2 and T^0_3 units.

In order to confirm the high stability of the low molecular species (**4**) and (**5**) we have also examined hydrolysis of $MeSi(OEt)_3$ in water at room temperature. Initially two distinct layers were observed (water and alkoxysilane) (Figure 5a). After 18 hours the system became homogeneous and two resonances were observed, corresponding to (**4**) and (**5**) as well as one signal originating from T^0_2 unit (Figure 5b). After washing the reaction mixture with diethyl ether, the organic phase was concentrated at 60 °C. ^{29}Si NMR spectra showed only two broad signals, corresponding to T^0_2 and T^0_3 units, indicating the total transformation of silanol groups and formation of high molecular weight species (Figure 5c). Chojnowski *et al.* [34,35] reported that once one alkoxy group in tetraethoxysilane was substituted by OH, the next ones were hydrolyzing very fast. It explains the lack of other resonances, which would correspond to low molecular species with single OH and OEt groups. The ^{29}Si NMR assignments are confirmed by CI-MS analysis of the above mixture of hydrolysis and condensation products. The spectra were obtained at chemical ionization, using direct inlet (Figure 6a and b) (Scheme 9). Silanetriol and its dimer appeared at m+1 = 95 and 171. The former corresponds to protonated methylsilanetriol while the latter to its protonated dimer. Signals at higher m/z originate from the silanetriol dimer, containing still some ethoxy groups. Fully ethoxylated dimer was observed as well (at m+1 = 283). Although the mass spectrometric studies were run for a mixture of products, they correspond well to the results obtained for analogous systems of OH containing silanes [37,38].

Our model studies have shown that the persistent presence of hydroxyl groups would enable the forming resin to react with OH groups present on the surface of the soil particles [37] as shown by us [22] (Scheme 10). Silanol groups are more stable in water emulsion than in organic solvent due to extensive formation of hydrogen bonds [39,40].

The presence of a large content of silanol groups in the reaction mixture of $MeSi(OEt)_3/H_2O = 0.1$ after 18 hours of mixing at room temperature was also confirmed by the IR spectrum, which showed a sharp band of Si-OH stretching at 910 cm^{-1} and a broad band of hydrogen-bonded O-H stretching centred at 3430 cm^{-1} (Figure 7).

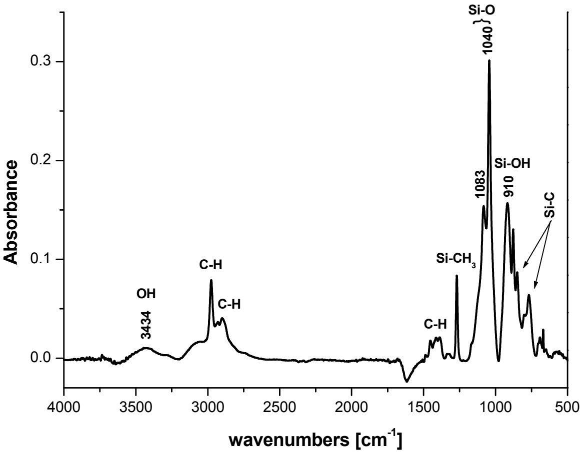
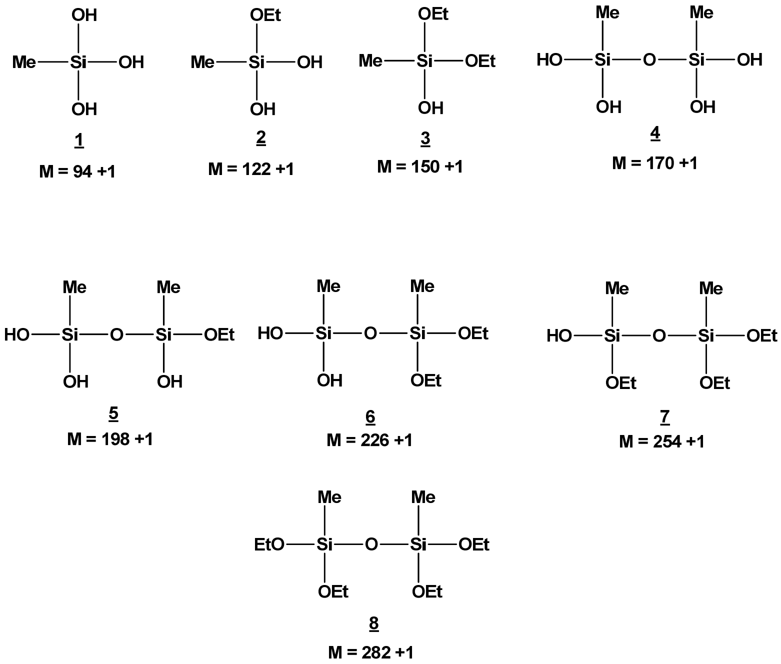
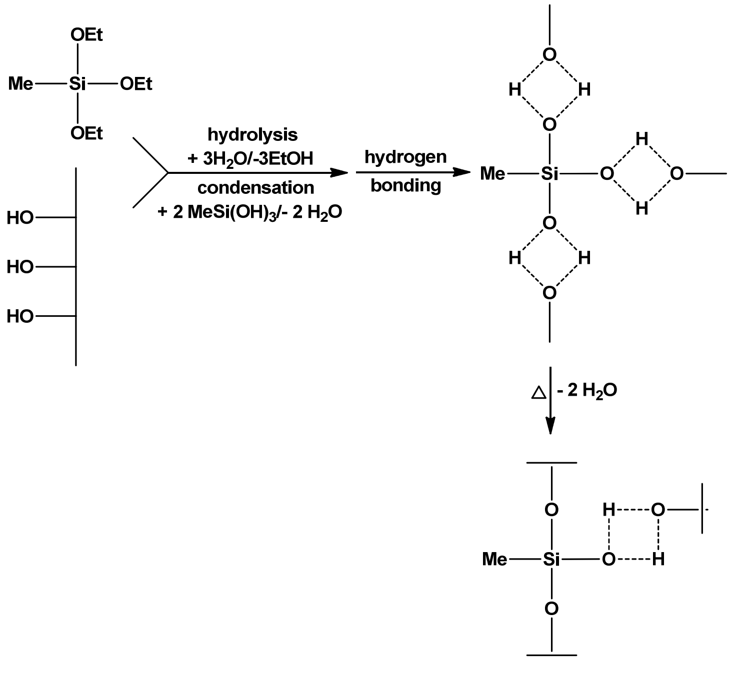


Figure 7. IR spectrum of the reaction mixture of $MeSi(OEt)_3$ in water (Molar ratio $MeSi(OEt)_3/H_2O = 0.1$), after 18 hrs of reaction at room temperature.



Scheme 9



Scheme 10

4. Conclusion

These studies present an effective and a low cost synthetic method for preparation of ethoxysilanes from mono-functional (Me_3SiCl), bi-functional (Me_2SiCl_2) and tri-functional ($MeSiCl_3$) chlorosilanes. The process involves a room temperature, so-called "reverse addition" –where an appropriate chlorosilane is introduced to the reaction vessel containing alcohol under its surface. This method limits the contact of alkoxysilanes with water vapours, and hydrochloric acid, which usually leads to a number of subsequent reactions. The side product (HCl) is removed from the reaction by the nitrogen spurge and it is absorbed in water in a scrubber. Chlorosilanes were introduced during ~2 hours at the rate of 2.5 mL/min. This method allows for over 90% yield of the pure alkoxy compounds containing a small amount of its condensation products: dimer and trimer, as shown by GC and GC-MS. The methyltriethoxysilane prepared by this method was used to make an aqueous water emulsion. Hydrolysis and condensation processes taking place during aging of the emulsion were studied by ^{29}Si NMR. The detailed studies of a model system, involving hydrolysis of $MeSi(OEt)_3$ in water, demonstrated that low molecular silanols are stable in the aqueous mixture for a long time and can be detected by ^{29}Si NMR, MS and IR. The presence of silanol species in the aqueous emulsion of methyltriethoxysilane, which are capable to form covalent bonds with OH group on the surface of inorganic materials, rationalize, why such emulsion are so effective in hydrophobization of building materials and soil.

Acknowledgements

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