

Iron Oxyhydroxide Aerogels and Xerogels by Hydrolysis of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in Organic Media: Early Stages

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Abstract: Formation of iron oxyhydroxide aerogel and xerogel by hydrolysis of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ was studied in organic media using water available solely from the starting iron salt. Ethylene glycol (EGLY), dimethyl sulfoxide (DMSO) and dimethyl formamide (DMFA) solvents were used. Products were analysed with specific surface area and TEM measurements. Early stages of hydrolysis and progress of gelation were followed by Mössbauer spectroscopy of frozen reaction mixtures. Presence of transient species and increase of the probability of the Mössbauer effect was observed in the early phase (0–60 min). Hydrolysis and gelation were the faster in EGLY, proceeded with medium rate in DMSO and were the slowest in DMFA.

Keywords: iron hydrolysis, transient components, organic solvents, recoilless fraction, Mössbauer spectroscopy.

INTRODUCTION

HYDROLYSIS of iron in organic solvents may attract distinguished interest since the process provides a suitable mean to prepare iron oxyhydroxide aerogels. In a sort of preparation methods limited amount of water is used. As an extreme, amount of water solely present in common crystalline iron salts as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ or $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ can be sufficient. Due to the dominance of the organic solvent, loose network of oxo-hydroxo bridges forms in the process. The loose network can be preserved by careful removal of the solvents by applying extraction with supercritical carbon dioxide. Propylene oxide or epichlorohydrine are essential promoters for this process since they scavenge protons produced in the course of hydrolysis.^[1–4] Synthesis of aerogels is performed usually at ambient temperature, therefore mostly oxyhydroxide forms. In order to obtain oxide aerogels moderate temperature (< 250 °C) treatments can be applied for removal of excess water with preservation of the high porosity.^[5,6]

Xerogels can also be formed by the same manner. The only exception is the final step, which is more simple, namely ethanol can be used to remove the organic solvents instead of extraction with supercritical CO_2 . In consequence, the obtained oxyhydroxide gel is more compact, although the first stages of formation, the process of hydrolysis are the same for both substances.

Hydrolysis of iron in aqueous media is well described. α , β , γ hydroxides (goethite, akageneite, lepidocrocite, respectively) form usually at slightly elevated temperature (< 80 °C).^[7,8] Below this temperature usually ferrihydrite develops.^[9] Careful study on early steps of hydrolysis of iron was carried out by laborious separation of hydrolysis products into < 1k, 1k – 10k, 10k – 20k, 20k – 50k, 50k – 100k, 100k – 300k and > 300k molecular weight fractions with diafiltration and subsequent freeze drying, the obtained samples were analysed primarily with Mössbauer spectroscopy.^[10] This technique has also been successfully applied for studying the hydrolysis in aqueous media, by recording spectra on frozen solutions and reaction mixtures.^[11,12]

One sole publication has been reported for analogous application of the Mössbauer method for studying the hydrolysis of iron in frozen organic media by our best knowledge so far. Namely, that is our recent communication in which early stages of hydrolysis of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ are described. The most interesting features were found in DMFA media. Appearance of transient species was observed in the 8 – 80 min time slot after mixing the reaction components, they exhibit rather large quadrupole splitting in respective Mössbauer spectra ($1.3 < \Delta < 1.7 \text{ mm s}^{-1}$). Furthermore, simultaneous increase of the recoilless fraction (*f*-factor) was observed with the progress of hydrolysis.^[13] In the present work results obtained in the first stages of hydrolysis of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in different solvents (ethylene glycol, EGLY, dimethyl sulfoxide, DMSO and dimethyl formamide, DMFA) are compared and reported in more detail.

EXPERIMENTAL

Sample Preparation

6 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 12 ml of solvent (EGLY, DMSO or DMFA) and after dissolution of the salt 3.7 ml of epichlorohydrin was dropwise added with stirring. Gel formation had taken place within 4 – 6 hours. Samples were aged for 2 – 3 further days. For aerogel preparation the organic solvent was exchanged for methanol then gradually to dry acetone. The gel was placed to an autoclave, then liquid CO_2 was introduced at *ca.* 50 bar pressure. The acetone solvent was removed as a separate phase. The temperature was increased to 80 °C afterwards, where CO_2 supercritical phase exists. CO_2 was slowly decompressed

and cooled, thereby monolithic aerogel could be obtained after evaporation.

Xerogel samples were prepared by replacing the final extraction with supercritical CO_2 to extraction with ethanol repeated 3 – 4 times. Ethanol was evaporated by storing the sample at ambient conditions for 3 – 4 days. *Ca.* 50-fold contraction has taken place as compared to the volume of the original gel.

The process of hydrolysis was followed in another series of measurements. *Ca.* 1 ml samples were taken from the reaction mixture at different periods after addition of epichlorohydrin. These samples were immediately frozen with immersion to liquid nitrogen (and were measured later with Mössbauer spectroscopy).

Sample Characterization

Specific surface area/BET and pore size distribution measurements on aerogel samples were performed by using a Quantachrome Nova 2200e surface area and porosity analyzer using nitrogen gas as sorbent at 77 K. Prior the measurements samples were outgassed at 50 °C in vacuum for 3 hours.

TEM measurements were performed by using either a Philips CM20 200kV conventional Transmission Electron Microscope (point resolution 0.24 nm) or a JEOL 3010 300 kV high resolution TEM (point resolution 0.17 nm).

Mössbauer spectra were obtained both on frozen samples and the final aerogels and xerogels as well. A KFKI spectrometer equipped with a 0.5 GBq $^{57}\text{Co}/\text{Rh}$ source was used. Spectra were decomposed to Lorentzian lines. The accuracy of positional data is *ca.* $\pm 0.03 \text{ mm s}^{-1}$, isomer shift values are related to metallic alpha-iron.

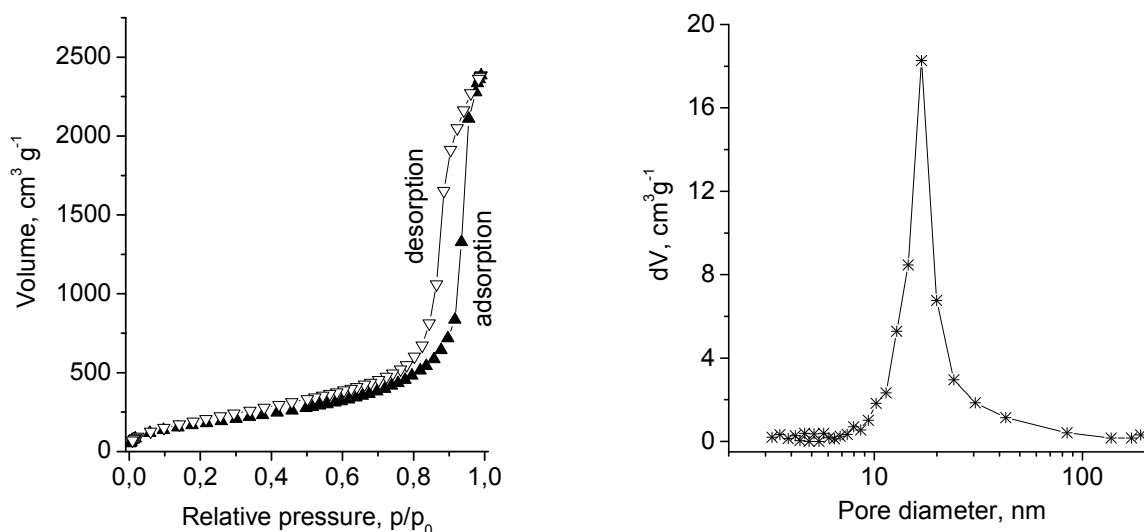


Figure 1. Results of sorption measurements on the aerogel prepared in DMSO media. Sorption-desorption isotherms (left), and pore diameter distribution determined from the desorption branch (right).

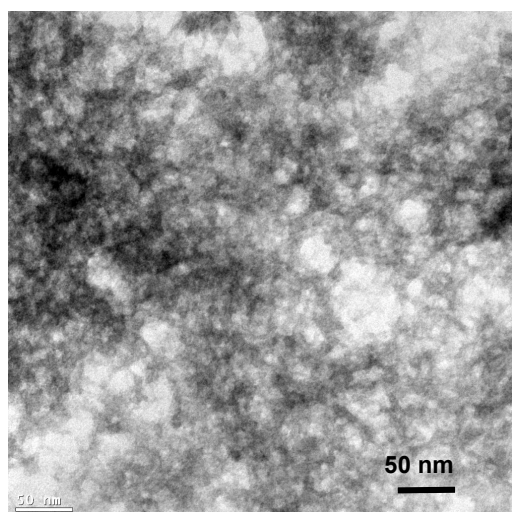


Figure 2. TEM image recorded on the aerogel prepared in DMSO media.

RESULTS

Formation of Aerogels

Aerogels could be prepared in different organic solvents. For illustration typical results of surface area measurements obtained on an aerogel prepared in DMSO media are presented. The product is a light substance with a density of *ca.* 0.1 g cm⁻³. Sorption measurements provided 895 m² g⁻¹ specific surface area and 3.74 cm³ g⁻¹ pore volume values on the sample after extraction of the organic solvent with supercritical CO₂ and subsequent evacuation for 2 h at 50 °C. Sorption isotherms and pore diameter distribution for this sample are also shown in Figure 1.

TEM images were also recorded. The typical loose structure and pores with various sizes are represented in Figure 2.

Mössbauer spectra can also be recorded on the light, loose aerogel sample prepared in DMSO media.

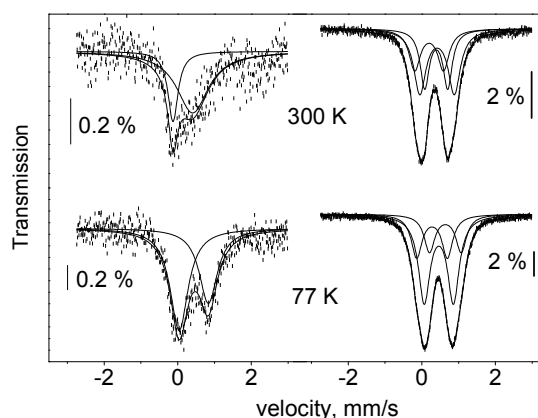


Figure 3. Mössbauer spectra of the aerogel sample prepared in DMSO media recorded at 300 and 77 K. Pristine sample (left side), and the same sample after compression with 100 MPa (right side). (Figure taken from Ref. [13]).

Spectra obtained on the pristine sample at room temperature and at 77 K are shown in Figure 3 (left). Asymmetric doublets can be recorded with poor statistics, *i.e.* with very small recoilless fraction values. In contrast, the probability of the Mössbauer effect increases more than ten times upon compressing the same sample with 100 MPa (Figure 3, right). The comparison of the two sides of Figure 3 attests for the loose, light structure of the pristine aerogel. Data extracted from decompositions of spectra of Figure 3 are shown in Table 1.

Formation of Xerogels

Xerogels were also prepared by hydrolysing FeCl₃ · 6 H₂O in various solvents. Early stages of hydrolysis are similar both for xerogels and aerogels. Structural differences among them are primarily due to the differences in the subsequent drying processes. This can clearly be demonstrated with comparison of corresponding TEM images. For illustration, image obtained on a xerogel sample

Table 1. Data extracted from spectra of aerogel sample prepared in DMSO media shown in Figure 3. (δ : isomer shift, Δ : quadrupole splitting, FWHM: line width – Full Width at Half Maximum).

Sample	T / K	Comp.	δ / mm s ⁻¹	Δ / mm s ⁻¹	FWHM / mm s ⁻¹	Rel. Int. / %	mean δ / mm s ⁻¹
Pristine	300	Fe ³⁺ (I-1)*	-0.13	-	0.34	28	0.26
		Fe ³⁺ (I-2)*	0.41	-	1.03	72	
	77	Fe ³⁺ (I-1)*	0.04	-	0.59	57	
		Fe ³⁺ (I-2)*	0.83	-	0.61	43	
Compressed	300	Fe ³⁺	0.23	0.79	0.38	40	0.45
		Fe ³⁺	0.41	0.67	0.31	30	
		Fe ³⁺	0.45	0.95	0.38	30	
	77	Fe ³⁺	0.37	0.73	0.38	44	
		Fe ³⁺	0.46	1.29	0.34	15	
		Fe ³⁺	0.54	0.74	0.36	41	

* For simplicity spectra of pristine sample are described by two singlets to provide a mean to obtain the mean isomer shift of them.

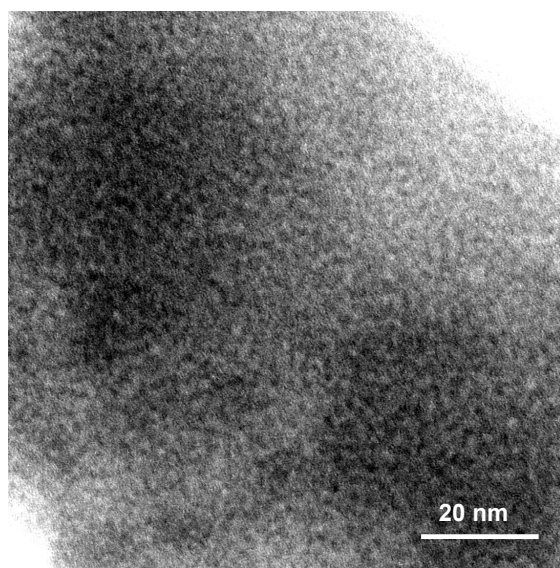


Figure 4. TEM image obtained on xerogel prepared in ethylene glycol media.

prepared in EGLY is shown in Figure 4. Comparison of Figure 4 with Figure 2 (aerogel in DMSO) clearly demonstrates the mentioned structural difference. Namely, porous structure cannot be observed, instead, dense agglomeration of globuli, composed from oxyhydroxide

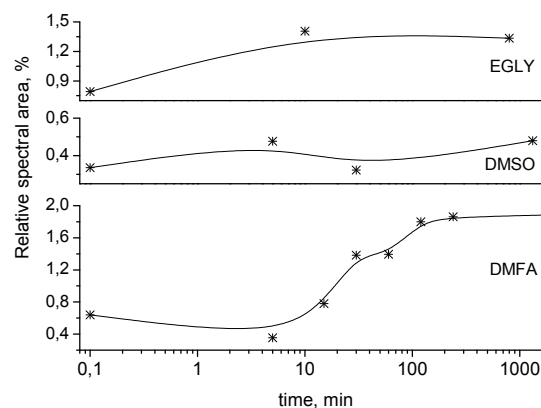


Figure 6. Dependence of the recoilless fraction in the progress of gelation in various solvents. Increase of the relative spectral area in 77 K Mössbauer spectra with time spent after mixing the components.

particles with similar, 2 – 3 nm diameter are shown in Figure 4.

The corresponding Mössbauer spectrum of the EGLY xerogel (with TEM image shown in Figure 4) is similar to that shown for compressed DMSO aerogels in the right side of Figure 3. Namely, the 77 K spectrum is composed from two doublets with parameters of $\delta_1 = 0.48$, $\Delta_1 = 0.57$ and $\delta_2 = 0.48$, $\Delta_2 = 0.97$ mm s⁻¹.

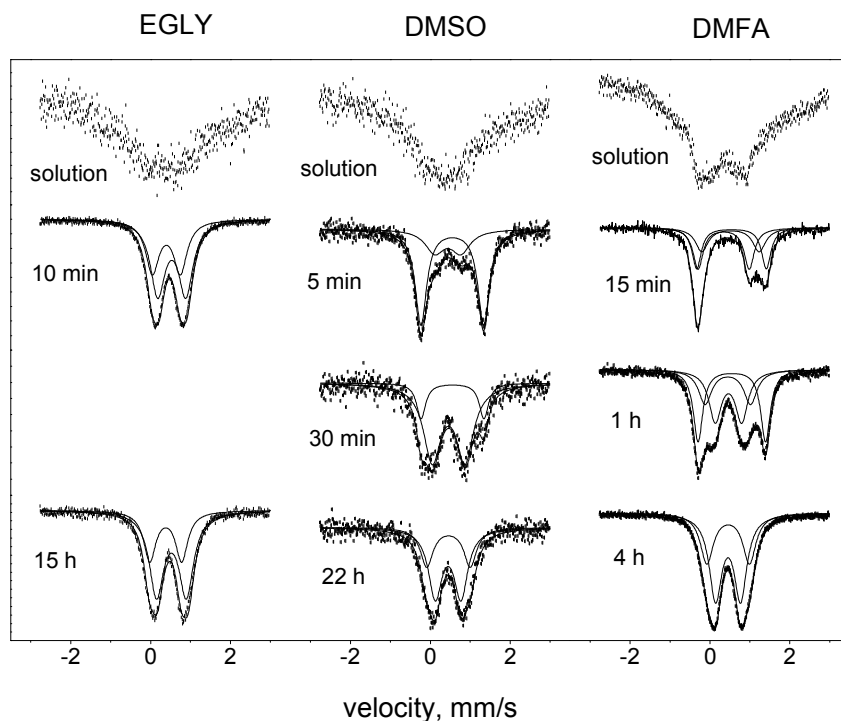


Figure 5. 77 K Mössbauer spectra of frozen samples of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in EGLY, DMSO and DMFA media. First row: spectra of solutions. Spectra shown in 2nd, 3rd and 4th rows are taken on samples frozen at the indicated time intervals elapsed after mixing the solution with epichlorohydrin.

Formation of Xerogels

Process of hydrolysis can be followed by recording Mössbauer spectra on frozen samples, obtained by freezing with immersion to liquid nitrogen after different intervals following the initiation of the hydrolysis with addition of epichlorohydrin proton scavenger into the $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ / organic solvent solution. Spectra obtained on the starting frozen solutions of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in EGLY, DMSO and DMFA are also shown in Figure 5 (first row).

The extents of recoilless fractions are low in solutions, as poor statistics indicate. Hydrolysis is fast in EGLY, parameters of doublets characterizing the product after 10 minutes of mixing do not change significantly later on (see corresponding data in Table 2). Hydrolysis in DMSO is slower, a transient species with large quadrupole splitting ($\Delta = 1.57 \text{ mm s}^{-1}$) dominates the spectrum recorded after 5 minutes of mixing, and is still present after 30 minutes (Figure 5, middle column). Hydrolysis is the slowest in DMFA, three types of transient species can be distinguished, and the more stable of them is still present with *ca.* 40 % share in the spectrum recorded at 1 h after mixing the reactants.

Values of average recoilless fractions may also provide information on the progress of hydrolysis. Increase of the average recoilless fraction can be assumed as di- and oligomerization proceeds. Corresponding values of the relative spectral areas are shown in Figure 6. *Ca.* 50 % increase can be found for spectrum recorded after 10 minutes of mixing the components in comparison to the

spectrum of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ solution in EGLY (Figure 6 top). In DMSO the situation is mixed, an increase but some subsequent decrease can also be detected. However, in the net of the process an increase of the average spectral area can be observed. The most expressed (*ca.* 6-fold) increase is found in DMFA when comparing the average relative spectral area of the final gel to that found in the spectrum of the starting solution (Figure 6, bottom).

DISCUSSION

Formation of Aerogels and Xerogels

Successful preparation of aerogels in our experiments is proven. Namely, Figure 1 (left side) attests for the high specific surface area, and Figures 1 (right side) and 2 for the porous structure. Low recoilless fraction is found in corresponding Mössbauer spectra, similarly as reported in Ref. [4]. A further particular feature is presented in Figure 3, namely asymmetric doublet appears for the aerogel sample. Similar asymmetry is attributed to emergence of temperature dependent spin-spin relaxation times.^[14] Further on, the extent of the probability of the effect can be increased *ca.* 10 times by compression, and the asymmetry disappears simultaneously, *i.e.* relaxation phenomena disappear (Figure 3). A further structural effect of compression can also be revealed apart of the increase of the Mössbauer effect and disappearance of relaxation phenomena. Namely, the mean isomer shift value is consistently

Table 2. Mössbauer parameters of products of hydrolysis of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in different organic media obtained from decomposition of spectra shown in Figure 5. (δ : isomer shift, Δ : quadrupole splitting, FWHM: line width, Full Width at Half Maximum).

Solvent	Time	Comp.	$\delta / \text{mm s}^{-1}$	$\Delta / \text{mm s}^{-1}$	FWHM / mm s^{-1}	Rel. Int. / %
EGLY	10 min	Fe^{3+}	0.38	0.70	0.37	40
		Fe^{3+}	0.56	0.70	0.39	60
	15 h	Fe^{3+}	0.36	0.80	0.33	33
		Fe^{3+}	0.55	0.78	0.40	67
DMSO	5 min	$\text{Fe}^{3+}(\text{t})^*$	0.55	1.57	0.35	72
		Fe^{3+}	0.44	0.65	0.58	28
	30 min	$\text{Fe}^{3+}(\text{t})^*$	0.56	1.57	0.28	20
		Fe^{3+}	0.46	0.82	0.52	80
	22 h	Fe^{3+}	0.45	0.64	0.41	65
		Fe^{3+}	0.46	1.09	0.38	35
DMFA	15 min	$\text{Fe}^{3+}(\text{t-1})^*$	0.33	1.31	0.30	37
		$\text{Fe}^{3+}(\text{t-2})^*$	0.52	1.43	0.39	28
		$\text{Fe}^{3+}(\text{t})^*$	0.55	1.71	0.28	34
	1 h	$\text{Fe}^{3+}(\text{t})^*$	0.55	1.69	0.29	38
		Fe^{3+}	0.46	0.66	0.38	35
		Fe^{3+}	0.45	1.14	0.42	27
		4 h	Fe^{3+}	0.45	0.63	0.38
Fe^{3+}	0.46		1.07	0.40	38	

* Fe(t), Fe(t-1), Fe(t-2): transient components in the spectra.

increased with $0.09 - 0.07 \text{ mm s}^{-1}$, depending on the temperature of measurement (last column in Table 1). This modest increase of the isomer shift can probably be related to increase of the filling of coordination shell in the near environment of iron.

Xerogels are composed from aggregated globuli of iron oxyhydroxide particles of 3–4 nm diameter, as the TEM image in Figure 4 clearly demonstrates. In correspondence, their Mössbauer spectra exhibit large recoilless fraction, and no signatures of relaxation features are observed. The obtained Mössbauer parameters are similar to those reported for iron oxyhydroxides.^[15,16]

Early Stages of Hydrolysis – Comparison of Different Solvents

The first stage of the process is the dissolution of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in the organic solvents. Broad lines with low recoilless fraction appear in the first row of Figure 5, indicating that Fe^{3+} ions are solvated directly with the EGLY and DMSO solvents. Corresponding spectrum in DMFA exhibits an additional doublet component (Figure 5, top right), which may probably be attributed to stabilization of a combined Fe : DMFA-2 : 3 complex.^[17]

Commencement of hydrolysis results in significant increase of recoilless fractions in the spectra, *i.e.* the organic ligands are replaced with hydroxo- and/or with oxo bridges (Figure 6). The differences in the rate of hydrolysis can be compared and interpreted in the three solvents in further details. In particular, the process is fast in EGLY, the spectra hardly change in the 10 min – 15 h range (Figure 5 left, and Table 2). The size of ethylene glycol molecules is small in comparison to the other two organic solvents, hydroxo and oxo bridges may easily develop. The obtained quadrupole splitting values ($0.7 - 0.8 \text{ mm s}^{-1}$) are in good correspondence with those reported for early products separated in aqueous media for < 500 molecular weight fraction.^[10] Furthermore, only a slight increase of the recoilless fraction is observed in the process (Figure 6, top).

In contrast, transient components appear in DMSO and DMFA solvents exhibiting $1.3 < \Delta < 1.7 \text{ mm s}^{-1}$ quadrupole splitting values. These two solvent molecules are more voluminous, iron centers are more separated, the process is slower. Appearance of the $1.3 < \Delta < 1.7 \text{ mm s}^{-1}$ transient components can probably be attributed to partial decomposition of the DMSO and DMFA solvated iron complexes, with simultaneous formation of hydroxo and oxo bridges. More exactly, formation of μ -oxo bridges can be suggested, since μ -oxo bridged dinuclear iron complexes display similar large quadrupole splitting values, whereas, in comparison, μ -hydroxo bridged dinuclear complexes exhibit only $0.25 - 0.56 \text{ mm s}^{-1}$ values for their quadrupole splitting values.^[18] Thus, probably the very first stages of hydrolysis, formation of μ -oxo-bridged di- and oligomers are manifested in the

appearance of the transient components exhibiting $1.3 < \Delta < 1.7 \text{ mm s}^{-1}$ quadrupole splitting values.

The second solvent, DMSO, forms stable complexes, the molecular weight of *e.g.* the $[(\text{DMSO})_5\text{FeCl}]$ complex is large^[19]. Thus, the vibrating mass is large even for the starting state, in correspondence the recoilless fraction can also be large, the further increase during the di- and oligomerisation does not result in significant increase in the recoilless fraction^[20] (Figure 6, middle).

The process is the slowest in DMFA, existence of transient species can be observed for rather long interval (5 – 120 min). The main controlling effect is probably the relative stability of the Fe-DMFA complex.^[17] DMFA is composed from light atoms (C, N, O and H) the vibration states can probably be influenced significantly by the oligomerization and chain growth during hydrolysis as compared to DMSO. Thus, the increase of the probability of the Mössbauer effect can be the most expressed in this case (*ca.* 6-fold, Figure 6 bottom).

All the previously mentioned considerations concern the first steps of hydrolysis when larger μ -oxo di-, and oligomers form in liquid media. The reaction mixture is still fluid in that first stage, gel formation is completed later, after *ca.* 4 hours.

As for the mass of the primary particles a rough estimation can be provided based on the TEM images presented in Figures 2 and 4 (and HRTEM in Ref. [13]). *Ca.* 10k molecular weight range can be estimated by combining the average particle size extracted from TEM images either of aerogel or xerogel (3 – 4 nm), and lattice distances of ferrihydrite.^[7] The 1 – 10 k molecular weight fraction is the second lightest one in Ref. [10] in the case of aqueous media. Decomposition of spectra reported in Ref. [10] results in similar components as detected in our case, for hydrolysis dominantly in organic media.

Process of gelation takes place subsequently in a secondary stage. The primary agglomerates grow, get into touch, adjoin each other and form a loose network full of voids filled up with the original organic solvent (and unreacted epichlorohydrine, or formed chloropropanol and chloropropanediol). The network is rather loose, it can be preserved during the delicate supercritical extraction by forming an aerogel, as demonstrated in Figure 1. If more polar solvent is used for the removal of the organic phase the delicate network of oxyhydroxide particles collapses, more dense conglomerate, *i.e.* xerogel, forms from the primary oxyhydroxide particles, as demonstrated in Figure 4.

CONCLUSIONS

Iron oxyhydroxide aerogels can be prepared in organic solvents by hydrolysing iron with consuming water molecules available solely from crystals of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$.

Early stages of hydrolysis were studied and compared in frozen samples of EGLY, DMSO and DMFA solutions. Hydrolysis is fast in EGLY, instant formation of final oxyhydroxide species was observed. The process is slower in DMSO, presence of a transient component exhibiting high quadrupole splitting value ($\Delta = 1.57 \text{ mm s}^{-1}$) is observed. Hydrolysis is the slowest in DMFA. Existence of three transient species ($\Delta_1 \sim 1.3$, $\Delta_2 \sim 1.43$ and $\Delta_3 \sim 1.6 \text{ mm s}^{-1}$) can be detected, some of them is still present even after 2 h from initiation of hydrolysis. Presence of transient components exhibiting high quadrupole splitting values is attributed to appearance μ -oxo bridged dimeric complexes in the early stages of hydrolysis. Differences in the rate of hydrolysis are related to variations in the stability of starting complexes, formed by solvation in EGLY, DMSO and in DMFA.

Simultaneous variations in the mean recoilled fractions were also monitored. In general, a significant increase (ca. 50 %) was found with the progress of di- and oligomerization in EGLY and DMSO. Extremely large (ca. 6-fold) increase of the mean recoilled fraction is detected in DMFA. The increase is in good correlation with the previously mentioned appearance of the transient components. Namely, as transient components are converted to oxyhydroxide chains and networks the effective vibrating mass in the Mössbauer process is increased, as indicated clearly in the increase of the recoilled fraction. Variations in the extent of the increase can be correlated to the structure of the starting solvated complexes, too.

Formation of aerogels and xerogels proceeds probably in two stages. First, oxyhydroxide particles form with 3–4 nm average particle size, whilst the reaction media is still liquid. Gelation takes place subsequently, when the growing particles get into touch, join each other and form a loose network.

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