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FTIR spectroscopic study on liquid silica solutions and nanoscale particle size determination

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Silica gel is a very important material in technology. Usually tetraethyl orthosilicate (TEOS) is used as precursor in the sol-gel science. But silica gel can also be formed by liquid silica solutions, like alkali silica solutions and silica sols. Due to their importance in paint technology and as a constituent in building material, we investigated alkali silica solutions (especially potassium water glass) and the silica sol Levasil 300. The gel formation process of inorganic silica solutions is quite different to gel formation from TEOS. Gel formation by TEOS is due to polymerization of monomers, whereas the gel formation process of inorganic silica solutions is due to condensation of dense SiO_2 particles with particle diameters of a few nanometers. Fourier transformed infrared (FTIR) spectroscopy proved to be a powerful tool to obtain information on the structure of these liquid silica solutions and their sol-gel processes. Most information could be derived from the main silica peak at $\sim$1070 cm^{-1}. This peak can be assigned to the TO_3 vibration mode of silica. In silica solutions and in silica gels this peak is composed of different peaks. Compared to earlier studies an additional peak can be found at $\sim$1040 cm^{-1} in potassium silica solutions. By comparison of FTIR spectra of related silica glasses and their liquid solutions the peak at $\sim$1027 cm^{-1} can be assigned to vibration modes of SiO_2 on the surface of silica particles. The intensities of these individual peaks contain information on the degree of polymerization and the particle size of the silica particles in the liquid solutions. The information about particle size is limited to nanosized particles between 2 and 6 nm. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

In paint technology potassium silicate solutions are used for silicate paints. Potassium salts, which can be formed in building materials after application of silicate paints, are less harmful for the masonry than sodium salts. Newer developments in silicate paints use a mixture of silicate sol and potassium silicate solution with less alkali content as silica source.

Physical and chemical properties of soluble silicates are discussed in previous papers [1, 2]. Most structural information of the sol-gel process are based on silica gels made of TEOS [2–7] and sodium silicate solution [8, 9].

Informations on the structure of potassium silicate solutions are scarce because of their hitherto less industrial importance [8].

Most informations of the structural properties of silica solutions are obtained by 29Silicon nuclear magnetic resonance spectroscopy or combining NMR with FTIR spectroscopy [9, 10].

These authors correlate ^{29}Si-NMR data with the main infrared absorption bands between 700 and 1300 cm^{-1} of the FTIR measurement and conclude that FTIR spectroscopy is a useful tool to obtain structural information on highly diluted silicate solutions. Band assignment to individual ^{29}Si-NMR peaks is less clear in higher concentrated silicate solutions due to a higher degree of polymerization.

The band assignment of FTIR data of solid silica gels is discussed in several papers [11–17]. The main absorption band in silica gels between 1300 and 800 cm^{-1} consists of several bands. The most dominant band is assigned to the asymmetric stretching vibrations of Si–O–Si (TO_3 mode) in the range of 1130–1060 cm^{-1}. At the high frequency side of this band there is a shoulder, which is related to skeletal stretching vibrations [12, 14]. Other authors assign this mode to the LO_3 mode of the Si–O–Si stretching vibration [13, 15, 16]. Usually LO_3 modes are not infrared active, but as a result of gel porosity this mode occurs as proofed by oblique incident

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FTIR spectroscopy [16]. A supplementary band between LO_3 and TO_3 mode is found by some authors [13, 15, 16] too. The shape of this band is influenced by the porosity of the silica gel. The shoulder at the low frequency side is assigned to the Si-O stretching vibration of surface silanol groups [12, 14–16]. A second, very weak band related to the silanol vibration could be observed in the range of 900-880 cm^{-1}. This band is assigned to the bending vibration of the silanol group [17].

Structural information about silica solutions and the sol-gel process are usually obtained by small angle *x*-ray scattering (SAXS) and small angle neutron scattering (SANS) measurements [18–20].

No FTIR data exist on concentrated silica solutions. Therefore the aim of this study is to obtain structural informations on potassium silicate solutions, silica sols and their mixtures by FTIR spectroscopy. In comparison to other analytical methods as NMR, SAXS or SANS this is a quick, less expensive and easy to use method.

2. Experimental

Potassium silicate solution HENKEL TYPE 2830 and the corresponding alkali silicate glass, with a molar ratio SiO_2:K_2O of 4:1, were used. The silica sol was LEVASIL 300 from BAYER with a molar ratio SiO_2:Na_2O of 100:1. The average particle size of LEVASIL 300, according to suppliers date, is 9 nm. The particle size of the potassium silica solution is about 2 nm [21]. For comparison silica sol SYTON X30 from MONSANTO with a particle size of 25 nm, according to suppliers data was used.

Mixtures of potassium silica solutions and LEVASIL 300 were used for preparing silica solutions with different particle size. The silica solutions have got a potassium content from 0 to 8 w% K_2O and a silica concentration of 20%. An alkali content of 0% K_2O is equal to diluted Levasil 300, 8% is equal to the potassium silicate solution Type 2830.

FTIR spectra were collected with a BRUKER EQUINOX 55 FTIR spectrometer in the range of 4000–400 cm^{-1} with 64 scans and a resolution of 4 cm^{-1}. The samples were prepared as thin liquid films between two polyethylene foils. The PE-foils were measured as background. The spectra were processed by baseline adjustment and subtracting the spectra of pure water with the program OPUS from BRUKER. The peak fitting was done with the program PEAKFIT from SPSS Inc.

Peak fitting was done using a Gauss-Lorentz sum function. Fitting was undertaken until reproducible results were obtained with squared regression coefficient of r_2 greater than 0.995.

Degree of polymerization and particle size of the primary particles in silicate solutions were measured with the molybdic acid method [22–24].

TABELE I FTIR band assignment for silicate solutions

wavenumber [cm^{-1}]	assignment
1225–1180	Si-O-Si asymmetric stretching vibration (LO_3-mode) [14–16]
1175–1138	skeletal Si-O stretching vibration [12,14] LO_3-TO_3 splitting band [13,15,16]
1126–1078	Si-O-Si asymmetric stretching vibration (TO_3 mode) [12–16]
1070–1020	TO_3 mode of surface Si-O-Si (this study)
955–940	Si-O stretching vibration of surface silanol groups [12,14–16]
895–880	Si-OH bending vibration [17]

3. Results and discussion

3.1. IR band assignment

The main IR absorption band of silica can be found in the mid-infrared spectrum from 800 to 1300 cm^{-1}. This absorption band is a superimposition of several individual peaks. In solid silica gels usually 4 peaks at ~1200 cm^{-1}, ~1150 cm^{-1}, ~1100 cm^{-1} and ~ 950 cm^{-1} were found to be sufficiant for fitting the spectrum (Table I).

In potassium silicate solution a supplementary peak at 1027 cm^{-1} occurs in the spectrum which is also the most intense peak. This peak is located between the asymmetric stretching vibration TO_3 at 1087 cm^{-1} and the stretching vibration of the silanol group at 942 cm^{-1} (Fig. 1). In silica sols with very low alkali content (0,1 M Na_2O) the peak intensity of this band is lower and the peak is shifted to 1060 cm^{-1} (Fig. 2). In this spectra the asymmetric Si–O–Si stretching vibration at 1126 cm^{-1} is the most intense band. A comparison of the spectra of the potassium silicate solution with the spectra of the corresponding solid alkali silica glass and the spectra of the silica sol (Fig. 3) indicates that the position of the asymmetric Si–O–Si stretching vibration is strongly correlated with the potassium ion in glass and in solution. In the alkali rich potassium silica solution and the corresponding potassium silica glass the peak maximum

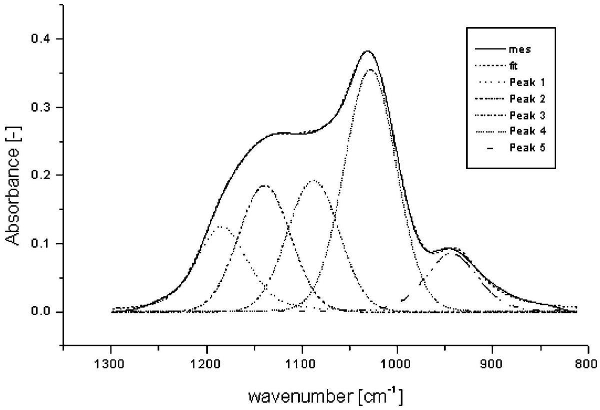

Figure 1 FTIR spectrum of a potassium silicate solution ($SiO_2 : K_2O =$ 4:1). The most intense band at 1027 cm^{-1} is very weak or not observed in silica gels. This band is assigned to the asymmetric stretching vibration of Si–O–Si groups at the surface of the silica particle.

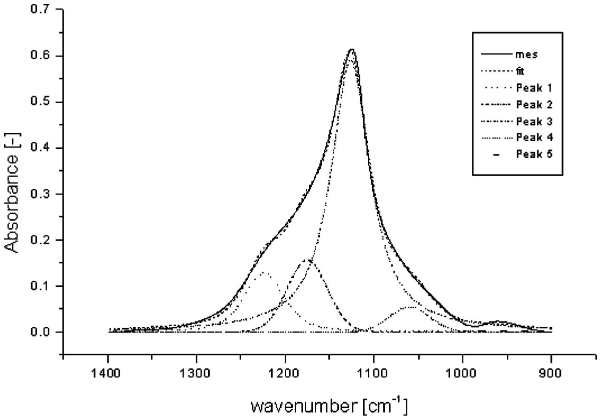

Figure 2 FTIR spectrum of the silica sol LEVASIL 300 ($SiO_2 : Na_2O = 100:1$). The band at 1065 cm^{-1} is comparable with the band at 1027 cm^{-1} in the spectrum of the potassium silicate solution. The shift is due to the lower content of alkali ions in the silica solution. This band is much weaker than in potassium silica solutions.

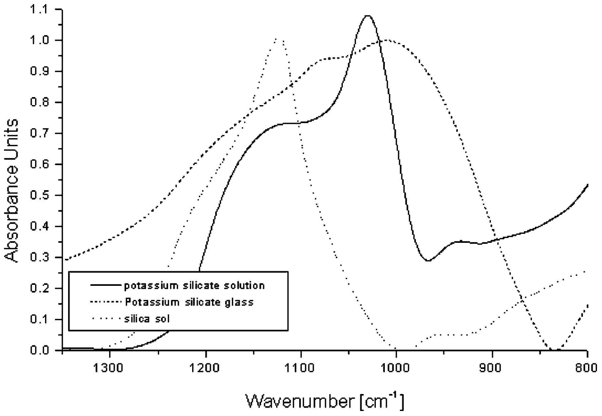

Figure 3 FTIR spectra of silica sol, potassium silicate solution and the corresponding potassium silicate glass. The most intense band at 1027 cm^{-1} of the potassium silicate solution is near the band maximum of the potassium silicate glass, which is assigned to vibrations of Si–O–K groups in the glass.

is shifted to lower wavenumbers. This shift is due to the elecronegativity of the potassium ion.

In silica solutions the silica particles are composed of polymerized SiO_2 units without alcali ions inside the particle [9, 21]. In these solutions the positively charged potassium ion is located at the negatively charged Si–O-groups on the surface of the silica particles. The average particle size of LEVASIL 300 is 9 nm. In the potassium silicate solution the particle size is about 2 nm, so the surface:volume ratio is 0.75 in comparison to 0.167 in Levasil 300. The potassium silica solution therefore has a 4.5 times larger surface area than the silica sol with the same silica content. Due to this, the peak at 1027 cm^{-1} in alkali silicate solutions must be assigned to Si–O–Si vibrations at the particle surface. The potassium ions located on the surface of the silica particles weakens the bond strength of neighboring Si–O–Si groups, so the vibration mode of this peak is shifted to lower wavenumbers. Therefore this band is assigned to the asymmetric stretching vibration of SiO_2 groups on the surface of the silica particles. A summary of the bands and their assignment used in the peak fitting procedure is given in Table I.

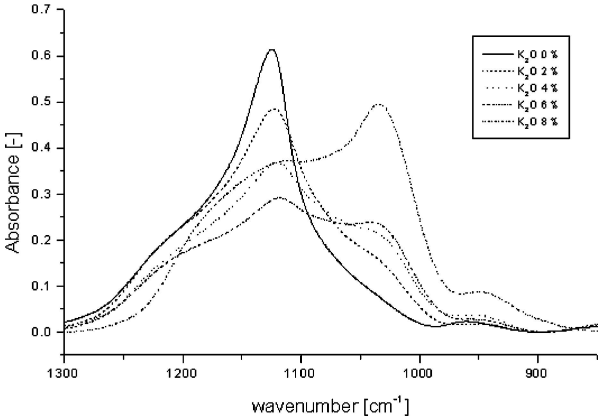

Figure 4 Variation of the TO_3 band with rising K_2O content. The peak at ~1120 cm^{-1} decreases with rising K_2O content, the surface peak at ~1027 cm^{-1} increases.

3.2. Particle size in silica solutions

The particle size of alkali silica solutions is determined by the alkali content and the silica concentration of the solution. A simple but time consuming method to determine particle sizes is measuring the reaction rate of molybdic acid with silicic acid [21–23]. This method was used to determine the particle size of alkali silica solution with K_2O contents varying from 0% to 8%.

FTIR spectra of these solutions show great variations in band shape and band location between 800 and 1400 cm^{-1}. Peak positions are generally shifted to lower wavenumbers with rising K_2O content and the peak intensity of the asymmetric Si–O–Si stretching vibration of inner SiO_2 groups at ~1100 cm^{-1} and of the surface SiO_2 groups at ~1040 cm^{-1} varies strongly (Fig. 4).

These changes can be used for determination of the particle size of the silica solutions. The band assigned to the TO_3 vibration of surface Si–O–Si bonds at ~1040 cm^{-1} increases in intensity with decreasing particle size and therefore increasing surface:volume ratio (Fig. 5a). The TO_3 vibration of inner Si–O–Si bonds at ~1100 cm^{-1} decreases in intensity with decreasing particle size (Fig. 5b). As the particle size is directly dependent from the potassium concentration in the solution, a linear correlation between peak intensity of the TO_3 mode of surface Si–O–Si bonds and the potassium concentration could be observed (Fig. 5c).

The sensitivity of particle size determination is high for very small particles below ~6 nm. For bigger particles the asymmetric Si–O–Si stretching mode at ~1100 cm^{-1} gets dominant in the spectra whereas the surface mode at ~1040 cm^{-1} vanishes. A comparison of the spectra of

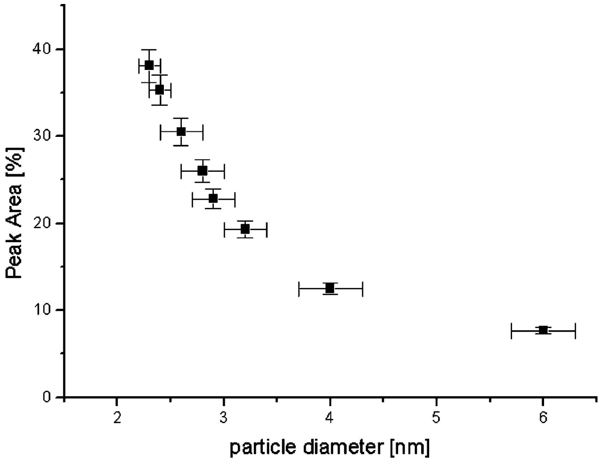

Figure 5a The peak intensity of the asymmetric stretching vibration of Si–O–Si groups at the surface of the silica particles (1070–1020 cm^{-1}) decreases with increasing particle size.

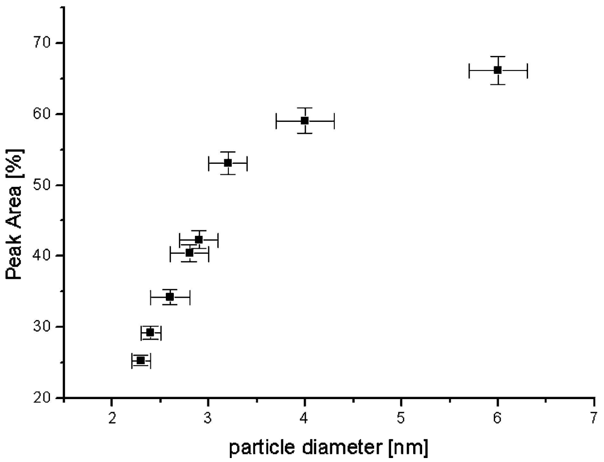

Figure 5b The band intensity of the asymmetric stretching vibration of Si–O–Si groups in the interior of the silica particles (1126–1078 cm^{-1}) increase with particle size.

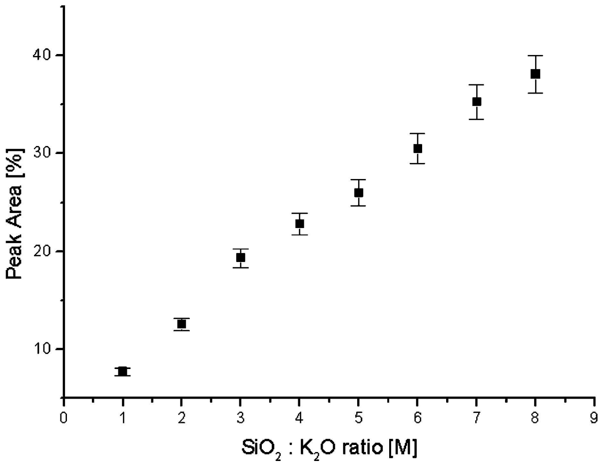

Figure 5c The particle size is correlated with the potassium concentration which is directly correlated with the peak intensity of the band intensity between 1070 and 1020 cm^{-1} .

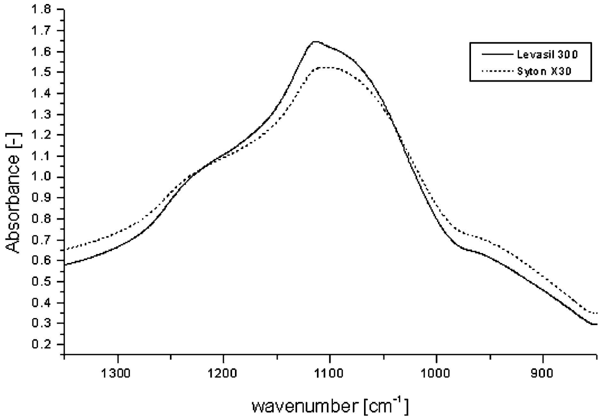

Figure 6 TO$_3$ band of Levasil 300 with 9 nm particle size and Syton X30 with 25 nm particle size. No significant differences are observable.

LEVASIL 300 with 9 nm particle size and SYTON X30 with 25 nm particle size shows no significant difference (Fig. 6). Due to the smaller changes in surface to volume ratio with rising particle size, the changes in peak intensity of the surface mode at ~1060 cm^{-1} are small.

Unfortunately the correlation function between peak intensity and particle size is only true for silica solutions with the same silica content. Solutions with another silica content show other correlations. This is due to differences in sample-matrix ratios which affect band intensity and shape. For quantitative particle size measurements with FTIR spectroscopy it is necessary to measure correlation functions for each silica concentration separately.

4. Conclusions

FTIR Spectroscopy is a useful method to determine the particle sizes of alkali silica solutions. The band between the TO$_3$ vibration and the vibration of the Silanol group, which is dominant in alkali silicate solution, is strongly correlated with the surface:volume ratio of the primary silica particles in the solution and therefore with the particle size. As the particle size is correlated with the alkali content of the solution, this peak intensity could also be used for determination of the alkali content. Due to sample-matrix effects the correlation between this mode and particle size is only correct for solutions with the same silica concentration.

The resolution of particle size measurement is best below ~6 nm. Above a particle size of ~6 nm the band intensity of the asymmetric Si-O-Si streching vibration of surface SiO$_2$ groups is low, so the strong water vapor absorption below 1000 cm^{-1} has got an influence on peak shape and position, which makes particle size measurement insecure.

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