The role of cations in the formation of aqueous silica-gels

Citation for published version (APA):

Wijnen, P. W. J. G., Beelen, T. P. M., Rummens, C. P. J., & Santen, van, R. A. (1993). The role of cations in the formation of aqueous silica-gels. *Journal of Non-Crystalline Solids*, 152(2-3), 127-136.
[https://doi.org/10.1016/0022-3093\(93\)90241-O](https://doi.org/10.1016/0022-3093(93)90241-O)

DOI:

[10.1016/0022-3093\(93\)90241-O](https://doi.org/10.1016/0022-3093(93)90241-O)

Document status and date:

Published: 01/01/1993

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

The role of cations in the formation of aqueous silica gels

Peter W.J.G. Wijnen, Theo P.M. Beelen, Kees P.J. Rummens and Rutger A. van Santen

Schuit Institute of Catalysis, Department of Chemical Engineering, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Received 17 January 1991

Revised manuscript received 15 September 1992

The influence of alkali metal cations and polyvalent cations (i.e., Al^{3+} and Mg^{2+}) on the aggregation kinetics of aqueous silicate solutions is discussed in terms of the fractal properties of the silica aggregates formed. At pH = 4.0, alkali metal cations appear to have little or no effect on the aggregation kinetics and fractal dimensionality of the aggregates. Aluminum and magnesium on the other hand retard the aggregation process considerably. In this study, it is shown that aluminum gives rise to the most predominant effect as a result of the highest ionic charge. At low aluminum–cation concentration ($\text{Si}/\text{Al} = 100$) the aggregation process is inhibited by charge stabilization of the primary particles by selective adsorption of aluminum cations on the surface of oligomeric silicate anions. The aggregates initially formed at these low aluminum contents show very low fractal dimensionalities ($D \approx 1$). Increasing the aluminum content also increases the rate of aggregation, and aggregates with higher dimensionalities are observed. Homogeneous formation of amorphous, uncharged aluminosilicate oligomers prevents charge stabilization at the polymerization conditions chosen.

1. Introduction

The introduction of the concepts of fractal geometry in physics and chemistry has ushered new perspectives in the study of preparation and transformation reactions of silica gels [1]. Fractal objects intrinsically have the property that very large surface areas can be obtained through the structural arrangement of elementary building units, thus resulting in an open packing of primary building units. In physics, mass-fractal objects are different from Euclidean or non-fractal objects in the way mass and density are related in the structure. In a mass-fractal object, density decreases from the center of mass towards the object's peripheral sites via non-integer, power-law behaviour.

Equation (1) describes analytically this power-law behaviour of mass, M , and density, ρ , in case the object is embedded in three-dimensional Euclidean space:

$$M \propto r^D \rightarrow \rho \propto r^{D-3}, \quad (1)$$

where r is radius of the primary particle and D is fractal dimensionality. Since the value of the fractal dimensionality is < 3 (often ≤ 2), a mass-fractal aggregate of primary building units has a very open and ramified structure, with large crevices at the outer parts of the aggregates (see fig. 1). Most applications of silica gels are concerned with high specific surface areas of the material. In heterogeneous catalysis, for instance, one is interested in structures exposing maximum surface area per unit mass. The above-mentioned property of mass-fractal objects might thus be very suitable for applications as supporting material in heterogeneous catalysis.

The influence of (polyvalent) cations on the polymerization kinetics of aqueous silica gels is of interest, not only because the development and

Correspondence to: Dr T.P.M. Beelen, Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands. Tel: +31-40 473 008. Telefax: +31-40 455 054.

broad applicability of catalytical reactions demands well defined carrier material having as low concentrations of impurities as possible but also because it enables one to construct fractal silica aggregates which might have interesting catalytical properties in themselves. Further, the development and application of new zeolitic structures (i.e., crystalline alumino-silicates) in acid and shape-selective catalysis has gained much interest [2]. Cations play a predominant role in the synthesis of these crystalline materials. Since the formation of gel precursors of zeolites in essence involves the same reactions as the formation of silica gels, molecular chemical concepts of poly-

merization of silicic acid may be expandable to the synthesis of zeolites.

New spectroscopic techniques, such as silicon-29 nuclear magnetic resonance and small angle scattering, have contributed to new and deeper insights in the *molecular* and *colloidal* aspects of silica gel formation and transformation. Especially on an atomic level, much knowledge was gained from aqueous silicate solutions which were enriched in silicon-29. Knight [3] and Kinrade and Swaddle [4,5] have proposed a reaction scheme between a large number of structurally different silicate anions in solution at equilibrium state.

Fig. 1. Mass-fractal structure built by diffusion limited aggregation of particles to one cluster.

Polymerization processes taking place in alcoholic silicate solutions have been successfully studied on atomic scale using ^{29}Si -NMR [6–14] and on colloidal scale applying small angle scattering (SAS) spectroscopy of X-rays and neutrons (SAXS and SANS, respectively) [15–29]. From SAS it soon became apparent that aggregates formed in the polymerization process of silica solutions induce, in a certain range of the scattering vectors, non-classical, power-law behaviour of the scattered intensities indicating mass-fractal dimensionalities of the structure [30]. However, the majority of publications concerning silica gel formation and the description on molecular and colloidal scales deals with gels prepared from alcoholic precursor solutions [1] (tetra alkoxy or-tho silicates).

In this paper, the application of SAXS is discussed with respect to the investigation of the polymerization process of aqueous silicate solutions, since, on bulk scale, silica gels are prepared from aqueous silicate solutions (water glass) as well [31]. In a previous study [32,33], we have already pointed at the influence of cations on the composition of water glass solutions. The present study is focused on the role of cations in the aggregation kinetics of aqueous silicate solutions and structural transformations taking place during aggregation of the building units (particles).

2. Experimental

Silica gels were prepared by acidification of water glass solutions. The aqueous silicate solutions were prepared through dissolution of amorphous pyrogenic silica gel (Aerosil 200 and 380 ex Degussa) in the appropriate alkali metal hydroxide (sodium hydroxide, potassium hydroxide: Merck, p.a. and lithium hydroxide (99.99%), rubidium hydroxide and cesium hydroxide (50 wt% aqueous solutions): Janssen Chimica) or in tetramethylammonium hydroxide (Janssen Chimica). In the case that the effect of polyvalent cations was to be investigated, the appropriate salt (e.g., MgCl_2 , CaCl_2 and $\text{Al}_2(\text{SO}_4)_3$, Merck p.a.) was first dissolved in hydrochloric acid (1.0 N). To prepare the silica gels, a calculated quantity of

water glass was added to the acidic solution under vigorous stirring. Adjustment of the pH-value to $\text{pH} = 4.0$ was obtained by addition of small amounts of the hydroxide solution. In the experiments described, calculated quantities were in good agreement with the actually added quantities assuring similar SiO_2 concentrations in all systems.

SAXS-spectra were recorded at the Synchrotron Radiation Source in Daresbury, UK, using the 'Dutch' beamline NCD 8.2. The camera-length (i.e., sample to detector distance) was chosen such that a large range in scattering vectors, Q , was covered (typically $0.05\text{--}2\text{ nm}^{-1}$). Acquisition times needed to record SAXS-spectra with satisfactory signal to noise ratio typically amounted to 1 min in case the synchrotron was operated in multi-bunch mode and 10 min in case single bunch radiation was available. Unless stated differently, samples were introduced as quickly as possible in the sample holder (cell sealed by mylar windows) after which acquisition took place. Typically, the time span between reaching the appropriate pH-value of the silicate solution and recording of the first spectrum amounted to 5 min. In the descriptions and discussions of experiments, correction for this time span was made. The raw data-set was corrected for background and parasitic scattering occurring from mylar-windows, water solution and slits. Analysis of the corrected SAXS-curves was performed using the procedure provided by Freltoft et al. [34] and Teixeira [35].

3. Results

Silica gels are formed by polycondensation reactions of silanol groups ($-\text{Si}-\text{OH}$) of silicate species in solution. The tetrafunctional monosilicic acid polymerizes into three-dimensional particles of (sub-) colloidal size [31]. For a certain pH-value and cation content, the formed silica particles become unstable with respect to Van der Waals forces between individual particles, according to the Deryagin-Landau-Verwey-Overbeek (DLVO) theory of double-layer stabilization [36]. From that moment on, clustering of

Fig. 2. Simulated SAS curve using the expression for scattering from fractal objects given by Freltoft et al. [34] and Teixeira [35]. The fractal object is characterized by $D = 2.25$, $r_0 = 3$ nm and $\xi = 250$ nm. For a description of regions I, II and III, see text.

the particles occurs, resulting in aggregates of elementary particles. Modelling the scattering curve of fractal objects yields three possible regions of scattering (see fig. 2). Information on structure and size of the primary building units is obtained from region I, presenting (in this particular case) the form-factor of spherical, primary particles. The fractal dimensionality of the aggregates can be obtained from the slope of the linear relationship between $\log Q$ and $\log I$ (region II). In this region and in region III, the structure factor of scattering primary particles (particle-particle correlations) is involved in the process of scattering. From region III, an impression of the size of the aggregate can be obtained.

Figure 3 presents a typical SAXS spectrum of a situation in the polymerization process of aqueous silica gel prepared from a potassium water glass ($\text{SiO}_2/\text{K}_2\text{O} = 3.0$) at $\text{pH} = 3.91$ at ambient temperature. Comparing this spectrum with the model spectrum depicted in fig. 2, we observe two of the three regions in the SAXS curve. Region I as referred to in fig. 2 was not detected since the particles constructing the aggregates are so small that the scattering vectors at which scattering from these small primary particles should be detected were not captured by the linear position sensitive detector available at Daresbury Laboratories. The smallest length scales observable by the experimental set-up are ≈ 0.5 nm, indicating

that the primary particles are smaller than 0.5 nm in radius (molecular sizes).

Although the range of length scales is in most cases less than a decade, we ascribe the linear region in a double-log plot to fractal properties of the aggregates. This confidence is based on SAXS spectra measured on similar systems with potassium cations [37,38]. By combination of measurements at different camera lengths, extending the Q -range two decades upwards, we did observe a growth of fractal aggregates all over this range. Ultra small angle scattering experiments even indicate sizes of 200–300 nm for the fractal aggregates [37] but, due to the very different experimental conditions, we are not conclusive if linearity is extended over the entire range from 200 to 0.5 nm.

Depending on the concentration ($[\text{SiO}_2] > 0.2$ wt%), gelation always occurred, often during the in situ experiments. In accordance with Cabane et al. [24], no indication of the liquid to gel or sol to gel transition could be detected from the SAXS spectra. However, according to Martin and Hurd [30], the fractal dimensionalities of gelating and non-gelating systems should differ substantially if the size distribution in gelating solutions is con-

Fig. 3. Typical experimental SAXS spectrum of acidified aqueous silicate solution ($\text{pH} = 3.91$, $\text{SiO}_2:\text{K}_2\text{O} = 3.0$). The solid line presents the simulated SAXS curve. Due to the small size of the primary particles, region III of fig. 2 cannot be observed.

Fig. 4. (a) Fractal aggregate dimensionality and (b) fractal aggregate size for different alkali metal silicate solutions as a function of reaction time; $\square$, Li; ∇ , Na; $\diamond$, K; $\triangle$, Rb; $\circ$, Cs. pH = 4.0, $T = 300$ K.

Fig. 5. (a) Fractal aggregate dimensionality and (b) fractal aggregate size for different concentrations of tetramethyl ammonium cations: $+$, merely K; ∇ , TMA/Si = 0.01; $\diamond$, TMA/Si = 0.04; $\square$, TMA/Si = 0.10. pH = 4.0, $T = 300$ K.

Fig. 6. (a) Fractal dimensionality and (b) fractal size for sodium silicate solutions containing different polyvalent cations: $+$, K^+ ; $\triangle$, Mg/Si = 0.01; $\bullet$, Al/Si = 0.1. pH = 4.0, $T = 300$ K.

siderably different from a power-law with exponent $\tau = 2.0$. For a percolating network with $\tau = 2.2$, this indeed might be expected.

This controversy can only be resolved by assuming that the fractal dimensionality of the gel structure manifests itself at a much larger length scale than the relatively small length scale probed in our SAXS experiments [39,40].

Figure 4 shows the development of fractal dimensionality of the aggregates (fig. 4(a)) and the size of the aggregates (fig. 4(b)) as a function of reaction time from initial mixing of silicate solution, employing different water glass solutions with respect to the alkali metal hydroxide.

Aqueous silicate solutions polymerizing in the presence of tetramethyl ammonium (TMA) cations show different aggregation behaviour as can be concluded from fig. 5. Figure 5(a) presents the fractal dimensionality of polymerizing silicate solutions as a function of reaction time for different concentrations of tetramethyl ammonium cations (TMA/Si = 0, TMA/Si = 0.01, TMA/Si = 0.04 and TMA/Si = 0.1). Potassium hydroxide was used as the main base for silica water glass formation. In fig. 5(b), the size of the fractal aggregates as a function of reaction time is shown for different concentrations of tetramethyl ammonium cations.

Addition at low pH-values ($\text{pH} = 4.0 \pm 0.1$) of polyvalent cations (e.g., Mg^{2+} and Al^{3+}) to the

aqueous silicate solutions initially suppresses growth of the fractal aggregates, as can be concluded from fig. 6. For aluminum cations, we observe a predominant effect at already minor concentrations. The fractal dimensionality (fig. 6(a)) of initially formed silica aggregates is very low ($D \approx 1$) when 0.01 mol Al^{3+} per mol silica is added to the silicate solution. Care should be taken, however, with the interpretation of this fractal dimensionality. The fractal dimensionality of silica aggregates formed during the very first stages of the aggregation process (immediately after mixing of the two solutions) was obtained from SAXS curves exhibiting power-law behaviour over a very limited Q -range. The error made in the determination of these fractal dimensionalities is large. However, we might mention as well that, from silicate solutions containing no aluminum cations, fractal dimensionalities almost as high as the final dimensionality could be determined (see fig. 4(a)) from the very start of polymerization.

Further, the way in which the aggregate structure develops with reaction time depends strongly on the concentration of polyvalent cations present in solution. Figures 7(a) and 7(b) show the experimental parameters (fractal dimensionality and aggregate size, respectively) obtained from SAXS curves of polymerizing silicate solutions to which different concentrations of aluminum

Fig. 7. (a) Fractal dimensionality and (b) fractal size for sodium silicate solutions containing different amounts of aluminum cations as a function of reaction time: +, Al/Si = 0; ■, Al/Si = 0.01; △, Al/Si = 0.04; ●, Al/Si = 0.10. pH = 4.0, $T = 300$ K.

cations were added. Obviously, these figures show a large influence of the amount of aluminum present in the solution

4. Discussion

4.1. Alkali metal cations

From fig. 4 it becomes clear that no obvious differences in growth and structure development of fractal aggregates can be determined when different monovalent cations (as Li, Na, K, Rb and Cs) are present in polymerizing aqueous silicate solutions. Almost instantaneously the final value for the fractal dimensionality ($D = 2.21 \pm 0.05$) is found indicating reaction-limited aggregation to occur from the very start of polymerization. At the pH-value used in this study, we do not observe any differences in polymerization behaviour of the different alkali metal silicates. This can be explained by the fact that, at this low pH-value (pH = 4.0), only minor quantities of the surface silanol (Si-OH) groups are ionized. Thus, adsorption of monovalent alkali metal cations to the silica-particle surface is in the aggregation of silica particles at this pH-value, a process of minor importance. Differences, with respect to aggregation kinetics, between alkali metal cations (similar to effects of different alkali metal hydroxides observed for silica gel dissolution [32,33]) thus are not to be expected.

Comparing the final fractal dimensionality obtained from these experimental SAXS curves with values reported for aggregates generated by computer simulation (reaction limited cluster-cluster aggregation [41]) reveals, within the experimental error, almost the same dimensionality: $D_{\text{exp}} = 2.21$ and $D_{\text{sim}} = 2.08$. In case structural rearrangement of computer-simulated aggregates is taken into account, fractal dimensionalities similar to the experimental value are obtained [42].

4.2. Tetramethylammonium cations

From experiments described earlier [32,33] concerning the dissolution of amorphous silica gel in TMAOH, we concluded that TMA cations

Fig. 8. Size of fractal aggregates as a function of TMA concentration. Data obtained from spectra recorded 60 min after initial mixing.

preferentially adsorb on the silica gel surface, inducing inhibition of the dissolution reaction. Concerning the aggregation processes occurring in acidified silicate solutions, preferential adsorption on silica surfaces may occur, due to the low polarity of methyl groups of the tetramethyl ammonium cation. This effect was also shown by measuring the ζ -potential of silica gels [43]. The influence of variation of TMA concentration on the aggregate size measured 60 min after initial mixing are shown in fig. 8. The size of the silica aggregates determined after 60 min of polymerization increases with increasing TMA concentration. Moreover, one observes that addition of relatively small amounts of TMA induces an increase in rate of aggregation. This effect of small quantities of TMA can be explained on the basis of the structure of water surrounding the silicate particles. Hydrophobic hydration [44,45] does not play an important role since this phenomenon is only observed for tetraalkyl ammonium cations whose alkyl chains are larger than those of tetrapropyl ammonium. Adsorption of TMA cations causes the water structure to be disturbed and thus induces destabilization of the colloidal particles. The activation energy for coagulation is decreased by the adsorption of TMA cations and thus coagulation is accelerated [31].

4.3. Aluminum (III) cations

Combining the data showing the development of the fractal dimensionality (fig. 7(a)) with data

representing the development of the size (fig. 7(b)) for silica aggregates that are grown in solutions containing small quantities of aluminum cations ($\text{Si}/\text{Al} = 100$), we may conclude that at the onset of polymerization (i.e., aggregation), an inhibition of aggregation occurs. In this time period and at this low aluminum concentration, we attribute the observed inhibition of the aggregation process to the reaction of aluminum cations with silica (oligomers and sub-colloidal particles) to form isolated patches ('islands') of aluminosilicates on the surface of the small silica particles. Reaction of aluminum cations with the silicate oligomers is fast compared with the aggregation rate of silicate particles [31]. The rate of aggregation is now decreased since the primary silica particles are stabilized against aggregation through the positive charges on the particles, induced by the aluminum cations. The low fractal dimensionality as observed during the first period of aggregation can be explained by a model of screened aggregation [46,47]. This model predicts very tenuous structures with correspondingly low fractal dimensionalities. After some 20 min of reaction, an increase in aggregate size is observed. Now all aluminum has reacted with oligomeric silica in forming tenuous aggregates and the aggregation process is continued just by silicate oligomers. This process causes the aluminosilicate aggregates to become enveloped by oligomeric silica, forming aggregates which are as active in further aggregation as the non-aluminum-containing silica particles and aggregates. Because no classical Porod-law behaviour was observed in the scattering region investigated ($0.06 < Q < 1 \text{ nm}^{-1}$) primary particles have to be of molecular size ($< 1 \text{ nm}$) in all systems.

Minor amounts of aluminum cause a significant decrease in aggregation rate, whereas increasing amounts of aluminum cause this inhibition effect to become less obvious. Moreover, at 0.10 mol aluminum per mol silica, no differences in aggregation kinetics can be observed compared with silicate solutions containing only sodium cations. Fractal dimensionality as well as aggregate size are not influenced by the addition of 0.10 mol aluminum per mol silica. This may indicate a fast reaction between aluminum cations

Fig. 9. Size of fractal aggregates of aluminum containing sodium silicate solutions after 60 min of reaction at $\text{pH} = 4.0 \pm 0.1$ as a function of aluminum content.

(whether or not in polycationic form [31]) and silicate species present in the solution. Aluminum is now more equally divided over the silicate species, by contrast with the low concentrations of aluminum. At low concentration, primary silica particles become covered by the aluminum cations causing ionic stabilization of the particles whereas, at high aluminum concentrations, the primary particles consist of aluminosilicates which at $\text{pH} = 4.0$ are nearly charge neutral at the surface, thus causing no stabilization of the particles. Figure 9 shows the size of silica aggregates after 60 min of polymerization reaction as a function of aluminum content. It can be seen that minor amounts of aluminum give rise to an inhibition in cluster growth.

5. Conclusions

Using small angle X-ray scattering in the in situ study of polymerization (aggregation) occurring in acidified aqueous silicate solutions, differences in rate of aggregation and in development of (fractal) structure are recognized, when polyvalent cations or strongly adsorbing cations (TMA) are added to silicate solutions. No differences are found for polymerization reactions taking place in aqueous silicate solutions in which different monovalent alkali metal cations are present. At relatively low pH-values ($\text{pH} \approx 4.0$), ionization of surface silanol groups is of relatively minor im-

portance and thus adsorption of monovalent cations and differences in adsorption behaviour are of minor importance as well; the majority of the cations can be considered as solvated cations which, at these low pH-values, show almost no interaction or bonding with the silicate particles. According to the DLVO theory, particles bearing some charge are relatively stable and this indicates that, at these low pH-values, aggregation is a process controlled by reaction kinetics for formation of clusters of colliding particles or clusters. Breaking of the water structure surrounding the silica particles and subsequent formation of siloxane bridges between the two colliding particles causes aggregation to be reaction-limited. Monovalent alkali metal cations play a minor role in the aggregation kinetics at low pH-values.

Additions of small concentrations of tetramethyl ammonium cations at low pH values show an increase in rate of aggregation, as was also suggested by Iler [31]. This is attributed to the lower energy of activation to disturb and break the less predominant water structure surrounding the primary silicate particles in case TMA cations are adsorbed on the silica surface. Aggregation results in the same fractal dimensionality as encountered for silicate solutions merely incorporating alkali metal cations.

Aluminum (III) cations at low concentration induce inhibition of the aggregation process. Therefore the three-dimensional polymerization process of silicate solutions is strongly limited and causes initially formed structures to be very ramified (almost linear), as is reflected in very low fractal dimensionalities ($D \approx 1$) of aggregates. On the other hand, when the concentration of aluminum cations is increased, a recovery in polymerization rate is observed. This effect is attributed to a different, homogeneous distribution of aluminum in the silica particles. At low concentration, aluminum will preferentially interact with the surface groups of silica particles, thus forming a surface alumino-silicate. Stabilization against aggregation is achieved through positive charges on the particles. Only after a certain time period is this surface structure replaced or reorganized through addition of active silicate species (small oligomers) from solution. From

that moment, equivalent aggregation kinetics are observed as in the cases where no aluminum was added. Addition of larger amounts of aluminum cations leads to less predominant inhibition of aggregation kinetics. This is attributed to a more equal distribution of aluminum throughout the particles; not only surface sites become alumino-silicate groups, but gradually the entire primary particle becomes an alumino-silicate because of reaction between aluminum and dissolved silicate oligomers.

This study has shown the value of fractal analysis in the study of aggregation phenomena occurring in polymerizing silicate solutions. Differences in rate of aggregation and in structural aspects of the aggregates are reflected in the fractal properties and in the small angle scattering profile. Application of small angle scattering to the in situ study of zeolite synthesis is very promising.

Financial support was given by the Netherlands' Department of Economic Affairs, in terms of the 'IOP-Katalyse' program. Beamtime at Daresbury Laboratories was provided by the SERC/NWO agreement on synchrotron use. Dr Wim Bras is gratefully acknowledged in assisting on the use of Beamline NCD 8.2.

References

- [1] L.L. Hench and J.K. West, *Chem. Rev.* 90 (1990) 33.
- [2] W.F. Hölderich and H. van Bekkum, in: *Introduction to Zeolite Science and Practice*, ed. H. van Bekkum, E.M. Flanigen and J.C. Jansen (Elsevier, Amsterdam, 1991) p. 631.
- [3] C.T.G. Knight, *J. Chem. Soc., Dalton Trans.* (1988) 1457.
- [4] S.D. Kinrade and T.W. Swaddle, *J. Am. Chem. Soc.* 108 (1986) 7159.
- [5] S.D. Kinrade and T.W. Swaddle, *Inorg. Chem.* 27 (1988) 4253, 4259.
- [6] G. Engelhardt, W. Altenburg, D. Hoebbel and W. Wicker, *Z. Anorg. Allg. Chem.* 428 (1977) 43.
- [7] R.K. Harris and C.T.G. Knight, *J. Chem. Soc., Chem. Commun.* (1980) 726.
- [8] I.L. Svensson, S. Sjöberg and L.-O. Öhman, *J. Chem. Soc., Faraday Trans. 1*, 82 (1982) 3635.
- [9] C.J. Creswell, R.K. Harris and P.T. Jageland, *J. Chem. Soc., Chem. Commun.* (1984) 1261.
- [10] G. Engelhardt and O. Rademacher, *J. Molec. Liq.* 27 (1984) 125.

- [11] I. Artaki, S. Sinha, A.D. Irwin and J. Jonas, *J. Non-Cryst. Solids* 72 (1985) 391.
- [12] L.W. Kelts, N.J. Effinger and S.M. Melpolder, *J. Non-Cryst. Solids* 83 (1986) 353.
- [13] S.D. Kinrade and T.W. Swaddle, *J. Am. Chem. Soc.* 108 (1986) 7159.
- [14] J.C. Pouxviel, J.P. Boilot, J.C. Beloeil and J.Y. Lallemand, *J. Non-Cryst. Solids* 89 (1987) 345.
- [15] R.H. Bragg, I. Corvin and J.W. Buttrey, *J. Appl. Phys.* 31 (1960) 1183.
- [16] O.L. Brill, C.G. Weil and P.W. Schmidt, *J. Coll. Interf. Sci.* 27 (1968) 479.
- [17] C.J. Brinker, K.D. Keefer, D.W. Schaefer, C.S. Ashley, R.A. Assink and B.D. Kay, *J. Non-Cryst. Solids* 48 (1982) 47.
- [18] C.J. Brinker and G.W. Scherer, *J. Non-Cryst. Solids* 70 (1985) 301.
- [19] A. Dager, F. Chaput, J.C. Pouxviel and J.P. Boilot, *J. Phys. (Paris)* C8 46 (1985) 455.
- [20] M.A.V. Axelos, D. Tchoubar and R. Jullien, *J. Phys.* 47 (1986) 184.
- [21] J.E. Martin, D.W. Schaefer and A.J. Hurd, *Phys. Rev.* A33 (1986) 3540.
- [22] J.D.F. Ramsay and M. Scanlon, *Coll. Surf.* 18 (1986) 207.
- [23] M.A. Aegerter, D.I. Dos Santos, A.F. Craievich, T. Lours and J. Zarzycki, *Diff. Def. Data* 53&54 (1987) 427.
- [24] B. Cabane, M. Dubois and R. Duplessix, *J. Phys. (Paris)* 48 (1987) 2131.
- [25] K. Wong, B. Cabane and R. Duplessix, *J. Coll. Interf. Sci.* 123 (1988) 466.
- [26] B. Cabane, K. Wong, T.K. Wang, F. Lafuma and R. Duplessix, *Coll. Polym. Sci.* 266 (1988) 101.
- [27] S. Ciccariello, J. Goodisman and H. Brumberger, *J. Appl. Crystallogr.* 21 (1988) 117.
- [28] P.W. Schmidt, A. Höhr, H.B. Neumann, H. Kaiser, D. Avpir and J.S. Lin, *J. Chem. Phys.* 90 (1989) 5016.
- [29] F. Chaput, J.P. Boilot, A. Dager, F. Devreux and A. de Geyger, *J. Non-Cryst. Solids* 116 (1990) 133.
- [30] J.E. Martin and A.J. Hurd, *J. Appl. Crystallogr.* 20 (1987) 61.
- [31] R.K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).
- [32] P.W.J.G. Wijnen, T.P.M. Beelen, J.W. de Haan, L.J.M. van de Ven and R.A. van Santen, *Coll. Surf.* 45 (1990) 255.
- [33] P.W.J.G. Wijnen, T.P.M. Beelen, J.W. de Haan, C.P.J. Rummens, L.J.M. van de Ven and R.A. van Santen, *J. Non-Cryst. Solids* 109 (1989) 85.
- [34] T. Freltoft, J.K. Kjems and S.K. Sinha, *Phys. Rev.* B33 (1987) 269.
- [35] J. Teixeira, *J. Appl. Crystallogr.* 21 (1988) 781.
- [36] E.J.W. Verwey and J.Th.G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).
- [37] P.W.J.G. Wijnen, thesis, Eindhoven University of Technology (1990).
- [38] P.W.J.G. Wijnen, T.P.M. Beelen, C.P.J. Rummens and R.A. van Santen, *J. Non-Cryst. Solids* 136 (1991) 119.
- [39] T.P.M. Beelen, P.W.J.G. Wijnen, C.P.J. Rummens and R.A. van Santen, *Mater. Res. Soc. Symp. Proc.* 180 (1990) 273.
- [40] T.P.M. Beelen, W.H. Dokter, H.F. van Garderen, R.A. van Santen, M.T. Browne and G.R. Morrison, to be published in *Mater. Res. Soc. Symp. Proc.* (1992).
- [41] P. Meakin, *Adv. Coll. Interf. Sci.* 28 (1988) 249.
- [42] P. Meakin, in: *Phase Transitions*, Vol. 12 (Academic Press, New York, 1988) p. 335.
- [43] J.C.J. van der Donck and H.N. Stein, personal communication.
- [44] E.M. Flannigen, *Adv. Chem. Ser.* 121 (1973) 119.
- [45] E.G. Derouane, S. Detremmerie, Z. Gabelica and N. Blom, *Appl. Catal.* 1 (1981) 201.
- [46] M. Axelos, D. Tchoubar, J. Bottero and F. Fiessinger, *J. Phys. (Paris)* 46 (1985) 1587.
- [47] J.Y. Bottero, D. Tchoubar, M.A.V. Axelos, P. Quienne and F. Fiessinger, *Langmuir* 6 (1990) 596.