

Silica gel dissolution in aqueous alkali metal hydroxides studied by silicon-29 NMR

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SILICA GEL DISSOLUTION IN AQUEOUS ALKALI METAL HYDROXIDES STUDIED BY ^{29}Si -NMR

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The rate of silica gel dissolution in aqueous alkaline media was investigated using ^{29}Si nuclear magnetic resonance spectroscopy. A profound difference of alkali metal hydroxides on the dissolution rate of amorphous silica gel was observed. The dissolution rate increases in the order $(\text{LiOH} \approx \text{CsOH}) < (\text{RbOH} \approx \text{NaOH}) < \text{KOH}$, as was confirmed by the β -silicomolybdate complexation method. Silica gel dissolution involved formation of monomeric silicic acid, Q^0 . The monomeric anions oligomerise into dimer species, which in turn form cyclic and linear trimer species. The structure of highly polymerised silicate species depends on the alkali metal cation, i.e. low pH silicate solutions have structurally different silicate species as a function of alkali metal hydroxide, as is shown by ^{29}Si -NMR spectroscopy. Potassium cations gave rise to more polymerised silica species compared with other alkali metal cations studied. On the contrary, when lithium hydroxide and silica gel are mixed in a molar $\text{SiO}_2/\text{Li}_2\text{O}$ ratio = 1:1, a microcrystalline phase is formed which consists of lithium silicate crystals. Crystallisation of the lithium silicate proceeds via monomeric silica being in solution.

1. Introduction

Silica is a commonly used material that exhibits a large variety of applications due to a large diversity in surface structure, porosity and texture. Numerous investigations on this diversity in silica systems have been reviewed by Iler [1], who also reviewed the complicated silica polymerisation.

Since slight variations in precursor composition may have profound effects on the final silica products, knowledge about the physical chemistry of the starting compounds is also required, in order to obtain insight in the polymerisation pathway of aqueous silica [e.g. 2,3]. For example, salts such as sodium chloride tend to increase the rate of silica gel dissolution [4], whereas zinc and aluminum cations retard dissolution reactions [5].

In this paper we describe the results of a study on the dependence of silica gel dissolution on different alkali metal hydroxides, i.e. we investigated the dissolution of amorphous silica gel in LiOH , NaOH , KOH , RbOH , CsOH at two different silica to base ratios. Our results obtained from ^{29}Si -NMR experiments were confirmed by results from the β -silicomolybdic acid analysis [6] of dissolving suspensions, c.q. gel systems.

In 1971, Engelhardt et al. applied ^{29}Si -NMR for the study of aqueous silica solutions [7]. Many investigations followed [e.g. 8] and much knowledge was gained from silica solutions in a steady state. Investigations on ^{29}Si enriched solutions have led to structural assignments of resonance frequencies [9-11]. It was pointed out that aqueous silica solutions always consist of a variety of oligomerised silica species of subcolloidal size (< 1 nm) which tend to form cyclic, cubic or cage-like structures or even colloidal particles. Recently,

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Knight et al. used 2D Correlated (COSY) and Exchange Spectroscopy (EXSY) to investigate the structure of and exchange reactions between silicate anions in aqueous solutions [12,13]. These investigations were carried out on aqueous silica solutions being in thermodynamical equilibrium and thus primarily inform about the composition and exchange reactions at equilibrium.

Our work can be considered as an application of these results to the study of silica gel dissolution.

2. Experimental

A series of inorganic silica gel precursors (water glass solutions) was prepared by adding appropriate quantities of alkali metal hydroxide to a suspension of very pure, pyrogenic silica (Aerosil 380 ex Degussa. *Pro analysi* alkali metal hydroxides were obtained from Merck (NaOH, KOH) or Janssen Chimica (LiOH, RbOH, CsOH). Teflon PTFE containers were used to avoid any metal ions leaching out of the container wall. The overall, molar composition of the well mixed suspension was $1M_2O : 3SiO_2 : 108H_2O$ in the case of the low alkaline suspensions and $1M_2O : 1SiO_2 : 35H_2O$ in the case of high alkaline suspensions. In these formulas, M denotes the alkali metal used, i.e. Li, Na, K, Rb or Cs. The solute compositions are comparable with commercially silica solutions. Also, these compositions can be referred to precursor solutions used in zeolite synthesis.

The well mixed suspensions were introduced into a Bruker CXP 300 NMR spectrometer as quickly as possible, using alumina spinners in a double air bearing magic angle spinning (MAS) probe. MAS was applied to average chemical shift anisotropies, which might occur in viscous fluids. The same applies to dipolar interactions between either ^{29}Si and 1H , which are, however, small. Since our starting material consists of solid silica gel in aqueous alkali metal hydroxides, the first stages of the dissolution reactions proceed in highly viscous suspensions, requiring magic angle sample spinning. The spin frequency was 1500 ± 100 Hz. The resonance frequency for ^{29}Si was 59.63 MHz (field strength 7.05 T) whilst spectra were re-

corded using the quadrature detection mode. All suspensions were measured under the same experimental conditions ($T = 296$ K and atmospheric pressure) using the same one pulse excitation program: 3 μs pulse duration (45° flip angle), 4 s pulse delay, spectrum width 20 kHz. In the case of the $1M_2O : 3SiO_2 : 108H_2O$ samples, an acquisition time of 25 ms was taken and after collecting the appropriate amount of FIDs (free induction decays), the 1 K data set was zero-filled to 8 K. Since the intrinsic line widths of the silicate species decrease with increasing pH value of the suspension, an acquisition time of 410 ms was needed for the $1M_2O : 1SiO_2 : 35H_2O$ samples. Unless stated differently, 1500 pulses were required for the $1M_2O : 3SiO_2 : 108H_2O$ suspension and 200 pulses were required for the $1M_2O : 1SiO_2 : 35H_2O$ suspensions. For data obtained from $1M_2O : 3SiO_2 : 108H_2O$ suspension a Lorentzian filter of 20 Hz was applied prior to zero filling.

In order to quantify dissolved silica species, the suspensions were analysed by the β -silicomolybdate complexation method after Alexander et al. [6]. One ml of the silica gel suspension was added to 50 ml of 1.5 N sulphuric acid p.a. From this solution 1 ml was added to 50 ml of the molybdc acid reagent. The absorption at 410 nm was recorded by a Hitachi 150-20 UV-VIS spectrometer.

3. Results and discussion

3.1. Dissolution with molar ratio = 3

In fig. 1(a-e), natural abundance ^{29}Si -MAS-NMR spectra of aqueous silica solutions with different alkali metal cations are shown after 17 h of reaction. Since the spectra of the different cations are normalised and since all solutions contain the same initial concentration of silica gel and hydroxyl anions (pH is equal for all solutions), the spectra are directly comparable.

In general, ^{29}Si -NMR spectra of aqueous silica solutions exhibit several resonances corresponding to structurally different sites of the ^{29}Si atom [8]. The differences in resonance frequencies are mainly caused by the local environments of the

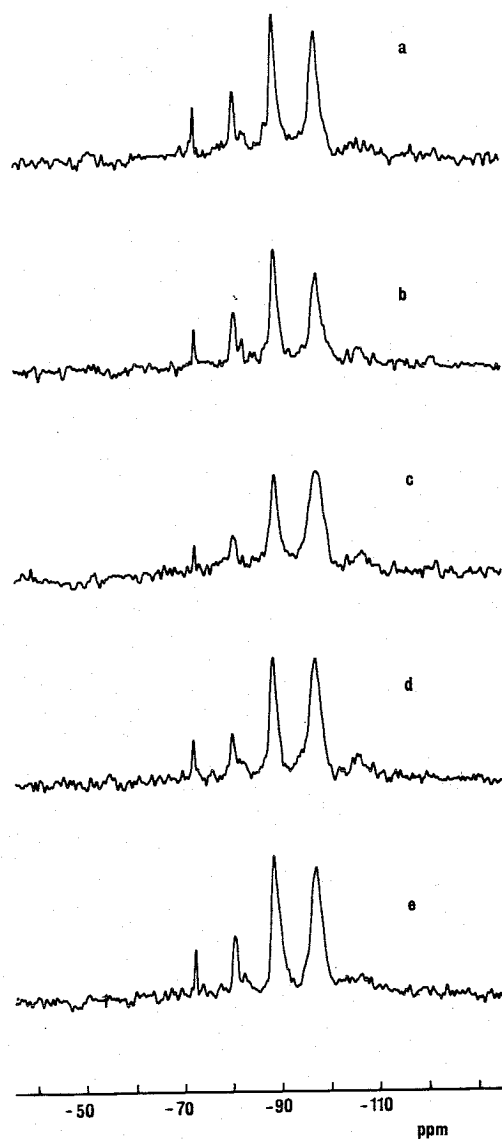


Fig. 1. ^{29}Si -NMR spectra of aqueous silicate solutions 17 h after initial mixing of silica gel and (a) LiOH, (b) NaOH, (c) KOH, (d) RbOH, and (e) CsOH in a molar ratio $\text{M}_2\text{O}:\text{SiO}_2 = 1:3$. Number of scans 1500.

atoms considered, e.g. depending on the number of siloxane bondings ($=\text{Si}-\text{O}-\text{Si}=\text{}$) surrounding the ^{29}Si atom, the nuclear magnetic resonance frequency is shifted. In the following, Q^i corresponds to the nomenclature introduced by Engelhardt et al. [14] for silicate species with i siloxane ($=\text{Si}-\text{O}=\text{}$) linkages. A subscript refers to the

number of Q^i sites within the silicate species. For example, Q_4^2 and Q_3^2 represent the ^{29}Si nuclei in the cyclic tetramer and the cyclic trimer respectively. Moreover, several configurations for Q^1 to Q^4 sites are possible, i.e. in linear, cyclic, or cubic species, which all give slightly different resonance frequencies. Hence, resonance bands for Q^1 to Q^4 may broaden more or less proportionally to the number of different structural sites belonging to one resonance (Q^i) group. Most pronounced extra chemical shifts are generated by three-membered ring structures, indicated by the subscript Δ . Table 1 presents the chemical shift values for resonance peaks in the ^{29}Si -NMR spectrum of aqueous alkali metal silicate solutions.

Silica can readily be dissolved in highly alkaline media ($\text{pH} > 11$). The hydroxyl anion is considered to be a catalyst for the dissolution reaction [1]. Hydroxyl anions increase the coordination number of a surface silica atom to more than four, thus weakening the oxygen bonds to underlying silicon atoms. As such, silica dissolves in the form of monomeric silica $\text{Si}(\text{OH})_4$ until the equilibrium concentration of monomeric silica is reached. However, prolonged dissolution causes significant oligomerisation of the monomer [1].

At the selected silica to base ratio of 3.0 and the experimental conditions ($T = 296$ K and atmospheric pressure), the silica solutions after 17 h of dissolution reaction are composed of monomeric as well as oligomeric silicate species (fig. 1(a-e)). Examination of the quantitative composition of the aqueous solutions shows that the type of alkali cation present in solution affects the distribution of the silicate species. In particular, the ratio of the amount of Q^2 and Q^3 sites is affected. Highly polymerised silicate anions (Q^3 sites) are favoured to a larger extent by potassium cations than by lithium, sodium and cesium cations. Rubidium hydroxide takes an intermediate position. Moreover, considering figs. 1(a, e), the solution containing lithium cations (fig. 1(a)) contains silicate species of the Q^3 resonance group resonating at the low frequency edge (δ more negative) whereas silicate solutions containing cesium cations (fig. 1(e)) possess silicate species resonating at the high frequency edge of the Q^3 -group. For clarity, fig. 2 shows the measured and simulated (deconvoluted)

Table 1
Chemical shift values for resonance peaks in the ^{29}Si -NMR spectra

Alkali metal cation	Silica to base ratio	Q^0	Q^1_2	Q^1	Q^2_3	Q^2_4	Q^2	Q^3
Li	3:1	-72.11	-	-80.3	-	-82.13	-88.58	-97.12
	1:1	-71.54	-79.46	-79.25	-81.55	-81.31	-86.7-89.1	-
Na	3:1	-71.13	-	-79.32	-	-81.1	-87.58	-96.26
	1:1	-71.36	-79.35	-79.2	-81.32	-81.2	-86.9-89.1	-
K	3:1	-72.12	-	-80.3	-	-82.02	-88.57	-97.24
	1:1	-71.52	-79.54	-79.25	-81.52	-81.20	-86.9-89.1	-
Rb	3:1	-71.04	-	-79.11	-	-81.16	-87.36	-96.00
	1:1	-71.55	-79.48	-79.2	-81.54	-81.23	-86.7-89.1	-
Cs	3:1	-72.12	-	-80.22	-	-82.25	-88.34	-97.01
	1:1	-71.66	-79.48	-79.27	-81.59	-81.32	-86.7-89.1	-

NMR spectra for the Q^2 and Q^3 sites of lithium (fig. 2(a)) and cesium (fig 2(b)) silicate solutions, stressing the compositional dependence of silica solution on cations present in solution. These differences in peak asymmetry are significant since all experiments were performed at least in duplo. The observations described above show that alkali metal cations influence the silicate anion distribution (Q^2/Q^3). Also it is clear that the contact between cations and silicate anions is close enough to influence the ^{29}Si -NMR chemical shift of the anions in a way specific for the alkali metal cation. We surmise that this latter effect is only possible assuming cation specific, slight changes in anion geometries (e.g. by partial overlap of inner solvation shells).

The progress of silica gel dissolution in alkali metal hydroxides was followed by ^{29}Si -MAS-NMR. The initial viscosity of the silica suspensions depends on the alkali metal hydroxide used, indicating an effect of the alkali metal cations already at the very first stages of the reaction. Figures 3(a-f) shows ^{29}Si -MAS-NMR spectra obtained from a depolymerising silica suspension after 100, 200, 300, 400, 800 and 1000 min of reaction in lithium hydroxide. The maximum concentration of monomeric silica is reached already within the first 100 min of reaction as is indicated by the Q^0 -resonance frequency. This relatively high concentration of monomer suggests that (at this silicate to base ratio) the dissolution of silica

gel with formation of monomeric silica, is considerably faster than oligomerisation of the latter to dimer, etc. This observation was encountered regardless of the type of alkali metal hydroxide used. Dissolution of the silica gel proceeds until a steady state situation is established between the different kinds of oligomers. However, in the case of lithium hydroxide at a silica to base ratio = 3 (fig. 3), a steady state is not fully encountered within 17 h in contrast with silica gel dissolution in NaOH, KOH, RbOH and CsOH.

In the first stages of dissolution, we observe rather large differences in the composition of the liquid phase between the different alkali metal hydroxides. Figures 4(a-e) show spectra of silica gel suspensions, obtained 100 min after mixing. From these spectra we learn that silica gel has dissolution rates which depend on the alkali metal cation. Figure 5 represents the normalised dissolution rates which show a dependence [16] on the alkali metal cation. The rate of dissolution is maximum for the potassium cation.

Observations described above are confirmed by the analysis of depolymerising suspensions, using the β -silicomolybdic acid complexation method [6]. This method may be seen as a standard method of determining active silica in aqueous solutions [1], we will not discuss the results in detail. Complexation of monomeric silica by heptamolybdate anions yields the β -silicomolybdic acid, the amount of which is measured photometrically. Oligomeris-

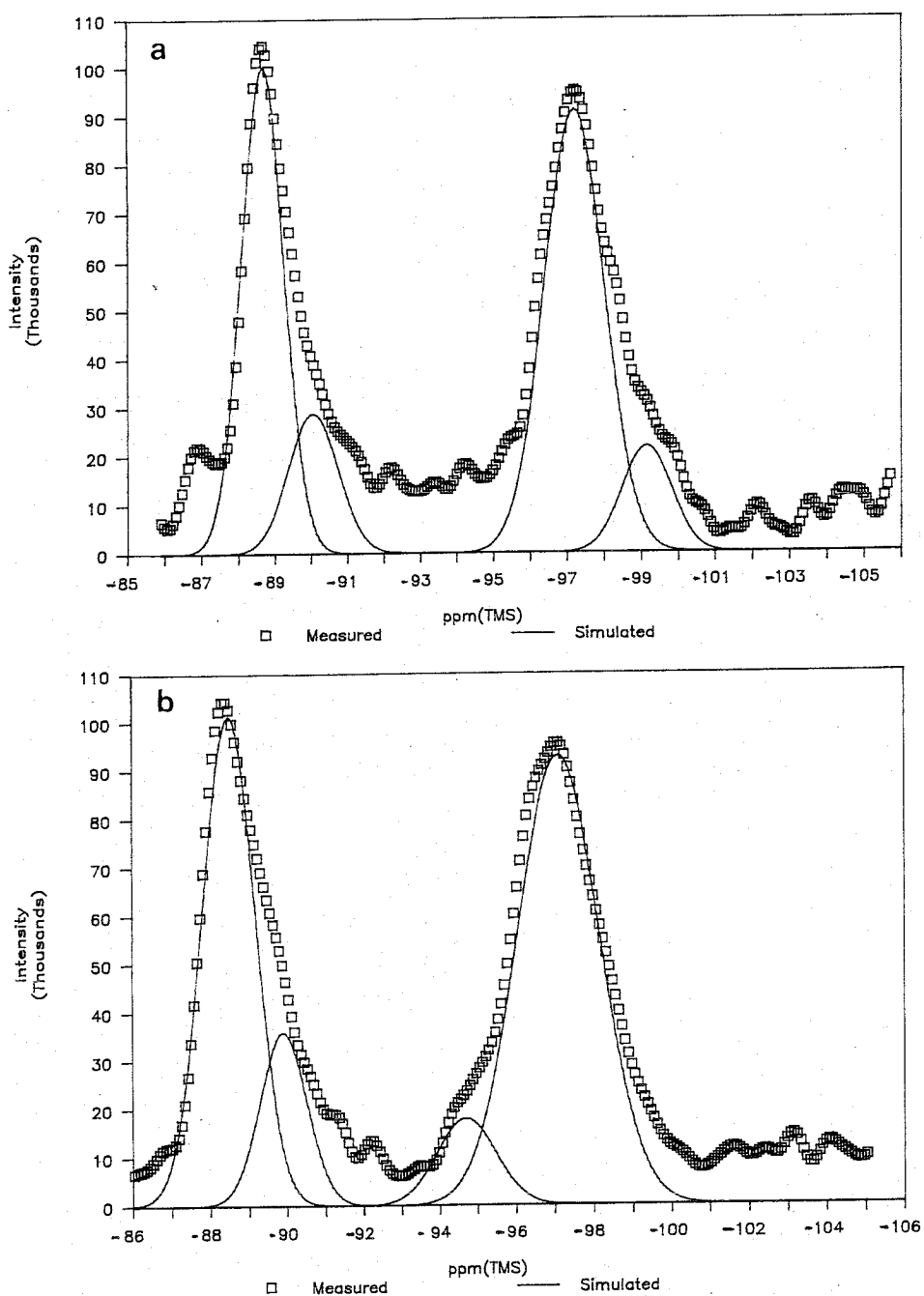


Fig. 2. Comparison between the steady state situations of lithium (a) and cesium (b) silicate solutions (silica to base ratio = 3:1). Symbols: measured spectrum, lines: simulated spectrum. Only the Q^2 and Q^3 ranges of the spectra are shown.

ed silicate species first have to dissolve to form monomeric silica, before a reaction with heptamolybdate can occur. We observed that only a

minor part of dissolved silica forms highly polymerised silica (colloidal silica). However, the amount of (sub)colloidal particles present in solu-

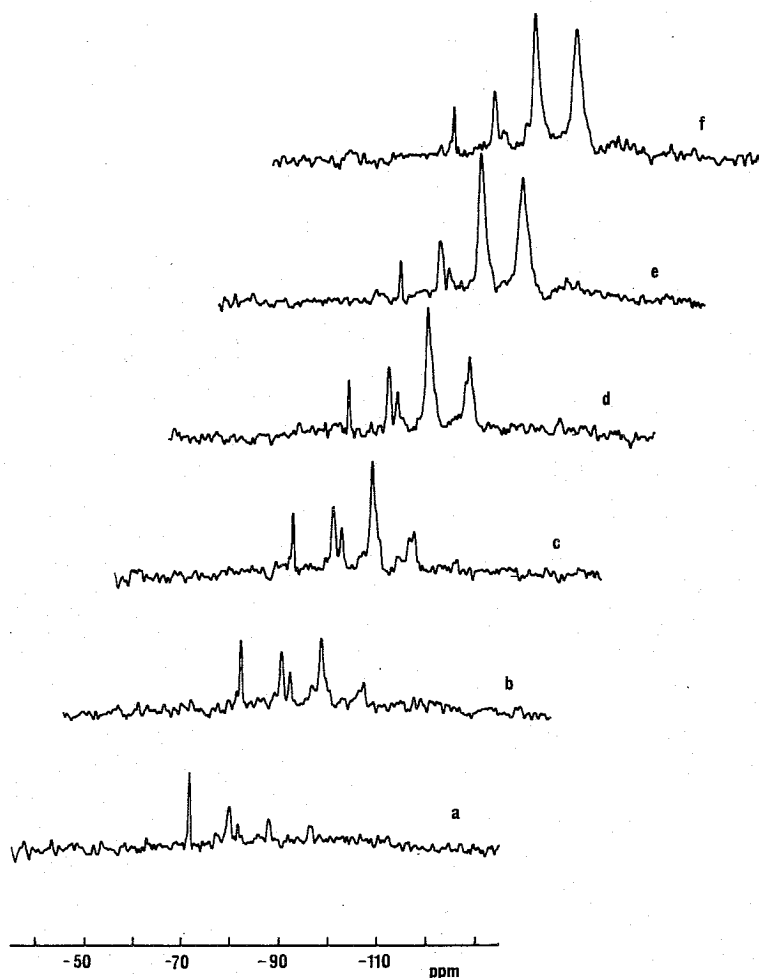


Fig. 3. Dissolution of amorphous silica gel in lithium hydroxide after (a) 100, (b) 200, (c) 300, (d) 400, (e) 800, and (f) 1000 min of reaction as followed by ^{29}Si -NMR. Molar ratio $\text{Li}_2\text{O}:\text{SiO}_2 = 1:3$. Number of scans 1500.

tion increases with reaction time, since colour development decreases with reaction time. This observation is consistent with the increase of intensities of Q^2 and Q^3 resonance groups in our NMR data.

The observed differences in silica gel dissolution by the different alkali metal hydroxides cannot simply be explained by differences in adsorption behavior of the alkali metal cations on the silica gel surfaces [17–20]. Adsorption on silica gel surfaces decreases uniformly with the intrinsic alkali metal cation radius in the order $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$ [19]. Obviously, this cannot explain the

maximum observed for K (fig. 5). So, alkali metal cations have to promote dissolution of silica gel surfaces with different efficiencies. The strength of the promoting effect appears to relate to the effective cation radius instead of the intrinsic cation radii. The effective radius of an alkali metal cation is at a minimum for potassium. Lithium and sodium are strongly hydrated whereas there is a break in hydration at the potassium cation. Lithium and sodium cations are known as water structure formers, whereas potassium, rubidium and cesium cations are known as water structure breakers [21]. This effect is well in accordance

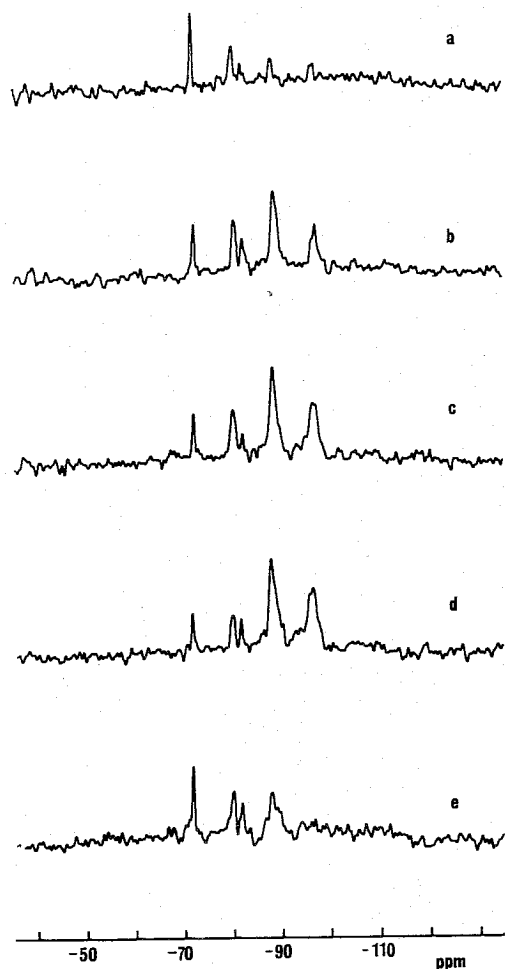


Fig. 4. ^{29}Si -NMR spectra of aqueous silicate solutions 100 min after initial mixing of silica gel and (a) LiOH, (b) NaOH, (c) KOH, (d) RbOH, and (e) CsOH in a molar ratio $\text{M}_2\text{O}:\text{SiO}_2 = 1:3$. Number of scans 1500.

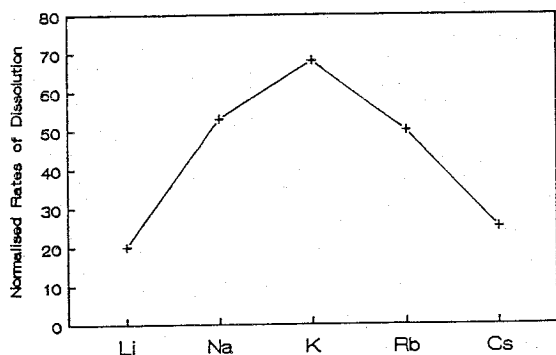


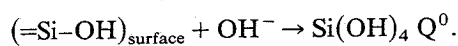
Fig. 5. Normalised rate of dissolution, obtained from ^{29}Si -NMR spectra, as a function of alkali metal hydroxide.

with the rate of silica gel dissolution in alkali metal hydroxides.

3.2. Dissolution with molar ratio = 1

Figures 6(a-f) shows a series of subsequent spectra of silica gel dissolving in cesium hydroxide at a molar $\text{SiO}_2/\text{Cs}_2\text{O}$ ratio = 1 (high pH). In contrast to the spectra shown in fig. 3(a-f), the spectral resolution is much better. Line widths of the different ^{29}Si resonances decrease considerably when the pH of the solution is increased, and when the ratio, $\text{SiO}_2/\text{M}_2\text{O}$, is lowered. This effect may be attributed to the decrease in viscosity introduced by higher pH values or to a decrease in chemical exchange rates between silicate species in solution. This decrease in either viscosity or rates also results in a fairly good signal to noise ratio, which makes data accumulation relatively fast (15 min between two successive spectra) for observation of the reactions involved in the dissolution of silica gel. From these spectra and the peak assignments after Harris [10] and Knight [12], we are able to postulate a mechanism for the dissolution of silica gel and the subsequent oligomerisation of aqueous silicate species, induced by saturation of the alkaline solution by monomeric silica.

At the very first stage of silica gel dissolution, $=\text{Si}-\text{O}-\text{Si}=\text{O}$ linkages are hydrolysed and primarily, monomeric silica is dissolved from the silica gel/water interface:



The concentration of monomeric silica increases as is seen in figs. 6(a, b). With the increase in monomer concentration, the dimer (Q_2^1) species becomes evident (fig. 6(c)). During formation of the dimer, the monomer concentration still increases, indicating that, in contrast to the dissolution reaction with molar ratio = 3, the dissolution reaction is slower than the oligomerisation of monomer.

Almost simultaneously with dimer formation, a small amount of linear trimer Q_2^1Q_1^2 is being formed. The rate of formation is much faster for the Q_2^1 species than for the Q_2^1Q_1^2 species. After formation of a considerable amount for dimer species, cyclic trimer species Q_3^2 become evident in

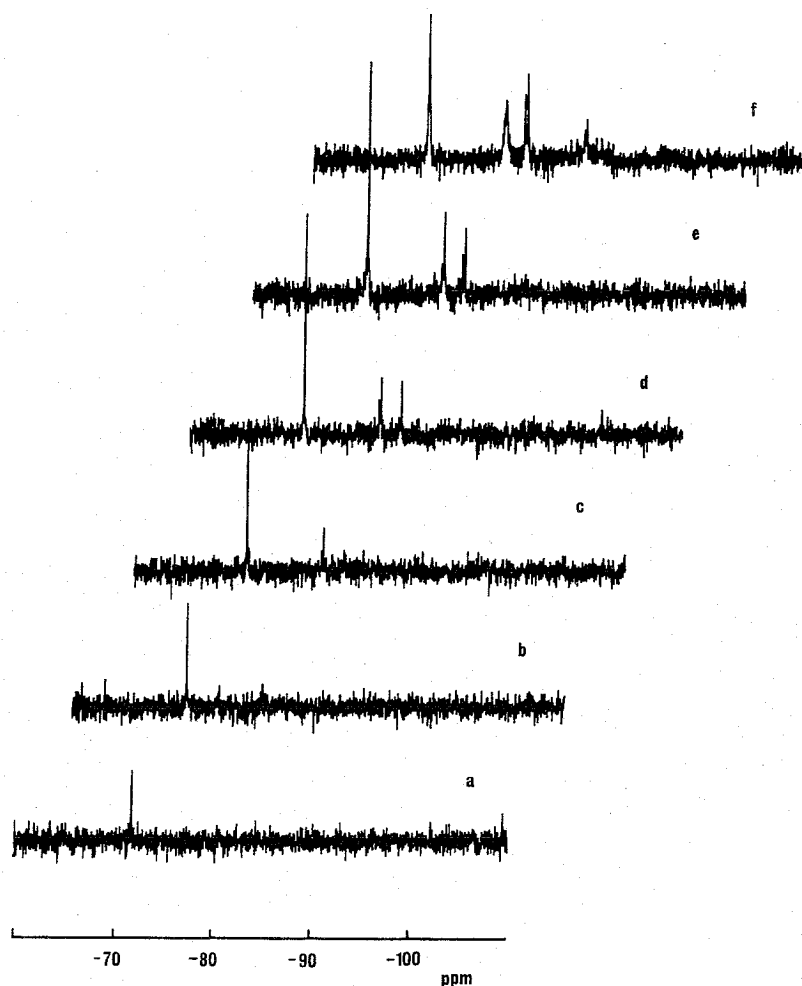
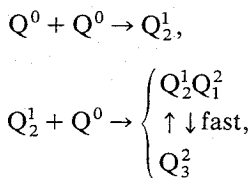


Fig. 6. Dissolution of amorphous silica gel in cesium hydroxide after (a) 15, (b) 30, (c) 60, (d) 105, (e) 165 min and (f) 17 h of reaction as followed by ^{29}Si -NMR. Molar ratio $\text{Cs}_2\text{O} : \text{SiO}_2 = 1 : 1$. Number of scans 200.

the spectra (fig. 6(d)). The increase in cyclic trimer concentration involves an increasing concentration of linear trimer species too, indicating simultaneous formation of, or a fast equilibrium between the two. Recently, Knight et al. [13] used ^{29}Si -2D-EXSY-NMR to examine chemical exchange pathways of steady-state aqueous silica solutions in a very elegant way. They found evidence for the chemical exchange between the monomer Q^0 and the dimer Q_2^1 and between monomer Q^0 and trimer $Q_2^1Q_1^2$. Our results in combination with the results of Knight lead to the conclusion that the oligomerisation reactions after the first stage of dissolution, proceed *via* the same

reaction pathway as the equilibrium reactions in steady state solutions. The first two steps in the oligomerisation of monomeric silica proceed *via* formation a (a) dimer, and (b) linear trimer and cyclic trimer:



After reaching the maximum concentration of the cyclic and linear trimer species, new Q^2 reso-

nances become evident in the spectra (fig. 6(e)). According to the assignments of Harris et al. [10] Q^2 resonances arising in this frequency region correspond with silicate cages and multicyclic silicate structures. Knight et al. [13] concluded from their 2D experiments, that chemical exchange occurs between the bicyclic pentamer $Q_3^2Q_2^3$ and the double three-membered ring Q_6^3 . However, their study does not mention a reaction pathway for the formation of the bicyclic pentamer, although its presence in the equilibrium solution was established unequivocally. Our results from natural abundance ^{29}Si -NMR at 7.05 T are insufficient to postulate a subsequent reaction of the cyclic trimer (poor signal to noise ratio in the region concerned). We observe simultaneously with the formation of Q^2 species, formation of species resonating in the -80ppm region. Substitution of cyclic trimer yields structures with Q_4^2 , Q^1 and Q^3 resonances. However, since the Q^3 resonance originates from a Q^3 site within a three-membered ring, this resonance is positioned in the " Q^2 region" of the spectrum. Prolonged dissolution of the starting silica gel yields a rather broad range of aqueous silicate structures, which are difficult to resolve, since the low concentration of these compounds and the minor differences in resonance frequencies obscure the individual NMR lines in natural abundance spectra.

Figure 7 shows ^{29}Si -MAS-NMR spectra of steady state aqueous silicate solutions at high pH as a function of alkali metal cation. In case of higher pH solutions, silicate species are more ionised, locating the counterion, i.e. the alkali metal cation, more closely to the silicate anion. From the Q^3 -peak asymmetry of spectra presented in fig. 1, we learned that the alkali metal cation must be in close contact with the bigger, Q^3 -site bearing silicate species. Aqueous silicate solutions with molar ratio = 1 however, hardly contain any species with Q^3 sites as is seen in fig. 7. However, observing the Q^2 region (ca. -90 ppm) critically, minor differences in silicate species containing Q^3 sites and substituted three-membered ring structures are noticeable in the case of sodium, potassium and rubidium cations present in solutions; solutions containing lithium and cesium cations, however, differ substantially. Comparing fig. 7(c)

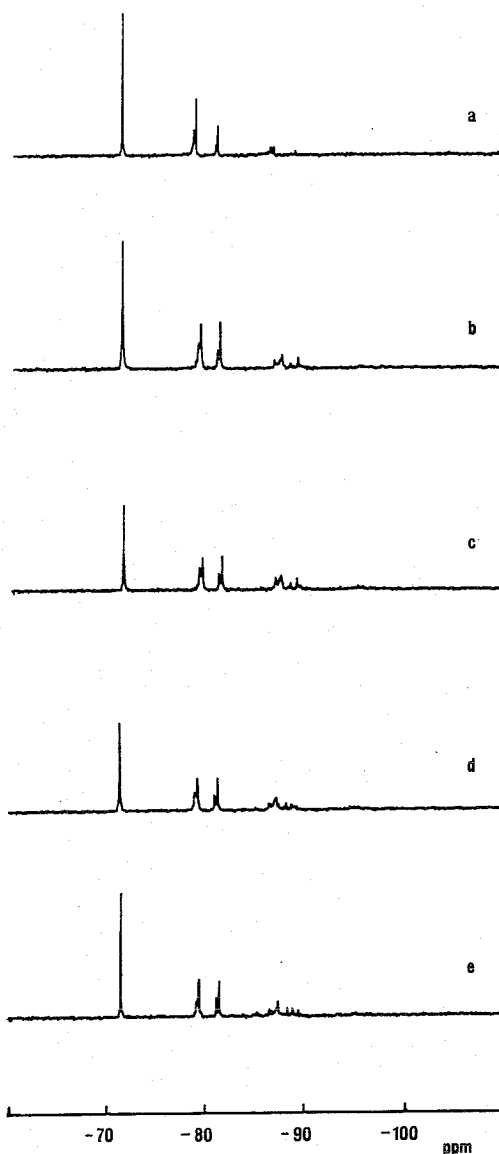


Fig. 7. ^{29}Si -NMR spectra of aqueous silicate solutions in steady state situations: (a) LiOH, (b) NaOH, (c) KOH, (d) RbOH and (e) CsOH; molar ratio $\text{M}_2\text{O}:\text{SiO}_2 = 1:1$. Number of scans 1500.

(silica in potassium hydroxide) with spectra obtained by Knight et al. [13], we observe rather large differences in peak intensities which might be due to structures containing two Q^1 sites.

The rate of dissolution however, exhibits the same dependence on the type of alkali metal hydroxides as was found for the suspension with

molar $\text{SiO}_2/\text{M}_2\text{O}$ ratio = 3; potassium hydroxide dissolves silica gel at a faster rate than lithium, sodium, rubidium and cesium hydroxide do. However, the differences in dissolution rates between either potassium and sodium or potassium and rubidium decrease, suggesting that at these high cation concentrations, differences in promotion effects of the different alkali metal cations are small compared with the overall rate of silica gel dissolution.

At a molar ratio $\text{SiO}_2/\text{Li}_2\text{O} = 1$, lithium silicate is found to precipitate. The precipitate consists of microcrystalline, single chain lithium silicate (Li_2SiO_3) [22] as was deduced from X-ray diffraction analysis and IR spectroscopy.

4. Conclusions

The rate of silica gel dissolution in aqueous alkali metal hydroxides depends on the type of alkali metal hydroxide in solution. An optimum for the dissolution rate at molar ratio $\text{SiO}_2/\text{M}_2\text{O} = 3$ was found for potassium hydroxide.

The compositions of aqueous silicate solutions in steady state situations depend on the type of alkali metal cation present in solution as is concluded from ^{29}Si -NMR peak asymmetries of polymerised silicate species. Minor differences in composition occur for more alkaline solutions (molar ratio $\text{SiO}_2/\text{M}_2\text{O} = 1$). At the molar ratio $\text{SiO}_2/\text{M}_2\text{O} = 1$, the rate of dissolution shows a similar dependence on intrinsic alkali metal cation radius as in the case of low alkaline solutions. At this high pH the differences in dissolution rates between the alkali metal hydroxides NaOH, KOH and RbOH decrease, due to the increased rates in the presence of higher hydroxyl concentrations.

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References

- [1] R.K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).
- [2] L.S. Dent Glasser and G. Harvey, *J. Chem. Soc. Chem. Commun.* (1984) 664.
- [3] L.S. Dent Glasser and G. Harvey, *J. Chem. Soc. Chem. Commun.* (1984) 1250.
- [4] J.A. van Lier, *The solubility of Quartz* (Kemink, Utrecht, 1965).
- [5] B. Sasaki, *Bull. Chem. Res. Inst., Non-Aqueous Solutions* (Tohoku Univ.) 2 (1952) 113.
- [6] G.B. Alexander, *J. Am. Chem. Soc.* 75 (1953) 5655.
- [7] G. Engelhardt, H. Jancke, M. Mäge, T. Pehk and E. Lippmaa, *J. Organometal. Chem.* 28 (1971) 293.
- [8] G. Engelhardt, W. Altenburg, D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.* 428 (1977) 43; R.K. Harris and C.T.G. Knight, *J. Chem. Soc. Commun.* (1980) 726; I.L. Svensson, S. Sjöberg and L.-O. Öhman, *J. Chem. Soc. Faraday Trans. 1*, 82 (1982) 3635; C.J. Creswell, R.K. Harris and P.T. Jageland, *J. Chem. Soc. Chem. Commun.* (1984) 1261; G. Engelhardt and O. Rademacher, *J. Molec. Liq.* 27 (1984) 125; R.K. Harris, M.J. O'Connor, E.H. Curzon and O.W. Howart, *J. Magn. Res.* 57 (1984) 115; I Artaki, S. Sinha, A.D. Irwin and J. Jonas, *J. Non-Cryst. Solids* 72 (1985) 391; R.H. Mainhold, H.P. Rothbaum and R.H. Newman, *J. Coll. Interfac. Sci.* 108 (1985) 234; L. Griffiths, C.S. Cundy and R.J. Plaisted, *J. Chem. Soc. Dalton Trans.* (1986) 2265; L.W. Kelts, N.J. Effinger and S.M. Melpolder, *J. Non-Cryst. Solids* 83 (1986) 353; S.D. Kinrade and T.W. Swaddle, *J. Am. Chem. Soc.* 108 (1986) 7159; J.C. Pouxviel, J.P. Boilot, J.C. Beloeil and J.Y. Lallemand, *J. Non-Cryst. Solids* 89 (1987) 345; C.W. Turner and K.J. Franklin, *J. Non-Cryst. Solids* 91 (1987) 402.
- [9] R.K. Harris, J. Jonas and C.T.G. Knight, *J. Molec. Struct.* 69 (1980) 95.
- [10] R.K. Harris and C.T.G. Knight, *J. Chem. Soc. Faraday Trans. 2*, 79 (1983) 1525, 1539.
- [11] R.K. Harris and C.T.G. Knight, *J. Am. Chem. Soc.* 103 (1981) 1577.
- [12] C.T.G. Knight, *J. Chem. Soc. Dalton Trans.* (1988) 1457.
- [13] C.T.G. Knight, R.J. Kirkpatrick and E. Oldfield, *J. Magn. Res.* 78 (1988) 31.
- [14] G. Engelhardt, D. Zeigan, H. Jancke, D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.* 418 (1975) 17.
- [15] A.V. McCormick, A.T. Bell and C.J. Radke, *Mat. Res. Soc. Symp. Proc.*, Vol. 121 (to be published).
- [16] T.A. Pecoraro and R.R. Chianelli, *J. Catal.* 67 (1981) 430.
- [17] H. Ti Tien, *J. Phys. Chem.* 69 (1965) 350.
- [18] Th.F. Tadros and J. Lyklema, *J. Electroanal. Chem.* 17 (1968) 267.
- [19] J. Depasse and A. Watillon, *J. Coll. Interfac. Sci.* 33 (1970) 430.
- [20] Yu.A. Shchipunov, *Adv. Coll. Interfac. Sci.* 28 (1988) 135.
- [21] J.B. Nagy, P. Bodart, E.G. Derouane, Z. Gabelica and A. Nastro, *Proc. 7th Int. Zeolite Conf.* (Elsevier, Amsterdam, 1986) p. 231.
- [22] F. Liebau, *Structural Chemistry of Silicates* (Springer, Berlin, Heidelberg, New York, 1985).