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Silicate complexes of aluminum(III) in aqueous systems

Thomas W. Swaddle *

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Dedicated to Professor A.B.P. Lever on the occasion of his 65th birthday

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Abstract

Aluminum(III) forms complexes with aqueous silicic acid in neutral or mildly acidic media, and these species are important in the protection of plant and animal life against aluminum toxicity. In highly alkaline media, surprisingly high concentrations of various

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* Tel.: + 1-403-2205358; fax: + 1-403-2841372.
E-mail address: swaddle@ucalgary.ca (T.W. Swaddle).

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aluminosilicate solute species can be achieved at least temporarily, the lifetime of the homogeneous solution depending on the pH, the nature of the cation(s) present, and the Al and Si concentrations. The longevity of aluminosilicate complexes in solution may have technological consequences — for example, in causing silica carryover in the Bayer process for aluminum production. The kinetics of silicate exchange on small, acyclic aluminosilicate solute species in alkaline solutions are much faster than on either the corresponding all-silicate ions or cyclic aluminosilicate species. The kinetic lability of small aluminosilicate species is attributable in part to the ability of Al^{III} to expand its coordination number easily from four to six in acyclic structures, but also to the availability of –OH groups for condensation reactions on aluminate centers, even at high pH where ≡Si–OH functions become deprotonated. One implication is that, contrary to the traditional picture of zeolite formation from structured 'secondary building units' pre-existing in solution, cyclic and cage-like aluminosilicate solute species are not directly involved in the crystallization of solid aluminosilicates such as zeolites from aqueous solutions but simply serve as reservoirs for small, active, acyclic species responsible for crystal growth.

Keywords: Aluminosilicates; Aluminum in biology; Silicon in biology; Aluminum and dementia; Zeolite synthesis; Bayer process

1. Overview

Aluminosilicate minerals are dominant in the crust of the Earth, and are commonly regarded as being very poorly soluble in water. Nevertheless, complexes of aluminum(III) species with silicic acid or silicate anions do exist in aqueous solutions, and in certain strongly alkaline media concentrations of several tenths of moles per liter can be achieved. Such solutions, however, are generally metastable, eventually depositing gels which, at elevated temperatures, may crystallize as zeolites, smectites, etc. [1–6]. Indeed, the underlying theme of this article is that knowledge of the kinetic properties of aqueous aluminosilicates is essential to the understanding of their chemical and biological behavior.

1.1. Industrial and geochemical relevance

The existence and behavior of aqueous aluminosilicates is of practical importance in many diverse contexts. The author's interest in the topic derives from local industrial initiatives to exploit the Athabasca Oil (Tar) Sands of northern Alberta, a vast deposit of very viscous petroleum in a sandy matrix (quartz plus minor amounts of dolomite, clay minerals, etc.). A favored method of recovering the hydrocarbons from the deeper-seated deposits involves injection of water or steam at high temperature and elevated pH, and collecting the oil with the produced water [7]. The matrix, however, is attacked by the hot water, and hydrothermal reactions lead to deposition of voluminous solid aluminosilicates (smectite, analcime, etc.) that can block the production pathway. This could arguably be advantageous in sealing off exhausted parts of the formation, but in any event an understanding of the solution-phase chemistry, in particular of whether transport of Al and Si as long-lived aluminosilicate solutes can lead to deposition in remote sites, is desirable. Similar considerations emerge in fouling of process equipment by glassy aluminosilicates deposited from alkaline liquors in kraft pulp and paper plants [8,9], and also in the Bayer process for making pure alumina from bauxite for aluminum production [10–12] — if long-lived aqueous aluminosilicate species exist in the highly alkaline aluminate solutions, they may cause carryover of Si beyond the 'red mud' stage at which any Si^{IV} present is normally deposited as solid aluminosilicates along with iron(III) wastes.

In the context of geology, environmental geochemistry and oceanography [13–20], the possibility of the involvement of soluble aluminosilicates in weathering processes is of obvious importance. For example, Faimon [19] was able to model the oscillations of aqueous [Al] and [Si] in the experimental weathering of granodiorite, amphibolite, and feldspar samples in terms of the polymerization of aqueous aluminosilicate species.

Aluminosilicate solutions, or gels formed from them, are precursors for the hydrothermal syntheses of zeolites, microporous aluminosilicate solids ('molecular sieves') that are widely used in industry as desiccating agents, ion exchangers, and above all as solid, noncorrosive, shape-selective Lewis-acid catalysts [4,21–25]. The role and mechanism of action of soluble aluminosilicate species in the construction of elaborate zeolite frameworks are not entirely clear [26–33], but, since neither the aqueous aluminosilicate species nor indeed the zeolite products are thermodynamically stable under the reaction conditions, the kinetics and mechanism of substitution at Si and/or Al centers must determine the course of reaction and the nature of the product.

1.2. Toxicity of aluminum

In biology, medicine, and agriculture, aluminum(III) is recognized as being highly cytotoxic to plant and animal life alike [34–47]. The toxicity may have several origins [48], but the strong affinity of Al^{III} for phosphate in phosphorylated biomolecules such as adenosine 5′-phosphates (AMP, ADP, ATP) provides one likely mechanism [49–51]. The binding strengths of Al^{III} with these and other biomolecules are higher, and the associated reaction kinetics are slower, than for the biologically essential ions Mg^{2+} and Ca^{2+}, with the result that Al^{III} can disrupt biological processes that depend on these cations [34]. In humans, Al^{III} is known to be severely neurotoxic, leading to dementia, osteomalacia, and ultimately death when the natural protection of the intestinal and blood-brain barriers is bypassed (as in kidney dialysis treatment with Al^{III}-containing water, since the patients cannot excrete the Al^{III}) [36]. Thus it is also possible that Al^{III} is involved in Alzheimer's disease, in which extreme dementia is associated with the formation of neurofibrillary tangles and senile plaques of amyloid protein in the brain [38,44,45,52]. It is known that Al^{III} can induce formation of similar plaques. Furthermore, absorption of Al^{III} from normal dietary intake is significantly increased in patients with Alzheimer's disease and other forms of dementia [53], and the incidence of Alzheimer's disease in Norway, Canada, the United Kingdom, and southwestern France correlates with the Al^{III} content of drinking water [47,54,55] (but see below). Nevertheless, the possibility of an involvement of Al^{III} with Alzheimer's disease has largely been discounted by the medical community since 1992, when a scanning electron microprobe study failed to detect any Al in plaque cores [56], but Birchall [57] has pointed out that the limit of Al detection of this technique (10^{-4} mol l^{-1}) is considerably higher than Al levels that are known to induce biological effects. Conversely, the sheer ubiquity of Al in the environment makes it difficult to measure low Al burdens reliably — in some cases, the Al contents of control samples have exceeded those of the actual specimens. Thus, while there can be no doubt that Al^{III} is neurotoxic, the question of a link between Al^{III} and Alzheimer's disease remains open but highly controversial.

Yet, in healthy people, ingestion of Al^{III} in amounts far in excess of the potentially toxic level — for example, through consumption of baked goods made with baking soda containing Al^{III} as the source of acid for CO_2 release, of processed cheeses, of nondairy creamers, or of $Al(OH)_3$-based antacids — normally leads to no ill effects. Indeed, despite the correlation noted above of $[Al^{III}]$ in drinking water with the incidence of Alzheimer's disease, the dosage of Al^{III} from drinking water is small compared with that from other food sources, and paradoxically there appears to be no correlation between dose from all sources and disease. It should be borne in mind that the chemical mechanisms of toxicity of the relatively low in vivo Al concentrations derived from dietary sources may differ from those associated with massive doses administered therapeutically, but the potential for toxic effects from even low levels of ingested Al^{III} is evident. Organisms have necessarily evolved with barriers to reject potentially lethal Al^{III} concentrations, and in humans the relevant barriers are the gut epithelium, the skin, and the blood-brain barrier. Soluble Al^{III} in the intestines is mostly absorbed by epithelial mucosal cells, which die and are excreted; only about 2 μg Al per day gets past the intestinal barrier (mainly through loose junctions in the epithelium), whereas some 20 μg per day can normally be excreted in the urine. In the gastrointestinal tract, the pH can range as low as 1 (in the stomach), at which Al^{III} would ordinarily be present as the highly cytotoxic $Al(H_2O)_6^{3+}$, or as high as 7–8 at which the speciation of $Al^{III}(aq)$ in equilibrium with the poorly soluble $Al(OH)_3(s)$ is overwhelmingly $Al(OH)_4^-$ (see below) [58,59]. Also present in foods, however, are chelating ligands such as citrate [60–62] or maltol [63,64] that strongly sequester Al^{III} as uncharged complexes; the speciation of Al^{III} (and, separately, of Si^{IV}) in the presence or absence of such ligands has been the subject of a 34-article series of publications by Öhman and coworkers [65]. In blood serum, a large fraction of the Al^{III} burden is carried by the protein transferrin, but the main small-molecule vehicle for Al^{III} is citrate [36]. Aluminum(III) may penetrate biological barriers in the form of these uncharged chelates, and again it is the citrato complex that seems to be responsible for most of the flow of Al^{III} through the intestines into the blood stream [35]. Such complexes may therefore contribute to neurotoxic effects but by the same token can provide a vehicle for urinary excretion of Al^{III} in healthy individuals (indeed, aluminum tolerance has been induced in papaya and tobacco plants by genetically engineering them to produce excess citric acid in the roots, thereby removing excess Al from the growth tips of the roots [66]). Nevertheless, it would seem unwise for humans to ingest deliberately foods or medicines containing high levels of Al^{III} simultaneously with large amounts of citrates or other chelating agents that bind through oxygen atoms — for example, the use of citrates as flavoring agents for $Al(OH)_3$-based antacids is inadvisable.

Evidence is accumulating, largely through the pioneering work of the late J.D. Birchall and coworkers, that silicic acid ($Si(OH)_4(aq)$) interacts with aqueous Al^{III} so as to reduce the bioavailability (and hence the toxicity) of the latter and, by the same token, to increase the bioavailability of the essential element phosphorus [47,57,67–79]. For example, Birchall et al. showed that the acute toxicity of $Al^{III}(aq)$ to fish (a serious ecological problem in some surface waters because low pH levels produced by acid precipitation release Al^{III} from soils) can be eliminated by silicic acid, which has 'a strong and unique affinity for Al^{III}' [69]. Similarly, the growth rate of the green alga *Chlorella vulgaris* in the presence of Al^{III} was found to be stimulated by $Si^{IV}(aq)$, and the effect was shown to be correlated with an increase in the bioavailability of phosphate [79]. Sequestration of Al^{III} by Si^{IV} appears to protect conifers against damage by Al^{III} [80]. In humans, silicic acid seems to reduce gastro-intestinal absorption of Al^{III} and to enhance its excretion through the kidneys [74,75]. A recent epidemiological study [55] of 3777 subjects aged 65 and over, resident in southwestern France, has confirmed a clear positive correlation of dementia with $[Al^{III}] \geq 0.1$ mg l^{-1} (which may represent a threshold level), and an inverse correlation with $[Si^{IV}]$ (independent of $[Al^{III}]$), in drinking water. Thus, $Si^{IV}(aq)$ appears to be nutritionally essential to a wide variety of life forms as an antidote to Al^{III} [81], and, to the delight of chemistry students, it has been pointed out that, because grasses such as barley concentrate silica, an excellent dietary source of bioavailable silica is beer [82].

It is reasonable to suppose that the biological role of $Si^{IV}(aq)$ as an antidote to Al^{III} involves complexation of Al^{III} by silicic acid or silicate anions to form aqueous hydroxyaluminosilicate species (HAS). (Williams [83], however, has cautioned that this supposition may be simplistic inasmuch as Si^{IV} seems to provide some protection against Al^{III} even at pH < 5.5, where, as noted below, HAS formation is relatively unimportant.) This review seeks to summarize what is known about such aqueous complexes, particularly with regard to the rates at which they form and break up.

2. Speciation of Al^{III} and Si^{IV} in aqueous solution

2.1. Aluminum(III)

The speciation of Al^{III} in aqueous solutions over a wide range of pH has been reviewed by Martin [36,84]. In brief, for dilute solutions above pH 3, the only detectable form of aqueous Al^{III} (in the absence of complex-forming counter-ions) is $Al(H_2O)_6^{3+}$, while at pH 4–5 the loss of a proton to form $Al(H_2O)_5OH^{2+}$

becomes significant, and in the range pH 5–7 these ions coexist with $Al(H_2O)_4(OH)_2^+$, $Al(OH)_3(aq)$, and $Al(OH)_4^-$ in varying proportions. Around pH 5, polymeric cations including the Keggin cation $Al_{13}O_4(OH)_{24}(OH_2)_{12}^{7+}$ (described below) can form, but anticipated species such as $(H_2O)_4Al(OH)_2Al(OH_2)_4^{4+}$ appear to be unimportant [6,85]. In this respect, and also in the narrowness of the pH band in which any Al species other than $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$ and $Al(OH)_4^-$ are significant, Al^{III} differs sharply from Fe^{III} [84], which is about three orders of magnitude more acidic.

On the alkaline side, there is very little evidence for the existence of Al^{III} species other than the tetrahedral $Al(OH)_4^-$ over the entire accessible pH range [86]. In particular, ^{27}Al-NMR and infrared–Raman spectra are inconsistent with the existence of the putative linear 'AlO_2^-' ion often invoked in the older literature. ^{27}Al-NMR evidence suggests the presence of minor amounts of $(HO)_3AlOAl(OH)_3^{2-}$ at high Al^{III} concentrations (6 mol l^{-1}) [86] (the solid potassium salt of this anion is known [87]) and of $Al(OH)_6^{3-}$ at extreme alkalinities (23 mol l^{-1} NaOH) [85], but these observations simply reaffirm that $Al(OH)_4^-$ is the only Al^{III} species of any significance in alkaline aqueous solution from physiological pH (ca. 7.4) up to the very high alkali concentrations typical of the Bayer process. There is no evidence for the existence of deprotonated aluminate species such as $Al(OH)_3O^{2-}$ in alkaline solution, although dielectric relaxation studies indicate that proton exchange on $Al(OH)_4^-$ is rapid in solutions of alkalinity around 1 mol l^{-1} [88].

It may be noted that there is a shift in preferred coordination number of Al^{III} as the degree of deprotonation increases. Thus, Al^{III} is six-coordinate in $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5OH^{2+}$, both six- and four-coordinate in $Al_{13}O_4(OH)_{24}(OH_2)_{12}^{7+}$ (in which a central tetrahedral AlO_4 unit is linked to four surrounding $Al_3(OH)_8(OH_2)_3$ blocks that contain Al in octahedral environments), and four-coordinate in $Al(OH)_4^-$.

2.2. Silicon(IV)

Silicic acid ($Si(OH)_4$), which exists as such only in solution, is isoelectronic with $Al(OH)_4^-$ but, because 'Si^{4+}' is smaller than Al^{3+}, there is little tendency toward six-coordination, and the higher charge-to-radius ratio results in a greater acidity ($pK_a(1) = 9.5$–9.9 depending on the medium, $pK_a(2) \sim 12.7$, $pK_a(3) \sim 15$ [89]) for the neutral $Si(OH)_4$ than for the anionic aluminate. Thus, in alkaline solutions, $Si(OH)_4$ is deprotonated to various degrees whereas $Al(OH)_4^-$ is not. In dilute neutral or acidic solutions, silicic acid is present as monomeric $Si(OH)_4$, but unlike the aluminate ion it undergoes various degrees of oligomerization at higher concentrations, the oligomers being more acidic than the monomer, $pK_a(1)$ values as low as 6.5 having been reported [89]. Molecular mechanics simulations of chain branching in the oligomerization process confirm the experimental activation energy of 50 kJ mol^{-1} for gelation [90,91].

In alkaline solution, a striking variety of oligomeric silicate anions has been shown to exist, primarily by ^{29}Si-NMR spectroscopy (Fig. 1) [6,92–96]. The degree of connectivity n of a particular Si atom to other Si centers (via bridging O atoms) is conventionally represented as Q^n, and one typically finds ^{29}Si resonances corresponding to Q^0 (monomer), Q^1 (terminal), Q^2 (singly bridging) and Q^3 centers (corners of cage structures). Q^4 Si centers are not usually seen in ^{29}Si-NMR spectra of homogeneous alkaline silicate solutions [95], probably because formation of a Q^4 center would be a starting point for gelation, but Harris and coworkers [96] have detected Q^4Si^{IV} in highly concentrated sodium silicate solutions with a high molar ratio of SiO_2 to Na_2O; these Q^4 centers may, however, be present in colloidal silicate sols, in keeping with the expectations concerning gelation. The observed coordination number of Si^{IV} in silicate solutions is invariably four, although higher coordination numbers may be energetically accessible since five- and six-coordinated silicate species have been produced in solution by chelation of silicate

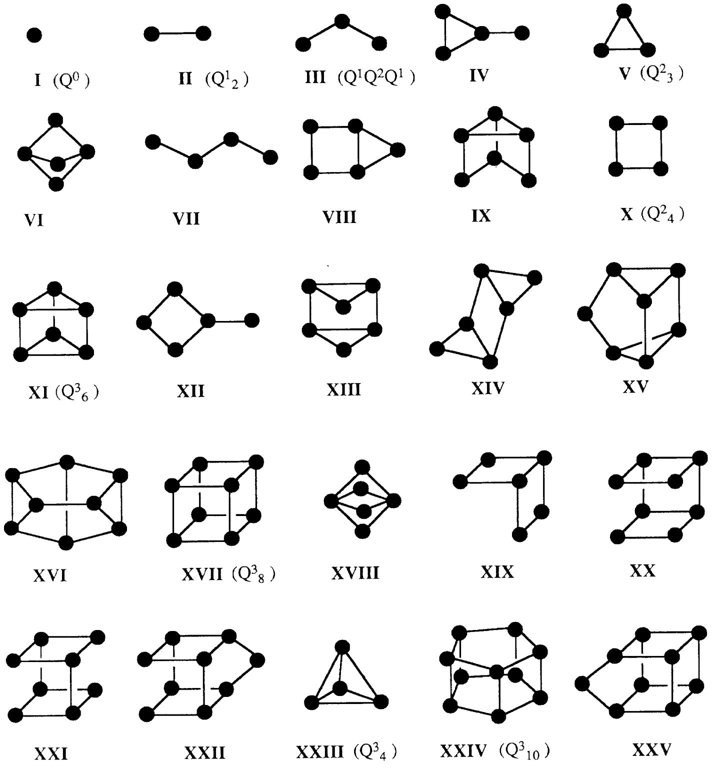

Fig. 1. Silicate anions that have been detected in aqueous alkaline media by ^{29}Si-NMR [92–96]. Filled circles represent Si atoms, tetrahedrally surrounded by oxygen atoms; connecting lines represent links though shared oxygen atoms. From Ref. [6] — reproduced by permission of The Royal Society of Chemistry.

monomer with polyols [97,98] and five-coordinate Si^{IV} has been inferred as an intermediate state in silicate condensation and hydrolysis [99].

The larger silicate oligomers are favored by high [Si^{IV}], low alkalinity, and low temperatures [6,95]. Particular structures may be favored by the nature of the cation present; for example, tetramethylammonium cations favor the cubic octamer Q_8^3 (species XVII in Fig. 1) [100,101], but simple rationales of the relative effects of various quaternary ammonium ions and of alkali metal cations are elusive [102]. In alkali metal hydroxide solutions, the proportions of the Si^{IV} present as the putative tetrahedral Q_4^3 species XXIII [95] as well as the cubic octamer XVII are markedly enhanced when the cations are sequestered with cryptand-2.1.1 or -2.2.2 [103]. The assignment of the ^{29}Si resonance to species XXIII has recently been questioned on the grounds of computations that suggest that a Q_4^3 species would be more strained than other Q_x^3 species and so unlikely to coexist with them in solution [104]; however, the anion XXIII ($Si_4O_{10}^{4-}$) is isoelectronic and isostructural with the very stable, adamantane-like P_4O_{10}, and besides organosilicon compounds having the same Si_4O_6 core have long been known [105,106].

It should be noted that Q^3 centers in silicate anions are necessarily unprotonated in even moderately alkaline solutions, and Q^2 centers may have one proton at pH ~ 10–11 but none at high alkalinities. This may have an important bearing on the reactivities of cage and cyclic silicates and aluminosilicates, as discussed below.

2.3. Aluminosilicates in neutral or acidic solution

Definitive information on the identity, structure, and thermodynamic properties of aqueous hydroxyaluminosilicates (HAS) in acidic or neutral solutions is elusive because the HAS concentrations involved are too low for their direct detection by Raman or either ^{29}Si- or ^{27}Al-NMR spectroscopy, while the lack of redox activity of HAS precludes their direct electrochemical characterization. One must therefore resort to indirect experimental methods. Thus, Yokoyama et al. [107] used gel chromatography with flow injection analysis to demonstrate the existence of HAS in solutions containing Al^{III} and silicic acid at pH 8. Exley and Birchall [108,109] used dialysis, ion exchange and membrane filtration techniques to demonstrate qualitatively that HAS do form in solutions of low (near-physiological) Al^{III} concentrations over the pH range 3.0–9.0. Pokrovsky and coworkers [18] interpreted the decrease of the completely polarized Raman band at 785 cm^{-1} (assigned to $Si(OH)_4(aq)$) in the presence of added Al^{III} at $0 \leq pH \leq 8$ in terms of the formation of $(H_2O)_5AlOSi(OH)_3^{2+}$:

$$Al(H_2O)_6^{3+} + Si(OH)_4 \Leftrightarrow (H_2O)_5AlOSi(OH)_3^{2+} + H^+ + H_2O \quad (1)$$

The equilibrium constant (K) estimated from the Raman data for reaction (1) was in good agreement with that obtained in the same laboratory by potentiometric pH measurements ($\log K = -2.38 \pm 0.10$ at 25°C; $\Delta H = 66.6$ kJ mol^{-1}, 25–150°C) [17]. These data in turn agreed well with those obtained by Farmer and Lumsdon [14] by potentiometric pH measurements ($\log K = -2.48 \pm 0.07$ at 25°C), but were markedly lower than those obtained by Browne and Driscoll [13] using the fluorescence of the complex of Al^{III} with morin ($\log K = -1.07 \pm 0.06$ at 25°C). Exley and Birchall [110] have pointed out that the discrepancy may have originated in Browne and Driscoll's assumption that the Si–Al ratio in the HAS formed in their experiments was 1:1; in fact, it may have been higher and variable, as was suggested by the results of ion-exchange studies [109]. This conclusion receives strong support from the spectrophotometric study of Taylor et al. [111], in which 1,2-dimethyl-3-hydroxy-4(1*H*)-pyridineone (DMHP) and silicic acid competed for Al^{III} at pH 7.2, and which showed that oligomeric forms of silicic acid were some 10^6-fold more effective at scavenging Al^{III} than was monomeric $Si(OH)_4$. Farmer and Lumsdon [112] stress that the solutions used in their measurements [14] were designed to avoid forming colloidal material, and that their system is correctly represented by Eq. (1).

In summary, there is general agreement [14,108–112] that the equilibrium constants of Pokrovsky et al. [17,18] and Farmer and Lumsdon [14] for the formation of $(H_2O)_5AlOSi(OH)_3^{2+}$ are accurate, which means that this species is of negligible importance in natural waters ($[Si^{IV}]$ typically $< 2 \times 10^{-4}$ mol l^{-1}) at 25°C and pH less than about 4.0, but that about 90% of Al^{III} would be complexed as $(H_2O)_5AlOSi(OH)_3^{2+}$ at pH 7 (assuming $[Al] \ll [Si]$). Thus, on the basis of reaction (1) alone, silicic acid in biological fluids at physiological pH can afford a significant degree of protection of living organisms against Al^{III} toxicity, just as has been inferred on biomedical grounds as noted above. For warm-blooded animals, protection via reaction (1) would be more complete, since the reaction is quite strongly endothermic [17], and by the same token the importance of reaction (1) would be greatly increased under the hydrothermal conditions typical of many geological processes. Furthermore, the results of Taylor et al. [111] indicate that reaction (1) represents the minimum efficacy of silicic acid in sequestering Al^{III}, since oligomeric Si^{IV} can be up to six orders of magnitude more effective. At present, however, there is little information on the simultaneous multiple interactions that are likely to occur in biological systems between Al^{III}, Si^{IV} and various biomolecules such as phosphorylated proteins [113] and chelating agents such as citrate [114] or catechol [115].

These observations can explain the correlation noted in Section 1.2 between the incidences of ostensibly Al^{III}-related afflictions (including Alzheimer's disease, Parkinsonism, osteomalacia, and ischaemic heart disease [34]) and the Al^{III} content of public water supplies despite the lack of any dose–effect correlation in total Al^{III} intake. Birchall and Chappell [47] were the first to recognize that, because the Al^{III} and silicic acid contents of natural waters are inversely related, the epidemiologically significant factor is probably not the Al^{III} content per se but rather the lack of biologically available silicic acid that would otherwise provide protection against Al^{III} poisoning. Thus it is that silicon must be regarded as a biologically essential element [70–74,81].

In their study of the mechanism of HAS formation, Exley and Birchall [109] made the significant observation that silicic acid inhibited the formation of aluminum hydroxide precipitates by replacing hydroxylated Al^{III} at growth sites in the lattice surfaces. Swaddle and Oltmann [116] reported a similar inhibitory effect of silicate ions on the hydrothermal conversion of maghemite (nominally γ-Fe_2O_3) to hematite (α-Fe_2O_3); although the conversion proceeded by a dissolution pathway, the action of silicate evidently involved attack of silicate on the solid phases rather than formation of ferrisilicate species in solution. A secondary pathway in which maghemite yielded goethite (α-FeO(OH)) was also suppressed by silicate. Schwertmann and Taylor [117] found that Si^{IV} also inhibited the conversion of lepidocrocite (γ-FeO(OH)) to goethite in aqueous media; again, the conversion was solution-mediated, but the action of Si^{IV} was ascribed to the suppression of nucleation of goethite, i.e. to a surface phenomenon rather than complexation of Fe^{III} by silicate in solution. The importance of these observations is at least twofold: (a) in the natural environment, the ubiquitous Si^{IV} can seriously retard aqueous reactions involving solid minerals; and (b) laboratory studies of the interconversion of solid oxide/hydroxide phases in aqueous environments must be carried out with strict exclusion of Si^{IV} — thus, conventional glassware must not be used at any stage, especially where alkaline media are involved.

2.4. Aluminosilicates in alkaline solution

The thermodynamic data [17] governing reaction (1) suggest that, in strongly alkaline media, aqueous Si^{IV} will be a very effective scavenger for Al^{III} and vice versa, particularly under hydrothermal conditions (for example, in zeolite synthesis) since ΔH is $+67$ kJ mol^{-1}. The relevant monomeric reactants, however, will now be $(HO)_{4-x}SiO_x^{x-}$ and $Al(OH)_4^-$, and moreover the reactants as well as the aluminosilicate products are subject to variable degrees of polymerization, so a general quantitative treatment is not feasible, particularly at high [Si^{IV}]. Yokoyama et al. [118], using ^{27}Al-NMR with very dilute solutions (0.001 mol l^{-1} Al^{III}, Si–Al ratio ranging from 1 to 5), obtained a formation constant of 22.8 l mol^{-1} for the presumed reaction in 0.10 mol l^{-1} NaOH.

$$(HO)_{4-x}SiO_x^{x-} + Al(OH)_4^- \Leftrightarrow (HO)_3AlOSiO_x(OH)_{3-x}^{(x+1)-} + H_2O \qquad (2)$$

They also found evidence for aluminosilicate polymers in 0.015 mol l^{-1} NaOH, but could not detect complex formation in 1.0 mol l^{-1} NaOH, suggesting that reaction (2) may be less favored for higher values of x. For the more concentrated solutions typical of (say) zeolite synthesis, however, Al^{III} will be complexed strongly by an excess of silicate ions, and conversely minor amounts of silicate in alkaline aluminate solutions (for example, in Bayer process liquors) will, similarly, be scavenged to form aluminosilicate ions. Such simple considerations, however, may be complicated by slow rates of formation of the aluminosilicate solute species. Furthermore, given the very low solubility of many solid aluminosilicates, precipitation of solid products may occur, though not necessarily rapidly. Indeed, the nature of the actual (as distinct from the thermodynamically possible) products may well be determined by reaction kinetics, and this is the thrust of Section 3.

Evidence for the existence of aluminosilicate solutes in alkaline aqueous solutions has come from Raman [119] and ^{27}Al-NMR spectroscopic studies [118,120–123] as well as solubility measurements [8,9,15,124] and trimethylsilylation techniques [125], but detailed information on the nature of the aluminosilicate solute species requires ^{29}Si-NMR spectroscopy [126–132] because the ^{29}Si (nuclear spin quantum number 1/2) gives sharp, relatively well-resolved NMR signals whereas the quadrupolar ^{27}Al nucleus gives broad overlapping resonances. Unfortunately, the ^{29}Si nucleus (natural abundance 4.6%) has rather low receptivity as well as fairly long spin–lattice relaxation times T_1 (typically 3–5 s) in solution, so that long accumulation times as well as quite high Si concentrations are needed to give useful NMR spectra. These factors presently preclude the use of ^{29}Si to characterize HAS in neutral or acidic solutions, in which the solubilities of HAS are low, but Dent Glasser and Harvey [1–3] showed that under strongly alkaline conditions metastable solutions containing up to a few tenths of moles per liter aluminosilicate solutes could be obtained. The studies of Dent Glasser and Harvey [1–3] have recently been extended to higher alkalinities and a wider range of Si–Al ratios by North et al. [5]. The lifetimes of such solutions before gelation or precipitation sets in depend in a complicated way on the nature of the alkali metal cation M^+ present as well as on the temperature and the concentrations of SiO_2, Al_2O_3, M_2O and H_2O (this terminology is used because of the need to define solution compositions unambiguously at high solute concentrations and because the degrees of protonation and oligomerization of the silicate and aluminosilicate solutes are normally not known) [5].

Thus, by judicious choice of solution composition, it is possible to obtain ^{29}Si spectra that allow identification of several aluminosilicate solute species [126–132] and even to follow the kinetics of silicate exchange in these species [133]. The low receptivity of ^{29}Si, however, restricts measurements to the Si-rich side of the Si–Al composition continuum, and furthermore it transpires that aluminosilicate solute species are much more labile in silicate exchange than are their silicate analogues [133], so that extreme chemical exchange line broadening makes it impossible to obtain useful ^{29}Si spectra from concentrated solutions having Si–Al ratios close to 1 despite the anomalously long lifetimes of such homogeneous solutions [5]. By working at temperatures low enough to minimize chemical exchange line broadening (but not so low as to cause viscosity line broadening — in a recent study [133], -5 to $+5$°C was found to be acceptable), at very high alkalinities to reduce the number of oligomers present [95,127], and with high Si–Al ratios, it is possible (but barely so) to obtain aluminosilicate ^{29}Si spectra sufficiently well defined to allow measurement of the rates of silicate exchange on the simplest aluminosilicate species [133]. In other words, extraneous factors limit the power of NMR to characterize aluminosilicate species in alkaline solutions even when there is independent evidence to indicate that they are present in high concentrations.

From experience with the ^{29}Si-NMR of solid aluminosilicates [134], we can expect the resonance frequency of a silicon atom attached to an Al^{III} atom to increase by 4–5 ppm relative to the same site in the equivalent all-Si anion. Thus, we are able to use well-established assignments of silicate ^{29}Si resonances in solution to identify Al-substituted analogues. The number of species present, however, must be kept to a minimum to avoid overlapping resonances. Aluminosilicate solute species that have been identified at least tentatively on this basis [127,129–133] are sketched in

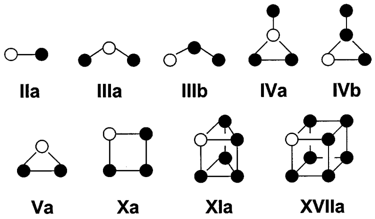

Fig. 2. Aqueous aluminosilicate anions for which ^{29}Si-NMR evidence has been presented [127–133]. Symbols as in Fig. 1, but with open circles representing Al atoms tetrahedrally surrounded by oxygens.

Fig. 2. These assignments can usually be supported by ^{27}Al spectra [120,127,133], but in general ^{27}Al-NMR can only confirm that Al^{III} occupies certain generic Q^n sites, possibly representing several anions simultaneously, and cannot identify individual aluminosilicate anions structurally.

Finally, it may be noted that isolable and fully characterizable organo-derivatives of aluminosilicate cores (e.g. the $(AlOSiO)_2$ ‘4-ring’) have been prepared, and may be of assistance in assigning ^{29}Si resonances in some aqueous aluminosilicate structures [135,136]. Such comparisons, however, may not be realistic; the hexagonal-prismatic double-three-ring core $(SiAl_2O_3)_2$ reported by Roesky and coworkers [136] has ≡Al–O–Al≡ links, whereas linked tetrahedral AlO_4 centers are extremely rare in solid inorganic aluminosilicates and never occur in zeolites [24] (this is known as Loewenstein’s rule [137], which has a sound theoretical basis [138,139]).

3. Kinetics of silicate exchange

3.1. Silicate exchange in alkaline aqueous silicates

^{29}Si-NMR spectra of alkaline aqueous silicate solutions at moderate alkalinities, near-ambient temperatures, and $[Si^{IV}]$ high enough for the convenient signal accumulation times show the presence of too many different silicate solute species to give decipherable information on the kinetics of exchange of SiO_4 units. However, at high alkalinities, moderate $[Si^{IV}]$ and elevated temperatures, the number of species present can be reduced to a manageable few [6,95], and retardation of silicate exchange rate by the high pH offsets the temperature effect to keep the rate within a tractable NMR time-frame [140,141]. In principle, silicate exchange rates can be deduced from the broadening of the ^{29}Si line-widths, but line broadening can be also be induced by anion–cation interactions [142,143] and by adventitious traces of paramagnetic impurities [144–146]. The chief source of paramagnetic impurities in silicate solutions is usually the alkali, and when very high $[M_2O]$ are used this effect is demonstrably strong enough to invalidate line-shape analyses of ^{29}Si spectra in terms of chemical exchange dynamics [146]. Thus, the kinetic information reported from an early study in our laboratory [140,141] should be regarded as semiquantitative, although alkali concentrations in that study were moderate and the results probably were not seriously in error.

The technique of selective inversion recovery (SIR), introduced in silicate chemistry by Harris and coworkers [144], avoids the problems associated with line-shape analysis. In silicate ^{29}Si-NMR, the population of one particular kind of ^{29}Si magnetic site (typically, but not necessarily, the silicate monomer) is inverted with a 180° radiofrequency pulse, and the transfer of magnetization from the inverted site to others is followed through ^{29}Si-NMR spectra taken after selected delays. Because the transfer of magnetization occurs specifically through chemical exchange, unambiguous chemical rate constants (k) can be obtained for the various silicate–silicate exchange modes from the time dependence of the magnetizations M_i of Si sites of the ith kind if the initial (post-pulse) and equilibrium M_i values as well as the longitudinal magnetic relaxation times $T_1(i)$ and stoichiometric silicate concentrations can all be accurately measured [146]. The mathematical analysis of the NMR data is therefore a daunting task unless very few silicate species are present (implying in practice the use of very high alkalinities) and was not attempted in detail in early silicate ^{29}Si-SIR studies [141,144].

Vallazza et al. [146] applied the ^{29}Si-SIR technique to solutions containing 2.8 mol (kg water)$^{-1}$ of Si^{IV} and with a [K$_2$O]:[Si] ratio of 2.3, at 60–90°C. Use of KOH from different manufacturers and of different purity gave different ^{29}Si line widths, and furthermore the correspondingly inconsistent apparent rate constants extracted by line-shape analysis were much faster than those obtained by SIR, which were independent of the source of alkali within the experimental uncertainty (about $\pm 10\%$) — a clear demonstration of the susceptibility of line widths to impurities in the alkali. Under the selected experimental conditions, the only ^{29}Si resonances seen were those due to the monomer (I in Fig. 1), dimer (II), and cyclic trimer (V), with a minor contribution from the acyclic trimer (III). Unfortunately, the weak terminal (Q^1) and bridging (Q^2) Si resonances of III, though clearly resolved at ~5°C where the rate of chemical exchange was negligible, were effectively lost within the broadening envelopes of the II and V resonances, respectively, at 60–90°C. Thus, although III is a likely intermediate in the reaction of I and II to give V, its inclusion in the mechanism for SIR analysis could only be made artificially but fortunately did not significantly change the quantitative picture given by a mechanism involving only the monomer, dimer, and cyclic trimer. True rate constants could be obtained only for the monomer–dimer exchange: $k_1(90°\text{C}) = 0.13\ \text{kg mol}^{-1}\ \text{s}^{-1}$ and $\Delta H_1^{\ddagger} = 67\ \text{kJ mol}^{-1}$ for the formation of the dimer; k_{-1} as $(90°\text{C}) = 1.4\ \text{s}^{-1}$ and $\Delta H_{-1}^{\ddagger} = 65\ \text{kJ mol}^{-1}$ for the dissociation of the dimer. The degrees of protonation of I, II, and V under the experimental conditions are not known; thus, the k_1 and k_{-1} values are conditional. Comparison with the rate constants reported by Harris and coworkers [144] for the same [Si^{IV}] but a lower [K$_2$O]:[Si] ratio of 1.9 therefore cannot be interpreted in detail; however, the rate data given by Harris and coworkers [144] are 2.6–2.9 times faster than those of Vallazza et al. [146] extrapolated to the appropriate temperatures, so demonstrating clearly that deprotonation retards silicate exchange. In other words, silicate exchange at rates measurable on the NMR time-scale requires the availability of $\equiv$Si–OH functions.

An important qualitative observation from ^{29}Si-NMR is that the formation of the cubic Q_8^3 cage species XVII, which is dominant in tetramethylammonium silicate solutions at equilibrium at ambient temperature, occurs only slowly (over many hours, and at the expense of the smaller oligomers and the monomer) in solutions that have been equilibrated to 100°C (which favors the monomer and small oligomers) and then quenched to 20°C [101]. The kinetic inertness of Q_n^3 cage species may reflect the rigidity of the structures, which would inhibit substitution by associative attack (commonly thought to be the primary mode of substitution at Si^{IV} centers [6]). In addition, however, it may be noted that silicate–silicate bond formation is a condensation reaction:

$$\equiv\text{Si–OH} + \text{HO–Si}\equiv \Leftrightarrow \equiv\text{Si–O–Si}\equiv + \text{H}_2\text{O} \quad (3)$$

$$\equiv\text{Si–O}^- + \text{HO–Si}\equiv \Leftrightarrow \equiv\text{Si–O–Si}\equiv + \text{OH}^- \quad (4)$$

and consequently facile silicate exchange involves at least one bound proton, as the inverse pH dependence of the exchange rates confirms, whereas a Q_n^3 cage species is expected to have none even under moderately alkaline conditions ($\text{pH} > 10$). Quite likely, the inertness of Q_n^3 cage species reflects both factors.

Kinrade [147] has used ^{17}O-NMR to study speciation and O exchange kinetics in potassium silicate solutions ($[\text{OH}^-]:[\text{Si}^{IV}] = 1{:}1–2{:}1$) over the temperature range 275–425 K. Oxygen exchange between silicate anions, solvent water, and OH appeared to be governed by reactions (3) and (4), with rates that were consistent with ^{29}Si exchange data and approximately uniform for all O sites (bridging or terminal) in silicate ions. In particular, there was no indication of the very slow O–O exchange found by Knight et al. [148] for the cubic Q_8^3 species XVII in tetramethylammonium hydroxide solutions, but XVII would not have been present in substantial amounts in Kinrade's KOH solutions.

3.2. Silicate exchange in alkaline aqueous aluminosilicates

In a study designed primarily to identify aluminosilicate solute species [127], it was noted that substitution of some Si^{IV} centers in aqueous silicate ions with Al^{III} led to a broadening of ^{29}Si resonances as well as the appearance of new ones. This suggested that Al-substituted silicate ions were undergoing silicate exchange much more rapidly than their parent silicate ions, with an apparent time-scale on the order of 0.1 s for the particular experimental conditions used. The problems that beset NMR studies of silicate exchange kinetics and the identification of aqueous aluminosilicate species, considered above, apply even more forcefully to the study of aluminosilicate Si exchange kinetics by ^{29}Si-NMR because the greater rates of exchange dictate the use of low temperatures (-5 to $+5$°C) together with very high alkalinities to minimize both the exchange rates and the number of solute species involved in the exchange cycles [133].

Harris et al. [122,123] were able to show, using two-dimensional ^{27}Al-EXSY spectra, that the more highly connected Al^{III} sites in aqueous aluminosilicates are relatively inert kinetically, approaching equilibrium only over many hours in aluminosilicate solutions prepared at room temperature, but that some exchange processes (apparently involving aluminosilicate species with low Al connectivity) were rapid. North and Swaddle [133] were able to study some of the latter processes using the higher resolution of ^{29}Si-SIR, but, as noted above, the rapidity of silicate exchange in small aluminosilicate species together with the need to delay gelation force the use of low temperatures, very high alkalinities, and large excesses of Si^{IV} over Al^{III}. Furthermore, under such circumstances, the monomer resonance dominates the ^{29}Si spectra, so that the precision of the SIR method is reduced and in practice one is limited to inversion of the monomer resonance only. The kinetic analysis is yet further complicated by the overlap of some ^{29}Si resonances, notably the Q^1 sites of species IIa, IIIa and IVa and also the Q^2 sites of species IVa and Va (Fig. 2). Thus, the amount of kinetic information on silicate exchange in aluminosilicates that can be extracted by NMR is very limited in extent and precision.

Nevertheless, for solutions of composition 3.0 mol kg^{-1} of SiO_2, 0.1 mol kg^{-1} of Al_2O_3, and 8.0 mol kg^{-1} of K_2O, rate constants $k'_1 = 2.0 \pm 0.2$ kg mol^{-1} s^{-1} and $k'_{-1} = 17 \pm 4$ s^{-1} were obtained for the forward and reverse reactions, respectively, of monomeric silicate with $(HO)_3AlOSiO_x(OH)_{3-x}^{(x+1)-}$ ($x = 2$ or 3) at 0°C to give the acyclic species IIIa [133] (species IIIb, Xa, XIa and XVIIa were not detected in these solutions). Direct comparison of these data with those for Al-free silicate systems is not possible, as the kinetic analysis of the latter could not fully distinguish the acyclic silicate trimer III from the cyclic trimer V and in any case the alkalinity was different. It was, however, clearly seen that the silicate monomer underwent rapid exchange with small aluminosilicate species under conditions for which no silicate–silicate exchange of any kind could be detected [133]. In general terms, small aluminosilicate species are some 10^4-fold more reactive than small all-silicate oligomers at 0°C. Put differently, the lability shown by small acyclic aluminosilicate anions at 0°C is matched by all-silicate oligomers only at about 90°C.

The greater lability of aluminosilicate solutes over silicates may reflect the ability of aluminate centers (by analogy with $Al(OH)_4^-$) to retain a full complement of protons even at high alkalinities and therefore to take part in condensation processes (cf. reactions (1)–(3)). Silicate centers, on the other hand, tend to become deprotonated at high pH; furthermore, the higher the connectivity of the Si center, the fewer the possible proton sites, leading to low reactivity for ring and cage structures. In addition, incorporation of a Si^{IV} center into a cage or ring structure will hinder the usual Si substitution mechanisms, as these involve expansion of the Si coordination number beyond four [141]. By contrast, Al^{III} centers in acyclic aluminosilicate species can expand their coordination number beyond four more readily than can Si^{IV}. On the other hand, when Al^{III} is constrained to be tetrahedral (as in the cyclic species IVa and Va), no silicate exchange is detectable at 0°C and high pH [133]. The picture that emerges, then, is that small, acyclic aluminosilicate species are much more reactive than any silicate oligomers, and that ring or cage structures are particularly unreactive, whether or not they contain Al^{III}.

3.3. Kinetics and mechanism of zeolite formation

There is general agreement that the growth of zeolite crystals from aqueous aluminosilicate gels is a solution-mediated process [21–32,124,149,150], although different mechanisms may prevail at different Si–Al ratios [24]. A significant implication of the conclusions of Section 3.2 is that the building of solid aluminosilicate structures such as zeolites from the solution phase is much more likely to proceed by addition to the growing surface of small aluminosilicate units such as species IIa than of ring or cage structures such as Xa or XVIIa, regardless of any structural features in the latter that may seem to relate to those of the solid phase. In other words, the concept of zeolite synthesis via ‘secondary building units’ — rings and cages pre-existing in the supernatant solution that resemble fragments of the zeolite frameworks that crystallize out [150] — is largely mistaken, as Knight has cogently argued [29]. It is well established that certain cations such as $(CH_3)_4N^+$ or other solute species can promote the formation of particular zeolite structures as well as specific silicate or aluminosilicate rings and cages in solution, but there is often no obvious correlation between the structure of the synthesized zeolite and solute speciation in the supernatant liquor. For example, three-ring species such as V and Va are prominent in many (alumino)silicate solutions, but do not occur in common zeolitic frameworks (an exception that proves the rule is ZSM-18, a seemingly unique case of highly specific templating) [24]. It would seem that ring and cage aluminosilicate solute species, like aluminosilicate gels [24], serve only as reservoirs for relatively slow replenishment of the supply of the active crystal-forming species such as IIa. Indeed, such slow-release mechanisms are usually required to minimize supersaturation and so allow the uniform growth of well-formed crystals.

The kinetics and mechanism of hydrothermal formation of the archetypal synthetic zeolite A ($Na_{12}[Si_{12}Al_{12}O_{24}]\cdot 27H_2O$) have been extensively studied [26–28,30–33,151], and the consensus is that the major (final) stage of crystal growth proceeds by addition of small solute aluminate and silicate or (more likely) aluminosilicate species to the seed crystal. Similar conclusions have been reached regarding the crystallization of analcime [124]. Ciric [28] has analyzed the kinetics of formation of zeolite A in some detail, and has concluded that the building block is indeed small, most likely a ‘dimer’ (presumably $(HO)_3AlOSiO_x(OH)_{3-x}^{(x+1)-}$) or possibly a ‘tetramer’. It should be recognized, however, that the relatively dilute solutions used by Ciric [28] may not be representative of the conditions used in practice for synthesis of zeolite A.

Formation of zeolite A is accelerated by increasing the pH [26,149], and this has been attributed to the breaking down of aluminosilicate polymers (i.e. the nutrient gel) by hydroxide attack [149]. Additionally, however, high pH favors small aluminosilicate anions over cage or cyclic solute species, and we saw in Section 3.2 that it is the smallest aluminosilicate solute species that are the most reactive.

The kinetics of crystal growth from solutions are usually interpreted in Nernstian fashion in terms of the degree of supersaturation of the solution with respect to the particular crystalline product, so that knowledge of the solubility of the solid is required. Sefcik and McCormick [151] report a solubility product $K_{sp} = [Si(OH)_4][Al(OH)_4^-][Na^+] = 1.2 \times 10^{-8}$ mol^3 l^{-3} at 80–90°C for zeolite A in highly alkaline media ($1 \leq [Na^+] \leq 4$ mol l^{-1}), but it is not clear how this is affected by pH, oligomerization, and aluminate–silicate complexation. In any event, the authors [151] caution that proper modeling (including solute speciation) of the immediate aqueous environment of the growing zeolite surface is necessary to obtain physically meaningful supersaturation data.

Newer experimental techniques are providing a more detailed picture of the zeolite crystallization process. For example, Carr and coworkers [30] observed the growth of zeolite A in situ in real time by solid-state ^{27}Al- and ^{29}Si-NMR as well as X-ray diffraction methods, and concluded that a solution-mediated mechanism, involving Q^0 silicate and aluminate ions (more likely $(HO)_3AlOSiO_x(OH)_{3-x}^{(x+1)-}$) produced by dissolution of the gel, was operative rather than a solid-phase hydrogel alternative. Bein and coworkers [33] used low-dose, high-resolution transmission electron microscopy to examine zeolite A nanocrystal growth from clear colloidal aluminosilicate sols. Zeolite A crystal nuclei formed inside amorphous gel particles (40–80 nm) inside three days at room temperature. The later stages of crystal growth (at 80°C) involved solution-mediated transport of the kind discussed above —in effect, growth of zeolite A crystallites occurred by Ostwald ripening fed from the reservoir of nanometer-sized particles. White and coworkers [31] used dynamic light scattering and small-angle X-ray scattering from clear zeolite A precursor solutions to study the growth kinetics of zeolite A crystals in the 80 nm to 2 μm size range, and obtained an activation energy of 75 kJ mol^{-1} for this stage of the growth process (71 kJ mol^{-1} for aged samples).

The question of the mechanism of action of cations and other solutes in determining the structures of both zeolite products and (alumino)silicate solute species is not simply answered, and will not be pursued here. Theories have been advanced variously for a templating, space-filling, or water-structure-modifying action of the structure-directing agent, and there is always the possibility that the agent works by suppressing alternative structures rather than by favoring the one that seems to be promoted. The design of procedures to produce specific zeolitic structures has been considered at length by Davis and coauthors [23,24,152].

3.4. Kinetics of Al^{III}–Si^{IV} interactions at neutral to low pH

As noted in Section 2.3, silicate complexes of Al^{III} are much less stable in acidic than in alkaline solution, and so very little information is available on the *rates* of silicic acid-aqueous Al^{III} interactions at pH < 7. Stone and coworkers [153], however, have examined the interactions of soluble Al^{III} species with silica gel at pH 3–4 using spectrophotometric (silicomolybdic acid complex) methods of detecting dissolved Si^{IV}. They found that both the total amount and the rate at which silica passed into solution can be substantially increased by the presence of hydrolyzed Al^{III} species in solution such as $(H_2O)_5AlOH^{2+}$, $(H_2O)_4Al(OH)_2^+$, and especially $Al_{13}O_4(OH)_{24}(OH_2)_{12}^{7+}$, but that no simple generalizations can be made because the dissolution of silica depended on the pH, the history of the sample (polymerization), the nature of the cation, etc. No direct NMR evidence for Al^{III}–Si^{IV} complexation in solution could be obtained, but strong solution-phase interactions were inferred, and the texture, charge, and reactivity of the silica surface were greatly influenced by the Al^{III}.

These dissolution reactions occurred over time-scales of many days; it is not clear, however, whether Al^{III}–Si^{IV} interactions in solution are also slow in the low-pH regime. On the contrary, the fact that increasing the pH on the alkaline side retards silicate exchange in aqueous aluminosilicates suggests that the analogous processes in neutral or acidic solutions should be fast. If, as argued above, the availability of –OH functions is a prerequisite for facile condensation reactions, then Al^{III}–Si^{IV} reactions at pH 7 should be highly favored mechanistically. An exception may be silicate exchange in oligomeric structures, since the results of Harris et al. [122,123] on alkaline Al^{III}–Si^{IV}solutions show that cage-like aluminosilicate ions in particular can be kinetically inert to substitution. The biomedical implications are therefore that simple HAS species probably form and dissociate quickly, so that their physiological behavior is thermodynamically controlled. However, the sequestration of Al^{III} by oligomeric Si^{IV}, which the results of Taylor et al. [111] suggest may be much more physiologically important (see Section 2.3), may yield kinetically inert HAS species — indeed, the apparently high stability of such complexes may well reflect very slow dissociation kinetics. Thus, a significant part of the protection afforded by silicic acid against Al^{III} toxicity in biological systems may derive from the inferred kinetic inertness of cage HAS structures which, once formed, may retain the Al^{III} for long periods.

4. Conclusions

Complexation of Al^{III} by monomeric aqueous Si^{IV} is not significant below pH 4, but increases in importance as the pH is raised with the result that $Si(OH)_4$ is an effective scavenger of cytotoxic Al^{III} at physiological pH. The efficacy of oligomeric Si^{IV} as an Al^{III} scavenger is evidently several orders of magnitude greater than that of the monomer. This may be related to the kinetic inertness of cage aluminosilicate structures relative to aluminosilicate species of low molar mass, such as has been demonstrated quantitatively by NMR methods for highly alkaline aluminosilicate solutions. The relative lability of small aluminosilicate species such as $(HO)_3AlOSiO_x(OH)_{3-x}^{(x+1)-}$ in silicate exchange implies that they, and not the ring or cage aluminosilicate solutes, are the active agents in the hydrothermal crystallization of zeolites (and presumably other solid aluminosilicates). Thus, the larger aluminosilicate solutes and colloidal particles, like aluminosilicate gels, may act merely as reservoirs for the slow hydrolytic release of the reactive small units. Conversely, however, the longevity of ring and cage aluminosilicate anions has implications for the carryover of Si^{IV} in the Bayer process, and for the fouling of process equipment by deposition of aluminosilicate scales.

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