

Silica dissolution as a route to octaanionic silsesquioxanes

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The octaanion, $[\text{OSiO}_{1.5}]_8^{8-}$ (OA) is a low cost, discrete nano silica particle that can be made directly from high surface area, amorphous silica reacted with Me_4NOH in water alcohol mixtures. It would be ideal if Me_4NOH could be formed *in situ* from, for example, Me_4NCl and NaOH , as long known in the literature. This process would reduce costs and enable recycling of Me_4NCl produced in the functionalization of OA with chlorosilanes, RMe_2SiCl , to form $[\text{RMe}_2\text{SiOSiO}_{1.5}]_8$ organic/inorganic hybrid nanobuilding blocks. Kinetic studies were conducted to assess base-promoted dissolution of fumed silica ($25 \text{ m}^2/\text{g}$) as a function of concentrations, times, etc., to form the octaanion $[\text{OSiO}_{1.5}]_8^{8-}$ using Me_4NOH , NaOH and mixtures of $\text{NaOH}/\text{Me}_4\text{NCl}$. Surprisingly, we find that small amounts of Me_4NCl greatly inhibit the dissolution reaction for reasons that are as yet unknown. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: octaanionic silsesquioxanes; nano building blocks; silica dissolution; tetramethylammonium hydroxide

INTRODUCTION

We recently described kinetic studies on RMe_3NOH ($\text{R} = \text{Me}$ or $\text{CH}_2\text{CH}_2\text{OH}$) promoted dissolution of rice hull ash (RHA) as a simple, direct and high yield route to the octaanions, $[\text{OSiO}_{1.5}]_8[\text{NMe}_3\text{R}]_8$.^{1,2} As a result of these studies, we suggested that the choline derivative ($\text{R} = \text{CH}_2\text{CH}_2\text{OH}$) resembles a potential intermediate in the mechanism whereby diatoms extract silica from seawater, and store and transport it prior to using it to form the intricate structures within which they live. The implication is that the biosilicification process wherein millions of tons of silica, present in seawater as $\text{Si}(\text{OH})_4$, is transformed into biological structures may use nanosized silica building blocks like $[\text{OSiO}_{1.5}]_8^{8-}$ in the process. Also of considerable importance is the fact that $[\text{OSiO}_{1.5}]_8^{8-}$ (OA) is a low-cost precursor to organic/inorganic nanobuilding blocks of the type $[\text{RMe}_2\text{SiOSiO}_{1.5}]_8$ where $\text{R} = \text{alkyl}$, alkenyl , epoxy , etc., which are of considerable potential for numerous academic and commercial applications.^{1–11}

As an extension of the initial work, we sought to produce Me_4NOH *in situ* by reaction of NaOH with Me_4NCl , coincidentally forming relatively insoluble and innocuous NaCl using the hydroxide synthesis process.^{12–14} NaCl was not expected to affect the process, although sodium ions are known to greatly change the composition of soluble silicate ions in solution.^{15–17} The impetus for this effort was to demonstrate the potential to recycle Me_4NCl , a byproduct of the formation of $[\text{RMe}_2\text{SiOSiO}_{1.5}]_8$ from OA and RMe_2SiCl . This approach would make the synthesis of the nanobuilding blocks $[\text{RMe}_2\text{SiOSiO}_{1.5}]_8$ highly cost-effective. We report here the surprising observation that the chloride ion greatly affects the extraction of silica from RHA to produce OA.

EXPERIMENTAL

Materials

All chemicals were reagent-grade, purchased from standard vendors and used as received except ethylene glycol (EGH_2). EGH_2 used in these experiments was: (1) purchased from standard vendors and used as received, or (2) recycled from reaction distillate by distillation under N_2 . The silica used here is fumed silica received as a gift from Cabot Inc. It is amorphous and its specific surface area is $25 \text{ m}^2/\text{g}$. All

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reactions were carried out under N_2 to minimize the chances of exposing the solution to air or moisture.

General methods

Standard conditions for kinetic studies

In a 100 mL round-bottom flask containing 50 ml EGH_2 and selected quantities of tetramethylammonium hydroxide hydrate [$Me_4NOH \cdot 5H_2O$], sodium hydroxide (NaOH) or tetramethylammonium chloride [Me_4NCl] were added. In order to dissolve $Me_4NOH \cdot 5H_2O$, NaOH or Me_4NCl , the solution was stirred for 3 h. Then 1.8 g of silica (30 mmol) was added to the flask and the mixture stirred for 10 min. The flask, equipped with magnetic stirring and standard distillation apparatus, was immersed in an oil bath preheated to $125 \pm 2^\circ C$ for a pre-set reaction time. The flask was then cooled quickly in ice water. The undissolved silica was separated from vacuum filtration. This undissolved silica was washed with 20 ml dry ethanol. The recovered silica was then dried at $130^\circ C$ for 1 h, weighed and the amount of silica dissolved determined. All experiments were repeated at least twice.

Effects of [$Me_4NOH \cdot 5H_2O$] on silica dissolution

SiO_2 (1.8 g, 30.0 mmol) and 33–100 mol% $Me_4NOH \cdot 5H_2O$ (1.8–5.5 g, 10–30 mmol) were added to 50 ml EGH_2 and standard reaction conditions were applied. The reaction time was set to 1 h. The results are shown in Fig. 2.

Effects of reaction time on silica dissolution

SiO_2 (1.8 g, 30.0 mmol) and 100.0 mol% $Me_4NOH \cdot 5H_2O$ (5.5 g, 30 mmol) were added to 50 ml EGH_2 and standard reaction conditions were applied. Reaction times were set to 1, 2, 3 or 4 h. The results are shown in Fig. 3.

Effects of [$Me_4NOH \cdot 5H_2O$] and [Me_4NCl] on silica dissolution

SiO_2 (1.8 g, 30 mmol), $Me_4NOH \cdot 5H_2O$ (5.5 g, 30 mmol) and 0–33.3 mol% Me_4NCl (0–3.3 g, 0–30 mmol) were added to 50 ml EGH_2 and reacted under standard reaction conditions. The reaction time was set to 1.0 h. The results are given in Fig. 4.

Effects of [NaOH] on silica dissolution

SiO_2 (1.8 g, 30.0 mmol) and 25–57.1 mol% NaOH (0.4–1.6 g, 10–40 mmol) were added to 50 ml EGH_2 and standard reaction conditions were applied. The reaction time was set to 1 h. The results are shown in Fig. 5.

Effects of [NaOH] and [Me_4NCl] on silica dissolution

Silica (1.8 g, 30 mmol) was mixed with 0–33.3 mol% Me_4NCl (0–3.3 g, 0–30 mmol) in 50 ml ethylene glycol and 1.2 g NaOH (0.03 mol) and reacted under standard conditions. The results are shown in Fig. 6.

Combined effects of [NaOH], [$Me_4NOH \cdot 5H_2O$] and [Me_4NCl] on silica dissolution

Silica (1.8 g, 30 mmol) was mixed with various amounts of $Me_4NOH \cdot 5H_2O$, Me_4NCl and NaOH in 50.0 ml ethylene glycol and reacted under standard conditions at 1 h. The results are shown in Fig. 7.

RESULTS AND DISCUSSION

We have previously shown that alkali and alkaline metal hydroxides or oxides and simple basic amine compounds can dissolve silica at $200^\circ C$ in EGH_2 to form both stoichiometric products and polyglycolate complexes per reactions (1)–(3) as shown below.^{18–20} The rates of reaction for the amines studies relate directly to their pK_b s (Scheme 1) and their ability to chelate silicon.¹⁹

In these amine promoted reactions, the rates of dissolution at $200^\circ C$ are those shown in Fig. 1. The amine dissolution rates are much smaller than those found for catalytic amounts of alkali hydroxides, which are up to 10 times faster under the same conditions.¹⁹ However, the activation energies for dissolution for all the reactions studied^{18–20} are much the same at $\sim 59 \pm 8$ kJ/mol, suggesting a common dissolution mechanism.

The search for ways to improve reactions rates and reduce temperature led to Me_4NOH , used extensively as a very strong base, especially in alcoholic environments.^{12–14,21} In such environments, its pK_b is not known but is probably of the order of MeO^- in methanol based on the work of Cluett among others.¹⁴ Note that the acidities and basicities of various organic species in nonaqueous solvents have been the subject of much study over long periods of time; however, the estimations of pK_a and pK_b and the corresponding solution pH values, especially for the systems studied here, remains quite difficult, especially where some water is present.^{21,22}

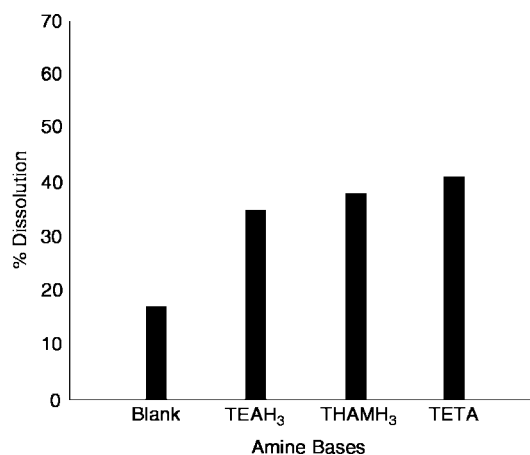
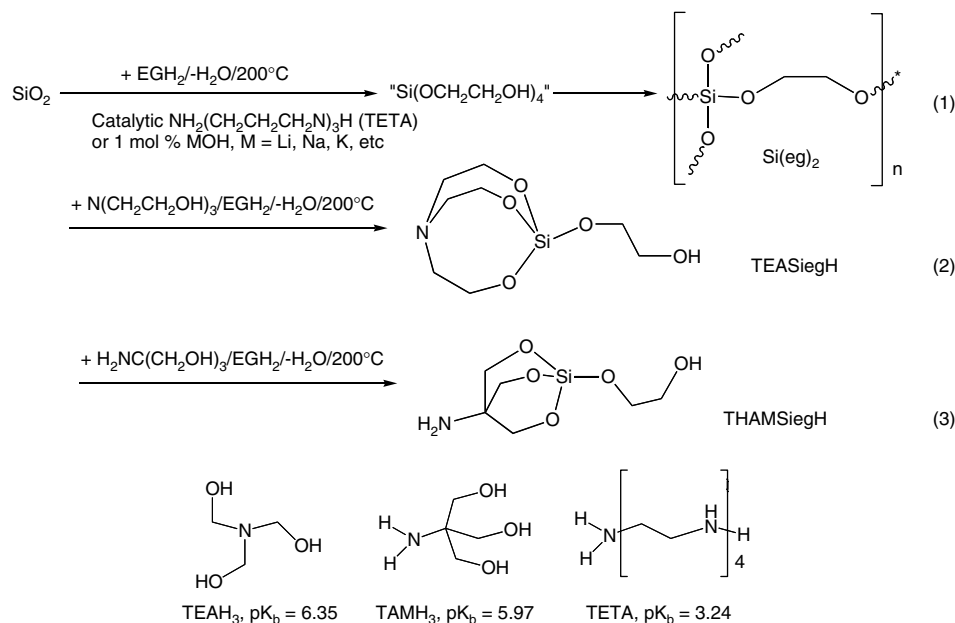


Figure 1. Dissolution of silica at $200^\circ C$ in EGH_2 promoted by amine bases from Reference 19.



Scheme 1. pK_bs of amines in reactions (1)–(3).¹⁹

As recently noted in our review on the subject,² tetraalkylammonium hydroxides to generate ammonium silicates have been studied extensively. Indeed, in preparing this paper, we discovered that the formation of ammonium polysilicates by reaction of silica with alkylammonium hydroxides was first described in 1951 by Merrill and Spencer,²³ some 20 years earlier than reported in our review.²

The goal of the work described below was to develop an understanding of the reaction of Me₄NOH with silica for the reasons discussed in the introduction. For example, we hoped to generate Me₄NOH *in situ* by mixing NaOH with Me₄NCl to form NaCl using the well-known ‘hydroxide synthesis’.^{14–16} This approach was predicated on the fact that NaCl is only modestly soluble in alcohols (1.4 g/100 ml MeOH, 7 g/100 ml EGH₂ at 25 °C)²⁴ thus creating the possibility of forming it *in situ* with the idea of using this approach to recycle Me₄NCl or its choline equivalent. A further goal was to compare silica dissolution with Me₄NOH with NaOH promoted dissolution in ethylene glycol (EGH₂) based on our previous work on this system.^{18–20} These goals provide the basis for the following sets of kinetic studies.

Standard conditions for kinetic studies

The first step was to establish standard conditions. Thus, all reactions were carried out as follows. A flask containing a mixture of 30 mmol silica and 50 ml EGH₂ with various amounts of NaOH, Me₄NOH·5H₂O or Me₄NCl was attached to a distillation apparatus above an oil bath pre-heated to 125 ± 2 °C. The bath was raised to immerse the flask and the reaction was run for a pre-set time. The flask was then cooled quickly in ice water. The undissolved silica yields were

then determined as described in the Experimental section and dissolution rates were then calculated. For silica dissolution to proceed, the reaction must be run under conditions where byproduct water is removed continuously. Before our studies began, it was necessary to confirm of the effect of H₂O contained in commercial Me₄NOH·5H₂O.

Commercially available anhydrous Me₄NOH dissolved in MeOH was distilled to remove methanol to produce solid (CH₃)₄NOH, presumably without waters of hydration. Thereafter, 30 mmol of this solid (CH₃)₄NOH and 30 mmol silica were added to 50 ml of EGH₂ and then the standard experimental procedure was run. These reactions were run several times and an average yield of 26.5 mol% for silica dissolution was obtained compared with a 27.4 mol% yield in case of the pentahydrate. This is within the error limits of our procedure. Thus, the pentahydrate has no apparent effect on silica dissolution. However, one must recall that fumed silica has significant amounts of Si-OH species on its surface and this likely serves as an additional source of water during the dissolution process. Because Me₄NOH is easily degraded to methanol and amine at temperature higher than 130 °C, the reaction temperature was restricted to 125 °C.²²

Effects of [Me₄NOH·5H₂O] on silica dissolution

The first set of kinetic studies established the effects of changes in Me₄NOH·5H₂O concentration on dissolution rates. Using the standard experimental procedure, 33–100 mol% Me₄NOH·5H₂O (vs SiO₂ added) was reacted with a known amount of silica with a reaction time of 1 h. The dissolution yields are plotted in Fig. 2 and indicate that there is a linear dependence on silica dissolution. As noted in our

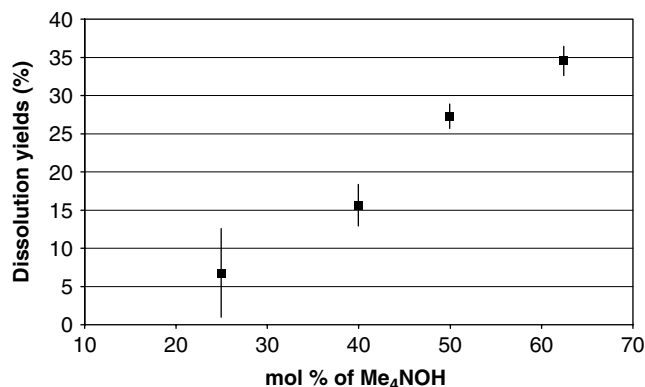


Figure 2. Dissolution of silica (mol%) as a function of Me₄NOH·5H₂O concentration. The plot is of mol% Me₄NOH·5H₂O vs mol% SiO₂ used.

previous work,¹⁹ and in contrast to the NaOH studies, Me₄NOH·5H₂O does not promote the catalytic dissolution of silica. Consequently the mechanism of dissolution must change, as discussed in our RHA dissolution paper.¹

Effects of reaction time on dissolution rates

In order to observe the effect of reaction time on silica dissolution, SiO₂ (1.8 g, 30.0 mmol) and Me₄NOH·5H₂O (5.5 g, 30 mmol) were added to 50 ml EGH₂ and reacted under standard conditions for periods of 1–4 h. As shown in Fig. 3, silica dissolution is linearly dependent with time. The intercept dissolution is about 15 mol% silica, as expected. This is identical within error limits to the blank studies done when NaOH was used to promote dissolution.¹⁹ These results confirm the fact that dissolution is a stoichiometric reaction, and also suggest that there is no degradation of Me₄NOH·5H₂O with time.

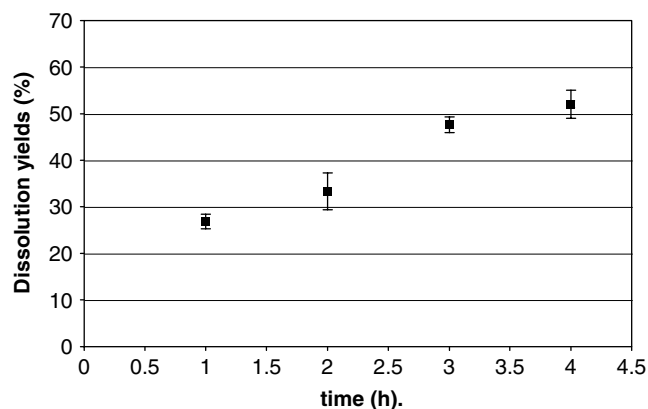


Figure 3. Dissolution of silica (mol%) as a function of time under standard conditions.

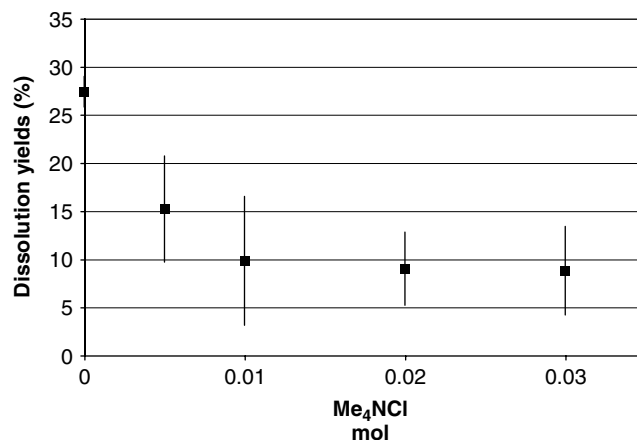


Figure 4. Dissolution of silica (mol%) vs added Me₄NCl under standard conditions.

Effects of added Me₄NCl on dissolution rates

A third set of kinetic studies was carried out to examine the combined effects of Me₄NCl and Me₄NOH·5H₂O on silica dissolution. In this set 5.5 g Me₄NOH·5H₂O (30 mmol) was used with incremental amounts of Me₄NCl added as shown in Fig. 4. Surprisingly Me₄NCl strongly inhibits silica dissolution as shown clearly.

We offer the following explanations but must emphasize that these are quite speculative. First, it is likely that Me₄NCl dissolves in relatively polar EGH₂ to form individual ions. Given that Me₄N⁺ is unlikely to form strong associations with any anion (including Cl⁻), this may leave the chloride free to act as a nucleophile with Si(O)_x surface species to preferentially form pentacoordinated [Si(O)_xCl]⁻ rather than [Si(O)_xOH]⁻ species. [Si(O)_xOH]⁻ may be the first intermediate formed during Me₄NOH promoted silica dissolution in analogy to the pentacoordinated glycolato-silicate species we proposed for alkali glycolate promoted dissolution of silica.¹⁹ Such a species would then coat the surface limiting access of Me₄NOH to the silica surface thereby inhibiting extraction of silicon species.

Alternately, a cluster complex may form between the Me₄NCl/Me₄NOH species, perhaps like a micelle, trapping all the ionic species in a 'hydrophobic' cage. Such behavior with alkyl ammonium species is known.²

A third explanation offered by one of the referees is that the TMACl may inhibit formation of silica intermediate species that form in solution and thereafter condense to OA by greatly reducing the solubility of these intermediates in solution. This may be equivalent to above suggestion about formation of [Si(O)_xCl]⁻ species.

Effects of [NaOH] on silica dissolution

Because we were interested in generating Me₄NOH from NaOH and Me₄NCl, the effect of chloride seems problematic;

nonetheless we attempted to add NaOH to the system to see if we could promote formation of Me_4NOH directly.

SiO_2 (1.8 g, 30.0 mmol) and 25–60 mol% NaOH (0.4–1.6 g, 10–40 mmol) were added to 50 ml EGH_2 and reacted under standard conditions. The reaction time was set to 1 h. The results are shown in Fig. 5 and are identical to our previous studies showing the same blank intercept and catalytic dissolution, something not possible with $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$.¹⁹

Another set of kinetic studies was carried out to examine the combined effects of Me_4NCl and NaOH on silica dissolution. Thus, 1.2 g NaOH (30 mmol) was used for this set of studies with incremental amounts of Me_4NCl . In this instance, the effect of Me_4NCl on silica dissolution is mixed per Fig. 6. For example, reacting 30 mmol of NaOH with 10 mmol of Me_4NCl leaves 20 mmol of unreacted NaOH which can

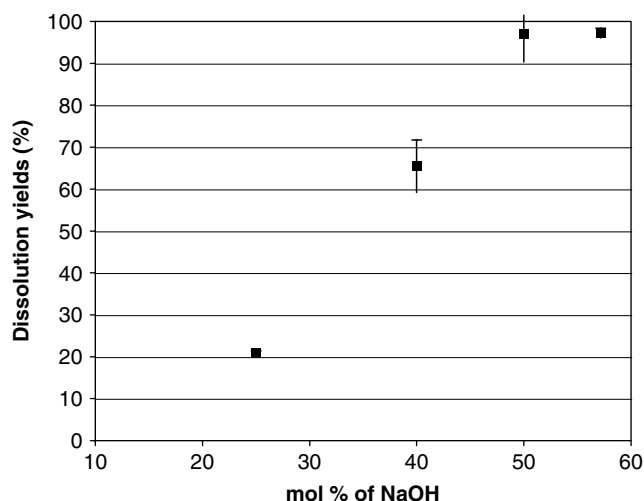


Figure 5. Dissolution of silica (mol%) as a function of added NaOH (mol%) under standard conditions. Data points with no visible error bars were reproduced within the data point size.

dissolve silica. In this case, the silica dissolution yield is ~30%. In contrast, in Fig. 5, the use of 20 mmol (20 mol%) NaOH gave 21% dissolution under standard conditions, about equivalent to a blank reaction. This suggests that the surface acidity of the silica itself may neutralize some of the base. Also, the improved yields with Me_4NCl , may again suggest that some form of complex with groups at the surface occurs. However, this is only speculative and requires further substantiation.

Combined effect of Me_4NOH and NaOH for silica dissolution

One final set of studies was run with a mixture to see if it was possible to observe silica dissolution from a combined system at various ratios. This has practical implications for using these materials for large scale synthesis of the octaanion and nanocomposite precursors thereafter as discussed above.

A set of kinetic studies was carried out using the compositions in Table 1, to examine the combined effect of $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$, and NaOH on silica dissolution at constant $[\text{Me}_4\text{NCl}]$. The resulting data are plotted in Fig. 7.

The efficiency of equimolar concentrations of NaOH and $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$ is higher than two equivalents of Me_4NOH and lower than two equivalents of NaOH. However, Hasegawa has already pointed out that the presence of Na^+ ions controls the equilibrium between formation of octaanion

Table 1. Effects of NaOH and $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$ on silica dissolution

Experiment number	1	2	3
NaOH (mol%)	40	20	0
Me_4NOH (mol%)	0	20	40
Me_4NCl (mol%)	3	3	3

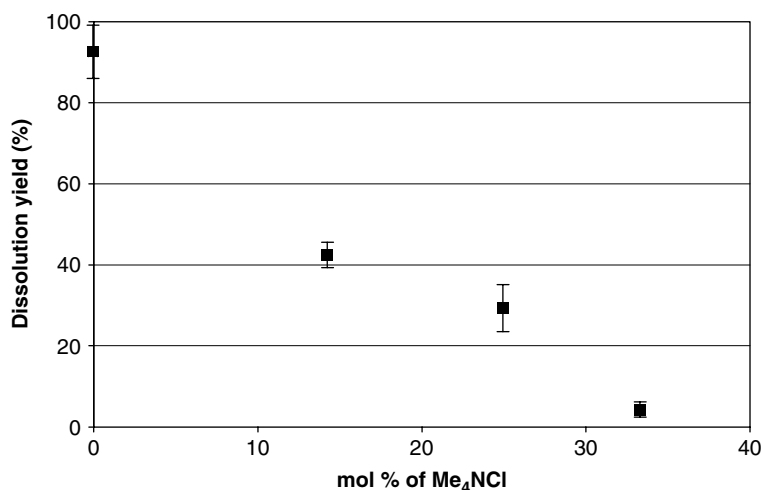


Figure 6. Silica dissolution vs added Me_4NCl with 0.03 mol NaOH under standard conditions.

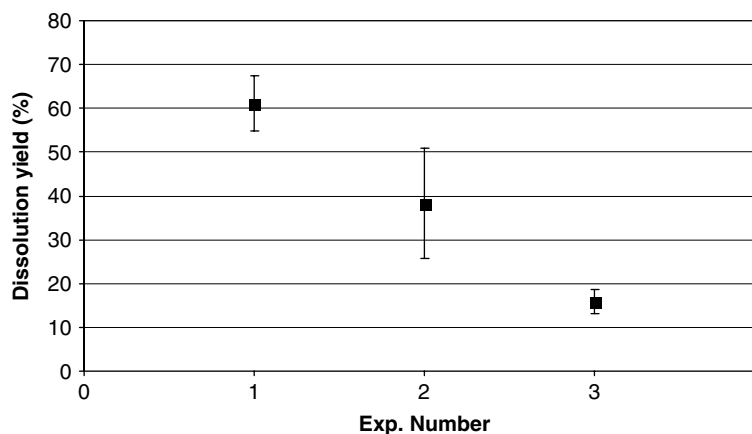


Figure 7. The effects of NaOH and Me₄NOH·5H₂O on silica dissolution.

and simple sodium silicates, suggesting that this approach while effective vis a vis silica dissolution will not offer improved yields of octaanion.

CONCLUSIONS

During studies designed to explore the *in situ* generation of Me₄NOH from NaOH and Me₄NCl, to promote silica dissolution with subsequent formation of the [OSiO_{1.5}]₈⁸⁻ nanobuilding block, we find that Me₄NCl strongly inhibits silica dissolution. These results are quite surprising and although no immediate rationale for this behavior can be offered, we suggest that the formation of some form of surface species prevents reaction of OH⁻ with the silica surface. It may be that Cl⁻ forms a pentacoordinate surface species in preference to a pentacoordinate hydroxide. This will require additional research to prove.

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