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ORIGINAL CONTRIBUTION

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# Depolymerization of soluble silicate in dilute aqueous solutions

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**Abstract** Experiments with diluted solutions of a customary water glass show that the rate of depolymerization depends not only upon pH and the $SiO_2$ concentration, but also varies systematically as a function of the type and concentration of an additional electrolyte. Increasing cation activities of metal chlorides are causing a decrease of the rate constant in the order 1) $Na^+, K^+$, 2) $Mn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}$, 3) $Zn^{2+}, Ni^{2+}, Ce^{3+}, Cu^{2+}$. With respect to anions of sodium salts the rate constants are increasing with increasing activities in the order $NO_3^-, HCO_3^-, Cl^-, SO_4^{2-}$, whereas $HPO_4^{2-}$ causes a decrease. The results permit to identify those components of water which are most responsible for a change of the depolymerization rate and may be used to evalute the properties of a water glass as a possible anti-corrosive agent for water supply systems.

**Key words** Soluble silicate (water glass) – depolymerization – rate constants – effects of electrolytes

## Introduction

Soluble silicate, also called water glass, is a viscous liquid from about 21 to 34 wt% $SiO_2$ and 6 to 18 wt% $Na_2O$. Beginning with a $SiO_2/Na_2O$ ratio of about 2, high molecular weight silicic acid dominates over low molecular weight species, essentially monomeric silicic acid. The high molecular weight, or polymeric silicic acid is supposed to act as an anti-corrosive agent for the pipes of water supply systems [1–3]. Unfortunately, it begins to decompose when diluted. In order to evaluate the possible anti-corrosive properties of a water glass the depolymerization rate must be known.

Previous work has been concerned with the depolymerization of soluble silicate, mostly as a function of pH and temperature, and in a number of cases in the presence of compounds such as NaF, NaCl, $NaHSO_3$, $Na_2S$, KBr, $NH_4F$, and $Al_2(SO_4)_3$ [4–8]. However, these results cannot be applied to the present case because soluble silicates of different composition and provenance have been used. Therefore, experiments have been made with one type of soluble silicate as a function of pH and in the presence of ions occurring in natural waters ($Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, SO_4^{2-}$) and other compounds.

## Analytical procedures

At low total $SiO_2$ concentrations the so-called reaction rate method must be used in order to distinguish between polymeric and monomeric silicic acid [4, 7, 9]. This method implies that the formation of ß-silicomolybdic acid from molybdic acid and either, polymeric or monomeric silicic acid, occurs according to an irreversible pseudo first-order reaction. Thus, the reaction of a mixture of polymeric and monomeric silicic acid may be expressed by two pseudo first-order parallel reactions which yield a common product, according to the equation

$$1 - X_r = \frac{[M]_0}{[T]} \cdot e^{-k_m \cdot t} + \frac{[P]_0}{[T]} \cdot e^{-k_p \cdot t}, \tag{1}$$

where $k_m$ and $k_p$ are reaction rate constants, and $[M]_0$ and $[P]_0$ are the concentrations of monomeric and polymeric silicic acid at the beginning of the measurement, respectively. The quantity $X_r$ is the fraction of silicic acid, relative to the total concentration $[T] = [P]_0 + [M]_0$, which has reacted to ß-silicomolybdic acid.

As in general, $k_m \gg k_p$, the first term of Eq. (1) can be neglected after a short time, so that the further evolution of the ß-silicomolybdic acid may be expressed by the equation

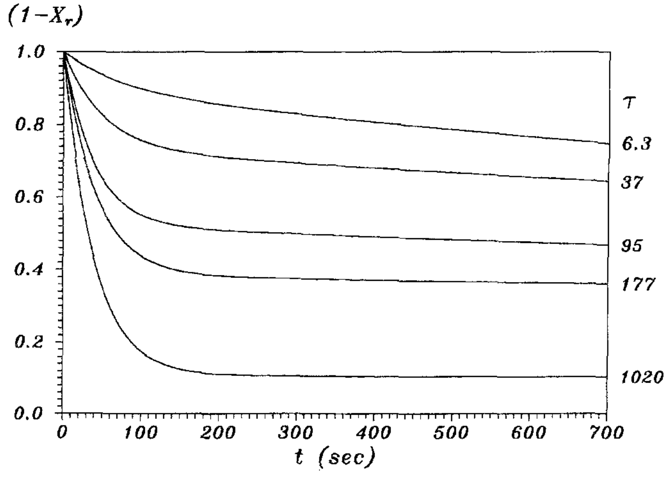
$$1 - X_r = \frac{[P]_0}{[T]} \cdot e^{-k_p \cdot t} \tag{2}$$

Extrapolating to $t = 0$ yields the $[P]_0/[T]$ ratio at the beginning of the measurement.

This procedure has been refined by measuring the evolution of the ß–silicomolybdic acid quasi continuously. For this purpose, in some experiments a ZEISS PMQ II, in others a PERKIN ELMER lambda 17 spectrophotometer was linked to a computer. Values for $k_m$ and $k_p$ were calculated according to Eq. (1), using the computer program SICALC [10]. An example for the formation of the ß-silicomolybdic acid is given in Fig. 1. All measurements yielded $k_m$ values close to 2 ($\text{min}^{-1}$), in agreement with other authors [e.g. 9, 11–13]. The $k_p$ values for the present solutions varied as function of the $SiO_2/Na_2O$ ratio from 0.015 ($\text{min}^{-1}$) at $SiO_2/Na_2O = 3.7$ to 0.031 ($\text{min}^{-1}$) at $SiO_2/Na_2O = 1.9$. Similar values have been reported by Hoebbel and Wieker [14]. The activation energy for the formation of the ß -silicomolybdic acid from polymeric silicic acid, obtained from measurements between 22° and 40 °C, increases from 68 kJ/mole ($SiO_2/Na_2O = 3.7$) to 120 kJ/mole ($SiO_2/Na_2O = 1.9$). The activation energy for the water glass under consideration ($SiO_2/Na_2O = 3.2$) is 80 kJ/mole.

For the measurements sample solutions were mixed with a stock solution (26 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (p.a.), 12.9 ml 25% $NH_3$ (suprapur), and 280 ml 3n $H_2SO_4$ (suprapur), diluted to 1 l). Two portions of this solution were mixed with three portions of a sample solution. The measurements were made at 390 nm. The extinction coefficient was 0.0298($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). pH was kept at 1.2 in order to rule out the formation of ß-silicomolybdic acid [15]. A stock solution containing 3n HCl instead of $H_2SO_4$ was used for the measurements of sulfate bearing sample solutions. Measurements in presence of phosphate were corrected considering the extinction of phosphate molybdic acid. The total $SiO_2$ concentration of the sample solutions was obtained by either AAS methods, or by measuring the ß -silicomolybdic acid evolved in solutions which had completely depolymerized over night at pH = 10.

**Fig. 1** Formation of ß-silicomolybdic acid. The curves represent sets of measurements of samples drawn in a single depolymerization experiment at time intervals, τ, between 6.3 and 1020 minutes. For simplicity eight additional curves have not been included. 1-Xr: see Eq. (1). pH = 5.74, 23 mg/l $SiO_2$. Waterglass WG 37/40



## Depolymerization experiments

The experiments were carried out in a 4-l PE-vessel at a temperature of 20 (+/−1)°C, stirring with a PTFE-propeller at 400 rpm (Fig. 2). The pH was recorded continuously and measured with WTWpH91 and INGOLD EQ-S7/1M-S7 electrodes. Buffer solutions or small quantities of HCl or NaOH added via a computer-controlled METHROM Titrino 702SM were used in order to keep pH constant. Water saturated $CO_2$–$N_2$ mixtures of defined compositions were bubbled through the solution in order to maintain a pH close to 7.

In each experiment the water glass was added to the solution while mixing vigorously at about 800 rpm for 10 s. After defined periods of time samples were withdrawn with a plastic syringe, acidified, and measured as described above.

## Starting material

In all experiments the customary water glass WG 37/40 was used. This product has a relatively low viscosity of 1.8 P [16]. A $SiO_2/Na_2O$ weight ratio of 3.15 and a $SiO_2$ content of 25.2 wt% were measured, as well as a density of 1.35 g/cm$^3$ and a refractive index of 1.389. The pH of the

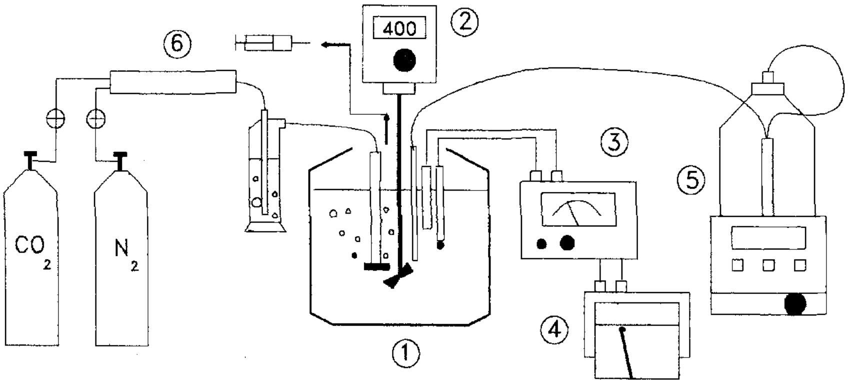


**Fig. 2** Setup for depolymerization experiments. 1: reaction vessel. 2: stirrer. 3: pH meter. 4: recorder. 5: titrator. 6: gas mixer

water glass is about 12. If diluted to 25 mg/l $SiO_2$ a constant pH = 9.3 is attained rapidly. The product contains about 10% monomeric silicic acid. The $k_p$ value immediately after dissolution is 0.0184 ($min^{-1}$). According to ILER [17] this value corresponds to a molecular weight of about 3800 g/mole. The pertinent polymer diameter is about 1.7 nm. Thus, the composition of the major portion of the polymers may be taken as $\{SiO_{1.6}(OH)_{0.8}\}_{56}$ [13].

## Kinetics of depolymerization

The depolymerization of silicic acid occurs via a number of complex reactions which have not been deciphered yet in detail, so that the kinetics must be treated empirically. Stade and Wieker [4] have observed that the overall reactions follow a pseudo first-order law. On the other hand, Baumann [5] describes depolymerization according to a pseudo second-order law. This latter case applies to the water glass under consideration.

Figure 3 shows the variation of the concentration of polymeric silicic acid according to the expression

$$\frac{[T]}{[P]_0} = [T]\cdot k_D\cdot \tau + \frac{[T]}{[P]_i} \qquad (3)$$

where $k_D$ is an overall reaction rate constant, and $[T]$ is the total concentration of silicic acid. $[P]_i$ is the concentration of polymeric silicic acid at the beginning, and $[P]_0$ is the concentration after a time period, $\tau$, of an experiment. It should be noted that $[P]_0$ in Eq. (3) has the same meaning as in Eqs. (1) and (2). The intercept of the straight line in Fig. 3 at $\tau = 0$ was $[T]/[P]_i = 1.123$, yielding an initial concentration of monomeric silicic acid close to 11%. ILER [17] reported the same percentage for a water glass with a rather similar $SiO_2/Na_2O$ ratio.

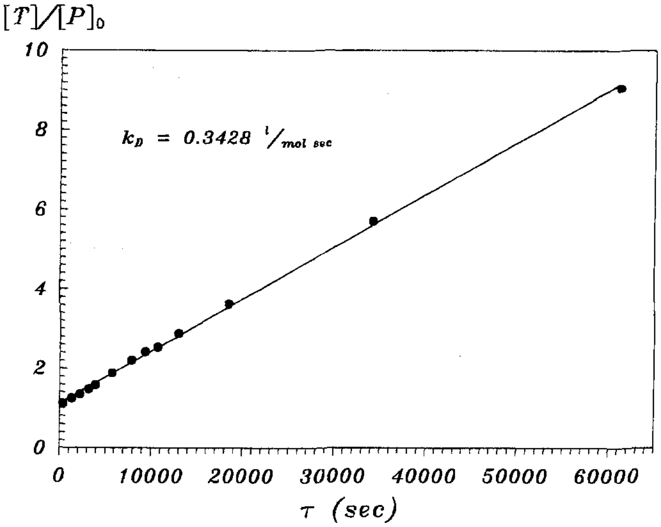


**Fig. 3** Depolymerization expressed according to a second order reaction (Eq. (3)). $[T]$ / $[P]_0$: ratio of total to polymeric silicic acid at any time, obtained from Eq. (1). Same experiment as in Fig. 1

## Depolymerization at various boundary conditions

In the following sections results from experiments are reported which have been made at different concentrations of silicic acid, as a function of pH, and at different compositions of the solution. The results are based on at least eight measurements for any experiment (e.g., Fig. 3). In all cases depolymerization occurred according to a pseudo second-order reaction, so that the results are discussed as variations of the $k_D$ values.

### Variation of $k_D$ as a function of pH

Figure 4 shows the variation of $k_D$ as a function of pH for two sets of experiments with different concentrations of

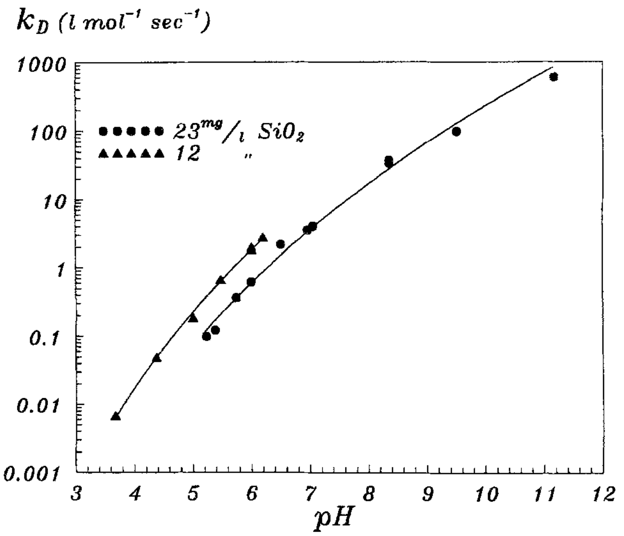


**Fig. 4** Variation of $k_D$ as function of pH at two different $SiO_2$ concentrations. At 12 mg/l $SiO_2$ reliable rate constants cannot be obtained above pH = 6.22 because depolymerization occurs rather rapidly

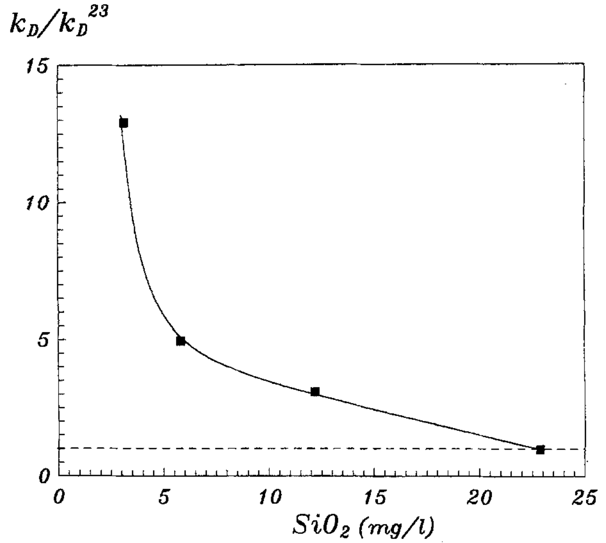


**Fig. 5** Variation of $k_D/k_D^{23}$ as a function of the $SiO_2$ concentration. pH = 6.22. $k_D^{23}$: rate constant for 23 mg $SiO_2$/l

silicic acid. With respect to 23 mg/l $SiO_2$ the $k_D$ values are increasing by almost 4 orders of magnitudes between pH = 5 and 11. With respect to 12mg/l $SiO_2$ an increase over 3 orders of magnitudes between pH = 5 and 11. With respect to 12 mg/l $SiO_2$ an increase over 3 orders of magnitude is observed in the acidic range. The relationship between pH and $k_D$ (l·mole$^{-1}$·s$^{-1}$) may be expressed by the equations

$$k_D = pH^{11.59}\cdot 1.814\cdot 10^{-9},$$

$$\text{pH: } 3.6 \text{ to } 6.2,\ 12\ \text{mg/l}\ SiO_2\ , \qquad (4)$$

and

$$k_D = pH^{11.61}\cdot 5.662\cdot 10^{-10},$$

$$\text{pH: } 5.2 \text{ to } 11.2,\ 23\ \text{mg/l}\ SiO_2\ , \qquad (5)$$

## Variation of $k_D$ as a function of the silica concentration

The above example shows that $k_D$ varies not only as a function of pH, but also depends upon the $SiO_2$ concentrations. This is confirmed by four sets of experiments with initial concentrations from 3.8 to 23 mg/l $SiO_2$, at a constant pH of 6.22. Figure 5 shows that the $k_D$ values are decreasing with increasing $SiO_2$ concentration. The variation of $k_D$ relative to $k_D^{23} = 0.903$(l·mol$^{-1}$·s$^{-1}$) at 23 mg/l $SiO_2$ may be expressed by the equation

$$\frac{k_D}{k_D^{23}} = 290\cdot C^{-3.2} - 0.18\cdot C + 5.1\ , \qquad (6)$$

where $C$ = mg $SiO_2$/l. The half-life time $\tau_{1/2} = ([P]_i\cdot k_D)^{-1}$ is between 27 and 48 min.

## Variation of $k_D$ as a function of solution compositions

In order to pursue changes of depolymerization rates upon the addition of electrolytes, two sets of experiments have been made. In one set metal chlorides were used so that the observed variations may be attributed to effects produced by cations at a given anion. These experiments were carried out in solutions buffered at pH = 6.22 (0.01 mol/l sodium acetate, 0.0005 mol/l acetic acid). For these conditions constants for the formation of metal acetate complexes are well known, and the formation of hydroxides can be ruled out. In the other set of experiments sodium salts were used in order to evalute the effects produced by anions at a given cation. These experiments were made at a carbonate buffered pH = 8.33 (3.75 g $NaHCO_3$ in 1 l solution). At this pH, bicarbonate is dominating over any other carbonate species so that the effects produced by other anions can be compared to that produced by "pure" bicarbonate. In any case the initial $SiO_2$ concentration was 23 mg/l.

The results are reported as variations of $k_D^r = k_D^a/k_D^0$ as a function of ion activities ($k_D^a$, $k_D^0$: constants for a given ion activity and for the "pure" buffer system, respectively). The required activity coefficients have been calculated from the Davies equation [18] using the constants for the formation of complexes given by Sillen and Martell [19] and Kolat and Powell [20]. Table 1 summarizes $k_D^r$ values, concentrations, and activities. The relationship between

**Table 1** Rate constants, concentrations, and ion activities with respect to metal chlorides ($Na^+$ to $Pb^{2+}$) and sodium salts ($Cl^-$ to $HPO_4^{2-}$). $k_D^r = k_D^a/k_D^0$; $k_D^0 = 1.83\ l \cdot mol^{-1} \cdot s^{-1}$ for cations; $k_D^0 = 35.9\ l \cdot mol^{-1} \cdot s^{-1}$ for anions and $Mg^{2+*}$ ($MgCl_2$ at pH = 8.3)

| | Concentrations · $10^3$ mol/l | | | | Activities · $10^3$ mol/l | | | | $k_D^r$ $l \cdot mol^{-1} \cdot s^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Na^+$ | 5 | 10 | 50 | 100 | 4.41 | 8.68 | 40.3 | 76.4 | 0.866 | 0.851 | 0.653 | 0.580 |
| $K^+$ | 5 | 10 | 50 | 100 | 4.40 | 8.64 | 39.7 | 75.0 | 0.965 | 0.873 | 0.735 | 0.416 |
| $Ca^{2+}$ | 1 | 5 | 10 | 50 | 0.597 | 2.63 | 48.7 | 17.2 | 0.634 | 0.171 | 0.139 | 0.123 |
| $Mg^{2+}$ | 1 | 5 | 10 | 50 | 0.592 | 2.70 | 50.1 | 19.5 | 0.716 | 0.316 | 0.113 | 0.0843 |
| $Mg^{2+*}$ | 10 | 15 | 20 | | 3.51 | 5.19 | 6.82 | | 0.824 | 0.641 | 0.443 | |
| $Sr^{2+}$ | 1 | 5 | 50 | | 0.587 | 2.60 | 16.0 | | 0.582 | 0.140 | 0.107 | |
| $Mn^{2+}$ | 1 | 5 | 50 | | 0.556 | 2.49 | 16.4 | | 0.557 | 0.343 | 0.100 | |
| $Zn^{2+}$ | 0.1 | 0.5 | 1 | 5 | 0.596 | 0.293 | 0.576 | 2.57 | 0.365 | 0.295 | 0.285 | 0.220 |
| $Ni^{2+}$ | 0.1 | 0.5 | 1 | 5 | 0.0576 | 0.283 | 0.557 | 2.49 | 0.501 | 0.281 | 0.244 | 0.0599 |
| $Cu^{2+}$ | 0.1 | 0.5 | 1 | | 0.0440 | 0.217 | 0.429 | | 0.398 | 0.191 | 0.129 | |
| $Ce^{3+}$ | 0.1 | 0.5 | 1 | | 0.0247 | 0.0941 | 0.235 | | 0.579 | 0.199 | 0.229 | |
| $Pb^{2+}$ | 0.1 | | | | 0.0215 | | | | 0.476 | | | |
| $Cl^-$ | 10 | 20 | 100 | 200 | 8.03 | 15.8 | 72.9 | 137.5 | 1.04 | 1.153 | 1.26 | 1.28 |
| $NO_3^-$ | 25 | 100 | 200 | | 17.3 | 59.4 | 102.7 | | 1.08 | 1.14 | 1.20 | |
| $HCO_3^-$ | 22.3 | 44.6 | 66.8 | | 17.3 | 33.7 | 48.2 | | 1.11 | 1.20 | 1.21 | |
| $SO_4^{2-}$ | 10 | 50 | 100 | | 2.97 | 9.72 | 14.43 | | 1.03 | 1.30 | 1.49 | |
| $HPO_4^{2-}$ | 0.01 | 0.05 | 0.1 | | 0.00445 | 0.0222 | 0.0444 | | 0.753 | 0.736 | 0.652 | |

the relative rate constant and activities (pH and $SiO_2$ constant) may be expressed according to the empirical equation

$$\ln k_D^r = A \cdot (e^{(a) \cdot B} - e^{(a) \cdot C}) , \tag{7}$$

where $(a)$ denotes the activity of a given ion. Values for the constants A, B, and C are listed in Table 2.

Figure 6 compares $k_D^r$ values for the metal chlorides, derived from Eq. (7) up to an activity of $5 \cdot 10^{-4}$. Three groups of electrolytes may be discerned. The effect produced by NaCl and KCl is rather small up to activities of $5 \cdot 10^{-4}$. At higher activities the $k_D^r$ values are decreasing to 0.580 (NaCl) and 0.416 (KCl). A much stronger decrease of $k_D^r$ is exercised by the chlorides of the earth alkalines and manganese. The $k_D^r$ values are decreasing to about 0.1 up to activities of about 0.02 (Table 1). Cerium and the transition elements zinc, nickel and copper are causing a very strong and virtually identical decrease up to activities of about $5 \cdot 10^{-5}$. At higher activities the individual $k_D^r$ values are leveling out. Lead, added as acetate, probably shows a rather similar behavior as indicated by $k_D^r = 0.476$ at an activity of $2 \cdot 10^{-5}$ (Table 1).

Figure 7 shows the variation of the $k_D^r$ values as a function of anion activities of sodium salts, calculated from Eq. (7). The strongest effect is produced by hydrogenphosphate. Up to rather small activities of $5 \cdot 10^{-5}$ the $k_D^r$ values are decreasing by a factor of 0.7. However, the other anions are exercising a reversed behavior. Sulfate causes an increase of the rate constant by a factor of 1.5, up to an activity of 0.014. The effect produced by nitrate is much smaller so that rather high activities are required for a notable increase of the rate constant ($k_D^r = 1.2$ at an activity of about 0.1, Table 1). A similar increase is shown by bicarbonate added in excess to the amount present in the reference solution. Sodium chloride, which causes a decrease of $k_D^r$ at pH = 6.2 (Fig. 6), shows an increase of the rate constant at pH = 8.3.

The behavior of sodium chloride indicates that the rate of depolymerization may depend on both electrolyte concentration and pH. Figure 8 compares $k_D^r$ values for a constant NaCl concentration of 0.1 m as a function of pH. It

**Table 2** Coefficients for Eq. (7)

| | A | B | C | | A | B | C |
|---|---|---|---|---|---|---|---|
| $Na^+$ | 0.5057 | − 46.43 | 1 | $Cu^{2+}$ | 1.341 | − 23412 | 983.94 |
| $K^+$ | − 0.4067 | 15.60 | 1 | $Ce^{3+}$ | 1.4518 | − 18733 | 113.2 |
| $Ca^{2+}$ | 2.095 | − 578.9 | 1 | $Cl^-$ | − 0.2174 | − 54.82 | 1 |
| $Mg^{2+}$ | 2.474 | − 359.5 | 1 | $NO_3^-$ | − 0.1604 | − 31.44 | 1 |
| $Sr^{2+}$ | 2.254 | − 638.2 | 1 | $HCO_3^-$ | − 0.2069 | − 44.67 | 1 |
| $Mn^{2+}$ | 2.273 | − 287.4 | 1 | $SO_4^{2-}$ | 0.5009 | 41.74 | 1 |
| $Zn^{2+}$ | 1.188 | − 31006 | 94.82 | $HPO_4^{2-}$ | 0.2567 | − 4.00E5 | 11000 |
| $Ni^{2+}$ | 1.149 | − 33951 | 360.3 | | | | |

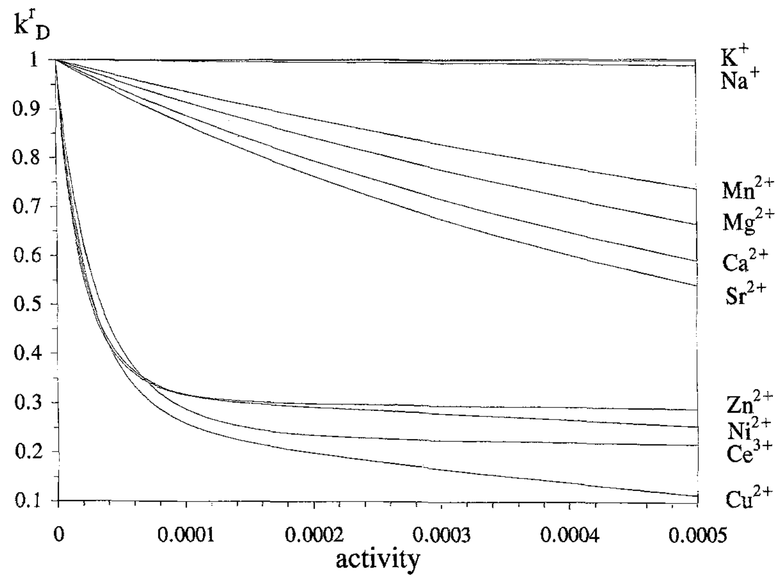


**Fig. 6** Rate constants as a function of cation activities of chlorides. $k^r_D = k^a_D/k^0_D$ ($k^a_D$, $k^0_D$ : constants for a given ion activity, for the pure buffer system). pH = 6.22. $SiO_2$ = 23 mg/l. Experiments with manganese and cerium were made under $N_2$ atmosphere

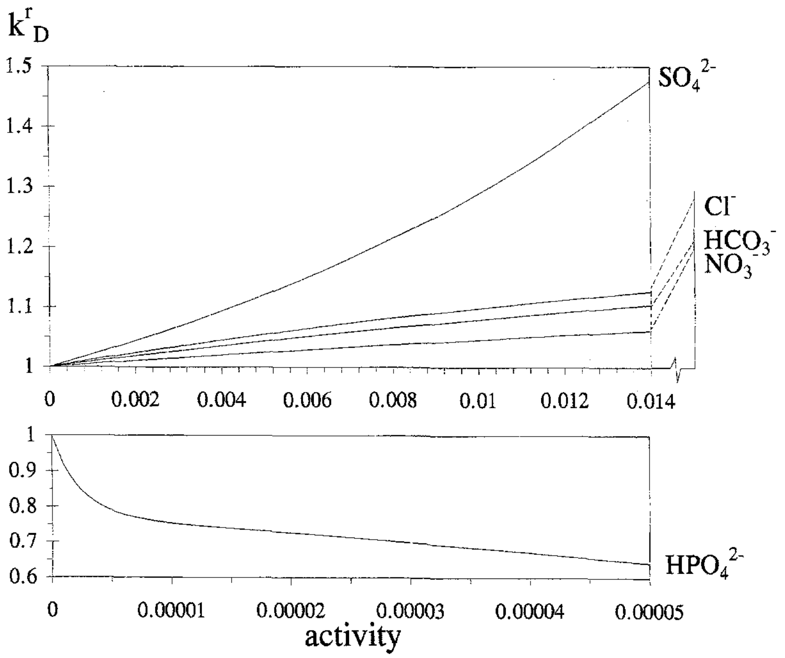


**Fig. 7** Rate constants as a function of anion activities of sodium salts. $k^r_D = k^a_D/k^0_D$ ($k^a_D$, $k^0_D$ : constants for a given ion activity, for the pure buffer system). pH = 8.33. $SiO_2$ = 23 mg/l

may be seen that the rate constants are increasing above pH = 7.7, whereas they are decreasing below this pH value. The overall change is $\Delta k^r_D/\Delta pH = 0.33$. Figure 9 compares the results for $MgCl_2$ at pH = 6.2 (Fig. 6) with those from experiments at pH = 8.3. At either pH the $k^r_D$ values are decreasing with increasing magnesium activity. However, at a given activity $k^r_D$ decreases considerably if pH increases, and vice versa.

## Summary and discussion

Depolymerization experiments were carried out using diluted solutions of a customary water glass with a $SiO_2/Na_2O$ weight ratio of 3.15 and a $SiO_2$ content of 25.2% (WG 37/40). All experiments show that the depolymerization is described best by a pseudo second-order

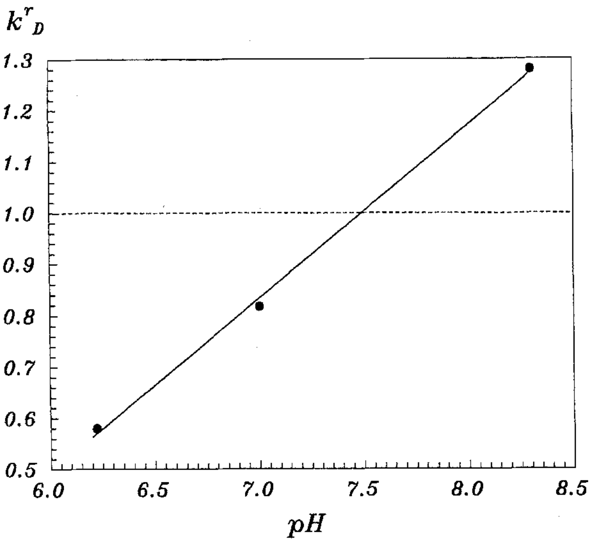


**Fig. 8** Variation of $k^r_D$ as a function of pH at 0.1m NaCl. $SiO_2$ = 23 mg/l

law. However, the reaction rate constant, $k_D$, varies as a function of pH, the initial $SiO_2$ concentration, and the type and concentration of an additional compound. This shows clearly that the kinetics of depolymerization do not follow strictly a "true" second-order reaction, but comprise a number of complex parallel and consecutive reactions which are most difficult, if not impossible to decipher. Nevertheless, the kinetics may be expressed by a pseudo second-order law for a given set of boundary conditions.

The depolymerization rates are related systematically to the above variables and may be expressed by empirical equations. The strongest control on the rate constant is exercised by pH. This is attributed to $OH^-$ which may act as a catalyst for either depolymerization or polymerization [21–22]. Values for $k_D$ vary from about 0.005 to 700 ($l \cdot mole^{-1} \cdot s^{-1}$) from pH about 3.5 to 11.3. Equations (4) and (5) permit to calculate $k_D$ for a given pH.

The relationship between $k_D$ and $SiO_2$ (pH = 6.2) may be expressed by Eq. (6). The values for $k_D$ increase by a factor of about 13 from 3.8 to 23 mg/l $SiO_2$.

The variation of the rate constant as a function of ion activities can be expressed by Eq. (7). With respect to metal chlorides three groups of electrolytes may be discerned: 1) NaCl and KCl which cause a rather small decrease of the rate constant, 2) the chlorides of earth alkalines and manganese which exercise a much stronger decrease, and 3) chlorides of transition elements and cerium which cause a very strong decrease. In general, the rate constants are decreasing in the order potassium, sodium, manganese, magnesium, calcium, strontium, zinc, nickel, cerium, and copper. With respect to anions the rate constants are increasing with increasing activities in the order sodium nitrate, -bicarbonate, -chloride, and -sulfate. The strongest effect is produced by sulfate. In contrast to the metal chlorides much higher activities are required to provoke a substantial change of the rate constant. However, rather small activities of hydrogenphosphate leads to a strong decrease.

The chemical mechanisms of the observed phenomena are still unknown, essentially. Nevertheless, the present study permits to identify those compounds of a water glass which are most responsible for a change of the depolymerization rate. Table 3 summarizes concentrations and activities of two different bicarbonate-sulfate ground waters. Experiments with the low concentrated ground water yielded $k_D = 28$, in close agreement with $k_D = 27$ calculated from Eq. (5) using $pH_{ex}$ (Table 3). It appears that the rate of depolymerization depends essentially on pH. The rather small activities of any of the ions are unimportant. With respect to the high concentrated ground water the measured rate constant is $k_D = 3$ versus a calculated value

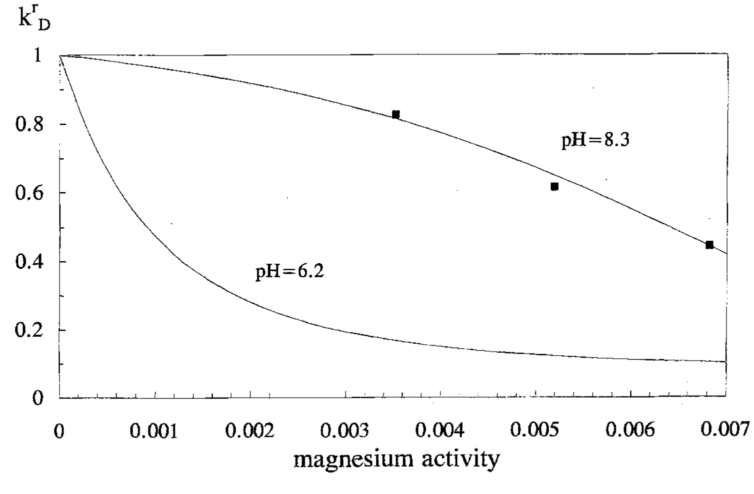


**Fig. 9** Variation of $k^r_D$ as a function of the cation activity of $MgCl_2$ at different pH values. $SiO_2$ = 23 mg/l

**Table 3** Ion concentrations and activities of two ground waters $W_1$ and $W_2$. $k_D$ is the measured depolymerization rate (1/mol s). $pH_s$: pH at sampling, $pH_{ex}$: pH after adding WG 37/40 to yield 23 mg $SiO_2$/l

| | Concentration (mg/l) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $pH_s$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $HCO_3^-$ | $SO_4^{2-}$ | |
| $W_1$ | 7.4 | 8.2 | 1.1 | 38 | 10 | 17 | 90 | 37 | |
| $W_2$ | 7.5 | 9.8 | 1.6 | 551 | 57 | 15 | 186 | 1362 | |
| | Activity (mmol/l) | | | | | | | | |
| | $pH_{ex}$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $HCO_3^-$ | $SO_4^{2-}$ | $k_D$ |
| $W_1$ | 8.3 | 0.33 | 0.03 | 0.68 | 0.30 | 0.43 | 1.4 | 0.25 | 28 |
| $W_2$ | 7.6 | 0.33 | 0.03 | 4.8 | 0.80 | 0.3 | 2.4 | 4.4 | 3.1 |

$k_D = 10$. This decrease must be attributed to the high concentrations of $Ca^{2+}$ and $Mg^{2+}$. It is certainly not caused by the even higher concentrations of sulfate (and bicarbonate) which should provoke a slight increase of the rate constant.

Manganese, strontium, zinc, nickel, cerium, copper and phosphate are trace components of natural waters. However, they may be applied in order to control the depolymerization rate of soluble silicate in industrial water systems.

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