

Analytical aspects of silica in saline waters — application to desalination of brackish waters

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Abstract

In several areas like water desalination and geothermal applications, the occurrence of silica in the used waters is undesirable. Many studies show the complexity and the diversity of the topic. For a better understanding of some of its analytical aspects the determination of amorphous silica content of natural waters, was carried out by various analytical methods. Amorphous silica solubility, at different temperatures, pH and ionic strength was studied. The heat of silica dissolution and the activity coefficient of dissolved silica were determined. A microcomputer program with the LabView graphical language was designed to calculate the solubility and concentration factors that indicate the limits above which silica precipitation occurs. This practical tool was applied to a variety of aqueous salt solutions and to some brackish waters from South Tunisia, at different temperatures. Predicted solubility values, using deduced silica activity coefficient, are in good agreement with experimental results.

Keywords: Amorphous silica solubility; Brackish waters; Concentration factor; Silica activity coefficient

1. Introduction

In many parts of the world including the South of Tunisia (North Africa), the efficient use

of water in desalination processes, by reverse osmosis and electrodialysis, and in geothermal applications is limited by the solubility of silica. Silica contained in brackish and geothermal waters may cause precipitation and/or fouling

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problems. To supply South Tunisian population with drinkable water, desalination of brackish waters is recommended. However, these waters contain a significant amount of silica. This means that pretreatment configurations have to take into account the amorphous silica scaling, in junction with the other known scales (especially calcium carbonate and calcium sulfate varieties).

Different analytical aspects of silica are reviewed in previous papers [1–4]. It appears that silica may occur in natural waters in different forms linked to a special terminology as follows:

- “Soluble” or “dissolved” silica containing monomers, dimers and polymers of silicic acid.
- “Insoluble” or “colloidal” silica, which results from high polymerization of silicic acid containing particles, and three dimensions gel networks.
- “Reactive” silica containing monomers and dimers forms that react with ammonium molybdate within 10 min. The other forms are referred to as “non-reactive” silica.

Silica presents with carbonic acid two weak acid-base systems, which are closely involved in the control of the pH and precipitation phenomena. Temperature, pH and ionic strength factors have substantial influence on the form and on the solubility of amorphous silica [4]. Many investigators are still interested in these parameters which continue to give place to recent works [5–9]. The form of silica in solution has significant influence on its determination methods (total, reactive or non-reactive silica) and on its removal systems (by warm and hot lime softening, ion exchange and activated alumina). Prediction and prevention of these phenomena require the study of the effect of different parameters on silica solubility. In such practical way data from published studies [4,11–13] and from our laboratory results, on silica solubility, were used to predict silica scaling. This preliminary attempt is necessary to include silica problem in a wider

and complex study devoted to the thermodynamic description of saline waters. Then, to predict and to avoid mineral scales, concentration factors that indicate the limits above which silica precipitation occurs, are calculated, using a microcomputer processing with a graphical language named LabView. This practical tool is applied, at different temperatures, to a variety of brackish waters from south Tunisia.

2. Material and methods

2.1. Chemical products

Demineralized water without silica and all solutions were stored in very clean polyethylene containers or bottles. The amorphous silica used was silica gel 40 (Fluka). Ammonium molybdate, sulfuric acid, fluorhydric acid, tartaric acid and all reagents used were Prolabo reagent grade.

2.2. Analytical procedure

For solubility determinations the mixtures of solid silica and solution (in the proportion of 5 g of solid for 1 l of solution) was stirred in a Prolabo thermostatted water bath for about 15 d as described previously [4]. The temperature of each system was kept constant to within $\pm 0.2^\circ\text{C}$. Three analytical methods were used for silica analysis:

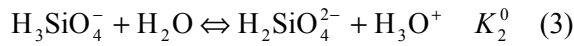
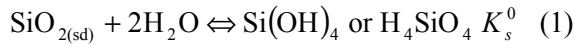
- Standard gravimetric method [14]
- Atomic absorption using a Perkin Elmer model AAS 3300 instrument [15] at 251.6 nm
- Spectrocolorimetric determination with a Perkin Elmer model 550 was used to measure the optical density of yellow or blue colored silicomolybdic acids [16]. The optical density of the yellow silicomolybdic acid was measured at 380 nm. The molybdenum blue, obtained by the reduction of the yellow colored silicomolybdic acid, with 1 amino-2 naphthol-4 sulfonic acid was measured at

810 nm. Tartaric acid was added to remove interference from phosphorous.

2.3. Silica solubility calculation

The present paper proposes a useful and practical tool for the prediction of amorphous silica solubility and concentration factors. An algorithm was developed which calculates the concentrations of all species present at specified temperature and pH. It was achieved on a Power Macintosh using the LabView graphical language. Calculations were based on analytical determinations, on data deduced from solubility measurements and the following equations with subsequent iteration procedure.

The hydrolysis of solid silica and the ionization of monosilicic acid in aqueous solutions are represented by the following equilibria:



The thermodynamic equilibrium constants concerned are:

$$K_s^0 = \frac{(\text{H}_4\text{SiO}_4)}{\text{SiO}_{2(\text{sd})} (\text{H}_2\text{O})^2} = \frac{\gamma_{(\text{H}_4\text{SiO}_4)} [\text{H}_4\text{SiO}_4]}{(\text{H}_2\text{O})^2} \quad (5)$$

$$= \frac{K_s}{(\text{H}_2\text{O})^2}$$

$$K_1^0 = \frac{(\text{H}_3\text{SiO}_4^-)(\text{H}_3\text{O}^+)}{(\text{H}_4\text{SiO}_4)(\text{H}_2\text{O})} = \frac{\gamma_{(\text{H}_3\text{SiO}_4^-)} [\text{H}_3\text{SiO}_4^-] [\text{H}_3\text{O}^+]}{\gamma_{(\text{H}_4\text{SiO}_4)} [\text{H}_4\text{SiO}_4] (\text{H}_2\text{O})} \quad (6)$$

$$K_2^0 = \frac{\gamma_{(\text{H}_2\text{SiO}_4^{2-})} [\text{H}_2\text{SiO}_4^{2-}] (\text{H}_3\text{O}^+)}{\gamma_{(\text{H}_3\text{SiO}_4^-)} [\text{H}_3\text{SiO}_4^-] (\text{H}_2\text{O})} \quad (7)$$

$$K_w^0 = \frac{(\text{H}_3\text{O}^+)(\text{OH}^-)}{(\text{H}_2\text{O})^2} = \frac{(\text{H}_3\text{O}^+) \gamma_{(\text{OH}^-)} [\text{OH}^-]}{(\text{H}_2\text{O})^2} \quad (8)$$

$$S = [\text{H}_4\text{SiO}_4] + [\text{H}_3\text{SiO}_4^-] + [\text{H}_2\text{SiO}_4^{2-}] \quad (9)$$

$$S = \frac{K_s^0 (\text{H}_2\text{O})^2}{\gamma_{(\text{H}_4\text{SiO}_4)}} \left\{ 1 + \frac{\gamma_{(\text{H}_4\text{SiO}_4)} 10^{\text{pH}} K_1^0 (\text{H}_2\text{O})}{\gamma_{(\text{H}_3\text{SiO}_4^-)}} + \frac{\gamma_{(\text{H}_4\text{SiO}_4)} 10^{2\text{pH}} K_1^0 K_2^0 (\text{H}_2\text{O})^2}{\gamma_{(\text{H}_2\text{SiO}_4^{2-})}} \right\} \quad (10)$$

The expressions of the variations of thermodynamic equilibrium constants with temperature are:

$$\log K_s^0 = 0.338 - 7.889 \cdot 10^{-4} T - \frac{3405.9}{T} \quad (11)$$

$$\log K_1^0 = 6.368 - 0.016346 T - \frac{3405.9}{T} \quad (12)$$

$$\log K_2^0 = 33.11 - 0.049581 T - \frac{8949.2}{T} \quad (13)$$

$$\log K_w^0 = 6.0875 - 0.01706 T - \frac{4470.89}{T} \quad (14)$$

3. Results and discussion

3.1. Typical analysis

The different analytical methods cited above were tested for silica analysis in the case of two artificial silica saturated solutions (at pH 7 and 10) and applied to two brackish waters from

South Tunisia. Analysis results for total, reactive and non-reactive silica are reported in Table 1. Table 2 reports some physico-chemical analysis of selected brackish waters from South Tunisia.

Gravimetry and atomic absorption give total silica contents. Spectrocolorimetry method is limited to reactive silica (monomeric and dimeric silicic acid).

At pH7, the same results are obtained by all methods. This reveals the absence of non-reactive silica at this pH. At pH 10, non-reactive silica is determined by difference between total silica (determined by gravimetry or atomic absorption) and reactive silica (determined by

the yellow or the blue silicomolybdic acid). A method for the conversion of non-reactive forms of silica to reactive forms was applied. Briefly, the method involves alkaline fusion with sodium hydroxide followed by the identical colorimetric method used for determination of reactive silica [14]. This confirm that in alkaline pH range internal condensation and cross-linking involved whereas at lower pH (2 to 3) chainlike or open-branched polymers are initially produced [1,3].

The analysis of brackish waters from South Tunisia shows that these waters contain a significant amount of dissolved silica in monomeric or dimeric silicic acid forms. Thus, as it is well

Table 1
Total, reactive and non-reactive amorphous silica determination

Concentration, mg.L ⁻¹	Gravimetry	Atomic absorption	Spectrocolorimetry		
	Total silica	Total silica	Reactive silica	Total silica	Non-reactive silica
Saturated solution, pH 7	116	116	116	—	0
Saturated solution, pH 10	889	889	860	889	29
Brackish water, well 2	24	24	24	—	0
Brackish water, well 4	33.7	33.7	33.7	—	0

Table 2
Analysis of brackish waters from South Tunisia

	Well 1	Well 2	Well 3	Well 4
Cations, mg.L ⁻¹				
Sodium	1,172	346	1,317	1,192
Potassium	46	15	47	70
Calcium	750	572	643	510
Magnesium	106	170	337	212
Anions, mg.L ⁻¹				
Chloride	1,548	603	1,491	1,899
Sulfate	2,200	1,770	3,470	1,600
Bicarbonate	221	107	227	128
Carbonate	0	0	0	0
Fluoride	0.9	1.2	1.4	0.7
Silica	27.4	24	28.7	33.7
pH	7.7	7.9	7.9	8.1
TDS	6,084	3,617	5,218	5,655
Ionic strength	0.14	0.10	0.19	0.13

known the use of spectrophotometry is restricted to solutions containing monomeric or dimeric silica forms. Total silica is determined by atomic absorption, gravimetry or by spectro-colorimetry after conversion of non-reactive to reactive forms.

3.2. pH and temperature effect on solubility

Amorphous silica solubility in aqueous solutions is studied at different temperature and different pH. Results are represented in Figs. 1 and 2.

If the influence of pressure upon silica solubility is neglected [17] then, the heat released per mole of silicic acid dissolved in reaction (1), corresponds to the heat of dissolution reaction and is determined graphically from the slope of a $\ln S$ vs. T^{-1} plot. According to the Van't Hoff equation [18]:

$$\frac{\partial \ln S}{\partial (1/T)} = -\frac{\Delta H}{R} \tag{15}$$

and Fig. 1, the experimental value obtained is $\Delta H=3.5 \text{ Kcal.mol}^{-1}.\text{K}^{-1}$. This value falls within the range of $2.65 \text{ Kcal.mol}^{-1}.\text{K}^{-1}$ [3] to $4.44 \text{ Kcal.mol}^{-1}.\text{K}^{-1}$ [19].

Silica dissolution is pH dependent. No significant variation is noted for pH values below 9. At higher pH there is an apparent increase in the solubility due to the formation of silicate ions in addition to monomers, which are in equilibrium with the solid phase.

3.3. Dissolved silica activity coefficient

The solubility measurements are performed in some salt solutions of interest because they constitute the major components of brackish waters and seawater. The activity coefficients for silica, summarized in Table 3, are determined in separate aqueous solutions of sodium chloride,

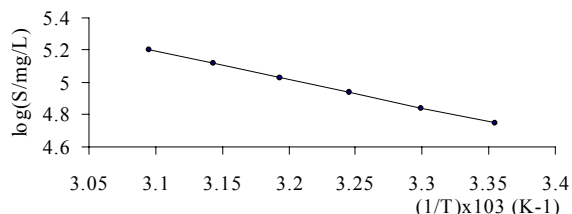


Fig. 1. Logarithm of molar amorphous silica solubility vs. $T^{-1} \text{ (K}^{-1}\text{)}$.

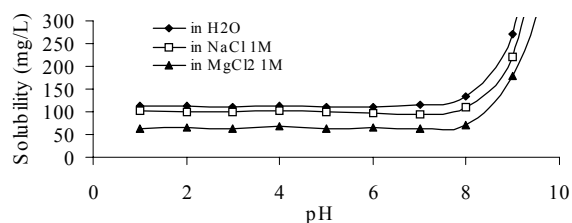


Fig. 2. Variation of amorphous silica solubility with the pH of aqueous solutions.

sodium nitrate, sodium sulfate, lithium chloride, lithium nitrate, potassium chloride, magnesium chloride and magnesium sulfate.

The activity coefficients for dissolved silica $\gamma_{\text{H}_4\text{SiO}_4}$ can be defined as the following ratio:

$$\gamma_{\text{H}_4\text{SiO}_4} = \frac{S_0}{S} \tag{16}$$

Where S and S_0 are the solubilities of the amorphous silica in salt and in distilled water.

These solubilities data for amorphous silica in single salts aqueous solutions are fitted to the empirical Setchénow equation [19]:

- in terms of molarity (M): $\log S = \log S_0 - D'.M$
- in terms of molality (m): $\log S = \log S_0 - D.m$

D or D' are parameters that vary only with temperature and salt type. The activity coefficients determined will be used in the next section to predict amorphous silica solubility.

Table 3
Dissolved silica activity coefficients in different salt solutions

Salt concentration, mol/l	NaCl	NaNO ₃	KCl	KNO ₃	LiCl	LiNO ₃	CaCl ₂	MgCl ₂	MgSO ₄
0	1	1	1	1	1	1	1	1	1
0.5	1.09	1.09	1.04	1.04	1.16	1.16	1.35	1.35	1.18
1	1.13	1.16	1.06	1.07	1.27	1.28	1.80	1.80	1.26
1.5	1.26	1.28	1.1	1.11	1.46	1.54	2.49	2.35	1.51
2	1.43	1.45	1.15	1.15	1.74	1.75	3.16	3.06	1.76
2.5	1.53	1.55	1.22	1.21	2.13	2.14	4.16	4.10	2.02
3	1.63	1.61	1.25	1.26	2.35	2.40	6.37	6.76	2.70
3.5	1.81	2.81	1.30	1.30	2.68	2.75	9.03	8.88	3.18
4	1.97	2.02	1.34	1.36	3.18	3.21	13.97	13.51	3.85
5	2.46	2.57	—	—	4.78	4.81	17.76	18.01	5.40

3.4. Solubility and concentration factors prediction

As described above [Eq. (10)], the calculation of solubility and concentration factors requires the knowledge of thermodynamic equilibrium constants and activity coefficients of H_4SiO_4 , $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ species. The activity coefficient $\gamma_{H_4SiO_4}$ is deduced from experimental solubilities (Table 3). Values of $\gamma_{H_3SiO_4^-}$ and $\gamma_{H_2SiO_4^{2-}}$ are estimated by the following Debye-Hückel equations:

$$\log \gamma_{H_3SiO_4^-} = \frac{-A\sqrt{I}}{1 + 4B\sqrt{I}} \quad (17)$$

$$\log \gamma_{H_2SiO_4^{2-}} = \frac{-4A\sqrt{I}}{1 + 5.4B\sqrt{I}} \quad (18)$$

Experimental and predicted values of amorphous silica solubility in NaCl, NaNO₃, KCl, KNO₃, LiCl, LiNO₃, CaCl₂, MgCl₂ and MgSO₄ aqueous solutions are represented in Fig. 3. Predicted solubility values given by the program

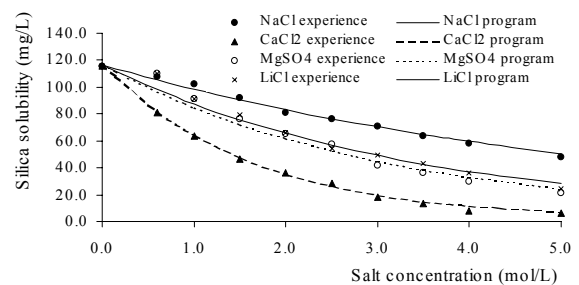


Fig. 3. Predicted and determined silica solubility vs. salt concentration.

are in good agreement with experimental results. We note:

- The decrease in solubility from that in water, at a given molarity is in the order of cation: ($Li^+ > Na^+ > K^+$). This order is the reverse of the ionic radii of the cation ($K^+ > Na^+ > Li^+$).
- Solubility in chloride and nitrate of a common alkyl ion (Li^+ , Na^+ or K^+) lie on a common line.
- Solubility of silica in $MgCl_2$ and $CaCl_2$ solutions are decreased to much lower values than are found using any of monovalent cation salts.

These results agree with those of Marshall and Varakomski [12] who observed a good correlation

with cation hydration numbers.

The developed program was applied to determine the concentration factor of amorphous silica in the case of some brackish water from South Tunisia (Table 2). Fig. 4 shows the increase of silica concentration factor with temperature. An increase of temperature from 15 to 40°C is accompanied with an increase of 2 or 3 factor concentration units. These temperatures correspond respectively to winter and summer average temperatures in South Tunisia. The dependence of the solubility on temperature has an important bearing in operational chemistry of desalination plants. Higher temperatures and lower cation concentration levels may inhibit deposition of silica from brine solutions in desalination plants.

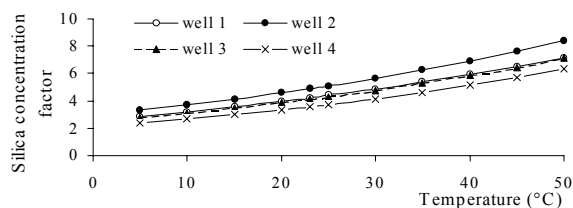


Fig. 4. Silica concentration factor vs. temperature.

4. Conclusion

Solubilities of amorphous silica were determined at different temperatures, pH and ionic strength. Heat of silica dissolution and the activity coefficient of dissolved silica were determined. A microcomputer program with the LabView graphical language was developed to predict the solubility and the concentration factors. This practical tool was applied to a variety of aqueous salt solutions and some brackish waters from South Tunisia, at different temperatures. Predicted solubility values, using deduced silica activity coefficient, are in good agreement with experimental results.

5. Symbols

ΔH	— Heat of amorphous silica dissolution
γ_i	— Activity coefficient of species i
(i)	— Activity of species I
$[i]$	— Concentration of species i
A, B	— Debye-Hückel parameters for the activity coefficients
I	— Ionic strength of solution
K_i^0	— Thermodynamic equilibrium constant for the ionization i of silicic acid
K_s^0	— Thermodynamic equilibrium constant for silica solubility
K_w^0	— Thermodynamic equilibrium constant for water ionization
\ln	— \log_e
\log	— \log_{10}
pH	— $-\log(\text{H}^+)$
R	— Gas constant $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$
S	— Equilibrium solubility of silica in salt solution
S_0	— Equilibrium solubility of silica in pure water
T	— Absolute temperature in Kelvin
TDS	— Total dissolved salts

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