CORROSION OF SILICA GLASS BY AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS

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The effect of solutions of salts of organic acids (citric, oxalic, lactic, ascorbic, tartaric, gluconic, ethylene- diaminetetraacetic) on the dissolving of silica glass was studied on powdered samples of the glass at 98 °C. All of the compounds were found to accelerate the dissolution of silica glass in neutral and alkaline solutions, and the effect decreased in the following sequence: citrate, oxalate, lactate, disodium salt of EDTA, ascorbate, tartrate, gluconate. More detailed attention was paid to citrate. Even its low concentrations in the leaching solution (0.1 wt.%) promote significantly the dissolution of silica glass. Concentration of SiO_2 in the citrate leachate increases with increasing pH of the solution. The rate of dissolution of silica glass in citrate solution is markedly higher than that of silica in crystalline form (quartz crystal).

INTRODUCTION

Glass comes into contact with organic compounds in the form of containers for foodstuffs, pharmaceuticals and chemicals, as laboratory and apparatus glass, and the like. The problem of the effect of chemical compounds on glass is important in particular with container glass for pharmaceutical purposes, where the minimum possible liberation of glass components is desirable. This applies especially to parenteral preparations (i.e. those applied in ways other than through the digestive tract), and to products to be sterilized in glass vessels. In the case of container glass for foodstuffs and beverages, the problems are basically concerned with the effect of organic compounds in the contents on the leaching of heavy metals from the glass (Pb, Cd, Ba, Cr, etc.).

The standard tests of chemical durability of glass include only tests of resistance to water and inorganic acids and bases. Of organic compounds, use is only made of acetic acid solution for determining the leachate of Pb, Cd and possibly also other heavy metals.

The literature dealing with the effects of organic compounds on glass is far from extensive, but some of the publications report that certain organic compounds promote the corrosion of glass. Bacon and Raggon [1] observed a strong aggressive effect of citrate solutions on dealkalized surfaces of soda-lime glass. Over the *pH* range in question (5 to 7.6) the corrosion increased with increasing *pH* of the solution. The authors also established a similar effect with neutral solutions of salts of other organic acids.

Ernsberger [2] found that aggressive effects on soda-lime glass were promoted by neutral solutions of

EDTA salts, while Olsen et al. [3] and Paul and Youssefi [4] established the same effect with lead crystal. Pineiro [5] discovered that SiO_2 from soda-lime, neutral and borosilicate glasses for medical purposes dissolves at a higher rate in solutions of glucose and calcium gluconate. Passl [6] observed that neutral solution (1.9 %) of potassium lactate had stronger aggressive effects on the dealkalized surface of soda-lime glass than the NaCl physiological solution of the same concentration. Paul and Yousseffi [4] reported more extensive leaching of calcium from soda-lime glasses in sugar solutions (0.5 mol l^{-1}) in an alkaline medium.

Lead and other components of lead crystals were found to be extracted at a higher rate by citrate and tartrate solutions [7]. Accelerated corrosion of glasses in the Na_2O-CaO-SiO_2-P_2O_5 system due to the presence of trishydroxymethylaminomethane (TRIS) as buffering agent in simulated body fluid was described in [8,9].

The general literature [10] mentions that a number of organic compounds, including some of those mentioned above, are capable of forming complex compounds with cations of many metallic elements, also those contained in glass (Ca, Mg, Al, Pb, Zn, Fe and others). This is why most of the authors [2 through 4] consider the higher aggressivity of the organic solutions to be due to formation of complex compounds of organic anions with the respective metal cations. In this way, the structure of glass in the surface layer is weakened and the other components, including SiO_2, are allowed to dissolve. The theory of the effect of complex forming compounds on glass is discussed by Paul [11].

On the other hand, Bacon and Raggon [1] assume that the given organic compounds form soluble comple-

xes also with silicon ions, and that this is the main reason of the higher rate of corrosion of silicate glasses. They offer as evidence the results of their experiments when neutral citrate solution promoted corrosion not only of soda-lime and borosilicate glasses, but also that of silica glass and pure crystalline SiO_2.

So far, no complex compounds of citrate or other anions with silicon ions have been described in the literature. However, a complex compound of catechol (o-dihydrobenzene) with silicon was already described in 1931 [12]. Data on the effect of catechol and other similar compounds on the dissolution of SiO_2 was summarized by Iler [13]. Formation of complex compounds of polyhydroaliphatic compounds with silicon was not so far described. Silicon complexes with organic compounds occur in some live organisms and plants, for example those containing lipids, cholesterol, and the like. Foucalte and Collette [13] reported on faster dissolution of SiO_2 in rat peritoneum than in a buffer solution of $pH = 7.4$. The authors assumed that this may be caused by the presence of organic compounds (similar in structure to catechol) in the live organism.

The present paper is concerned with studying the influence of aqueous solutions of some organic compounds (exhibiting more extensive aggressive effects according to the literature) on the dissolution of silica glass.

EXPERIMENTAL PART

In the experiments, use was made of clear silica glass of Czech manufacture (content of impurities approx. 10^{-2} %). Some of the comparison measurements were carried out on crystalline silica (Brazilian crystal).

Aqueous solutions of organic acids (citric, oxalic, tartaric, lactic, ascorbic, gluconic, ethylenediaminetetra-acetic) and their sodium salts (with the exception of potassium oxalate) were used as the leaching media. Solution of trishydroxymethylaminomethane (TRIS), often used as a buffering agent, was also chosen. In all instances, the concentration was 4 wt.%, except that with citrate also lower concentrations were tested (0.1 to 4 wt.%). The pH of solutions of salts was adjusted to approximately neutral or any other desired, by adding the acid or NaOH. Distilled water, whose pH was as necessary adjusted with NaOH or HNO_3 to correspond to the pH of the organic solution, was used for comparison in all of the instances.

The leaching conditions employed were the standard ones specified by ČSN ISO 719. Two grams of crushed glass (particle size 3-5 mm) were exposed to the leaching solution in teflon vessels with well sealing lids in a drying oven at 98 °C for a period of 1 to 24 hours. In the leachates, the concentration of silicon dioxide was determined by the photometric method to

ČSN 70 0527. In the case of leachates where the presence of the organic compounds could have an interfering effect on the determination, atomic absorption spectroscopy was used.

RESULTS AND DISCUSSION

The results obtained by leaching silica glass into the individual solutions (expressed in terms of SiO_2 concentration in the leachates) are summarized in table 1 for times of leaching of 6 to 24 hours. The results show that neutral 4 % aqueous solutions of the organic acids in question promote transfer of SiO_2 from the surface of silica glass into solution as compared to distilled water whose pH was adjusted with NaOH to the corresponding value.

Table 1. Concentration of SiO_2 in solutions after leaching silica glass. Temperature 98 °C. Concentration of organic solutions 4 wt.%.

solution	initial pH	time (hours)	SiO_2 (mg l^{-1})
distilled water	5.69	6	1.25
		24	21.6
distilled water with NaOH	6.90	6	5.8
		24	21.6
citrate	7.08	6	48.6
		24	224.6
citric acid	2.11	6	< 4.3
		24	< 4.3
tartrate	7.08	6	10.7
		24	78.5
tartaric acid	2.04	6	< 4.3
		24	< 4.3
lactate	6.80	6	28.1
		24	143.0
lactic acid	2.27	6	< 4.3
		24	6.4
gluconate	6.89	6	8.6
		24	42.8
gluconic acid	1.83	6	5.6
		24	8.6
ascorbate	6.67	6	16.5
		24	130.5
ascorbic acid	2.69	6	< 4.3
		24	< 4.3
oxalate	6.57	6	62.3
		24	165.8
oxalic acid	1.72	6	< 4.3
		24	< 4.3
disodium salt of EDTA	6.93	6	31.9
		24	134.3
TRIS	6.89	6	7.9
		24	16.5

In the case of solutions of organic acids with low *pH* values (1.83 to 2.69), the concentration of SiO_2 in leachates was lower than in that of water, and in most instances (with the exception of gluconic and lactic acids) and for the longest time of exposure (24 hours) was also below the determination limit of the AAS method employed (<4.3 mg SiO_2 l^{-1}). The highest concentration of SiO_2 was established in the leachate in the citrate solution. The aggressive effect of organic acids was decreasing in the sequence citrate, oxalate, lactate, disodium salt of EDTA, ascorbate, tartrate and gluconate. No increased aggressive effect was observed in the case of the TRIS solution. The relation between the effects of the individual solutions is comprehensively shown in figure 1 for the time of leaching of 24 hours.
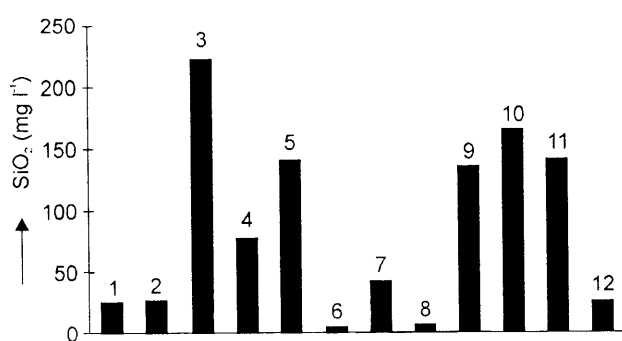

Figure 1. Concentrations of SiO_2 in silica glass leachates. Temperature 98 °C, time of leaching 24 hours.
1 - distilled water; 2 - distilled water with NaOH (*pH* = 6.90); 3 - citrate; 4 - tartrate; 5 - lactate; 6 - lactic acid; 7 - gluconate; 8 - gluconic acid; 9 - ascorbate; 10 - oxalate; 11 - disodium salt of EDTA; 12 - TRIS

Similar conclusions were reached from the time dependence of SiO_2 concentrations in leachates in the individual solutions. Figure 2 shows a comparison of the time dependence for 4 % citrate and lactate solutions
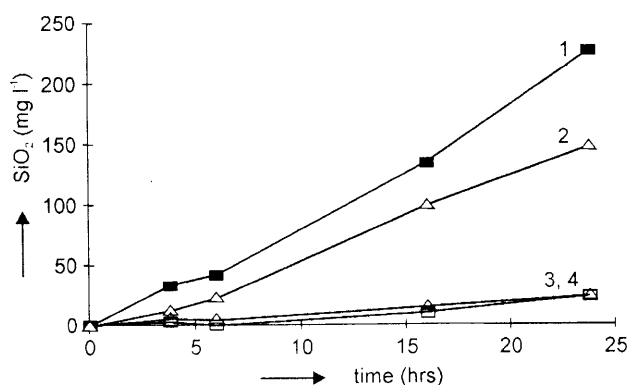

Figure 2. Concentration of SiO_2 in silica glass leachates vs. time of leaching. Temperature 98 °C.
1 - citrate; 2 - lactate; 3 - distilled water; 4 - distilled water with NaOH (*pH* = 6.90)

with that for distilled water, and that for distilled water whose *pH* was adjusted to approximately neutral with NaOH. In spite of the rather orientation character of the measurements due to the low number of the exposure periods employed, the rate of dissolution of silica glass in citrate and lactate solutions is clearly several times higher (by a factor of nine and five respectively) than for distilled water and neutral aqueous solution of NaOH.

Organic compounds are generally known to either suppress dissolution of SiO_2 by coating the surface with a firmly adsorbed film of an organic compound, or to accelerate it by removing the soluble $Si(OH)_4$, normally in equilibrium with the surface, in the form of a soluble complex compound. The present results indicate correctness of the assumption that the dissolution of silica glass is promoted by neutral aqueous solutions of the respective organic compounds in consequence of formation of some type of soluble organic compound of silicon.

As the most aggressive organic compound among those studied, citrate was further examined as to its effects in terms of concentration. Figure 3 shows the dependence of SiO_2 concentration in leachate in dependence on citrate concentration in the leaching solution for the temperature of 98 °C and the time of leaching of 6 hours. Already low concentration of citrate accelerate significantly the leaching process. For example, at a concentration of 0.1 wt.% citrate, the concentration of SiO_2 in the leachate was almost three times higher than in the distilled water leachate. At first, the concentration dependence shows a rapid increase, levelling off at the higher concentrations. This indicates that only a certain concentration of the organic compound is required for eliminating the soluble $Si(OH)_4$ by chemical reaction, and that further increasing of this concentration no longer results in any significant transfer of SiO_2 into solution. The effect of *pH* of citrate solutions on the dissolution of silica glass is shown in figure 4. This is the dependence of SiO_2 concentration in the leachate on *pH* for a 4 % citrate solution, and at the same time for citrate-free aqueous solutions whose *pH* was adjusted with HNO_3 and NaOH to approximately the same value as that of the citrate solutions. SiO_2 concentration in both types of leachates rises with increasing *pH* of the solution, the increase being faster with the citrate solution than with the citrate-free one. This may be due to increasing solubility of the arising organic silicon compound with increasing *pH* of the solution. The complex-forming capability is also generally known to increase with increasing *pH* [10].

Several measurements with crystalline quartz were carried out in order to assess the effect of citrate on the crystalline form of SiO_2. For example, the concentration of SiO_2 in leachate into a neutral 4 % citrate solution attained 26.5 mg mol^{-1} after 24 hours of leaching at 98 °C, whereas only 6.1 mg l^{-1} in the case of distilled
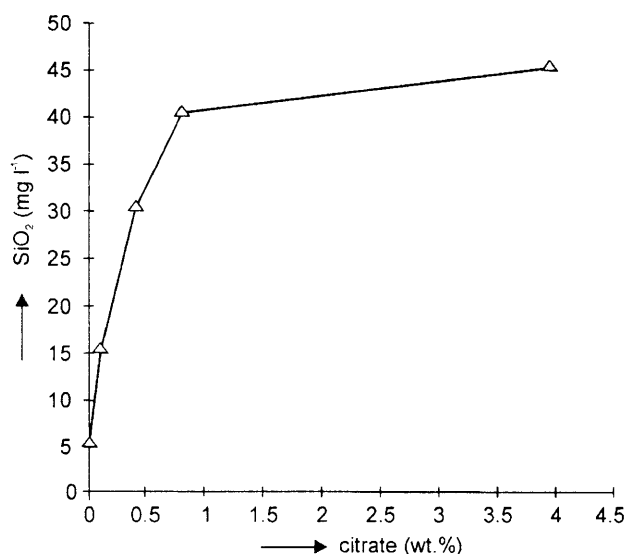
Figure 3. Concentration of SiO_2 in silica glass leachates vs. citrate content in leaching solution. Temperature 98 °C, time of leaching 6 hours.
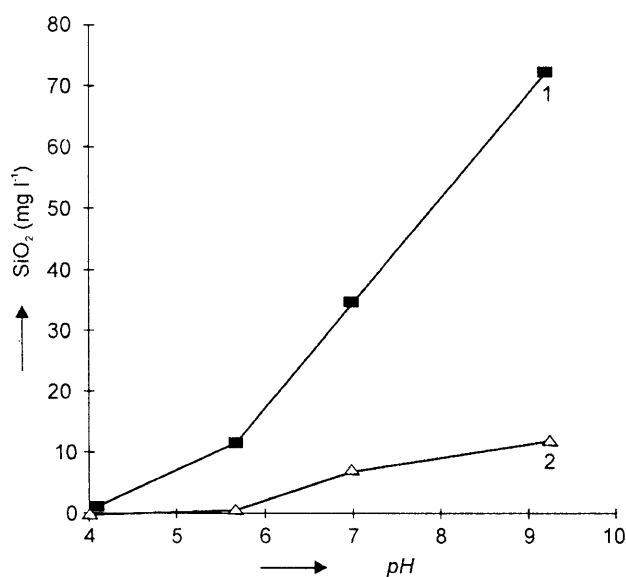

Figure 4. Concentration of SiO_2 in silica glass leachates vs. *pH* of leaching solution.
1 - citrate; 2 - inorganic solution

Figure 5. Comparison of the time dependence of SiO_2 concentration in silica glass and crystalline silica leachates. Temperature 98 °C, 4 wt.% citrate solution.
1 - silica glass; 2 - quartz crystal

water adjusted with NaOH to an approximately neutral *pH*. With crystalline SiO_2, the rate of dissolution is significantly lower than with silica glass, as illustrated by the comparison of time dependencies in figure 5. The lower rate of dissolution of crystalline SiO_2 was also observed with other types of solutions [13].
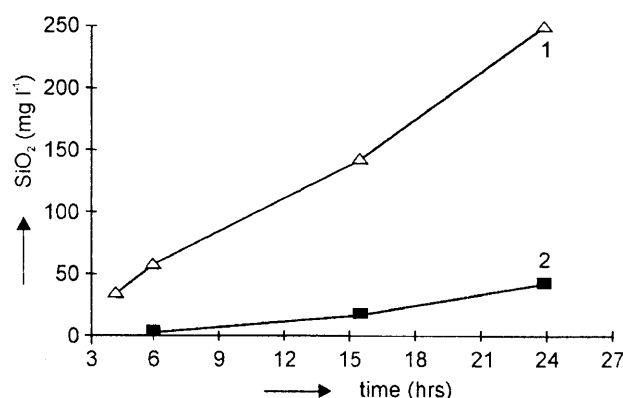
The assumption of formation of soluble complex silicon compounds with citrate and other similar organic anions was first suggested by Bacon [1], but such compounds have not so far been described in the literature, nor has the subject matter been dealt with in greater detail. However, the problems involved are of considerable interest and practical significance in view of the wide application of container glass in medicine and pharmacy, where it comes into contact with a wide range of organic chemical compounds. Further study of the issues thus seems to deserve further detailed study.

CONCLUSION

The results of the present study show that neutral and alkaline aqueous solutions of salts of the organic acids in question promote dissolution of silica glass, as well as that of crystalline forms of SiO_2. With the organic compounds studied, the aggressive effects decreased in the sequence citrate, lactate, sodium salt of EDTA, ascorbate, tartrate, gluconate.

The effects of citrate as the most aggressive compound among those in question were studied in more detail. Already low concentrations of citrate were found to speed up considerably the dissolution of silica glass. Concentration of SiO_2 in citrate leachates increases with increasing *pH* of the solution at a higher rate than in citrate-free aqueous solutions. The leaching rate in citrate solutions is significantly higher with silica glass than that with crystalline forms of SiO_2.

The results support the assumption [1] that under the effect of citrate and other similar ions on pure forms of SiO_2 in aqueous neutral or alkaline solutions, there arise some types of soluble organic compounds of silicon which speed up dissolution of these materials.

Acknowledgement

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KOROZE KŘEMENNÉHO SKLA VODNÝMI ROZTOKY ORGANICKÝCH SLOUČENIN

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O působení vodných roztoků organických sloučenin na sklo není v literatuře příliš mnoho údajů, i když je tato problematika důležitá z hlediska skleněných obalů pro farmaceutické účely. Je ale známo, že některé organické sloučeniny urychlují korozi skla. Patří k nim zejména neutrální roztoky solí některých organických kyselin. Názory na podstatu jejich působení na sklo ze zatím liší. Zvýšené korozní účinky vysvětluje většina autorů tvorbou komplexů organických aniontů s kationty kovových prvků ve skle, pouze ojediněle je předpokládán vznik komplexních sloučenin přímo s ionty křemíku.

V práci byl studován vliv vodných roztoků solí vybraných organických kyselin na rozpouštění křemenného skla, pro porovnání bylo provedeno několik měření také u čisté krystalické formy SiO_2 (křišťálu). Drťové vzorky křemenného skla (event. křišťálu) připravené standardním postupem podle ČSN ISO 719 byly louženy ve vodných roztocích (4 hmot.%) solí organických kyselin při teplotě 98 °C po dobu 1 až 24 h. Ve výluzích byla stanovena koncentrace SiO_2 buď fotometricky nebo pomocí AAS.

Bylo zjištěno, že neutrální roztoky solí sledovaných organických kyselin (citronové, šťavelové, mléčné, askorbové, vinné, glukonové, ethylendiaminotetraoctové) zvyšují přechod SiO_2 z povrchu křemenného skla do roztoku v porovnání s destilovanou vodou a destilovanou vodou s upraveným *pH* na přibližně neutrální hodnotu pomocí NaOH (tabulka 1.). Korozní účinek organických sloučenin klesal v pořadí: citrát, šťavelan, laktát, sodná sůl kyseliny ethylendiaminotetraoctové, askorbát, vinan, glukonan. U roztoků odpovídajících organických kyselin s nízkou hodnotou *pH* (1,83 - 2,69) byla koncentrace SiO_2 ve výluzích nižší než u vody. Porovnání účinku jednotlivých roztoků pro čas loužení 24 h je na obr.1.

Časové závislosti koncentrace SiO_2 ve výluzích do neutrálních roztoků citrátu a laktátu v porovnání s obdobnými závislostmi pro destilovanou vodu a destilovanou vodu s upraveným *pH* (*pH* = 6,90) jsou na obr. 2. Rychlost rozpouštění křemenného skla v roztocích citrátu a laktátu je několikrát vyšší než v destilované vodě i v destilované vodě s upraveným *pH*.

Podrobněji bylo sledováno působení citrátu jako nejagresivnějšího ze sledovaných činidel. Na obr. 3 je uvedena závislost koncentrace SiO_2 ve výluzích z křemenného skla na koncentraci citrátu v loužícím roztoku (teplota 98 °C, čas loužení 6 h). Již nízké koncentrace citrátu v roztoku výrazně urychlují rozpouštění křemenného skla, s rostoucí koncentrací citrátu v roztoku se ale růst koncentrace SiO_2 ve výluhu postupně zpomaluje. Koncentrace SiO_2 ve výluhu roste dále s rostoucím *pH* roztoku citrátu. Tento vzrůst je u roztoku citrátu výraznější, než u roztoku bez citrátu se stejným *pH* (obr.4). Přítomnost citrátu ve vodném roztoku urychluje i rozpouštění čisté krystalické formy SiO_2 - křišťálu. Z porovnání rozpouštění křemenného skla a křišťálu do roztoku 4 % citrátu na obr.5 je zřejmé, že křemenné sklo se rozpouští podstatně rychleji než křišťál.

Výsledky uvedené v předložené práci potvrzují, že citráty a soli dalších organických kyselin v neutrálních a alkalických vodných roztocích urychlují rozpouštění čistých forem SiO_2, jakými jsou křemenné sklo a křišťál. To podporuje předpoklad o tvorbě nějakého typu rozpustné organické sloučeniny křemíku s citrátovými a dalšími organickými anionty.