Influence of organic substances on the dissolution behavior of glasses

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In order to quantify the impact of organic substances on the dissolution behavior of glasses in aqueous solutions, long term corrosion corrosion experiments on chip samples of glasses of the system CaO-MgO-Al_2O_3-SiO_2 were performed. The organic acids in focus were lactic, oxalic, succinic, malic, tartaric and citric acid. The investigated glasses were from the main system CaO-MgO-Al_2O_3-SiO_2. The dissolution rates were determined as a function of glass composition, pH value and organic additive. As corrosion medium a physiological saline solution was used with the organic supplement, added at a concentration of $1 \cdot 10^{-3}$ mol/l. Experimentally obtained dissolution rates are compared to the hydrolytic stabilities calculated by a thermodynamic model.

1. Introduction

Organic substances in an aqueous environment can be found in various areas of science and technology. They occur naturally as products of metabolism of living organism and are therefore of interest for ecotoxicology. In everydays live, they act as preserving agents for foodstuff or as active ingredients for detergents. In laboratories, organic acids are technically used as buffering agents to maintain the pH of aqueous solutions[1]. In order to investigate the potential pathogenicity of mineral fibers, various in-vitro dissolution measurements in artificial lung fluids have been performed[2]. In a recent study, the dissolution behaviour of stone wool fibres in simulated lung fluid with different exclusions of organic components was investigated. The presence of sodium chloride lead to a dramatically lowered dissolution rate[3]. The present study comprises some of the organic components used for the simulated body fluids, like e.g. citric, tartaric and lactic acid; furthermore in order to fathom the fundamental mode of reaction of multifunctional organic species to the dissolution behavior of glasses, substances chemically related to the ones mentioned before are investigated (oxalic, succinic, malic acid). In contrast to the flow-through tests commonly used for biosolubility measurements of stone wool fibres, the corrosion experiments were carried out on chip samples.This procedure has the advantage to grant an accurate measurement of the dissolution rate. Due to the electronegative polarisation of the carboxylic functional group, organic acids can form strong complexes with many metal ions; Paul[4] calculated stability constants of metal-citrate-complexes. In our work we try to quantify the influence of such complex forming substances on the dissolution rate of glasses and include the organic components in the aqueous specification for the calculation of the stabilities of oxides.

2. Experimental

In order to quantify the influence of either lactate, oxalate, succinate, malate, tartrate and citrate in aqueous solutions on the dissolution behavior of glasses of the system CaO-MgO-Al_2O_3-SiO_2, long term corrosion experiments on chip samples were conducted. The preparation procedures are explained in earlier publications[5]. Dissolution rates are determined as a function of glass composition, complexing agent and pH value. The corrosion experiments were carried out for all of the five organic complexing agents at a concentration of $1 \cdot 10^{-3}$ mol/l at three different pH values (3, 5 and 11). The aqueous medium consisted of a physiological sodium chloride solution (0.154 mol/l) and the organic substances. The temperature was adjusted to 37 °C (certified within ± 1 K). The glass surface area to solution volume ratio (SA/V) was fixed to $s = 0.06\ cm^{-1}$ for all samples. The corrosion experiments were carried out in duplicate over a period of 63 days with the solution being replaced by fresh one every 7 days. Wide-neck PE bottles were used as reaction vessels. The sample holders were made of a HD-PE sheet. Evaporation losses were compensated by adding bi-distilled water. The pH values were checked every day. If necessary, they were adjusted by additions of HCl or NaOH solution; pH shifts never exceeded ± 0.5 units.

2.1 Materials

In table 1 the chemical compositions of the investigated glasses used for the experimental and theoretical part of this study are shown. Glass A is a typical composition of a mineral fibre with a low silica and high alumina and calcia content. Regarding the chemical composition by the approach of the thermodynamically modelled crystalline reference system, we find anorthite-akermanite-diopside as the main compounds. Glasses B to E have compositions identical with a single crystalline phase each of the C-M-A-S system.

Table 1. Chemical compositions of the glasses in wt.-%; R = K, Na; C = CaO, M = MgO, A = Al_2O_3, S = SiO_2

Glass	SiO_2	Al_2O_3	MgO	CaO	R_2O	constitutional compounds
A	42	20	7	19	4	CAS_2, C_2MS_2, CMS_2
B	56		19	26		CMS_2
C	44		15	41		C_2MS_2
D	43	37		20		CAS_2
E	22	37		41		C_2AS

2.2 Organic additives

In figure 1 the structural formulas of the organic components, which were added to the solutions are illustrated. The additives vary in the kind and number of functional groups as well as in the number of carbon atoms in the backchain. All of the substances have at least one acidic carboxyl group with combinations of hydroxyl groups. Lactic acid is a mono-hydroxycarboxylic acid, oxalic acid is the shortest di-carboxylic acid with only two carbon atoms, succinic, malic, tartaric acid are of four carbon atoms consisting di-carboxylic acids with none to two hydroxyl functions.

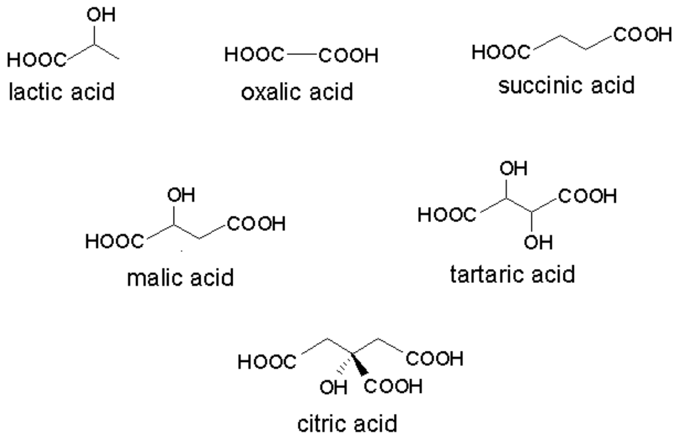

Figure 1: Structural formulas of the organic substances

3. Thermodynamic calculations

A thermodynamic approach published earlier[6] allows to calculate and predict many of the glass properties by the chemical composition. The chemical durability can be expressed by the Gibbs free energy of hydration ΔG_{hydr}[7], which is described by the following reaction:

$$\text{glass} + \text{aqueous solution} \xrightarrow{\Delta G_{hydr}} \text{aqueous species} \qquad [1].$$

This energy can only be calculated indirectly. The correlation between the different Gibbs energies is illustrated in figure 2. It is composed of the reaction enthalpy ΔG_s of the formation of the constitutional (crystalline) reference compounds (G_s) of the glass-forming oxides (G_{ox}), the vitrification enthalpy (G^{vit}) and the dissolution enthalpy ΔG_{aq} of the oxides in water. In terms of reaction paths, we find these free energies in the formation reactions of the oxides to the constitutional components of a glass:

$$\text{oxides} \xrightarrow{\Delta G_s} \text{constitutional components} \qquad [2],$$

and in the reaction of the constitutional components to a glass:

$$\text{constitutional components} \xrightarrow{G^{vit}} \text{glass} \qquad [3].$$

These formation energies are opposed to the energy of the dissolution reaction of the oxides in the aqueous system:

$$\text{oxides} + \text{aqueous solution} \xrightarrow{\Delta G_{aq}} \text{aqueous species} \qquad [4].$$

Up to now, for the calculation of the dissolution enthalpy only the reaction of oxides with water, hydroxide and protons have been taken into consideration. The addition of organic components changes the aqueous specification of the oxides and consequently alters the value for G_{aq}. The aqueous specification was revised for as many glass forming oxides as possible, the thermodynamic database for the organic aqueous species is unfortunately not stringent and complete[8].

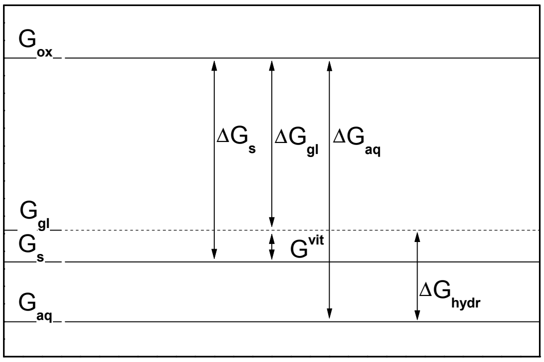

Figure 2. Overview of the Gibbs energies needed for the calculation of ΔG_{hydr}

The pH dependence of the hydrolytic stabilities of the glasses in aqueous solutions without any additions of organic substances are shown in figure 3. The calcia-magnesia-silicate systems have the same free energies over the acidic and neutral pH range and stabilise in the basic regime. The calcia-magnesia-silicates have range of low stability up to pH 4; a transitional increase in stability can be found in the neutral regime until the stabilisation at basic pH values occur. In figure 4 the thermodynamically modelled stabilities in the presence of $1 \cdot 10^{-3}$ mol/l organic additive for glass A and B are presented. An enormeous destabilisation occurs with the addition of citric and oxalic acid. A different behavior of the two glasses can be found in the near-neutral to basic regime. Compared to the solution without addition of organics, for glass B a relative stabilisation of the system is predicted. With the exception of succinic acid, for glass A the hydrolytic stability is decreased by the addition of the organic components at that pH range. In the strongly alkaline regime and without organic additions, the two glasses are expected todramatically increase in stability. This is not observed for the solutions containing organic acids.

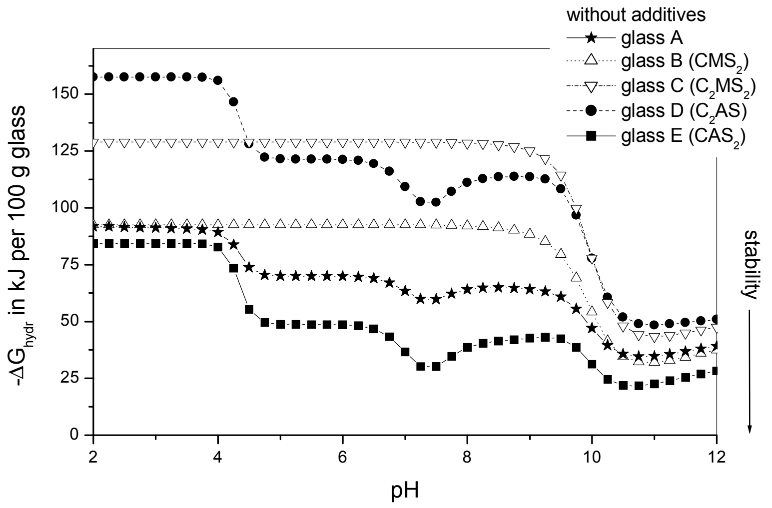

Figure 3. Gibbs energies of hydration without the presence of organic substances

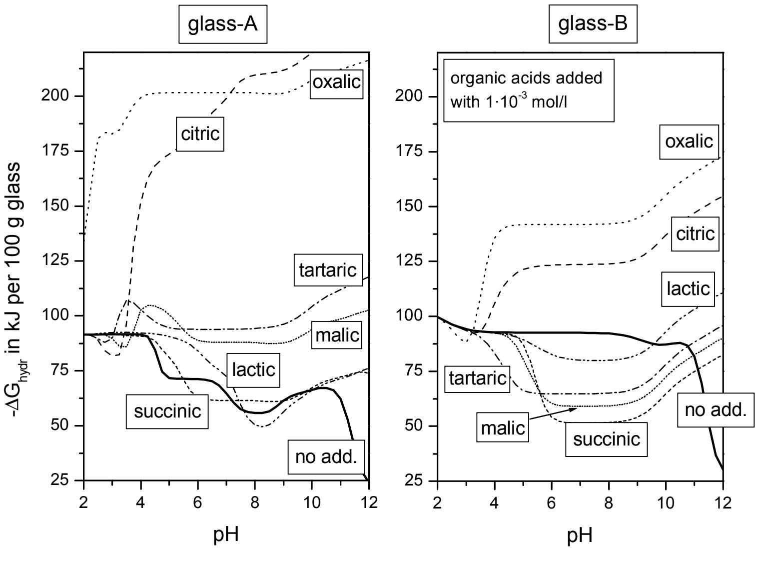

Figure 4. Gibbs energies of hydration for glasses A and B with additions of organic acids

4. Experimental Results

In table 2 the dissolution rates r of glass A and B are presented. The values are obtained by differentiation of the normalised mass losses for time in the range of 28 to 63 days. For glass A the typical pH dependence in a saline solution with no additives is still found with r (pH 3) > r (pH 5) ≈ r (pH 11). For glass B, the pH dependence of dissolution rate follows the range of sequence of pH 5 > pH 11 > pH 3, despite of the values for oxalic acid, which show the same pH-depending order like glass A. For malic acid, the dissolution is nearly independent of the pH.

Table 2. Measured dissolution rates for glass A and B in $mg/cm^2 \cdot d$

	glass A			glass B		
	pH 3	pH 5	pH 11	pH 3	pH 5	pH 11
lactic acid	0.72			0.06		
oxalic acid	0.76	0.04	0.05	0.41	0.22	0.20
succinic acid	0.74	0.00	0.05	0.12	0.42	0.36
malic acid	1.21	0.10	0.05	0.26	0.28	0.24
tartaric acid	1.03	0.06	0.05	0.06	0.22	0.13
citric acid	1.01	0.17	0.05	0.12	0.53	0.15

5. Conclusion and prospect

The comparison between the calculated hydrolytic stabilities of the glasses towards the solution and the measured rates shows that the reaction mechanism is not yet fully understood. The above calculations take into account that the organic agents enhance the solubilities of individual oxides only. For several cases, the enhanced solubility seems indeed to dominate (e.q. at pH = 3, except for oxalic acid) while for the other cases, an alternative mechanism overrules solubilities. We suggest that, depending on the charge balance at the glass surface, the organic agents may alternatively adhere to the surface (instead of complexing dissolved ions), thereby turning the surface hydrophobic and decreasing the dissolution rates. Future work will be devoted to clarifying this issue, especially with respect to the dissolution of further constitutional compounds of the CaO-MgO-Al_2O_3-SiO_2 system.

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