CHEMICAL DURABILITY OF THE GLASSES OF SYSTEM LiF - CaO - Al(PO₃)₃

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ABSTRACT Chemical durability of the glass 0.8 LiF - 0.2 Al(PO₃)₃ (designated below as LiF-80) was studied in water and in 0.01 mol dm⁻³ HCl solution (further 0.01 M). The experiments were carried out at 25, 40 and 60 °C with glass discs in unstirred solutions, which have been refreshed daily during a month. The methods used were mass loss measurements and determination of Li, F, and P₂O₅ concentrations in the solutions. The mean velocities and the apparent activation energies of the glass dissolution were estimated. The time dependencies of mass losses and leaching of the components were apparently linear. The ratios Li/F and Li/P₂O₅ in solutions tend to be twice in water and four times as large in HCl solution in comparison to such ratios in glass itself, i.e. the dissolution of the glass runs with a preferred leaching of Li⁺. Additions of 2 and 5 % CaO (over 100% by weight) increase slightly the chemical durability of the glass in unstirred 0.1 M HCl solution. In comparison with the glass LiF-80 the durability of the glass LiF-85 is much worse.

Glasses of the system LiF - Al₂O₃ - P₂O₅ attract attention thanks to their high Li⁺ ion conductivity¹ as solid electrolytes and material for selective Li⁺ sensors (glass electrodes) in water solutions ²,³. However their chemical durability was not studied yet.

EXPERIMENTAL The glasses have been synthesized in an electric oven for 30 min at 950 – 1000 °C using glassy carbon crucibles at dry argon atmosphere. The reagents were LiF, Al(PO₃)₃, and CaCO₃, chemical pure or pure for analysis grade. The specimens were glass discs 15 - 20 mm in diameter and 2-3 mm thick. They were obtained by moulding of glass melt in hot steel casts and then annealed. Their faces were polished (for details see¹). Areas of the samples were estimated; they were degreased with water and acetone. The weighed LiF-80 glass discs were hanged in 70 cm³ of distilled water or 0.01 M HCl in polyethylene or Teflon beakers with lids. The
beakers were posed in a water thermostat at temperature of 25, 40, or 60 °C. After a
day (sometimes after two or even three days) the discs were taken out, dried with filter
paper, air-dried and then weighed within ±0.05 mg. The solution was taken for
analysis. The discs were put in a fresh portion of the solution. No stirring was
employed.

The following methods of component analysis were used: Lithium was
determined with AAS-1N atomic-absorption spectrophotometer (Carl Zeiss, Jena,
Germany). The lower detection limit was $1 \times 10^{-6}$ M Li$^+$, and the accuracy was ±2%.
Fluoride was determined potentiometrically using home made F-selective electrode
with the membrane of LaF$_3$ (+ 0.2 % EuF$_2$). The citrate (Na$^+$, 0.4 M) - nitrate (K$^+$, 0.2
M) buffer was used for Al masking. Using the acetate buffer of the same ionic
strength and pH 5 – 6 instead of citrate one, we tried to estimate the amounts of F$^-$
bounded with Al. The accuracy of the calibration in the NaF solutions was within ±2%
for F$: Phosphorus (as P$_2$O$_5$) was determined by a method based on the photometry of
the blue phosphomolibdate solution. The spectrophotometer SF-46 was employed. To
transform the P, containing in analyzed solutions, in determinable form (PO$_4^{3-}$), the
solutions were acidified up to pH about 0 and boiled during 15 min before the
addition of all needed components$^4$. The accuracy of the method applied to standard
solutions was within ±3%.

Two samples of each glass (LiF-80, +2% CaO, +5% CaO, and LiF-85) were
also fully dissolved in 125 cm$^3$ of unstirred and not refreshed 0.1 M HCl at 25 °C,
with control of mass loss kinetics, considering the area alterations.

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**FIGURE 1.** Time dependence of mass losses at full dissolution of the glasses
LiF-80, +2% CaO, and +5% CaO in 0.01 M HCl (not refreshed) at 25 °C.

**FIGURE 2.** Time dependence of mass losses of the glass LiF-80 in
water refreshed daily.
RESULTS The results of the last experiments are shown in FIGURE 1. The inhibitory action of the products on the glass dissolution is seen in the case of CaO additions. The glass LiF–85 has been dissolved in such conditions for five days.

![Graph](image1)

FIGURE 3. Time dependence of F⁻ extraction from the glass LiF–80 in 0.01 M HCl at 40 °C

![Graph](image2)

FIGURE 4. Time dependence of P₂O₅ extraction from the glass LiF–80 in 0.01 M HCl at 40 °C

The typical results of the experiments with refreshed water and 0.01 M HCl solutions are represented in FIGURES 2 – 4. The time dependencies of mass losses of glass LiF–80 and component extraction from that are essentially linear. The mean velocities of these processes were calculated from the slopes of these and similar straight lines (see TABLES 1 and 2). The averaging–out was carried on two identical samples.

TABLE 1 Mean dissolution velocities (Vₚ), calculated from mass losses of the glass LiF–80 in water and in 0.01 M HCl.

<table>
<thead>
<tr>
<th>T / °C</th>
<th>Vₚ/ mg cm⁻² day⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.046 ± 0.004</td>
</tr>
<tr>
<td>40</td>
<td>0.121 ± 0.019</td>
</tr>
<tr>
<td>60</td>
<td>0.243 ± 0.073</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>9.8 ± 1.0</td>
</tr>
<tr>
<td>60</td>
<td>14.9 ± 1.9</td>
</tr>
</tbody>
</table>

TABLE 2. Mean velocities (Vᵢ) of extraction of glass LiF–80 components in water and in 0.01 M HCl.

<table>
<thead>
<tr>
<th>T / °C</th>
<th>Vᵢ/ mole cm⁻² day⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.06 ± 0.14</td>
</tr>
<tr>
<td>60</td>
<td>3.02 ± 0.38</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>60</td>
<td>1.0 ± 0.3</td>
</tr>
</tbody>
</table>

The part of F⁻ bounded with Al was estimated as 0.8 ± 0.1 after water and only 0.2 ± 0.1 after acid solution. The comparison of mass losses and the sums of revealed components in analyzed solutions (except Al) gave the following results. These
intermediate specific phenomena." We will try to study the phenomena and improve
the chemical durability of this type of glasses, so useful for making of them Li+-
selective glass electrodes\textsuperscript{2,3}.

REFERENCES
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