# Review Paper

## Interaction between glass and ethanol

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Dedicated to Prof. Dr. Franz Gebhardt on the occasion of his 60th birthday

The structural relationship between $H_2O$ and $C_2H_5OH$ molecules suggests certain similarity in their behavior. An evaluation of pertinent publications shows that this is really the case. The chemical interaction with absolute alcohol is minimal at room temperature but esterification can take place with increasing temperature accompanied by the formation of new Si–O–C bonds. Even small amounts of water lead to a predominance of reactions associated with $H_2O$. On the other hand, ethanol causes a dilution of the water, decreasing the reaction rate. Other phenomena are determined by the OH groups which are responsible for the formation of hydrogen bonds, e.g. by adsorption. Relationships also exist for gel layers, glass electrodes, silica gels, and the sol-gel process. Physical interactions, e.g. strength, fracture velocity, abrasion, are also influenced by the molecular properties of $C_2H_5OH$.

**Wechselwirkungen zwischen Glas und Ethanol**

Die strukturelle Verwandtschaft zwischen dem $H_2O$- und dem $C_2H_5OH$-Molekül läßt ein gewisses ähnliches Verhalten vermuten. Das ist wirklich der Fall, wie eine Auswertung einschlägiger Veröffentlichungen zeigt. Die chemischen Wechselwirkungen mit absolutem Ethanol sind bei Raumtemperatur gering, aber mit steigender Temperatur kann Veresterung eintreten unter Bildung neuer Si–O–C-Bindungen. Schon kleine Gehalte an Wasser ergeben eine Vorherrschaft der Reaktionen des $H_2O$. Andererseits bewirkt Ethanol eine Verdünnung des Wassers, wodurch die Reaktionsgeschwindigkeiten verringert werden. Andere Erscheinungen werden durch die OH-Gruppe bestimmt, die für die Bildung von Wasserstoffbindungen verantwortlich ist, z. B. bei der Adsorption. Zusammenhänge bestehen auch mit den Gelschichten, Glaselektroden, Kieselgelen und dem Sol-Gel-Prozeß. Physikalische Wechselwirkungen, z. B. Festigkeit, Bruchgeschwindigkeit, Abrieb, werden auch durch die molekularen Eigenschaften von $C_2H_5OH$ beeinflußt.

### 1. Introduction

The reason why glass has found a wide range of applications is because glass has proven itself to be inert to most agents with which it comes in contact during general use. Especially decisive for this was the good behavior of glass in the presence of water. Only in the 18th century it was recognized that glass can be attacked by water, a phenomenon the elucidation of which even today occupies numerous glass researchers. Much knowledge has been gained in meantime which indicates that in addition to purely chemical interactions between glass surfaces and water there exist additional interactions that also can markedly affect some of the glass properties. This raises the question whether similar effects can also be produced by other liquids. The present work attempts to compile and to confront some of these investigations. In doing so, the behavior of ethanol will stand predominantly in the foreground because, on one hand, it is the liquid which after water stands most frequently in contact with glass, even though mostly in diluted form; and because, on the other hand, there exist certain physico-chemical similarities between both liquids, caused by the OH groups.

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### 2. Chemical interaction

#### 2.1. Soda-lime-silica glasses

Due to the relatively late start of investigations on the durability of glass in water, it is not surprising that in these early studies side effects such as the influence of the solubility components were not being considered. This, however, changed at the beginning of the 20th century as the requirements became greater, and new problems arose with the introduction of fully automatic machines. This was also the reason for the lecture by Turner [1] in 1934 in the USA, in which he stated: "It is the object of this paper to comment on some of the more fundamental conditions, which should be understood in connection with the testing of glass containers." His comments were grouped into three main sections, with the special case of aqueous alcohols or of alcoholic preparations as the last one. The starting point is his statement that "there is very little information available in published literature about the action of alcohol and alcoholic solutions on glass. Such as there is would suggest that no marked corrosive action should be expected and this would probably be the normal view on physico-chemical

grounds. For whereas hydrolytic action, due to water, is clearly understood, equally marked behavior on the part of ethyl alcohol would not be predicted. In practice, the fact that whisky and other alcoholic spirits have for generations been stored in glass without suffering harm is an obviously powerful argument against any marked corrosive action on glass by ethyl alcohol".

This points not only to the practical objective, namely to investigate the long-time behavior of bottles filled with alcoholic spirits, but suggests also that essentially no hydrolytic reaction is to be expected. Controlled experiments were carried out with commercial 4-ounce bottles. After 24 h at 30 °C, for example, the soda contents in the extracts for a certain type of bottle were measured to be 0.15, 0.11, 0.07 or 0.03 mg $Na_2O$ when the test solution contained 0, 20, 40 or 60 vol% ethanol. This clearly indicates that ethanol does not enhance the extraction of alkali, but instead tends to retard it if one, in the first approximation, regards the addition of ethanol as "dilution" of the water.

In addition to the extraction of alkali, the experiments included visual observations, searching for the appearance of flakes. In the mentioned example, flakes appeared after about 8 d. With increasing ethanol contents these times became shorter, solution with 60 % ethanol exhibited flakes after 6 h. Turner does not give any explanation for this, but one must assume that in the presence of ethanol there is formed a reaction layer that is easily detached.

Similar investigations were reported a short time later by Bacon and Burch [2]. They, however, verified the above results only partially. The following observation is important: "The total corrosion of the bottles, as determined by the total amount of material extracted from each bottle, decreased slightly as the alcoholic content of the solution was increased from 0 to 20 % by volume, and it decreased rapidly as the percentage of alcohol was increased from 20 to 40 %". The following additional observation of them clearly differs from the results of Turner: "The resistance of glass to flaking when it is in contact with alcoholic solutions increases in general as the alcoholic concentration is increased. This, however, is not true of all glass compositions". An explanation for this discrepancy is not given. However, it is reminiscent of numerous investigations on chemical durability of commercial glasses which, according to published information, were carried out in similar manner but produced significantly different results. The reason for this is to be found in the complicated mechanism, or better in the complicated mechanisms of glass corrosion in which many parameters play a role, also secondary constituents that were not being considered or whose action was not known or also yet still not known.

Akagi [3] arrived at a similar result as Bacon and Burch: "The extent of corrosion of glass by water can be reduced by the addition of alcohol" and "It does not appear that the flakes are more easily formed in alcoholic solutions than in water". But it is to be considered that alcoholic solutions have a marked tendency to form the solid products such as a precipitate or turbidity consisting of fine and white amorphous particles. This can be accounted for by the poor solubility of calcium silicate compounds, formed in the reaction of the glass with water in alcoholic solutions.

Experiments with very high ethanol contents are difficult to perform on the usual hollow-glass compositions because the reactions in such solutions proceed extremely slowly. One can increase the reaction products by increasing the reaction temperature, but this involves the danger that other reaction mechanisms then become predominant. Another path is to change the glass composition, e.g. by increasing the alkali content and replacing CaO with other alkaline earth oxides. The latter approach was taken by Boksay et al. [4] with the glass (composition in mol%) 28 $Na_2O$, 4 SrO, and 68 $SiO_2$ at 40 °C. The subsequent analysis of the treated glass surface showed after 312 h in absolute ethanol only a very thin reaction layer with a steady increase of sodium content from zero in the surface to the starting concentration in the interior after 3 µm. A direct ion exchange $Na^+_{glass} \rightleftarrows H^+_{ethanol}$ is assumed responsible for this decrease in sodium concentration. However, only small amounts of $H_2O$, such as exist in an azeotropic mixture of 96 % ethanol, suffice for the formation of hydroxonium ions, $H_3O^+$, which can lead to a substantially quicker ion exchange. It can account for the 6 µm thick reaction layer observed after 168 h, as is typically observed during the extraction from soda-lime-silica glasses in water. According to Boksay et al. [4] the penetrating $H_3O^+$ ions bring about structural changes of the network in the reaction layer which cause a loosening of the entire structure and thereby facilitate the interdiffusion in such layer. (For comparison the corrosion layers after treatment with pure $H_2O$ are about 50 µm thick.) Such a structural change does not take place on treatment with absolute ethanol.

One can summarize these investigations by saying that the addition of ethanol to water decreases the corrosion rate of soda-lime-silica glass. The extraction is always determined by the ion exchange $Na^+ \rightleftarrows H^+ \cdot x\, H_2O$. A direct chemical action of $C_2H_5OH$ molecules in this reaction has not yet been demonstrated. Indirectly, the influences are possible in that the slower proceeding extraction leads to an altered structure in the reaction layer, and that for some compounds the solubility limits are exceeded as the ethanol content is being increased, causing them to precipitate. This makes variability in measurement

results comprehensible. Consequently, when carrying out practical related experiments with alcohol it should be kept in mind that additional components may be taking part in the reactions. Ethanol that is completely water free reacts very slowly, if at all. It still needs to be shown whether ethanol can provide protons for such ion exchange.

### 2.2. $SiO_2$ surface

The described experiments show that an alkali-impoverished surface layer results when alkaline earth alkali silicate glasses are subjected to aqueous solutions, and that the surface which is directly in contact with the solution consists essentially of $SiO_2$ or $SiO_2$ gel. Any further dissolution is then determined by the reactions with this layer. To obtain a more detailed explanation of the dissolution behavior, it consequently is justifiable to search the literature for information regarding the behavior of $SiO_2$ gel in alcohol or alcoholic solutions.

The information for this, however, is limited and deals chiefly with methanol. Iler [5] writes 1979: "At 25 °C, amorphous silica is essentially insoluble in methanol." The latter is consistent with data from Akagi [3] according to which 1.5, 1.1 or 0.5 ppm $SiO_2$ are dissolved from a silica glass flask at 50 °C in 150 h on exposure to slightly alkaline water, 20 or 33 % ethanol solution (initial pH value = 9.1, final pH value = 7.6), respectively. This upon first approximation suggests a dilution effect, but certainly also could be due to additional interactions. The esterification

$$\equiv Si-OH + C_2H_5OH = \equiv Si-O-C_2H_5 + H_2O$$

is discussed in connection with this. Azrak and Angell [6] attempted to show the formation of a Si–O–C bond by means of infrared spectroscopy, but unfortunately not with ethanol but with butanol and other larger alcohols and amines. One can generalize their results by stating that alcohols on $SiO_2$ gel surfaces at room temperature are essentially bound only by hydrogen bonds which indeed are not very stable.

A more stable bond on the $SiO_2$ surface occurs at temperatures above 100 °C. This was investigated especially by Kitahara et al. [7 to 9]. The reaction

$$\equiv Si-O-Si \equiv + 2\,MeOH \rightarrow 2 \equiv Si-O-Me + H_2O\,,$$

proposed in connection with this, explains the hydrophobic character of such surfaces. It namely was established during such experiments that the silica surface was covered with a close-packed layer of methyl and very probably also of ethyl groups. The esterification of the surface of their silica gel (preheated at 500 °C, and then heated with alcohol in an autoclave at 150 to 250 °C) yielded 5.0 methoxy groups per $nm^2$ or 3.0 ethoxy groups per $nm^2$. (An ethoxy group thus has a surface requirement of 0.33 $nm^2$, which for a circular arrangement corresponds to a diameter of 0.65 nm.)

If in the above equation not only one but numerous Si–O–Si bonds of the network are broken, in the limiting case all four bonds on one silicon, then there will take place cleavage of the network through the formation of smaller molecules. In the limiting case there will be $Si(OR)_4$ molecules which dissolve in alcohol. Such reactions are considered responsible, according to Kitahara [7], for the solubility of $SiO_2$ in alcohol. Under the experimental conditions mentioned above he found the following solubilities: methanol 1890, ethanol 164, and propanol 8 mg $SiO_2$ per liter alcohol. The smaller the alcohol molecule the more siloxane bonds in the silica gel are broken by alcoholysis. Thus, ethanol is capable of dissolving the $SiO_2$ surface by alcoholysis, but only at elevated temperatures.

### 2.3. Lead crystal glasses

It is also obvious to inquire into the behavior of ethanol with regard to lead crystal glass because of its frequent use as drinking vessel. Some years ago Dronsfield [10] discussed the possibility that a woman in the USA died of lead poisoning as a result of drinking cocktails from lead crystal glasses. This suspicion was shortly thereafter appropriately rejected in a note by Normandale [11] in which he referred to the International Standards and to the low lead release values of lead crystal tablewares. This is in agreement with the author's earlier measurements [12]. In comparison to standard test solutions the lead release in alcoholic drinks is only about one-third in magnitude.

Another communication by Newton [13] led to the following finding: "No ordinary user need fear lead poisoning from drinking cocktails out of lead crystal glassware". In connection with this he referred especially to the investigations of Paul and Youssefi [14] with a ternary $K_2O-PbO-SiO_2$ glass at 50 °C in 0 to 50 vol% $C_2H_5OH$ at pH values of 5 to 12. They found that only "the initial lead extraction in 50 % ethanol is higher than in alcohol free solutions. However, the lead extraction in the alcoholic solutions reaches a maximum in about 2 h and no further lead leaches from the glass, whereas the lead extraction in alcohol-free solutions increases continuously with time". As explanation they cite that "Ethyl alcohol favours rapid lead extraction at short times due to the formation of the soluble lead-ethyl alcohol complex. However, at long times (more than 2 h at 50 °C) a protective layer of insoluble ethyl silicate is formed on the glass surface, and this drastically reduces further lead release from the

glass". Especially the last condition is to be assumed the case for lead crystal vessels that have been used at least once. Thus, one can be in full agreement with the above conclusions by Newton.

### 2.4. Leached layers

It has already been pointed out several times that a leached layer results on exposure of alkaline earth alkali silicate glasses to aqueous solutions, that such layer is caused by ion exchange of alkali ions in the glasses with protons in the solution, that the protons are associated with $H_2O$ molecules, and that the number of such protons above all depends on the composition of the glass. In a recent compilation [15] it was pointed out that the interactions depend on many parameters. Special significance must be attached to the high mobility of water in the leached layer and the possibility of the rearrangement of the structure which leads to a phase separation.

The complexity of these reactions and the influence of the compounds dissolved in the water make it understandable that in alcoholic solutions the formation of a leached layer will proceed in a somewhat different manner than in pure water. Some of the phenomena were already pointed out in section 2.1. It should be only briefly mentioned here that in the literature the leached layers are frequently referred to as gel layers, which in view of their structures, microstructures and high water contents is justifiable.

The influence of ethanol on the formation of a leached layer was investigated especially by Boksay et al. [4] (see section 2.1.). Boksay [16] later reinforced his concept: "In the formation of the gel layer, the water has an outstanding role since in the absence of water, e.g. when absolute alcohol is used for leaching the glass, no sign of gel formation can be detected".

The latter reference leads directly to the glass electrodes since it is known that a proper determination of the potential and thus of the pH value is possible only when they have been sufficiently hydrated prior to first use. The fact that one can make measurements in water-free solutions led Schwabe [17] to assume that the glass electrodes used for such measurements already possess a hydrated layer. With increasing ethanol content one observes side effects, e.g. a shift in potential as a function of measuring time. Investigations regarding the reasons for this have not been made known, but it can be assumed that an increasing ethanol content changes the structure and microstructure of the leached layer.

The last conclusion can be generalized as follows: Each gel layer that has been formed in water will be altered when the water content is decreased by addition of ethanol. Consequently, it would be interesting to know what these changes are since they most likely also affect some of its properties.

## 3. Adsorption

Besides the occurrence of chemical reactions, one can reckon with adsorption phenomena because it is known from the $H_2O$ molecule that its tendency to form hydrogen bridges promotes adsorption, a property that to a certain extent also is characteristic for the alcohol molecules. Appropriate experiments generally involve the vapor phase, but despite this it is frequently possible to obtain additional insight regarding reaction mechanisms.

### 3.1. Solid glass surfaces

There are some publications concerning the adsorption on glass surfaces but only very few that deal with the behavior of alcohols. Sewell [18] uses polished sheet glass. In order to make a reproducible surface, the glass was first cleaned in carbon tetrachloride to remove grease and then immersed in distilled water at room temperature for further 16 h. As adsorbate he used, in addition to $CCl_4$, $CHCl_3$, and $C_6H_6$, also $CH_3OH$. The evaluation of the adsorption measurements with $CH_3OH$ led to a calculated surface of the glass which was nearly eight times that of the geometric surface. From this it follows that pores were formed in the glass surface on 16 h treatment in water and that methanol molecules penetrate these pores, indicating that the pores must have a diameter of over 0.5 nm.

The latter experiments unfortunately give no information whether ethanol molecules can also enter the leached layer. This does not appear to be the case according to Žhdanov [19], at least not for the silicate glasses that had been investigated by him. The pores in these leached layers must therefore be smaller than $C_2H_5OH$ molecules.

Glasses with standardized pore diameters can be prepared after phase separation and leaching. Yazawa et al. [20] have done so for the purpose of investigating the reaction with organic compounds. For glass with an average pore diameter of 4 nm there were no problems reaching a full coverage with ethanol molecules in the pores. The experiments were carried out in an autoclave at 150 °C. It is assumed that the alcohol molecules react with the surface silanol groups in the pores. From the complete degree of coverage which was measured, the surface requirement per $C_2H_5O$ group is 0.44 $nm^2$ (corresponding to a diameter of 0.75 nm).

From these limited investigations it can be concluded that $C_2H_5OH$ exhibits a similar behavior as $H_2O$, and that glass surfaces that have been altered prior to such investigations adsorb greater amounts than an ideal smooth surface. This is chiefly caused by pores in real surfaces in which the adsorbed amounts can vary significantly depending on both the size of the pores and the alcohol. By varying the alcohol molecules one can obtain information regarding the

microstructure of the surface layer. An increased adsorption of ethanol on commercial glass surfaces has not been reported. If this should be the case, it would be interesting to know how strong the $C_2H_5OH$ molecules are bound in these pores.

### 3.2. Silica gel

Leached glass surfaces show structural relationship to $SiO_2$ gels if one describes silica gels as did Iler [5], namely as a coherent, rigid three-dimensional network of continuous particles of colloidal silica, ranging from 1 to 100 nm in diameter. (The terms aquagel and alcogel refer to gels in which the pores are filled with the corresponding liquid, that is, water or alcohol. A xerogel is a gel from which the liquid medium has been removed, an aerogel is a special type of xerogel from which the liquid has been removed in such a way as to prevent any collapse or change in the structure as liquid is being removed.)

There are very many adsorption measurements on $SiO_2$ gels, but only very few with alcohol as adsorbate. Davydov and Kiselev [21] used Aerosil as adsorbent and followed the adsorption, among others, of ethanol in the vapor phase by infrared spectroscopy using the OH band in the region around 3300 $cm^{-1}$. The noteworthy result is that the adsorption of the $C_2H_5OH$ molecules does not occur on the bound hydroxyl groups of the silica surface but on their free hydroxyl groups forming new hydrogen bonds.

The methods of preparation and the aging conditions have a significant effect on the pore structure of silica gels, particularly on the pore size of the xerogels, investigated by Nakanishi and Soga [22]. Their gels were heated at a heating rate of 1 K/min to 500 or 800 °C in an electric furnace in air, held for 6 h, then slowly cooled to ambient temperature. For each measurement the gel sample was outgassed for 3 h at 150 °C under 0.013 mbar. The shape of the adsorption isotherms of methanol and ethanol on the gel, heat-treated at 500 °C, is type IV of BET classification, corresponding to the process of multilayer adsorption accompanied by capillary condensation. The calculated hydraulic pore radii were about 0.8 nm, e.g. $C_2H_5OH$ molecules still penetrate into pores having a diameter of only 1.6 nm.

These data show that one can obtain valuable information regarding the microstructure of fine-pored gels by adsorption experiments with ethanol. It verifies the conclusions from section 3.1.

## 4. Sol-gel process

A completely different interaction between silica and alcohol occurs in the case of the sol-gel process. It represents in a certain manner a reversal of the formation of alcoholates, as starting compounds to produce, among other things, glasses. Sakka and Kamiya [23] have described this. The process consists essentially of the following reaction steps: hydrolysis, gelling, and heating.

Alcohol or ethanol here plays a double role, once as component of the precursor ester tetraethylorthosilicate (TEOS) $Si(OC_2H_5)_4$, then also as solvent because TEOS is only moderately soluble in $H_2O$. Additional $C_2H_5OH$ produces a single phase solution of TEOS and $H_2O$, and hence a homogeneous gel. In addition to the numerous experimental parameters the proportions of the mixture of the three mentioned components play an important role as regards the structure and microstructure of the gels being formed and their sintering behavior. Shukla and Johari [24] found that especially the densification of the gel at room temperature strongly depends on the $C_2H_5OH$ concentration, which shows that there exists an interaction that cannot yet be explained in detail. But it is not absolutely necessary to add alcohol in this way. Avnir and Kaufman [25] namely point out that alcohol is formed on hydrolysis so that the system becomes homogeneous a short while after the reaction starts. Stirring, shaking, or subjecting to ultrasound increase the reaction rate.

The number of publications on the sol-gel process has markedly increased in the last years. It is hoped that a systematic evaluation with regard to the influence of ethanol will lead to profound knowledge.

## 5. Physical interactions

The physical interactions are manyfold. They are frequently determined by the transport of ethanol molecules at the glass surface and are sometimes obscured by chemical interactions.

### 5.1. Strength – fracture velocity

The influence of various organic liquids on the strength of glass has been investigated by Moorthy and Tooley [26]. They compared the tensile strength of glass rods taken from sheet glass in these liquids with the strength values obtained from measurements in water. In doing so the measurements in ethanol yielded about 30 % higher strength values, because the influence of water can hardly operate. The effect of a preceeding storage in these liquids led to contrary results, with water producing a higher tensile strength than alcohol (measured in methanol only). This is attributed to the fact that aging, which causes the strength increase, proceeds all the more rapidly the more $H_2O$ is available.

The influence of $H_2O$ on crack behavior has been known for some time and has been repeatedly investigated, among others by Wiederhorn et al. [27],

in connection with the influence of other dielectrics. When water is present in organic liquids, e.g. in ethanol, it remains the principle agent that promotes subcritical crack growth in glass. In crack growth region I with low crack velocities, subcritical crack growth is controlled primarily by the chemical potential of the water. Thus, at the stress-intensity factor $K_I$ of 0.5 MPa $m^{1/2}$ following crack velocities were measured in the system $H_2O-C_2H_5OH$ with 0, 30, 95, 99, and 99.8 vol% $C_2H_5OH$: $1.5 \cdot 10^{-6}$, $4 \cdot 10^{-7}$, $1.5 \cdot 10^{-7}$, $8 \cdot 10^{-8}$ and $<10^{-8}$ m $s^{-1}$, respectively. In the middle region II, crack growth is controlled by the concentration of water and the viscosity of the solution formed by the water and the ethanol. In region III with high crack velocities, where neither water nor ethanol affects crack growth, the slope of the crack-growth curves can be correlated with the dielectric constant of the liquid. Wiederhorn et al. suggest that these latter results can be explained by electrostatic interactions between the environment and charges that form during rupture of Si–O bonds. This is also the region where after Freiman [28] the chain length of the alcohols affects the result, and where crack velocity decreased monotonically with increasing chain length at a given stress-intensity factor $K$. This is also in agreement with measurements by Richter and Schinker [29].

### 5.2. Abrasion

Abrasion is a very complicated process which depends on many parameters. The obvious assumption that the formation of new surfaces by abrasion or by grinding can be related to the behavior of many small individual cracks is not sufficient because, according to that, one would expect that for primary alcohols abrasion would decrease with increasing chain length. The opposite is the case for alcohols with short chain lengths, according to measurements by Richter and Schinker [29]. Upon substitution of ethanol for $H_2O$ they observed a decrease in abrasion of about 30 %. Increasing the chain length raises the abrasion which with hexanol corresponds to that of $H_2O$. But small amounts of $H_2O$ cause an increase in abrasion with short chain alcohols. Also this influence of ethanol, which was found to be analogous upon measurement of the drilling rate of a borosilicate glass according to Cuthrell [30], requires still additional clarification.

## 6. Solubility of ethanol in glass

When a solid comes in contact with a liquid or a gas one must check whether the interaction is limited only to the surface of contact or whether the mobile partner has the possibility or ability to penetrate the solid. The investigations mentioned so far in this publication have not given any indications for this, if one does not count the penetration of ethanol molecules in the pores of the leached layer or gel layer. More extreme experimental conditions are indeed needed, especially higher pressures, before one can expect a dissolution of such molecules.

Such extreme experimental conditions exist in the hydration experiments carried out by Bartholomew et al. [31] in which alkali silicate glasses were heated at temperatures up to 300 °C in autoclaves in the presence of liquid or vapor of aqueous solutions containing a relatively short chain aliphatic alcohol. The resulting hydrated glass exhibited improved mechanical properties and, furthermore, also thermoplastic characteristics. The latter property is due to the high water content of the treated glasses, which amounted up to 40 wt%, rather than an eventual incorporation of ethanol in the glass structure. A dissolution of alcohol molecules does not take place according to Bartholomew [32]. The presence of alcohols, however, permits better control of water content absorbed in the glass and by this thermoplastic properties.

Nogami and Tomozawa [33] intensified the experimental conditions by placing $Na_2O \cdot 3\ SiO_2$ glass together with the desired amount of dehydrolysed pure ethanol in a sealed platinum tube and heating and pressurizing the charge to 900 °C at about 1 kbar for 7 h. Glasses with high ethanol content, such as 8.55 wt% were obtained. Their color was black and it was heterogeneous, however, glasses containing only 0.56 wt% ethanol consisted of the homogeneous single phase. The latter glass shows a weight loss of 0.25 % on heating at 550 °C for 30 min. This behavior is markedly different from that of the water-containing glasses in which water is completely evaporated at 550 °C. On heating at higher temperatures, a further weight loss of ethanol-impregnated samples took place, gradually accompanied by the change of the specimen color to gray or white. These phenomena suggest that ethanol reacted with glasses under hydrothermal conditions to result in the formation of new chemical bonds forming Si–O–C groups. This explains the increase in hardness and density with the first ethanol content. Therefore, the glasses became more brittle when impregnated with ethanol.

Thus, it is shown that in addition to the esterification and alcoholysis, such as were mentioned in section 2.2., a further reaction possibility occurs at the more extreme experimental conditions.

## 7. Summary – comprehensive remarks

In contrast to $H_2O$, practically no chemical interaction takes place with absolute $C_2H_5OH$ under normal ambient conditions. However, the presence of a small amount of $H_2O$ in pure alcohol is already sufficient to produce reactions that are attributable to such $H_2O$, and one can more or less perceive ethanol as "diluting

agent" for water, whereby the reactions are slowed down. In other words: In alcoholic solutions soda-lime-silica glasses exhibit better chemical durability. This statement also holds for lead crystal glass, but must be somewhat modified for initial contact with such solutions. It should be pointed out that the structure and microstructure of the leached surface layers is influenced by the presence of ethanol.

Owing to the OH groups, $C_2H_5OH$ has a similar adsorption tendency as $H_2O$ in which hydrogen bonding plays a substantial role. Surface Si–OH groups on glass can be esterified. Upon carrying out such experiments at elevated temperatures and pressures one observes that the esterification proceeds even further, resulting in a certain solubility of $SiO_2$ in $C_2H_5OH$. In the case of the latter reaction the formation of Si–O–C bonds is of interest.

The known influences of $H_2O$ on some physical properties, especially strength and crack velocity, make it clear that ethanol or alcoholic solutions always show corresponding actions when the effect is brought about by $H_2O$ or by OH groups. However, it should be pointed out that there are also effects that are influenced by the properties of $C_2H_5OH$ molecules.

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