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CONTRIBUTION TO THE KINETICS OF GLASS FORMATION FROM SOLUTIONS

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The different reaction steps during the formation of solid materials from metal alkoxides were investigated by IR and DSC methods. The kinetics of hydrolysis of the different components in the system $Na_2O/B_2O_3/SiO_2$ show, that the hydrolysis of $Si(OR)_4$ in alcoholic solution is the slowest reaction and may determine the way of cross-linking. The use of alcohol as a solvent leads to incomplete reactions and this, as a consequence, may disturb the process of glass formation. Concerning the glass transition, no difference in transition temperature between gel glasses and conventionally melted glasses could be observed.

1. Introduction

The formation of glass by the sol–gel process may be considered as a special case of the formation of inorganic amorphous and polymer solid materials. The principle of this reaction path is well-known, and takes place in nature, when materials like agate or chalcedony are formed [1], and it is used as a technique for the production of silica gels and aluminum oxides. Principally, the reaction starts from soluble monomeric or oligomeric components which are then reacted to solid materials (condensation reaction). The prerequisite with respect to the solvents only is a sufficient solubility of the monomers. Under certain circumstances the monomers themselves can serve as solvents.

A prerequisite for the condensation reaction is the presence of reactive groups and suitable reaction conditions. For example, silica gel will be formed by the reaction of $\equiv$SiOH-groups to a siloxane bond under the formation of water. Such $\equiv$SiOH-groups may just be present in a stabilized sol or may be formed by the reaction of derivates:

$$\equiv SiOR + HX \rightarrow \equiv Si - OH + RX, \qquad (1)$$

e.g. $R = CH_3$ and $X = OH$. Suitable reaction conditions may be created by exceeding the solubility (e.g. as a function of the pH-value) or by using special catalysts. It is not the intention of this paper to deal with the large number of possibilities of carrying out such reactions. However, interesting aspects result from the generalizability of this reaction principle. Instead of using silicic acid only as a cross-linking agent, it is possible to use other analogous reacting elements. The incorporation of non-cross-linking components is possible, and is not limited to oxide forming elements. In an analogous manner, the

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co-condensation of organic components may be performed. Another type of modification results from the use of substituted esters of silicic acid containing $\equiv$Si–C$\equiv$-bonds. By the combination of the described principles, so-called organic modified silicates can be prepared.

In this paper it will be demonstrated using purely inorganic models, how the mechanisms of the single reaction steps may effect the properties of the materials produced, how these properties may become understandable by the way of the reaction, especially when more than one component is used:

$$\begin{aligned} &n\underset{a}{\mathrm{Me^{III}(O}R)_3} + m\underset{b}{\mathrm{Me^{IV}(O}R)_4} + (3n+4m)\ \mathrm{H_2O} \\ &\quad \rightleftharpoons n\mathrm{Me^{III}(OH)_3} + m\mathrm{Me^{IV}(OH)_4} + (3n+4m)\ R\mathrm{OH} \qquad (2) \end{aligned}$$

$$n\underset{a'}{\mathrm{Me^{III}(OH)_3}} + m\underset{b'}{\mathrm{Me^{IV}(OH)_4}} \rightarrow \frac{n}{2}\mathrm{Me_2^{III}O_3} \cdot m\mathrm{Me^{IV}O_2} + \frac{3n+4m}{2}\mathrm{H_2O}. \qquad (3)$$

Reaction (3) may be defined as a condensation reaction and involves cross-linking when a′ and b′ are soluble. The type of cross-linking depends strongly on the rate of hydrolysis of a and b. Generally speaking, the reactions (2) and (3) define the primary structure of a gel. Other reactions may contribute further effects. As shown by Dislich, in certain cases the formation of complexes may occur [2]:

$$\mathrm{NaO}R + \mathrm{B(O}R)_3 \rightarrow \mathrm{Na^+[B(O}R)_4]^-.$$

Using metal alkoxides in organic solution leads to a quite generalizable way of producing gels. Only a cross-linking agent is necessary and for this, esters of silicic acid are very useful. For hydrolysis only water has to be added, and the reaction starts. Sometimes it is necessary to use catalysts. Acids as well as bases may be used. The only limitation is that no unsoluble salts should be formed.

In the literature there are numerous publications which describe the reaction of esters and other derivates of silicic acid [3–6]. Most of this work has been carried out in order to investigate the reaction mechanisms of the H^+-catalyzed as well as the OH^--catalyzed reaction. The results show, that as a function of the reaction conditions (solvent, temperature, concentration) different kinetics and mechanisms are proposed, which range from zero to third order, e.g. in H^+-catalyzed hydrolysis in the case of tetraethoxysilane. Almost no data about condensation kinetics and structural details are available.

More complex systems were described by Geffcken in 1939 for the preparation of metal oxide films from hydrolysable metal organic compounds [7]. In 1951 Roy described a method for preparing crystalline products by the gel route from organic solutions of metal salts [8]. The formation of thin films was especially developed by Schröder and Dislich [9,10]. Within the last 15 years many authors have been working on questions concerning the mechanisms of glass formation by the gel route. A matter of general interest is the gel–glass transition mechanism. In this connection the hydrolysis reaction of $Si(OR)_4$ is very often investigated. Some authors use the amount of water in the reacting system as an indicator. The measurement is normally done by chemical analysis [11–18].

The use of IR-spectroscopy for investigating the hydrolysis and condensation reaction by monitoring the H_2O-content of the reacting system [19] offers the advantage of very simple *in situ* observation, and furthermore, it will be possible to investigate systems under conditions, where the condensation to gels for glass formation occurs. For a better understanding of the reaction of complex systems, it seems to be necessary to start with single components. The system $Na_2O/B_2O_3/SiO_2$ was selected as a model.

2. Experimental

The preparation of solid materials from metal–organic compounds may be divided into two main steps: hydrolysis and condensation. The latter may be followed by other steps: densification, sintering, crystallization or vitrification. For monitoring the hydrolysis reaction the above mentioned IR-method was used. For measuring the condensation process and the influence of heat treatment, IR was used, too: KBr pellets were coated with gel solution by dipping the pellets into the liquid mixture and coating them with thin films. These films were heat treated in a closed infrared cell. Fig. 1 is a schematic representation of the measuring device.

As starting materials NaOMe, $B(OEt)_3$ and $Si(OMe)_4$ were used. The reactions were run at room temperature using ethanol or methanol as solvents.

The preparation of gels for monolithic glass pieces was performed at room temperature in closed systems using alcohols as the solvent; excess solvents were removed slowly using a light vacuum.

In order to characterize the monolithic gels produced the specific surface areas (BET area) were determined. The behaviour during temperature treat-

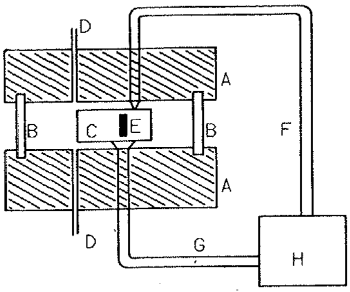


Fig. 1. Cell for IR-investigations at higher temperatures: A, cell housing with cooling system; B, KBr-windows; C, sample-holder (heatable); D, gas inlet/outlet; E, sample (coated KBr-pellet); F, thermocouple; G, heater; H, control unit.

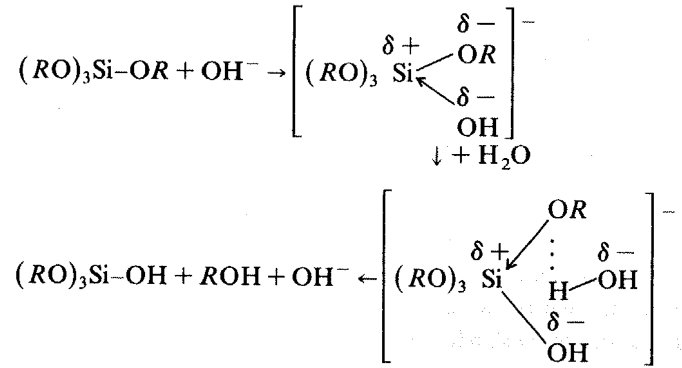
ments was determined by differential scanning calorimetry (Perkin Elmer DSC-2). The preparation of monolithic glasses was performed in a programmable and evacuable furnace.

3. Results

The rate of hydrolysis of ethyl silicate

$$\mathrm{Si(OEt)_4 + 4\,H_2O \rightleftharpoons Si(OH)_4 + 4\,EtOH} \tag{4}$$

in ethanol as solvent and with only water added is quite low as shown in previous experiments [4,19]. Addition of protons as catalysts leads to higher rates of hydrolysis. The analogous effect may be expected from OH^--groups, since they act as catalysts, too, as proposed in eq. (5):



(5)

In the system $NaOR/B(OR)_3/Si(OR)_4$ addition of water generates OH^--ions, so that in this system an alkaline catalysis takes place.

Investigations of the proton catalyzed hydrolysis of esters of silicic acid in ethanolic solution have shown a mainly first order reaction and a linear reaction rate dependence on proton concentration. Fig. 2 shows the OH^--catalyzed reaction of $Si(OR)_4$. The course of the reaction is not first order, that means no dependence on only one concentration of a reacting component is indicated. Also no second order dependence could be found. This is consistent with results of Aelion et al. [4], who found higher orders for NH_3-catalyzed hydrolysis of tetra-alkoxysilanes. Only during a very short period at the beginning of the reaction first order can be assumed. A rough computing of the reaction rate constants on this basis results in rate constants of about $10^{-4}\,s^{-1}$. The independence of these constants from the starting concentration of the water confirms the validity of the assumption.

The change of order might be explained by the beginning of other reactions like condensation; MS-investigations of the reactive system show that at the time when hydrolysis is not yet complete, condensation products as dimers of the type $(RO)_3\,Si–O–Si(OR)_3$ can be assumed.

The reaction rate itself is inversely proportional to the initial concentration

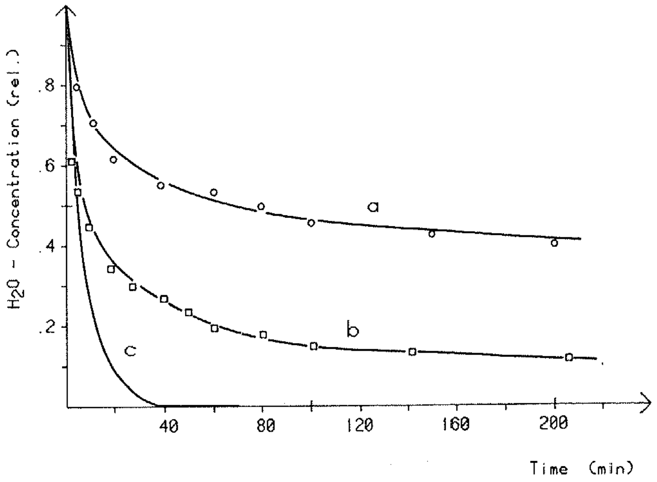


Fig. 2. OH^--catalyzed hydrolysis of tetraethoxysilane at 20°C in ethanol. $[OH^-]=5.5$ mMol/l. a, $Si(OR)_4:H_2O=1:4$; b, $Si(OR)_4:H_2O=2:4$; c, calculated H_2O-concentration after first order (analogous to curve b).

of the water. The latter effect was observed in the proton catalyzed reaction, too, and may be explained by a preferential coordination of OH^--groups to water in ethanolic solution, and as a consequence, a decrease in catalytic activity (nucleophilic attack on the Si atom).

In a series of investigations with different ester concentrations it could be shown that, as expected, with an increasing dilution the reaction rates become lower. The extent of the reaction also changes such that the reaction stops earlier. This can be explained since the solvent ethanol is a part of the reacting components, and determines the state of equilibrium [see eq. (4)].

The $B(OR)_3$ displays a completely different behaviour. Almost independent of the catalyst concentration the reaction reaches a steady state before the first infrared measurement (about 1 min after the starting point) was carried out, no complete reaction takes place:

$$B(OR)_3 + 3\,H_2O \rightleftharpoons B(OH)_3 + 3\,ROH. \tag{6}$$

NaO*R* undergoes almost complete hydrolysis. This reaction, as can be seen from IR-data, is finished within the first minute. The behaviour of $B(OR)_3$ and NaO*R* is demonstrated schematically in fig. 3. With regard to the overall reaction of metal alkoxides in the system $Na_2O/B_2O_3/SiO_2$, this means that the relatively slowly hydrolizing silicic esters face a reactive mixture of NaOH and $B(OH)_3$ or a complex $NaB(OH)_4$. Calculations of the equilibrium constants according to eq. (7)

$$k=\frac{[B(OH)_3][ROH]^3}{[B(OR)_3][H_2O]^3} \tag{7}$$

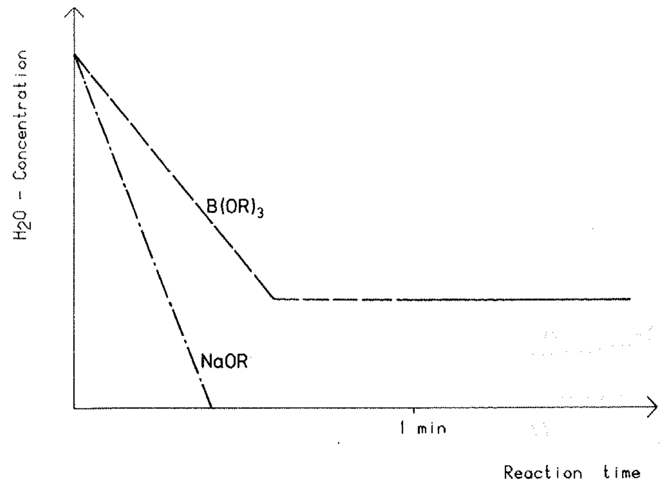


Fig. 3. Schematic course of the hydrolysis of ethylborate and sodium alcoholate in ethanol with water.

– stepwise hydrolysis and condensation is not taken into account – show constants independent of the concentration of the catalyst. These constants ($k \approx 10^4$) indicate a fairly incomplete hydrolysis. This may be explained by the effect of the ethanolic solution, where ethanol is a part of the reacting components.

The cross-linking reaction, which is very important as far as the material properties are concerned (homogeneity in the case of glass), may take place according to the obtained results in the three-component systems in two different ways: since satisfactory amounts of reactive boron acid are present, the further course of the reaction depends on the relative rate constants of the following reactions:

$$=\mathrm{B{-}OH} + \mathrm{HO{-}B}= \rightarrow\ =\mathrm{B{-}O{-}B}= + \mathrm{H_2O} \tag{8}$$

$$\equiv\mathrm{SiOH} + \mathrm{HO{-}Si}\equiv \rightarrow\ \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \tag{9}$$

$$=\mathrm{B{-}OH} + \mathrm{HO{-}Si}\equiv \rightarrow\ =\mathrm{B{-}O{-}Si}\equiv + \mathrm{H_2O}. \tag{10}$$

The reaction according to eq. (8) may take place only partially. The extent cannot be computed from the amount of water only, but if no external change in concentrations or temperature occurs, no change in the equilibrium will take place. A mass spectrometric control of the reacting system a few minutes after the starting point (when the steady state is already reached) shows no traces of dimeric or oligomeric species. The overall hydrolysis reaction of silicic esters is much slower than that of eq. (6). Thus, a mixture of boron and silicic ester should show an additive behaviour, if the reaction according to eq. (10) does not take place. Fig. 4 displays the change of water concentration of a mixture of boron and silicic ester (ratio 1 : 1). The strong decay in the beginning is due

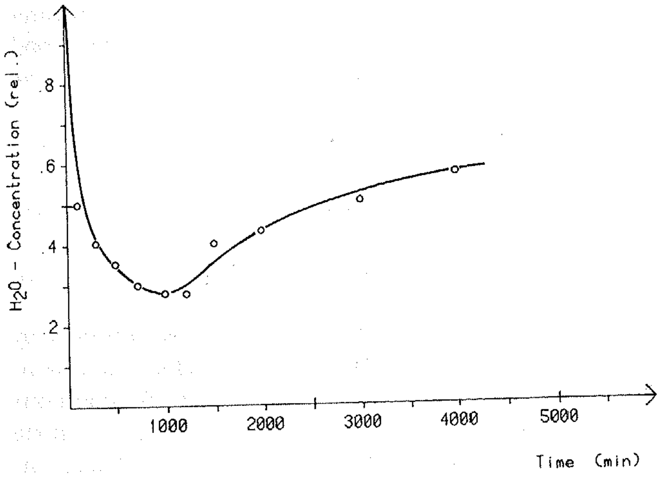


Fig. 4. Behaviour of an 1 : 1 mixture of ethylborate and tetramethoxysilane with water in ethanol.

to the hydrolysis of the boron ester. The following further decay results from the slower hydrolysis of the silicic ester. The subsequent increase of the water content, however, cannot be explained by the behaviour of the single components but might suggest the condensation reaction according to eq. (10). For a detailed explanation of this behaviour further investigations are necessary, especially with a system containing OH^--ions. The experiment schematically presented in fig. 4 was carried out without a catalyst in order to find out more

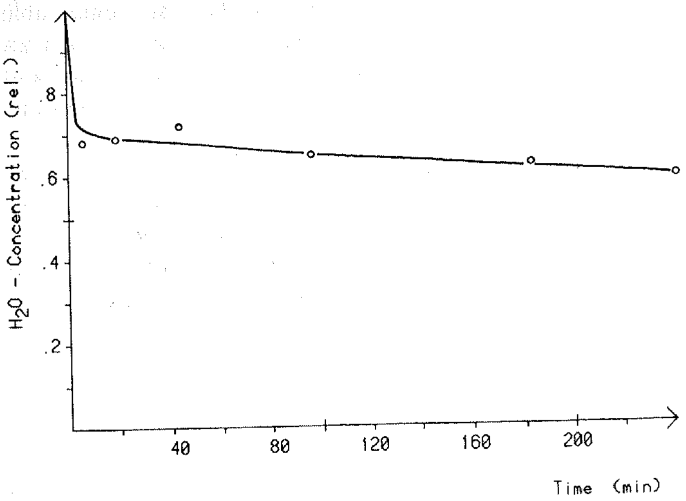


Fig. 5. Behaviour of the system $Na_2O/B_2O_3/SiO_2$ (weight-ratio 7:16:77): hydrolysis of the alkoxides in methanol with water.

details concerning the course of the reaction. The fact that no boron condensation products can be found at an earlier state of the reaction, should be a good hint that in boron silicate systems very homogeneous structures can be achieved by using the gel method.

The behaviour of the three-component system of composition (in wt%) 7 Na_2O; 16 B_2O_3; 77 SiO_2 is shown in fig. 5. The water concentration drops very rapidly due to the hydrolysis of $B(OR)_3$ and $NaOR$, followed by a lower decrease. Within the measuring time (the reaction was continued for about 20 h) no increase in the water content can be observed, whereas gelation occurred after a few hours.

Since the reaction in the liquid phase results in a steady state, where only an incomplete turnover is achieved, investigations of further condensation have to be performed by removing the solvent. This can be done under IR-conditions by using the cell described in fig. 1. As a consequence of the incomplete turnover, the gels formed contain larger amounts of unhydrolyzed and un-cross-linked components. Therefore, those gels contain organic residues which may disturb the glass formation reaction. Such groups may be detected by infrared-spectroscopy. Figs. 6a and 6b show the spectrum of a gel film dried at 70°C (line a). The spectrum shows that beside of high amounts of aliphatic hydrocarbons (2900 cm^{-1}) molecular water (δH_2O at 1650 cm^{-1}; νOH at 3500 cm^{-1}) is present. Further peaks between 1500 and 800 cm^{-1} are due to the $\equiv C–O–$, $= B–O–$ and $\equiv Si–O–$ bonds. The heat treatment of these films also is represented in fig. 6. At 200°C almost all the molecular water has disappeared.

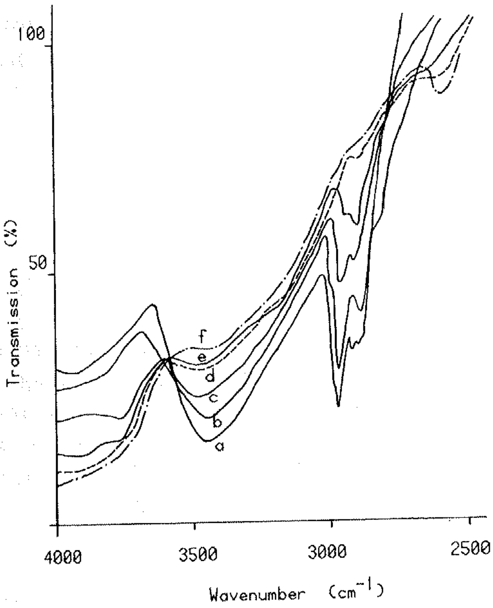
In contrast to this, one third of the hydrocarbons are still left and the OH^--groups at 3500 cm^{-1} still show intensive peaks. At 500°C almost no hydrocarbons are detectable, and the intensity of the OH^--groups has strongly decreased. The region between 1500 and 800 cm^{-1} offers no remarkable changes. The results show that even at higher temperatures it is pretty difficult to obtain water- and hydrocarbon-free gels, even if thin films (thickness about 30 μm) are applied. This fact may cause difficulties especially when monolithic glasses from gels should be obtained.

In order to find out whether it is possible to produce monolithic glass by this method, a series of experiments was carried out with different compositions. Thus (without using pressure), monolithic aluminum-, lead-, calcium- and phosphorus-containing glasses were prepared. Two types of gels (corresponding to borosilicate glasses) were used for further investigations (compositions in wt%):

1: 7 Na_2O; 16 B_2O_3; 77 SiO_2,

2: 15 Na_2O; 23 B_2O_3; 62 SiO_2.

Clear glass can be obtained by baking the gels at about 400°C in an O_2 atmosphere until all the hydrocarbons are oxydized, then evacuating the gels and heating until the shrinking and densifying of the glassy materials occur. Otherwise pyrolized carbon or bubbles resulting from the high porosity will be



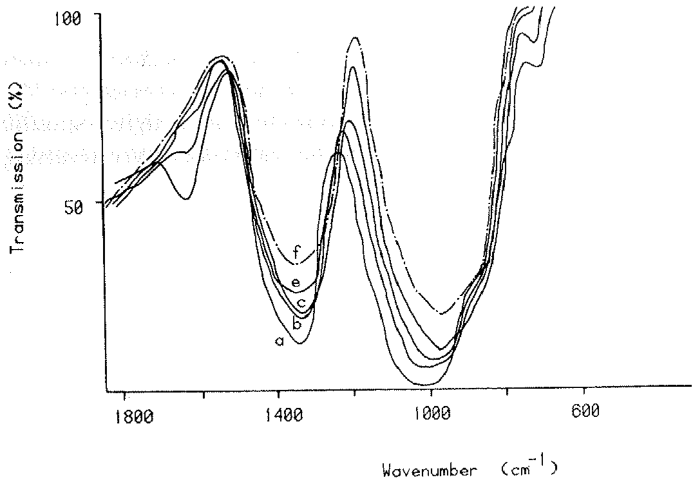


Fig. 6. (a) IR-spectra of gel films after heat treatment (15 min) at various temperatures in the range of 4000–2500 cm^{-1}. Gel composition (wt%): 7 Na_2O; 16 B_2O_3; 77 SiO_2. a, $T=70°C$; b, $T=100°C$; c, $T=200°C$; d, $T=300°C$; e, $T=400°C$; f, $T=500°C$. (b) IR-spectra of gel films after heat treatment (15 min) at various temperatures in the range of 1800–600 cm^{-1}. Indices according to the caption of fig. 6(a).

included. The gels regularly show a high porosity structure.

The investigation of the porosity of gels nos. 1 and 2 shows that the specific surface areas are 175 and 75 m^2/g after baking at about 300°C. Fig. 7 shows

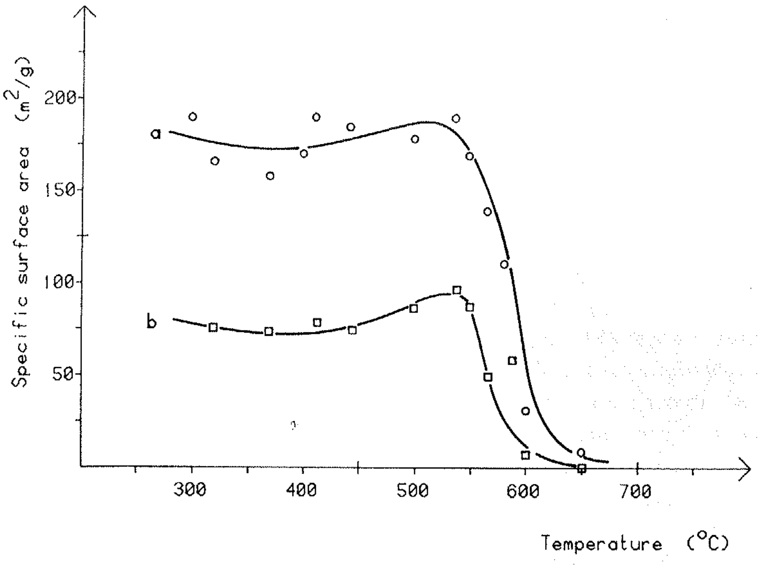


Fig. 7. Variation of the specific surface area of gel no. 1 (curve a) and gel no. 2 (curve b) after heat treatment at various temperatures (0.5 h in oxygen).

the breakdown of the specific surface area after heat treatment. Similar results with more complex systems were obtained by Brinker and Mukherjee [18].

As expected the glass with the higher silica content has a higher specific surface area, which may be explained by the more brittle structure resulting

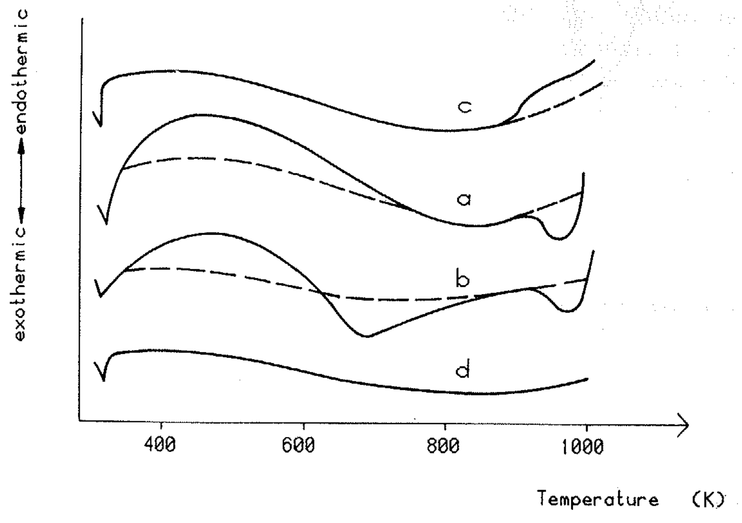


Fig. 8. DSC-runs of specimens of gel no. 1. Heating rate: 20 K/min. a, N_2-atmosphere; b, O_2-atmosphere; c, repetition scan of curve a (under N_2); d, baseline.

from a higher degree of cross-linkage because of the fourfold coordination of the silica. Both gels loose the main part of the accessible surface area between 550 and 600°C, but gel no. 1 still at a temperature of about 650°C has a measurable surface area. The resulting glasses were cloudy because of included microbubbles, since no vacuum treatment during heating was applied.

In order to investigate the gel–glass transition, DSC-scans with the gel type no. 1 were performed (fig. 8). The question, whether the high water content of the gels causes a lowering of the glass transition range is of special interest. Fig. 8 shows the DSC scans of different specimens. If the gel is heated under N_2 (curve a), a broad endothermic effect occurs between 300 and 700 K, indicating the loss of volatile compounds such as adsorbed water, solvents or oligomeric condensates. At about 960 K an exothermic peak appears. Repeating the scan with the same sample leads to curve c, where the exothermic effect at 960 K is no longer observed, but the transition temperature at about 900 K becomes visible. Within the precision of the measurement, no transition point at lower temperatures than shown in the repetition scan could be observed. The use of O_2 instead of N_2 only adds an exothermic effect at about 700 K, caused by the burning off of hydrocarbons. Analogous behaviour is shown by gel type no. 2. A baking out at 550°C with oxygen before the DSC scan does not lead to basically different curves: as shown in fig. 9, the exothermic effect at about 950 K is still present, though it is smaller. Computing the gain of surface energy leads to an order of magnitude that roughly agrees with the DSC measured energies, but in comparison with fig. 7 the temperature ranges differ for about 100 K. One interpretation might be that a stable closed pore system is formed during heating and the real loss of surface energy occurs at

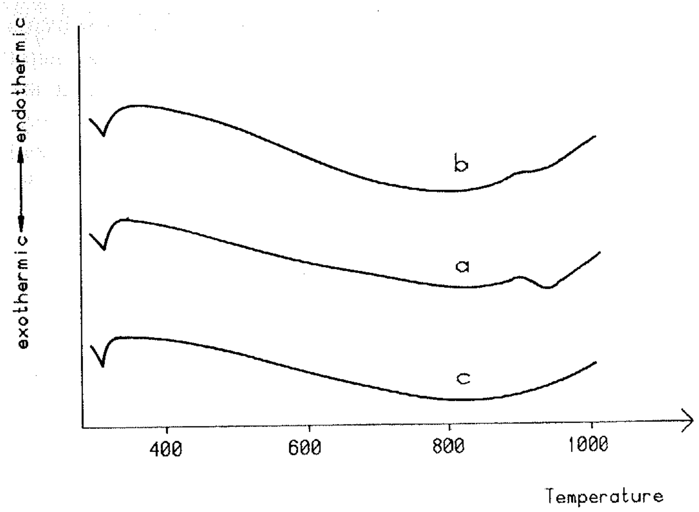


Fig. 9. DSC-runs of specimens of gel no. 2. Heating rate: 20 K/min. a, Pretreatment: 0.5 h at 550°C under O_2-flux; b, repetition scan of "a"; c, baseline.

higher temperatures, when the structure becomes more flexible, as indicated by DSC. Conventionally melted glasses did not display the exothermic effect, but did show an identical transition range.

4. Discussion

Investigations of model systems show that the hydrolysis and condensation processes of gel formation can be monitored by infrared spectroscopy and that statements about the overall reaction and the behaviour of the single components can be made.

Since the overall condensation process in multicomponent systems depends on the presence and reactivity of condensable intermediates, they play an important role for building up the structure of a gel and a glass prepared from this, when no melting process is applied. Structural details of the condensation process cannot be received from IR-data; but mass-spectroscopy seems to be a good tool for this: since oligomeric, $\equiv$Si–O–Si$\equiv$ containing compounds in a incompletely hydrolyzed system of ethyl silicate could be identified, there is a good chance that those structures will be later incorporated into the gel. In the case of boric acid esters, no condensation of hydrolyzed =B–OH forming =B–O–B= structure elements seems to take place at an early state of the reaction. This could lead to an homogeneous distribution at the beginning of the condensation reaction even at a molecular level. To confirm these first results, further investigations are necessary.

In the system $Na_2O/B_2O_3/SiO_2$ the hydrolysis reaction of methyl silicate is by far the slowest. That means that cross-linking can mainly occur as reactive silicic acids are produced, while homogeneously distributed reactive sodium- and boron-compounds are available. However, if alcohols are used as solvents (they are very convenient because of their good dissolving power for metal oxides, reactive intermediates, acids, and bases), they may take part in the reaction by influencing the hydrolysis equilibrium and keeping up a high content of unhydrolyzed educts even after the gel formation, as long as alcohol is present. These contents may strongly affect the glass formation, since by pyrolysis carbon will be developed. This seems to be a general disadvantage of the gel route, when using metal alkoxides for preparing monolithic glasses.

The achievable overall homogeneity seems to be good. In the case of boron silicate it seems to be understandable from mechanistic reasons, but more work has to be done to prove this. As a consequence of the high water content of the gels, a lowering of the glass transition temperature can be expected. DSC measurements, however, carried out with borosilicate gels do not show any change in the first run. The reasons therefore might be based on the limited sensitivity of the method or on the loss of water during the measuring procedure.

Finally some more general aspects should be mentioned: since the method of preparing solid material by hydrolysis and condensation is not only restricted to inorganic compounds, a wide variation of the composition is possible: thus, organic compounds may be introduced by co-condensation or by using substituted esters of silicic acid. A technologically very important example using $\equiv$Si–C$\equiv$-substituted monomers is the production of silicones. Making materials by the gel route leads to attractive aspects, when the behaviour of the single components and the influence of the reaction conditions are known. Taylor made materials with a wide range of properties should then be achievable.

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