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The problem of incorporating high levels of sodium nitrate into silica gels without segregation

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Na_2O–SiO_2 sols were prepared using silicon alkoxide and colloidal silica precursors with sodium nitrate as the salt. The experimental procedure carried out was changed depending on the precursors used. Several tests with dialysis membranes were performed in order to study the possibility of incorporating Na^+-ions into the sols. These ions were introduced into silica sols contained in membranes from an exterior solution. In addition, washing tests were carried out with Na_2O–SiO_2 sols contained inside the membranes and with several exterior washing solutions. Resistivity of the washing solutions was measured against time. The washing solutions were changed periodically. After drying and heat-treatment, Na_2O content in the gels was determined using flame photometry. The crystalline phases formed were detected by X-ray diffraction. The results show a small incorporation of alkaline ions in Na_2O–SiO_2 gels, even in those samples prepared through the dialysis membranes tests.

1. Introduction

During the last decade, the preparation of Na_2O–SiO_2 glasses through the sol–gel process has been studied extensively [1–4] in an attempt to incorporate the large concentrations of Na_2O, that are usual in conventional glasses, without seggregation. However, it has been generally observed that the sodium silicate glasses prepared via the sol–gel route show, from a stated Na_2O percentage, seggregation of the Na^+-ions in the form of salts (usually carbonates, bicarbonates and nitrates) [5–10]. The use of drying control chemical additives (DCCAs), by several authors [4, 11, 12], seems to favour obtention conditions for the gels, i.e. drying time, density evolution, weight loss, crack generation, etc. In this sense, the alkaline-ion seggregation process and its further crystallization, could be modified in order to carry out a gel–glass transition without such problems.

The Na_2O–SiO_2 glasses prepared by the sol–gel process are characterized by the presence of a phase separation similar to that of conventional glasses [13–15]. The trend to homogeneous droplet distribution and its amount was attributed to the high water level in the gels. On the other hand, Na_2O–SiO_2 gel glasses have higher electrical conductivity values compared with the glasses of the same composition prepared from oxide melts [16–18]. This is due to the lack of Na^+-ion incorporation into the silica gel structure. In addition, it was demonstrated that the weak alkaline ion incorporation causes a low hydrolytic resistance [10]. The $\equiv$Si–O^- groups, where alkaline ions could be bound, were blocked by the H^+ from the silicon alkoxide hydrolysis. One way to eliminate partially the H^+-ions and to favour Na^+-ion incorporation, is to carry out the heat-treatment densification of the gels in a helium atmosphere [19]. In this way it may be possible to release a great portion of the physically adsorbed water and, in the best case, the silanol groups.

In the sol–gel process, acid hydrolysis of a silicon alkoxide with sufficient quantities of water, results initially in the formation of the monomeric acid species (H_4SiO_4). The first protonation of this acid does not occur until the pH is above 9.5, because $pK_1 = 9.46$ [20]. Thus the monomeric species present under acid conditions are neutral species. Upon condensation, these monomeric species become dimeric, trimeric and, eventually, polymeric species. On ageing, polymeric species tend to lower their surface free energy and condense into spherical particles. The transition between the monomeric through the polymeric species to the particles, changes the Si/O ratio of the species. In the case of the monomer, the Si/O ratio is 1/4, and if one takes quartz (SiO_2) as the ultimate stable particulate species the Si/O ratio is 1/2. The isoelectric pH (pH_{IEP}) of silica particulate species is almost invariably between pH = 2.0 and 3.0 [21]. The pH_{IEP} is a measure of the acid–base properties of the solid surface and is thought to reflect the following reactions on the surface [22]:

$$SiOH_2^+ = SiOH^0 + H^+ \; pK_1 \qquad (1)$$

$$SiOH^0 = SiO^- + H^+ \; pK_2 \qquad (2)$$

and

$$pH_{IEP} = \tfrac{1}{2}(pK_1 + pK_2) \qquad (3)$$

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TABLE I Experimental conditions for the $10Na_2O \cdot 90SiO_2$ gels prepared from alkoxide

Sample no.	Hidroxide used*	Surfactant additive	Final pH
1	NH_4OH	–	4.5
2	NaOH	–	4.0
3	NH_4OH	Darvan 7	5.0
4	NaOH	Darvan 7	4.5

*NH_4OH concentration 0.2 N; NaOH concentration 0.1 N.

Whether or not there exist two surface protonation constants, one protonation constant, or several, is still a matter of continuing debate and outside the scope of this paper. Nonetheless, the pH_{IEP} is a measure of surface protonation. As in the case of monomeric or polymeric species, it is strongly a function of the Si/O ratio. Silicic acid is a very weak acid whereas the particulate silica species is a much stronger acid. Polymeric species, obviously lie somewhere in between these two extremes. Thus, in the sol–gel process, where there is a continual evolution of species, from monomeric through polymeric to particulate, there will be a concomitant change in charge associated with these species. At any given pH, this charge will reflect the degree of condensation or metal/oxygen ratios.

New routes of introducing positive ions into the gel structure are promised by the existence of polymers (oligomers) or particles with negative charge. The present paper focuses attention on the preparation and study of sol–gels in which the silica precursors and the preparation and gelling conditions were varied. Modification of the polymers or particles was attempted in order to make more efficient alkaline ion incorporation. On the other hand, several tests were made with a surfactant additive in order to disperse the polymers or particles, thereby forming smaller entities with high specific surface area with hopefully higher total negative charge.

2. Experimental details

2.1. Alkoxide gels

2.1.1. Sol preparation

The starting products employed for sol preparation were tetraethylorthosilicate (TEOS) and $NaNO_3$ as SiO_2 and Na_2O sources, respectively. The amounts of TEOS and $NaNO_3$ were adjusted in order to obtain $10 Na_2O \cdot 90SiO_2$ gels. 6N HCl, ethanol and Darvan 7 (trade mark for a polyelectrolyte dispersing agent of the R. T. Vanderblit co. Inc., USA) were also used as hydrolysis catalyst, interphase and surfactant additive, respectively.

On the whole, sols were prepared by previous hydrolysis of TEOS in an acid medium. The amounts of water, ethanol and 6 N HCl were adjusted to produce a molar ratio of TEOS: H_2O:EtOH of 1 : 4 : 1 and pH ~ 3. Then NH_4OH or NaOH was added until the pH was 4 (at this pH, the silica units should be relatively far from their isoelectric pH and would be expected to carry negative charges). Finally, the $NaNO_3$ solution with the surfactant additive, if any, was added. The final molar ratio TEOS: H_2O:EtOH was 1 : 12 : 1.

In the samples in which NaOH was used to increase the pH before the addition of $NaNO_3$, the Na^+ concentration was taken as the sum of the cations introduced by the two substances. The Na^+ content in the surfactant additive was determined by flame photometry and it was taken into account for the global Na^+ concentration. Table I shows the experimental conditions used.

2.1.2. Tests with dialysis membranes

The porosity afforded by dialysis membranes offers the capability of introducing several substances or ions from an exterior liquid to a sol placed inside a dialysis membrane. In addition, it is possible to extract from the sol inside the membrane certain ions or substances depending on the exterior and interior solute characteristics, as well as the charge on the macroion or particle contained inside. Another advantage of dialysis membranes is their use as a sol container during gelling and further drying. In this manner slow removal of water and alcohol can occur.

In this context, several tests have been carried out in order to introduce Na^+-ions from an exterior liquid to the silica sol inside the membrane. Such experiments should indicate, upon Na^+ content determination for the gel or solid inside the membrane, the alkaline ions that the silica sol admits under these conditions.

Pure silica sols were prepared from TEOS, water, ethanol and 6 N HCl. Molar ratio of TEOS : H_2O : EtOH was 1 : 4 : 1 and the pH ~ 2. Sols were poured into dialysis membranes (Tubing-Visking 3-20/32 in. in size), and they were tied at both ends. Each sol was suspended in a separate membrane in 500 ml of the respective exterior solution (Table II). Na^+-ion concentration in the solution was fixed for all the samples as twice that necessary to obtain $10Na_2O \cdot 90SiO_2$ gels. After suspending the samples for 40 min, the membranes were removed from the solution for subsequent drying and heat-treatment.

In another experiment, washing tests with $10Na_2O \cdot 90SiO_2$ sols were carried out. Three sols of compositions 1, 2 and 4 (see Section 2.1.1.) were prepared. The sols were poured into the same type of dialysis membrane. Table III shows the exterior washing solutions used and the molar ratios TEOS : H_2O : EtOH

TABLE II Exterior solutions used in order to introduce Na^+ into silica gels prepared from alkoxide

Sample no.	Exterior solution					
	NaCl (g)	$NaNO_3$ (g)	NaOH (g)	Darvan 7 (ml)	6 N HCl (ml)	pH
1′	36.69	–	–	–	4.27	2
2′	–	53.30	–	–	4.27	2
3′	–	–	25.08	–	–	10
4′	–	–	–	241.19	4.27	7

TABLE III Exterior washing solutions used for $10Na_2O \cdot 90SiO_2$ gels prepared from alkoxide

Sample no.	Exterior washing solution	Molar ratio TEOS : H_2O : EtOH
1″	H_2O	1 : 8 : 1
2″	H_2O + EtOH	1 : 12 : 1
4″	H_2O + EtOH + Darvan 7	1 : 8 : 1

of the sols. In the two last samples (2″ and 4″) the amounts of each substance in the washing solution were in the same proportions as in the sols, in order to eliminate the influence of water, ethanol and additive on Na^+-ion movement between sol and washing solution.

The washing solutions were changed three times, after each 45 min, for sample 1″ and twice after each 2 h, for sample 2″. Resistivity measurements and Na^+ analyses were performed on the solutions after washing. Analyses were carried out with a Micromeritics apparatus and by flame photometry, respectively. Resistivity measurements of each washing solution of sample 4″ were taken after each 5 min. The solution was changed three times, after each 30 min (90 min). The Na^+ content in this case was also analysed by flame photometry.

2.2. Colloidal gels

2.2.1. *Sol preparation*

Cabosil EH5 was used as a silica source and $NaNO_3$ as Na_2O precursor. The preparation procedure consisted of the addition of $NaNO_3$ solution (2.24 g in 100 ml water) to 6 g Cabosil. The milky suspension, pH ~ 4, was sonicated for 30 min. The pH was then adjusted to 5.8 using 2 N NaOH in order to obtain a stable suspension [23]. 35 ml of this suspension (sample A) was poured into a test tube, and maintained at room temperature until gelling occurred and during drying.

2.2.2. *Tests with dialysis membranes*

Two portions of approximately 35 ml suspension prepared previously were poured into dialysis membranes. One was placed in a forced air oven at 60° C (sample B) and the other was suspended for 3.5 h in distilled water (sample C). After washing, the second membrane was maintained at 60° C. Na^+ content was analysed after heat-treatment.

2.3. Gelling and heat-treatment

Once prepared, the sols produced as described in Sections 2.1.1 and 2.2.2 were poured into dialysis membranes. The membranes were closed by tying in both ends. Membranes with sols, both washed and unwashed, except for the sol produced as in Section 2.2.1, were hung inside a glass container, which was semihermetically closed with a plastic sheet. The membranes were placed in such a way that they were not in contact with the container wall.

On the whole, gelling takes place in a forced air oven at 60° C, at times varying between 1 and 10 h, except for sample 3′ which gelled with floccules in the first 15 min of suspending, sample 2″ which gelled at room temperature at the end of washing and sample A which gelled after 2 days at room temperature.

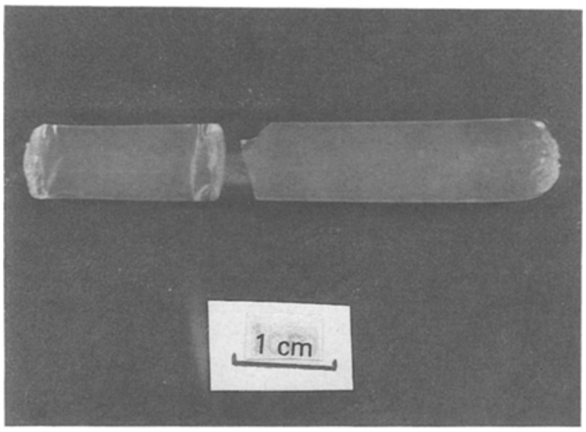

Figure 1 Sample 2″ heat-treated up to 200° C.

After drying for 8 days, the gels produced as in Section 2.1.1. were translucent. They had also shrunk and were monolithic. These characteristics were maintained until the drying cycle was over (1 mon). Of the samples prepared as in Sections 2.1.2, 1′ and 3′ gel membranes dropped from their hanging position during the last days of drying and could not be analysed. Samples 2′ and 4′ remained translucent and almost monolithic during drying. 1″, 2″ and 4″ gels were more transparent than the others and they showed a low tendency to crack (Fig. 1). The samples prepared from Cabosil were more porous, white and cracked. Drying schedules for these Cabosil samples were at room temperature and 50 days for sample A and 12 days at 60° C for samples B and C.

The heat-treatment was carried out in a forced air oven provided with a programmer. The heating rate was 0.1° C min^{-1} with stabilizations for 10 h at 120 and 200° C.

3. Results and discussion

3.1. Alkoxide gels

The weak bonds of the alkaline ions in silica gels [10] and its easy seggregation to form salts [4–9], make it difficult to incorporate such cations into the material. Actually, there are no forces sufficiently capable of retaining them effectively. The generation of negative charges over the silica particle surface, or in the silica polymers, would therefore appear to be a new route for introducing alkaline ions. In this context, the experimental procedure was selected to optimize this negative charge and electrostatically sequester the Na^+ counterion: sol pH was adjusted to 4 in order to favour the presence of negative charges in silica units before the addition of the Na_2O precursor, and, on the other hand, a surfactant additive was used to disperse the particles or polymers and thereby cause a greater total amount of exposed charge.

X-ray diffraction results (Table IV) of samples 1, 2, 3 and 4 heat-treated up to 200° C, showed the presence of $NaNO_3$. In this case, the relative percentages of crystallization were calculated semiquantitatively. Sample 2 was taken as reference with 100% $NaNO_3$ relative crystallization. After heat-treatment, these samples were white or translucent with several cracks and superficial white crystallizations ($NaNO_3$). Table IV shows that the relative percentages of crystallization are similar, although there is a trend to greater crystallization in samples prepared with NaOH as alkalifying substance. Probably this is due to the strong base character of NaOH in comparison with NH_4OH, which causes abrupt pH changes and thereby influences the Na^+-ion distribution. Samples 3 and 4, prepared with a small amount of surfactant additive, showed a yellowish colour on the external side.

In samples 2′ and 4′, in which Na^+-ions were introduced through a membrane from an exterior solution, no crystalline phase was detected by X-ray diffraction (Table IV). After heat-treatment to 200° C, gel 2′ was translucent and cracked in several pieces. Gel 4′ was brownish and monolithic with very few cracks. Combustion near 200° C of the organic groups from the surfactant additive can explain the yellowish or brownish colour in the respective samples.

Samples 1″, 2″ and 4″, washed with different exterior solutions, were the most transparent and monolithic without crystallizations. In effect, no crystalline phase was detected by X-ray diffraction (Table IV).

The final Na_2O content of the samples described in Section 2.1.2 is shown in Table V. Those results indicated, after heat-treatment to 200° C, that the Na^+-ions introduced into a silica sol contained in a membrane by means of an $NaNO_3$ solution (sample 2′), can produce a $6.8Na_2O \cdot 93.2\ SiO_2$ gel (mol %). However, a similar test performed with Darvan 7 as the exterior solution (sample 4′), yields a gel with ~1 mol % Na_2O. The complex composition of the polyelectrolyte dispersing agent probably determines the small mobility of the Na^+-ions. On the other hand, that mobility could be diminished if the alkaline ions were not dissociated in the aqueous solution as are the Na^+-ions of the $NaNO_3$. The total hydrolysis of this salt in water yields a relatively free Na^+-ion, which is able to be introduced through a porous membrane. By obtaining an amorphous material with 6.8 mol % Na_2O, using a porous membrane, we have achieved a slight increase in the Na^+-ions introduction without seggregation or precipitation of alkaline salts [4, 10].

Samples obtained after washing the sol contained in the membrane, by means of an exterior solution (samples 1″, 2″ and 4″), have between 1 and 5 mol % Na_2O (Table V). The greater the washing solution's resemblance to the sol medium, the higher are the final Na_2O percentages. Effectively, in sample 1″, washed with water, the percentage of Na^+-ions extracted during washing is higher than in sample 2″, washed with water and ethanol. In turn, sample 4″ has the greatest Na_2O percentage, because the corresponding sol was washed with water, ethanol and surfactant additive. These substances were in the same proportion as in the sol.

TABLE IV Crystalline phases detected by X-ray diffraction in the gels heat-treated to 200° C

Sample no.	Detected phase	Relative % of crystallization
1	$NaNO_3$	73
2	$NaNO_3$	100
3	$NaNO_3$	68
4	$NaNO_3$	91
2′	Amorphous	–
4′	Amorphous	–
1″	Amorphous	–
2″	Amorphous	–
4″	Amorphous	–
A	$NaNO_3$	not calculated
B	$NaNO_3$	not calculated
C	Amorphous	–

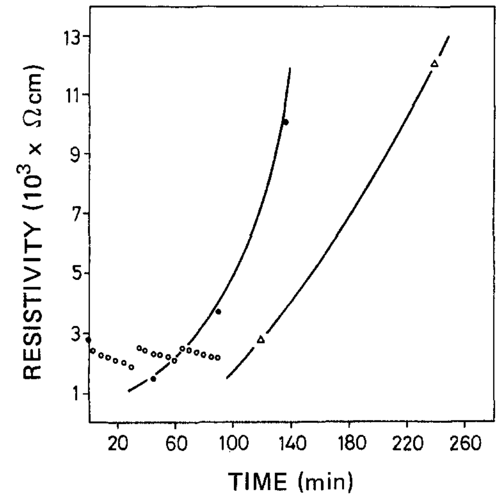

Figure 2 Washing solution resistivity of samples (●) 1″, (△) 2″ and (○) 4″.

Fig. 2 shows the resistivity values of the exterior washing solutions (water and water with ethanol, respectively) of the samples 1″ and 2″. Each experimental value corresponds to the washing solution resistivity after the membrane was immersed for the time indicated. Likewise, the resistivity values were measured from extractions taken every 5 min from sample 4″ washing solutions (water, ethanol and surfactant additive). The three plots for sample 4″ correspond to the three washing solutions that were used successively. Fig. 3a shows the Na^+ concentration (in $Na_2O\ g\,l^{-1}$) extracted by the washing solutions at the times indicated for samples 1″ and 2″. In Fig. 3b the same values are plotted for sample 4″.

The washing solution resistivity of samples 1″ and 2″ increases with immersion time. Thus, the greatest extraction of Na^+-ions occurs with the first solution and then diminishes with the subsequent extractions due to the decreased concentration of Na^+-ions in the sol. The same situation is also represented in Fig. 3a where Na_2O concentration also decreases with successive washings.

In the case of sample 4″, Fig. 2 shows three decreas-

TABLE V Na_2O introduced (samples 2′ and 4′) and remaining (samples 1″, 2″ and 4″) after the membrane tests

Sample no.	Na_2O	
	wt %	mol %
2′	7.00	6.80
4′	1.29	1.25
1″	1.07	1.04
2″	1.17	1.14
4″	5.01	4.86

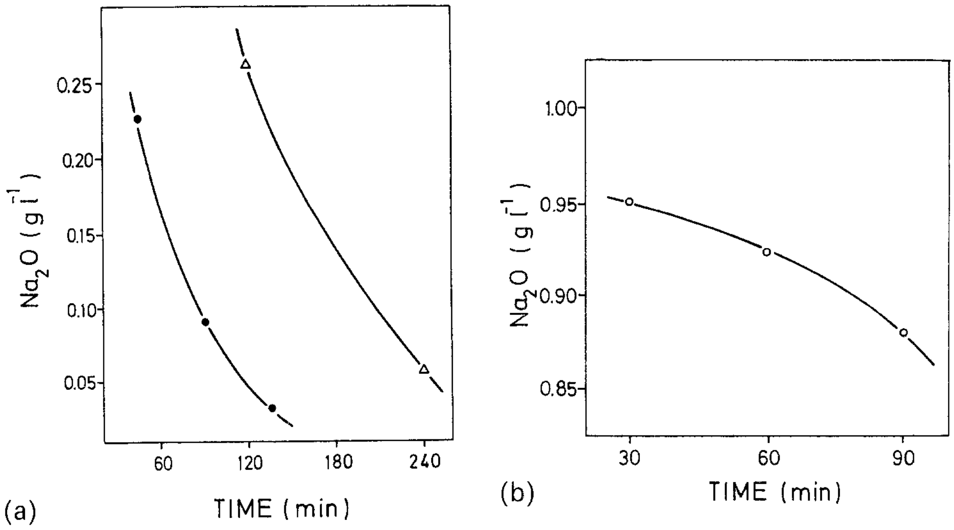

Figure 3 Na^+ concentration (as Na_2O in g l^{-1}) extracted plotted against washing time: (a) samples (●) 1″ and (△) 2″; (b) (○) sample 4″.

ing plots for every solution employed. This can be explained in terms of the progressive extraction of the ions. Fig. 3b also shows that Na_2O concentration diminishes with successive washings, due to the impoverishment of the Na^+-ions in the sol.

On the whole, the number of Na^+-ions extracted in comparison with the number of Na^+-ions initially introduced, is very high. This fact supposes that the alkaline ions are not linked to silica particles or polymers effectively, even in the case of sols prepared from TEOS at pH 4 and in the presence of a surfactant additive. These results indicate that there are insufficient negative charges to retain the alkaline ions in the silica particles or polymers.

3.2. Colloidal gels

Gel A heat-treated to 200° C, is white and porous. Sample B, obtained without washing, dried at 60° C and heat-treated to 200° C, is white, porous and has superficial crystallizations. Sample C, washed with water, is white with no crystals nor porous appearance. The crystalline phases detected by means of X-ray diffraction are shown in Table IV.

In samples A and B, no washing tests were carried out and their Na_2O content is about 11 mol %. These Na^+-ions were seggregated and precipitated as $NaNO_3$. In these samples, A and B, the alkaline ion content is very high and only a small proportion can be incorporated effectively. The other Na^+-ions appear as $NaNO_3$ after heat-treatment to 200° C. Sample C, after washing and heat-treatment, contains around 3.5 mol % Na_2O. Thus, the remaining Na^+-ions (the initial amount was 11%) were extracted by the washing solution. These results demonstrate that, even in the case of amorphous colloidal silica particles, alkaline ions could not be entirely linked by means of electrostatic attraction and only a very few Na^+-ions were capable of being incorporated into the final network.

4. Conclusions

The $10Na_2O \cdot 90SiO_2$ sols prepared from TEOS yield gels in which Na^+-ions are seggregated and crystallize as $NaNO_3$. This occurs even when the sol pH is increased and when a surfactant additive is added; this allows disperse particles or polymers to be obtained with a greater specific surface area and with a greater total quantity of negative charges.

The results obtained with pure silica sols prepared from TEOS, whose membranes were immersed into Na^+ solutions, demonstrated that the alkaline ions were introduced into the sol in small proportions (1 to 7 mol % Na_2O).

The $10Na_2O \cdot 90SiO_2$ samples, obtained using TEOS and washed with several solutions, lose the majority of the Na^+-ions that they contained initially. This was demonstrated by resistivity measurements and Na^+ analysis. Thus, there are insufficient negative charges in the silica polymers or particles to retain all the alkaline ions.

The gels obtained from Cabosil crystallize after the heat-treatment due to the alkaline ions. When the sol contained in the membrane was washed, an amorphous gel containing one third of the initial Na_2O content was obtained. Thus, the existence of a relatively low negative charge able to retain the Na^+-ions in the silica particles was shown.

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