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Effect of solvents and catalysts on monolithicity and physical properties of silica aerogels

A. VENKATESWARA RAO*, G. M. PAJONK, N. N. PARVATHY*
Laboratoire des Matériaux et Procédés Catalytiques, Université Claude Bernard Lyon I, 43, Boulevard Du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

The effect of various solvents and catalysts on the monolithicity and physical properties of silica aerogels is reported. The aerogels were prepared by hydrolysis and polycondensation of tetramethoxysilane, followed by hypercritical drying, using 6 solvents of different chain lengths, and 17 catalysts consisting of strong and weak acids, bases and their mixtures. It was found that solvents of longer chain lengths and strong basic catalysts resulted in semitransparent to opaque aerogels, whereas strong acids and their combinations with a weak basic catalyst produced transparent but cracked aerogels. While weak acids and their combinations with a weak base were found to produce shrunk and semitransparent (opaque for $CH_3COOH + NH_4OH$) aerogels, the best quality transparent, monolithic, low-density and refractive index, and large surface area aerogels were obtained for a combination of weak basic catalysts and solvents of shorter branching and chain lengths. The physical properties of the aerogels were studied by BET analysis, porosity, density, refractive index and optical transmission measurements.

1. Introduction

Silica aerogels are currently produced by hydrolysis and condensation of silicon alkoxides in the presence of an acidic or basic catalyst followed by supercritical drying in an autoclave. Either tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) is generally used as a silicon alkoxide precursor. The resulting silica aerogels are extremely porous, very low density and transparent solid materials consisting of more than 90% air with a refractive index varying between 1.01 and 1.1 [1, 2]. Their structural entities thus have to be smaller than the wavelength of visible light. In the infrared (IR) region of the spectrum, radiation is strongly attenuated by absorption. Therefore, silica aerogels are being used as superinsulated windows for house-wall insulations and covers on solar thermal energy systems such as hot-water collectors and solar ponds [3–8]. Because the thermal conductivity of silica aerogels is 100 times smaller than the densified glass and less than that of still air [9, 10], they are being considered for use in the bodies of refrigerators and refrigerated systems [11–14]. Silica aerogels are also being extensively used as Cerenkov radiation detectors in nuclear reactors [15–18]. However, one of the most important and recent applications of silica aerogels is their use as inertial confinement fusion (ICF) targets in energy-producing fusion reactors [19–21]. In addition, because of the large surface area ($\approx 1000\ m^2\ g^{-1}$), silica aerogels are being used as catalysts and catalytic supports [22–24], while opacified aerogel powders are being tested as substitutes for CFC-blown polyurethane foams [25, 26]. Recently, silica aerogels have been integrated into radioluminescent light and energy sources, which has resulted in a dramatic increase of the luminescence [27].

Silica aerogels were first produced by Kistler [28, 29] in the early 1930s, by mixing sodium metasilicate and an acid followed by alcohol substitution and super-critical drying. However, Kistler's method takes several weeks, and therefore Teichner and co-workers from our laboratory developed a faster method, using silicon alkoxides, to prepare silica aerogels within a day [30]. Since then various groups have been involved in the research work on silica aerogels [31–34]. However, the preparation of silica aerogels is still, to a great extent, an art, and much skill is required to obtain monolithic and transparent specimens with a good reproducibility. This is because of the many interdependent factors involved, beginning with preparation of solution and sol to the final stages of supercritical drying. It is, therefore, scientifically and technologically important to determine how the sol–gel parameters, such as solvents and catalysts, affect the monolithicity, transparency and physical properties of silica aerogels.

Even though silica aerogels have been prepared by Henning and Svensson [35], Poelz and Riethmuller [36], Prassas *et al.* [37] and van Lierop *et al.* [38],

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* *Present address*: Air Glass Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, India

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these investigators have not made detailed studies of the effect of various solvents and catalysts on the monolithicity, transparency and other physical properties of silica aerogels. For example, van Lierop *et al.* [38] have concluded that an initial inert gas pressure of around 1200 p.s.i. (10^3 p.s.i. = 6.89 N mm^{-2}) alcohol in the autoclave, resulted in zero shrinkage and monolithic aerogels. On the other hand, Laudise and Johnson [39] reported that crack-free silica aerogels were obtained when the autoclave was filled with 100% by volume of alcohol without using any initial inert gas pressure. We have obtained monolithic and transparent silica aerogels with an initial inert gas pressure as low as 45 p.s.i. and an alcohol amount of up to 25% of the autoclave inner volume. In the present paper, we report experimental results of the effect of various solvents and catalysts on transparency and other physical properties of silica aerogels.

2. Experimental procedures

2.1. Preparation of silica alco- and aerogels

The preparation of silica alcogels using the sol–gel process has been well described in the literature [40, 41], and will be briefly mentioned here. All the chemicals used in the present work were obtained from Fluka Company (Switzerland) with purity greater than 99.5%, except ethanol, methanol and ammonia ($>28\%$ in water) which were supplied by Prolabo (France) of AR grade. In all the experiments, the solutions were prepared in the amounts of precursor (TMOS): solvent: water: catalyst $= 1:12.25:4:6.5 \times 10^{-2}$ in molar ratios, unless otherwise specified. The solutions were mixed in a 250 ml Pyrex beaker with a magnetic stirrer. The mixing of the solutions was done in the following way: first, the required amount of precursor was taken in the beaker and then while stirring, solvent was added drop by drop. The stirring was continued for a further 5 min. Finally, a mixture of water and a catalyst was added drop by drop while stirring the solution mixture. The stirring of the whole solution was continued for 15 min in order to obtain a homogeneous and clear solution. The resulting sols were then transferred to Pyrex glass test tubes, 16 mm outer diameter and 160 mm height, with a wall thickness of 1.2 mm. The test tubes were hermetically closed with wooden corks. After setting, the gels were covered with their respective solvents and allowed to age for 15 days, in all cases. The time of gelation, T_g, depended upon the type of solvent and catalyst which varied from a few minutes to several days. In all, 6 solvents and 17 catalysts were used to prepare the alcogels.

To prepare aerogels, the solvent was removed from the alcogels by supercritical evacuation in an autoclave of 2 l capacity, specially designed and fabricated

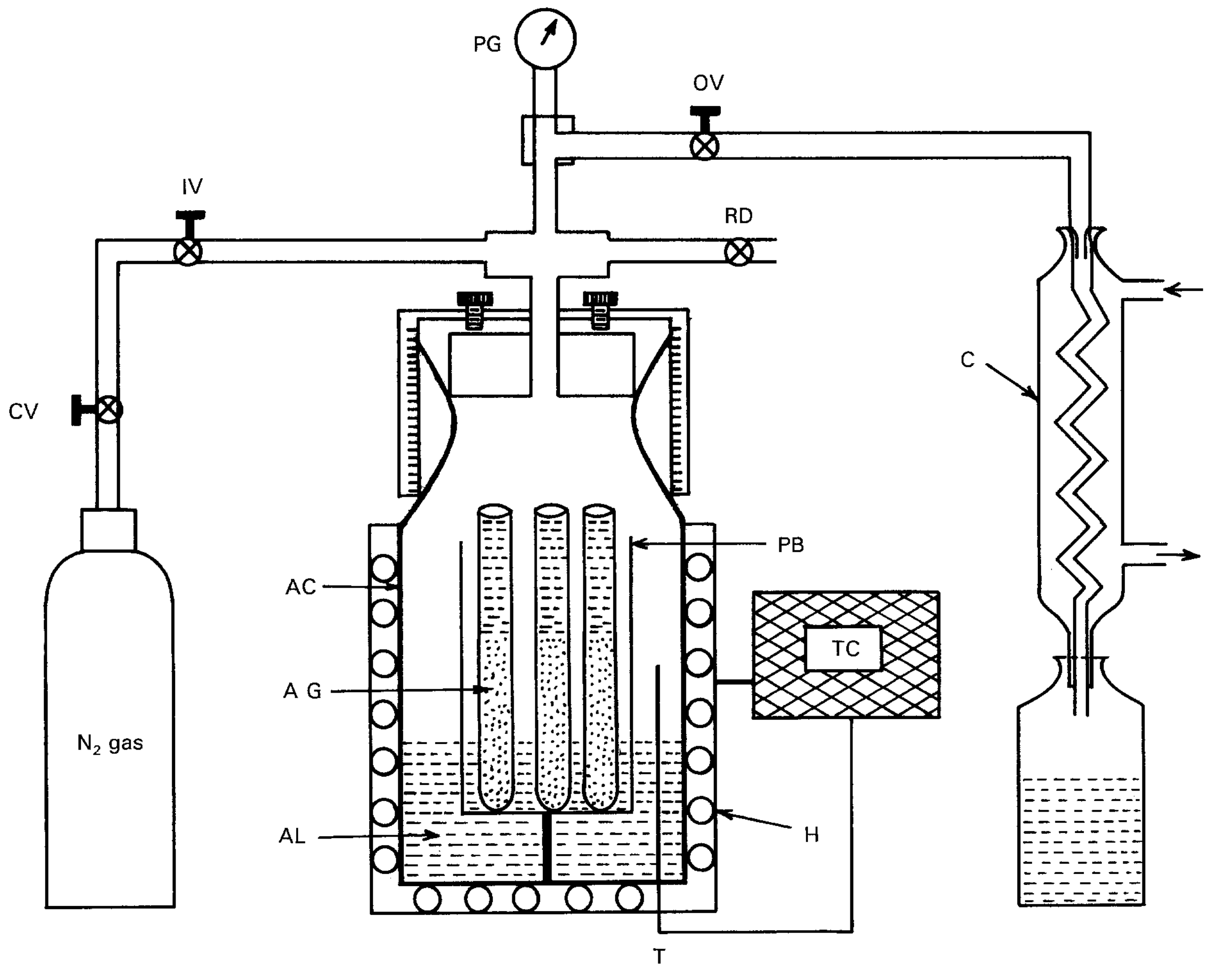

Figure 1 Schematic cross-section of the autoclave and accessories for supercritical drying of alcogels. CV, N_2 gas cylinder valve; IV, N_2 gas inlet valve; PG, pressure gauge; OV, outlet pressure release valve; RD, rupture disc; PB, Pyrex 250 ml glass beaker; H, heater; C, glass condenser; TC, heater temperature controller; T, thermocouple; AC, autoclave; AG, alcogel; AL, alcohol.

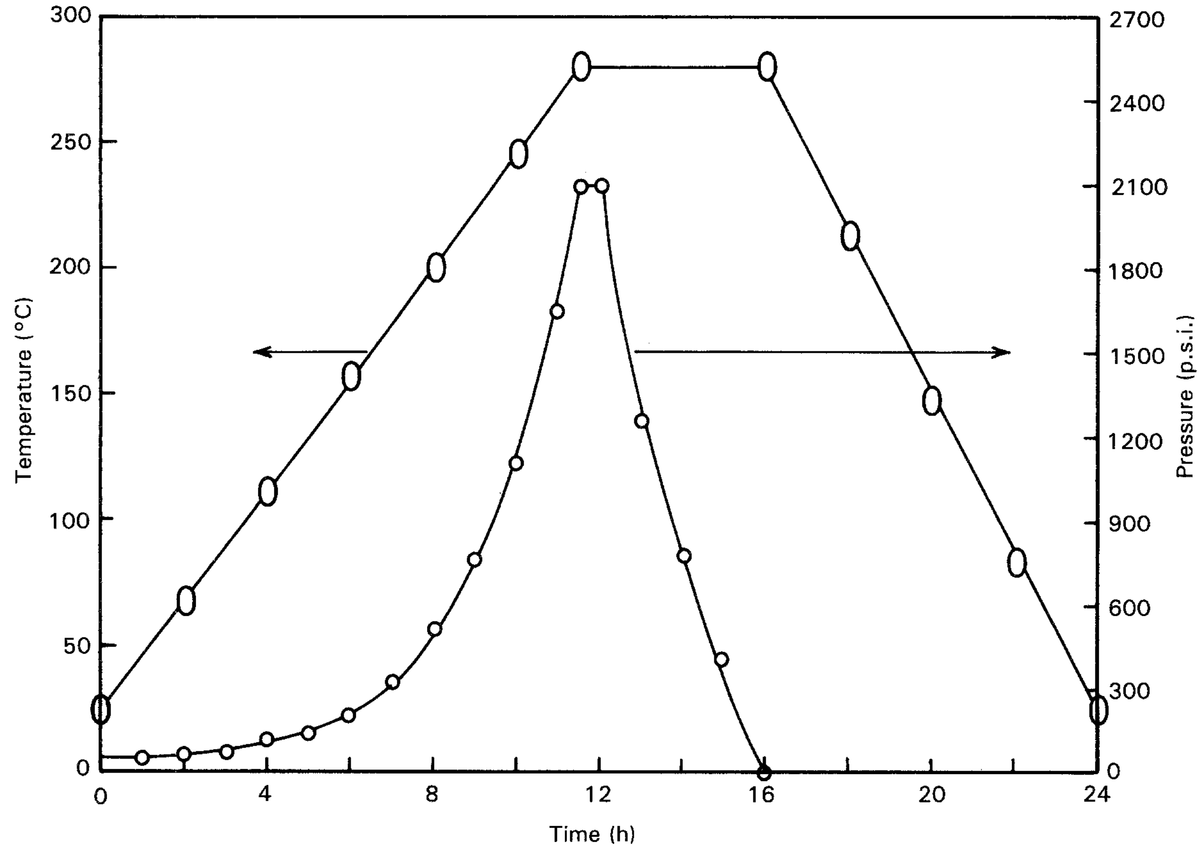

Figure 2 Temperature and pressure cycles as a function of time for the supercritical drying process.

in the workshop of our University (Lyon) using 316 stainless steel (Fig. 1). Eight test tubes at a time could be placed in the autoclave body in a Pyrex liner. The test tubes were completely filled with a solvent and an additional required amount of solvent was added in the autoclave. The total amount of solvent present in the alcogels and autoclave was 500 cm^3. This gives a pressure of 2100 p.s.i. at a temperature of 280 °C, which are much higher than the critical pressure ($\approx$ 1160 p.s.i.) and temperature ($\approx$ 240 °C) of methanol and other solvents. We have added an excess amount of solvent in the body of the autoclave instead of the glass liner because, by this process, first the solvent in the autoclave body is heated followed by that in the test tubes. This procedure has been found to be essential in order to obtain monolithic aerogels, because in the beginning the evaporation of the solvent from the gel during heating must be prevented. After tightly closing the autoclave, it was flushed three times with $\approx$ 15 p.s.i. dry nitrogen and finally pre-pressurized up to 45 p.s.i. N_2. The temperature of the autoclave increased, at a rate of 0.37 °C min^{-1}, to a temperature of 280 °C over a period of 11.5 h and the pressure in the closed system rose to 2100 p.s.i. After stabilizing the maximum temperature and pressure for about a half an hour, the vapour outlet valve of the autoclave was slowly opened to vent out the solvent to a condenser. All the solvent from the autoclave was evacuated in about 4 h at a constant temperature of 280 °C. Fig. 2 shows the temperature–pressure cycle. After reaching atmospheric pressure, heating was continued for about 15 min and finally the autoclave was flushed three times with $\approx$ 15 p.s.i. dry nitrogen in order to remove the remaining trapped solvent vapour.

2.2. Physical properties of aerogels

Bulk densities of all the aerogels were measured using a known volume of each silica aerogel sample. Surface areas and pore volumes of the aerogels were determined by BET analysis of nitrogen adsorption data collected at 77 K [42]. Depending on the bulk density (the lower the density the less is the amount) approximately 30–100 mg of each sample was accurately weighed out, with a microbalance, in an elongated Pyrex glass tube with a bulb at the bottom which contains the sample. The aerogels were outgassed at 300 °C under vacuum of $< 10^{-4}$ torr (1 torr = 133.322 Pa) for 12 h prior to each measurement. The evacuated sample was then allowed to cool before being placed in a dewar of liquid nitrogen and connected to the gas adsorption system. Preliminary helium isotherms were obtained to calculate the "dead space" due to the manifold volume. The calibration of the empty BET cell was done by helium which was stored in a calibrated vessel and depressurized into the cell. Nitrogen gas was then adsorbed on to the sample up to a pre-set pressure, and values of pressure and adsorbed volume (calculated from the flow rate of the gas with time corrected for the manifold volume) were collected by a computer. The saturation pressure, P_0, was measured continuously throughout the experiment by means of a tube containing condensed nitrogen and the sample was re-weighed after the experiment. Five adsorption points were collected at relative pressures between 0.05 and 0.30. The error in the fit of the BET equation to the adsorption points was around 1% for all the samples. The molecular cross-sectional area of the nitrogen molecule was assumed to be $0.162\ \mathrm{nm}^2$ [43]. The total pore volumes were determined by a single adsorption point at $P/P_0 = 0.995$. The percentages of porosity, P_r, were obtained from the values of the bulk, P_b, and skeletal, P_s, densities using the relation $P_r = 1 - P_b/P_s$. The refractive indices were determined using a He–Ne gas laser [35]. The optical transmittance measurements were performed with a Beckmann 5240 type spectrophotometer equipped with light sources covering the ultraviolet–visible and near infrared wavelength range from 300–2500 nm.

3. Results and discussion

TMOS polymerized in the presence of solvent, water and a catalyst by hydrolysis and subsequent spontaneous polymerization. TMOS was used because of its higher silicon dioxide content (39.5 wt% versus 28.8 wt% for TEOS) and chemical reactivity. The overall hydrolysis and polymerization reactions of $Si(OCH_3)_4$ may be written as

$$n\,Si(OCH_3)_4 + 4n\,H_2O \rightleftharpoons n\,Si(OH)_4 + 4n\,CH_3OH \tag{1}$$

$$n\,Si(OH)_4 \rightleftharpoons n\,SiO_2 + 2n\,H_2O \tag{2}$$

The reactions which usually occur in the hydrolysis of a methanol solution of silicon methoxide, however, are considered to be more complicated [44–46]. These reactions are very sensitive to various experimental conditions, such as the type of solvent, the presence of acidic or basic catalyst, the gelling temperature, the molar ratios of alkoxide to water and solvent. Hence, we have kept all the parameters constant and varied the type of solvent and catalyst separately. The time dependence of viscosity of the solutions prepared using various solvents and catalysts is shown in Fig. 3a and b. It is clearly seen from the figure that the viscosities increase very slowly with time at the initial stage, and sharply increase when the gels are formed. The gelation times of the sols, bulk densities, surface areas, pore volumes, refractive indices, transparencies and monolithicity of the obtained aerogels, varied with the presence of different solvents and catalysts, as shown in Tables I–IV.

3.1. Effect of solvents

It has been observed that the gelation time is directly proportional to the length and branching of solvent chain, and type of solvent molecules as shown in Table I. Out of the six solvents, methanol has been found to give rise to the lowest gelation time (2 h), and acetonitrile resulted in the longest gelation time (900 h). The differences in gelation times for various solvents can be explained by considering mainly three factors: (a) steric hindrence, (b) transterification and (c) hydrogen bonding. Firstly, according to Voronkov *et al.* [47, 48], any disturbance to the alkoxy group retards the hydrolysis of alkoxysilanes, but the lowest hydrolysis rate was obtained for the most branched and lengthy alkoxy groups. The branching and length of alkoxy group increases in the following order: $OCH_3 < OC_2H_5 < OC_3H_7 < OC_4H_9$ and therefore out of these four solvents, the shortest and longest gelation times were obtained with methanol and butanol, respectively. We have also used iso- and tertio-butanol as solvents. The gelation time using tertio-butanol is longer than *n*- and iso-butanol, which is due to the greater branching of tertio-butanol. Secondly, when TMOS is hydrolysed in alcohols containing larger alkyl groups, transesterification also occurs, as in the following chemical reaction

$$Si(OCH_3)_4 + R'OH \rightleftharpoons Si(OCH_3)_3OR' + CH_3OH \tag{3}$$

Therefore, we expect that substituents which increase steric crowding will decrease condensation of silanol groups and hence result in longer gelation times. Finally, Kirk observed that complexes were formed between silicic acid and esters through hydrogen bonding [49]. A quantitative comparison of the association of polysilicic acid with various solvents has been reported by Iler [50]. The relative effectiveness of hydrogen bonding activity is the lowest for methanol, 3, and highest for acetone, 17, and therefore the gelation time using acetone is about 830 h compared with the lowest value of 2 h for methanol. In the case of acetonitrile, probably there may be strong Si–N bonding which retards both hydrolysis and condensation reactions leading to the longest gelation time of 900 h compared to all other solvents used in the present work.

It can be clearly seen from Figs 4 and 5 that the aerogels prepared using methanol are more transparent than the other solvents. The results presented in Table II, clearly indicate that the aerogels obtained using methanol have lower density and refractive index, larger surface area, pore volume and porosity, compared to the aerogels obtained by all the other solvents. This is due to the fact that as the size of the alkoxy group increases, steric hindrence occurs, which will lead to larger pores and hence a decrease in transparency of the aerogels.

3.2. Effect of catalysts

Sols containing HCl, HNO_3, H_2SO_4, $C_2H_2O_4$ and the mixtures of these acids with NH_4OH, and all basic catalysts, remained clear during hydrolysis and polycondensation. Transparent gelled masses resulted. On the other hand, sols catalysed with CH_3COOH, HF and their mixtures with NH_4OH were clear just after preparation, but became faintly cloudy and the resultant gels were less transparent than the above acidic and basic catalysed gels. It has been observed that turbid alcogels were obtained for the mixtures of acids and bases at lower concentrations ($< 10^{-2}$ M). For all the catalysts, when the gels were set with very low catalyst concentration ($< 10^{-4}$ M), the gels became bluish with time. For catalyst concentrations greater

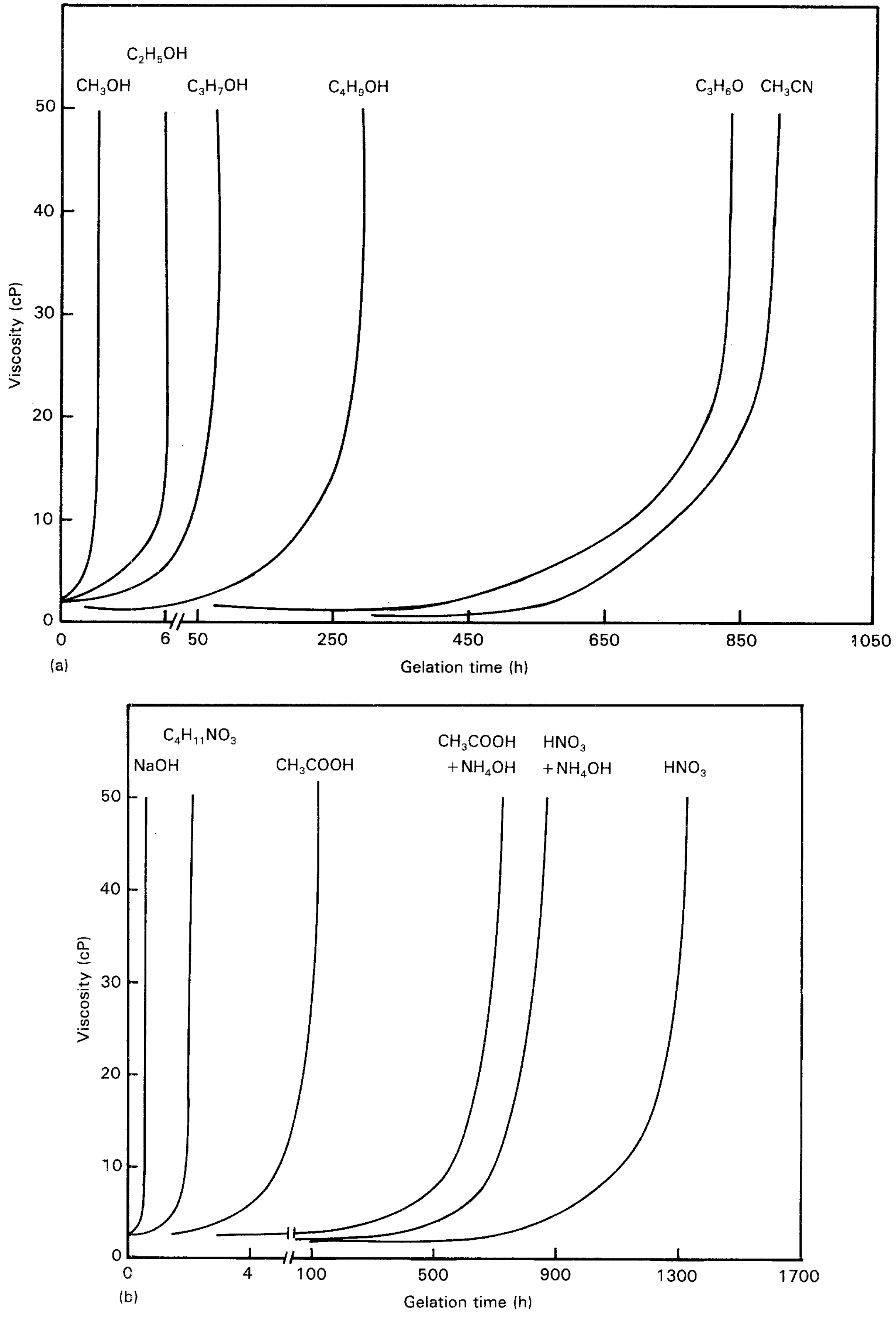

Figure 3 Viscosity as a function of gelation time (a) for different solvents, (b) for various catalysts.

than 1 M, the gels were transparent. The bluish colour of the gels may be due to the fact that at very low catalyst concentration, there may not be a continuous formation of polymer network; instead a group of localized polymer networks or primary particles form larger aggregates. The same arguments may hold good for CH_3COOH, HF and weak acidic–basic mixed catalysts.

TABLE I Effect of solvents on silica alco- and aerogels

	Solvent	Gel setting time, T_g (h)	pH of the sol	Remarks	
				Alcogels	Aerogels
1	CH_3OH	2	5.8	Transparent	Monolithic and transparent
2	C_2H_5OH	6	6.0	Transparent	Monolithic but transparency is less than the CH_3OH solvent aerogel
3	C_3H_7OH	70	6.0	Less transparent than the C_2H_5OH gel	Monolithic but less transparent than the above aerogel
4	C_4H_9OH	280	6.5	Less transparent than the above gel	Monolithic but less transparent than the C_3H_7OH aerogel
5	C_3H_6O	830	5.5	More transparent than the C_4H_9OH gel	Monolithic and transparent similar to the C_3H_7OH aerogel
6	CH_3CN	900	6.0	More transparent than the above gel	Monolithic and transparent similar to the C_2H_5OH aerogel

TABLE II Physical properties of silica aerogels prepared using various solvents (NH_4OH catalyst was used)

	Solvent	Density (g cm^{-3})	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Porosity (%)	Transmission (%) (at 900 nm)	Refractive index
1	CH_3OH	0.050	1050	19.32	97.5	85	1.012
2	C_2H_5OH	0.062	845	15.58	96.9	70	1.015
3	C_3H_7OH	0.073	758	13.14	96.5	65	1.027
4	C_4H_9OH	0.082	625	11.62	96	66	1.031
5	C_3H_6O	0.108	512	8.72	95	60	1.062
6	CH_3CN	0.062	830	15.65	96.9	70	1.015

TABLE III Effect of various catalysts on silica alco- and aerogels

	Catalyst	Gel setting time, T_g	pH of the sol	Remarks	
				Alcogels	Aerogels
1	HCl	45 days	3.2	Transparent alcosol and gel. The volume of the alcogel shrunk to 80% of the sol	Transparent aerogels but with multiple cracks. Total volume shrinkage is 5%
2	HNO_3	55 days	3.2	Same as above	Same as above
3	H_2SO_4	52 days	3.2	Same as above	Same as above
4	$C_2H_2O_4$	42 days	3.6	Transparent alcosol and gel. The volume of the alcogel shrank to 85% of the sol	Monolithic but less transparent than HF-catalysed aerogel. Total volume shrinkage is 10%
5	HF	15 hours	4.5	Alcosol is transparent but bluish in colour. After 10 days ageing the gel was loosened from the test tube	Monolithic and less transparent than strong acidic gels. Diameter shrinkage is 30%. Height shrinkage is 15%
6	CH_3COOH	5 days	4.1	Alcogel is transparent but more bluish than HF gels. After 6 days ageing, the gel was loosened and rose 1 cm distance from the bottom	Monolithic but less transparent than strong acidic aerogels. Diameter shrinkage is 40%. Height shrinkage is 25%
7	$HCl + NH_4OH$	10 days	4.3	Multiple cracks found in alcogel after 10 days ageing	Fragments in aerogel
8	$HNO_3 + NH_4OH$	36 days	4.3	Same as above	Multiple cracks in aerogel
9	$H_2SO_4 + NH_4OH$	35 days	4.3	Same as above	Same as above
10	$CH_3COOH + NH_4OH$	30 h	4.5	Gel is milky colour and turbid	Monolithic, opaque and white
11	$C_2H_2O_4 + NH_4OH$	9 days	4.4	Transparent alcogel without any cracks	Monolithic and less transparent than the $HF + NH_4OH$ catalyst aerogel
12	$HF + NH_4OH$	2.5 h	4.9	Transparent alcogel without any cracks	Monolithic and transparent
13	KOH	1 h	8.2	Transparent alcogel without any cracks	Monolithic but less transparent than NH_4OH incorporated aerogel
14	NaOH	0.5 h	7.5	Same as above	Few cracks in the lower half and the upper part is opaque
15	NH_4OH	2 h	6.0	Transparent and monolithic	Monolithic and more transparent than weak acids and their mixtures with NH_4OH-catalysed aerogel
16	$C_6H_{19}NSi_2$	1.5 h	6.0	Same as above	Monolithic and more transparent than the NH_4OH-catalysed aerogel
17	$C_4H_{11}NO_3$	2 h	5.8	Same as above	Monolithic and more transparent than the $C_6H_{19}NSi_2$-catalysed aerogel

TABLE IV Physical properties of silica aerogels prepared using various catalysts (CH_3OH solvent was used)

	Catalyst	Bulk density ($g\,cm^{-3}$)	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Porosity (%)	Transmission (%) (at 900 mm)	Refractive index
1	HCl	0.072	800	12.524	96.7	85	1.016
2	HNO_3	0.065	840	13.431	97	87	1.014
3	H_2SO_4	0.068	830	14.021	96.9	80	1.015
4	$C_2H_2O_4$	0.086	725	11.023	96	55	1.018
5	HF	0.105	618	9.001	95.2	60	1.021
6	CH_3COOH	0.120	545	7.680	94.5	57	1.025
7	$HCl + NH_4OH$	0.085	730	11.121	96.1	65	1.019
8	$HNO_3 + NH_4OH$	0.076	785	12.527	96.5	70	1.017
9	$H_2SO_4 + NH_4OH$	0.088	725	10.679	96	65	1.019
10	$C_2H_2O_4 + NH_4OH$	0.092	685	10.364	95	60	1.021
11	$CH_3COOH + NH_4OH$	0.082	425	6.012	93.1	5	1.052
12	$HF + NH_4OH$	0.095	630	10.024	95.7	65	1.032
13	KOH	0.086	545	7.328	94.2	50	1.036
14	NaOH	0.095	505	6.893	93.4	40	1.038
15	NH_4OH	0.062	1050	18.523	97.2	85	1.014
16	$C_6H_{19}NSi_2$	0.051	1175	19.468	97.7	90	1.012
17	$C_4H_{11}NO_3$	0.045	1200	21.538	97.9	90	1.011

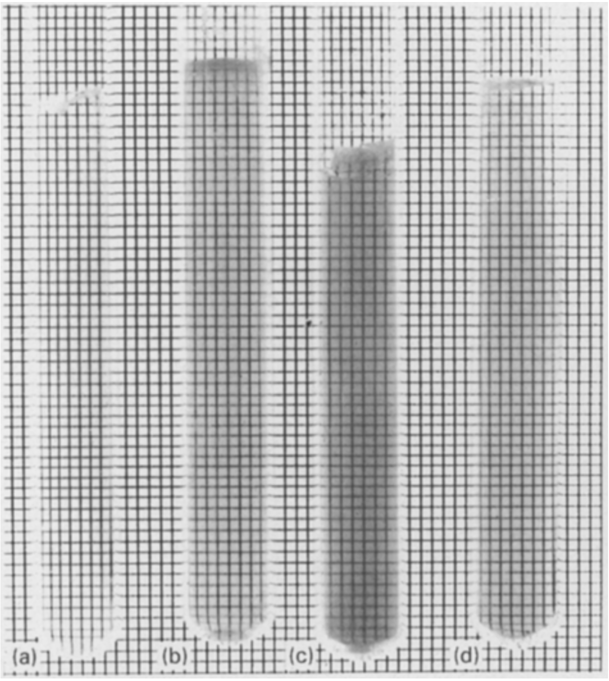

Figure 4 Silica aerogels obtained using different solvents: (a) CH_3OH, (b) C_2H_5OH, (c) C_3H_7OH, and (d) CH_3CN.

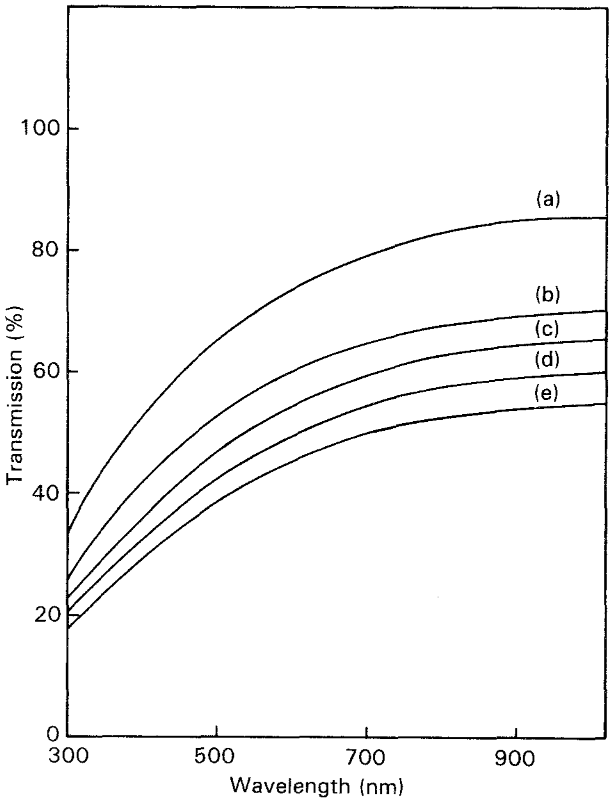

Figure 5 Percentage of transmission versus wavelength for five solvents: (a) CH_3OH, (b) C_2H_5OH, (c) C_3H_7OH, (d) C_3H_6O, (e) C_4H_9OH.

It has been observed that the hydrolysis and condensation reactions are different for acid and base catalysis of TMOS. In the case of acid catalysis, the condensation reaction tends to start at a fairly late stage (except at very low pH value of <0.05), whereas with basic catalysts, condensation starts relatively early [51]. Gelation times, T_g, pH of the sols and physical conditions of the alco- and aerogels are given in Table III. An interesting fact is that there is a wide variation of T_g values as a function of the type of catalyst. The time required for the gelation, T_g, is the shortest (30 min) for a strong basic catalyst such as NaOH, and longest (55 days) for a strong acidic catalyst such as HNO_3. For weak acids, bases and mixtures of acids and bases, the T_g values are in between the above limits. In general, for a condensation process (i.e. gelation) a maximum amount of OH^- groups and minimum amount of protons are needed [52]. Therefore, the shortest T_g (30 min) for strong bases may be due to the fact that these bases are strong proton acceptors and hence reduce the gelation time. On the other hand, the longest T_g (55 days) for strong acids is due to the fact that these acids are strong proton donors. In the former case, condensation is faster, whereas in the later case, hydrolysis is faster. These mechanisms can also be understood from the dissociation constants of various catalysts [53]. The T_g values for weaker acids are less than those for stronger acids, whereas the T_g values for weaker bases are larger than those for stronger bases. The lower and higher T_g values for weak acids and bases, respectively, are due to the fact that the anions of weak acids are basic and the cations of weak bases are acidic as in the following chemical reactions

$$F^- (aq) + H_2O (l) \rightleftharpoons HF (aq) + OH^- (aq) \quad (4)$$

$$NH_4^+ (aq) + H_2O (l) \rightleftharpoons NH_3 (aq) + OH^- (aq) + H^+ (aq) \quad (5)$$

It was found that the strong acidic and each of the acidic plus NH_4OH catalysts resulted in transparent but cracked and slightly shrunk ($\approx 5\%$) aerogels (Fig. 6). On the other hand, monolithic and less transparent aerogels were obtained using strong basic catalysts (Fig. 7). Sometimes one or two cracks were observed in the case of NaOH catalysed aerogels. In the case of weak acids ($C_2H_2O_4$, HF and CH_3COOH), monolithic but semitransparent (more transparent than strong bases and less transparent than weak bases) and shrunk (10%, 20% and 30% for $C_2H_4O_4$, HF and CH_3COOH, respectively, by volume) aerogels were obtained (Fig. 8), whereas for mixtures of each of the weak acids with NH_4OH, completely opaque and monolithic (for $CH_3COOH + NH_4OH$) and, transparent and monolithic (for $C_2H_2O_4 + NH_4OH$ and $HF + NH_4OH$) aerogels, were obtained (Fig. 9). With respect to weak bases, highly transparent (90% transmission at 900 nm) and monolithic aerogels were obtained (Fig. 10). The optical transparency of silica aerogels using various catalysts is shown in Fig. 11.

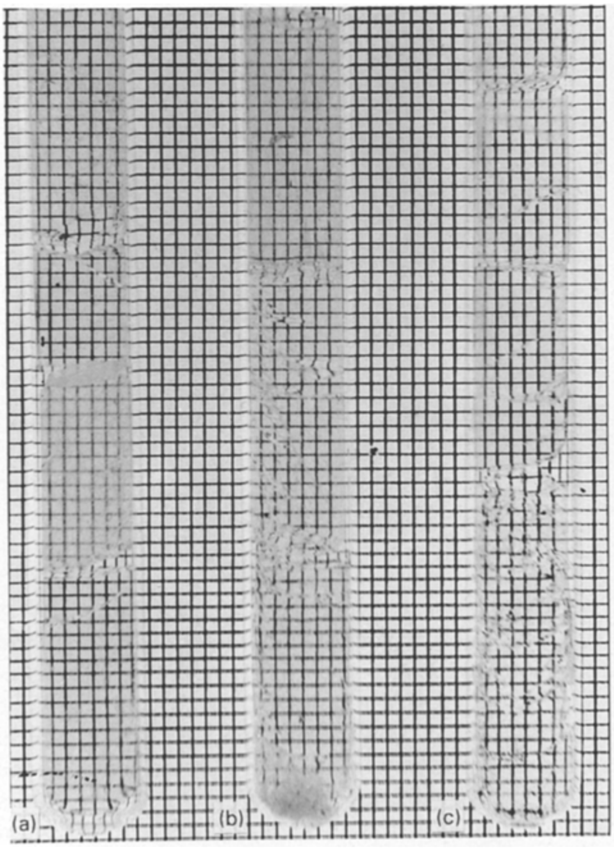

Figure 6 Silica aerogels obtained using three different strong acidic catalysts: (a) HNO_3, (b) H_2SO_4, and (c) $HNO_3 + NH_4OH$.

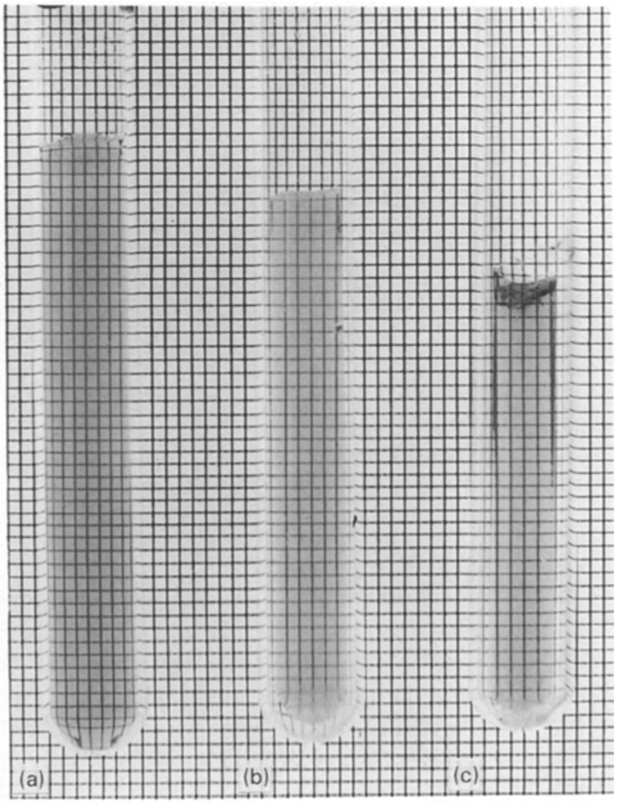

Figure 7 Silica aerogels produced by strong basic catalysts: (a) KOH, and (b) NaOH.

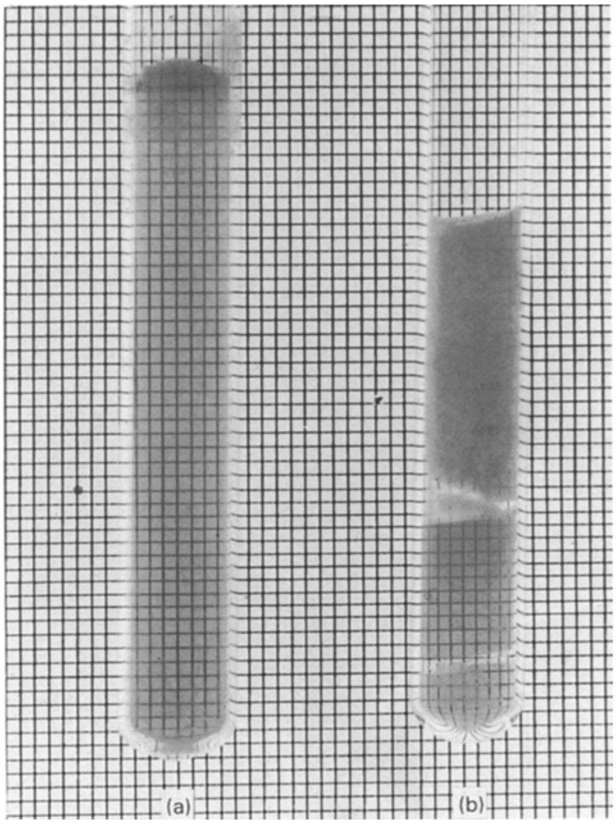

Figure 8 Silica aerogels prepared using weak acidic catalysts: (a) $C_2H_2O_4$, (b) HF, and (c) CH_3COOH.

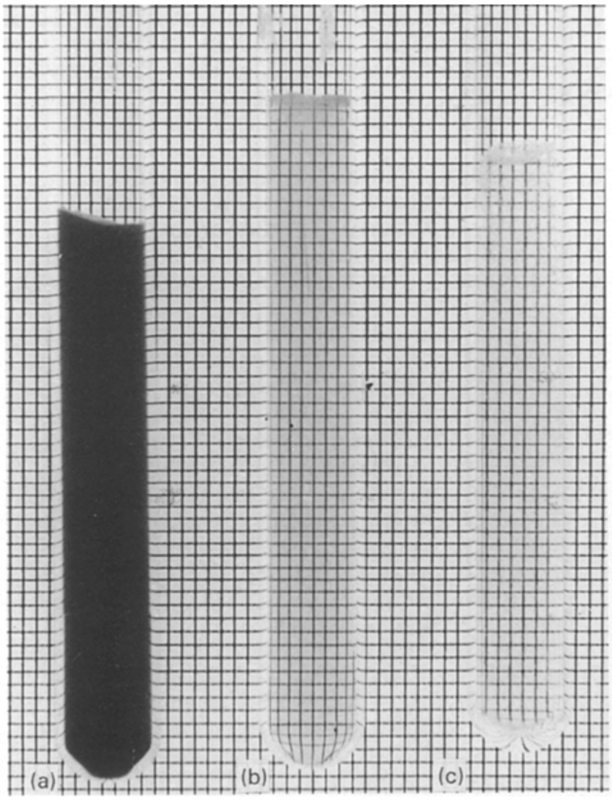

Figure 9 Silica aerogels obtained using a combination of weak acids and NH_4OH: (a) $CH_3COOH + NH_4OH$, (b) $HF + NH_4OH$ and (c) $C_2H_2O_4 + NH_4OH$.

Small-angle X-ray scattering studies [54] of both the acidic and basic catalysed gels and aerogels indicated that the acid-catalysed gels have smaller pores and hence the surface tension forces are larger and, as a result, the capillary pressure, P_r, during the evacuation of the solvent, increases according to the expression $P_r = 2\gamma \cos\theta/r$, where γ is the surface tension, r is the radius of the pore and θ is the solvent wetting angle. Because the pores are smaller in size, the acid-catalysed aerogels are cracked and transparent, as shown in Fig. 6 and hence they have large surface areas ($\approx 800\,m^2\,gm^{-1}$). On the other hand, base-catalysed aerogels (Porad slopes > -3) are highly branched and compact on a short-length scale, a result confirmed by nuclear magnetic resonance studies [55]. It is this branched, short-length scale structure that accounts for the ability to attain low-density, larger surface area ($\approx 1000\,m^2\,gm^{-1}$), transparent and monolithic aerogels from base-catalysed systems (Fig. 10). We can also attribute the differences between acid- and base-catalysed aerogels to the presence of unhydrolysed monomers during the base-catalysed condensation. The presence of these relatively unhydrolysed monomers means that the base-catalysed system can proceed by a monomer-cluster growth process which is known to produce more compact and cross-linked structure [56]. In acid-catalysed aerogels, by contrast, there is no preference for monomer-cluster growth, and the system simply continues to grow by conventional reaction-limited cluster–cluster kinetic growth. Therefore, these aerogels are prone to several cracks. The surface areas of transparent aerogels are around $1000\,m^2\,g^{-1}$. Aerogel samples that were white and opaque have surface areas around $400\,m^2\,g^{-1}$ which may be due to the larger pore sizes. All these results can easily be supported by the optical

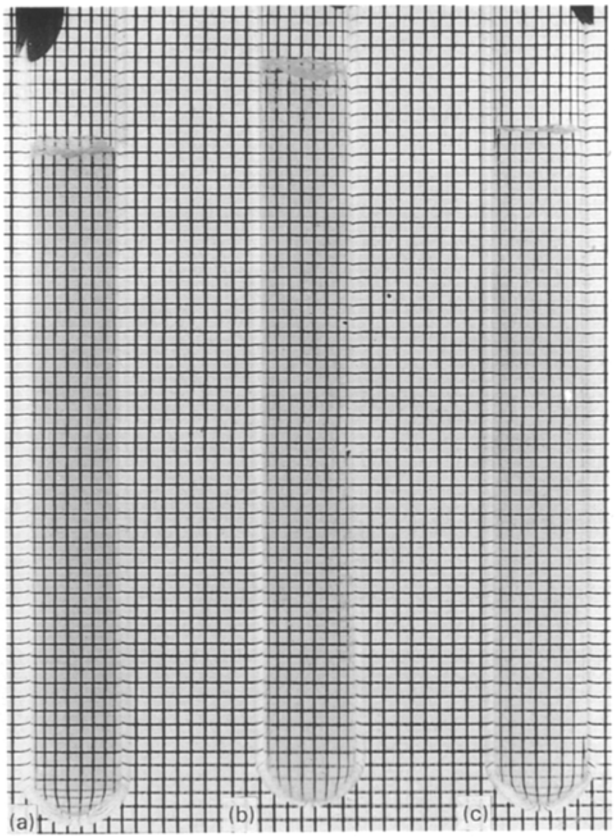

Figure 10 Silica aerogels obtained using three weak basic catalysts: (a) NH_4OH, (b) $C_6H_{19}NSi_2$, and (c) $C_4H_{11}NO_3$.

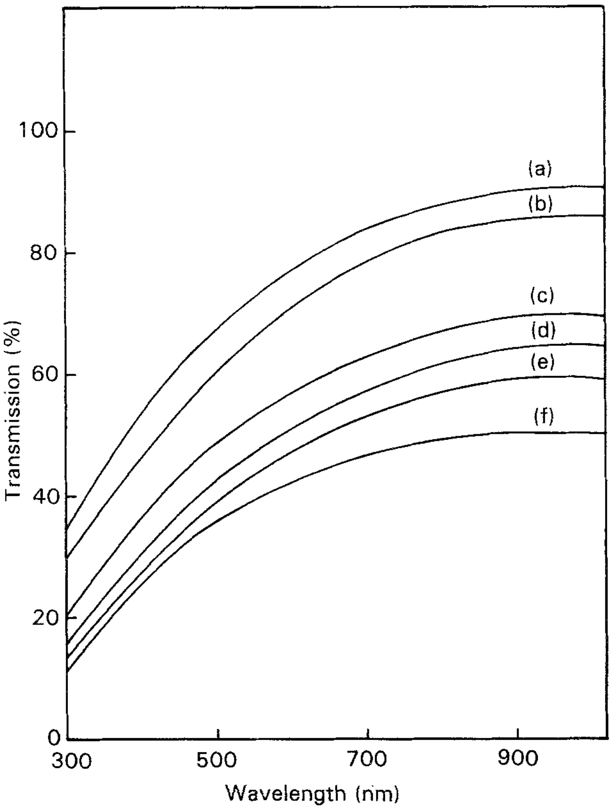

Figure 11 Percentage of transmission versus wavelength for six catalysts: (a) $C_4H_{11}NO_3$, (b) HNO_3, (c) $HNO_3 + NH_4OH$, (d) $HF + NH_4OH$, (e) HF, (f) KOH.

transmission, porosity and refractive index measurements as shown in Table IV. Mixtures of strong acidic and NH_4OH catalysts resulted in cracked aerogels which may be due to various sizes of the pores because of ammonium halide ions. If the alcogels contain pores of different sizes, then differential stresses develop which will result in cracks in the aerogels. The cracks and opacity in NaOH-catalysed aerogels may be due to larger sizes of Na^+ ions compared to K^+ ions; which will lead to pores of different sizes. The maximum transparency, the largest surface area and monolithicity obtained for the weak-base-catalysed aerogels may be due to the uniform porosity of these aerogels.

4. Conclusion

Silica aerogels of different physical properties have been produced using various solvents and catalysts. It was found that the gelation times, T_g, of the alcogels varied widely from a few minutes to several days, depending on the type of solvent and catalyst combinations, with shortest T_g being for methanol solvent and sodium hydroxide catalyst and the longest T_g for acetonitrile solvent and nitric acid catalyst. The lowest T_g observed is interpreted as the result of the shortest chain length and branching of the solvent, and proton acceptor capability of the catalyst. The longest T_g is explained on the basis of the Si–N bonding of the solvent and proton donor capability of the catalyst. In the case of strong basic catalysts, the gels with smaller cations (K^+) resulted in more transparent and monolithic aerogels compared to the gels with larger cations (Na^+). Strong acidic catalysts gave transparent but cracked aerogels, whereas weak acids yielded monolithic, transparent but shrunk aerogels. These results have been interpreted in terms of high and low cross-linkings for basic and acidic catalysts, respectively. The best quality aerogels, without any shrinkage, in terms of monolithicity and transparency have been obtained using weak basic catalysts, which has been attributed to the uniform pore sizes. Studies on fractal structure of the silica aerogels using low-frequency Raman scattering, small-angle X-ray scattering and electron microscopy techniques, are in progress.

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