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Stability of sol–gel derived porous silica monolith to solvents

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The mechanical stability of a dried silica gel monolith (with micropores ~16 nm average diameter, prepared from an $Si(OCH_3)_4$–$(CH_3)_2NCHO$–CH_3OH–H_2O–NH_4OH solution) on exposure to vapour and subsequent immersion in liquid, was examined using various solvents. The surface tension of the test solvent ranged from 17.1 dyn cm^{-1} for diethyl ether, to 72.8 dyn cm^{-1} for water. It was found that there is a distinct critical surface tension of the solvent in causing cracks in the gel on exposure to vapour and immersion in liquid for a particular shape of gel monolith. It has also been shown that the critical surface tension shifts to lower values when the gel is directly immersed in liquid, without prior exposure to solvent vapour, and that the critical surface tension also changes with the shape of the gel. The stability of the dried gel monolith to crack formation on exposure to solvent vapour and immersion in liquid solvent may be caused by the capillary force of the solvent filling pores on pore walls consisting of silica skeletons. The capillary force may be largely determined by the surface tension of the solvent. This may also explain the role of dimethylformamide as a component of the starting solution in producing dried gel rods used in this study without crack formation during the drying process.

1. Introduction

The fabrication of crack-free porous dried silica gel monolith by the sol–gel method using a $Si(OCH_3)_4$–$(CH_3)_2NCHO$–CH_3OH–H_2O–NH_4OH solution has been reported previously [1, 2]. The presence of dimethylformamide (DMF) is characteristic of the present solution. It has been shown that the DMF prevents the occurrence of cracks which are otherwise often seen during drying of a wet gel monolith. The present study was undertaken to examine the stability of the dried porous gel monolith to various kinds of solvents which have different polarities and surface tensions. It is expected that this study will yield useful information on the utilization of the gel as a porous material for various purposes, and elucidation of the nature of stresses generated in the drying process in the sol–gel preparation of the monolith.

2. Experimental techniques

2.1. Preparation of the sample

The dried gel monolith used in this study was prepared by the sol–gel method. A solution of composition $1Si(OCH_3)_4 \cdot 1(CH_3)_2NCHO \cdot 2CH_3OH \cdot 12H_2O \cdot 5 \times 10^{-4}NH_4OH$ was prepared using 148.8 ml (1 mol) $Si(OCH_3)_4$ (TMOS) as silica source. The solution was mixed by stirring at 50° C, and then cooled to 30° C, placed in a polytetrafluoroethylene (Teflon®) cylinder, 315 mm long and 49 mm i.d., sealed with aluminium foil, gelled at 30° C and aged by raising the temperature from 30 to 70° C in 24 h. The wet gel thus prepared was dried by perforating the aluminium foil cover with 15 pinholes of 1 mm diameter. The temperature was raised from 70 to 160° C over 9 days and held there for 24 h. The dried gel cylinder, opalescent in appearance, was 120 mm long and 32 mm diameter. Discs 8 mm thick and 32 mm diameter were cut from the dried gel cylinder and used for the experiment.

2.2. Pore size distribution of the sample

The size distribution of micropores in the dried gel monolith was measured using a Micromeritics Company Model AccuSorb 2100E surface measurement apparatus giving the adsorption isotherms of nitrogen gas at liquid nitrogen temperature.

2.3. Exposure and immersion tests

The gel discs have been dried in vacuum at 100° C for 12 h and then subjected to an exposure test in which a gel disc was exposed to vapour of a solvent for 48 h. The gel disc, suspended by wire and bar, was placed above the surface of 100 ml solvent in a beaker covered with aluminium foil. In order to generate vapour from the solvent, the beaker was heated in an oven at a temperature 20° C lower than the boiling point of the solvents with boiling points not higher than 101.3° C, and at 120° C for the solvents with boiling points higher than that. The exposure test was performed at room temperature (20° C) for diethyl ether (boiling point 34.6° C).

After the exposure test, the sample was subjected to

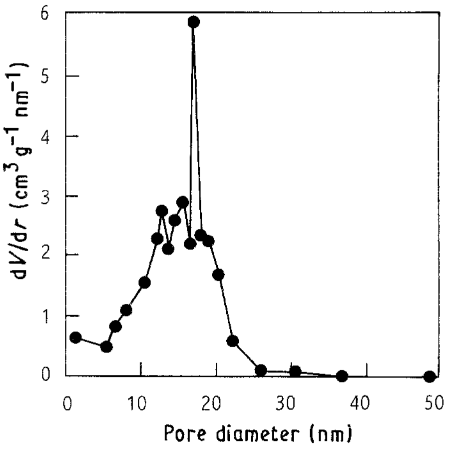


Figure 1 Pore size distribution of the gel monolith used in the experiment.

the immersion test, in which the sample is immersed in a liquid solvent at room temperature (25° C). In this test, a petri dish was filled with a solvent to about 4 mm deep, so that half the thickness of the disc could be immersed in the solvent. One surface of the exposed disc sample was immersed in the solvent, the other surface being kept clear of the solvent. It was suspected that immersion of the whole disc in the solvent may lead to crack formation due to the increased pressure of gases in pores when compressed by the intruding solvent from both surfaces of the disc.

2.4. Direct immersion of the gel in liquid solvent

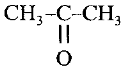
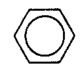
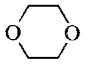
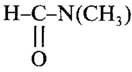
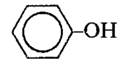
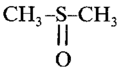
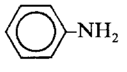
In order to examine the effect of direct immersion of the gel and the shape of the gel monolith on crack formation, rectangular plates of gel, 35 mm × 25 mm × 5 mm, and gel cylinders, 30 mm high and 32 mm diameter, were immersed in liquid solvents at 20° C without prior exposure to solvent vapour. Three kinds of solvents (diethyl ether, methanol and dimethylformamide) were used, whose surface tensions are 17.1, 22.6 and 36.8 dyn cm^{-1}, respectively. Only part of a rectangular plate or cylinder was immersed in the liquid, so that absorption occurred from the immersed bottom part.

3. Results

3.1. Characterization of the gel

The size distribution of micropores in the dried gel monolith is shown in Fig. 1. It is seen that the most frequent pore size (the average pore size) is 16 nm and the sizes of most pores are distributed in the range from about 5 to 25 nm.

TABLE I Structural formulae, surface tension at 20° C, boiling point of various solvents used in exposure and immersion, and crack formation in the gel disc 8 mm thick and 32 mm diameter

Solvent	Structural formula	Surface tension (dyn cm^{-1})	Boiling point (° C)	Crack formation in the gel	
				Exposure to a solvent vapour	Immersion in a liquid solvent
Diethyl ether	$C_2H_5\text{-}O\text{-}C_2H_5$	17.1	34.6	No crack	No crack
Di-iso-propylamine	$C_3H_7\text{-}NH\text{-}C_3H_7$	20.0*	83.4	No crack	No crack
Acetone	 $CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3$	23.7	56.2	No crack	No crack
Benzene		28.9	80.1	No crack	No crack
Dichloroethane	$Cl\text{-}CH_2CH_2\text{-}Cl$	32.2	83.5	No crack	No crack
Dioxane		34.5†	101.3	No crack	No crack
Dimethylformamide	 $H\text{-}\underset{\underset{O}{\|}}{C}\text{-}N(CH_3)_2$	36.8	153	No crack	No crack
Phenol		40.9	181.8	No crack	No crack
Dimethylsulphoxide	 $CH_3\text{-}\underset{\underset{O}{\|}}{S}\text{-}CH_3$	43‡	189	No crack	No crack
Aniline		44.5	184.7	No crack	No crack
Ethylene glycol	$HO\text{-}CH_2CH_2\text{-}OH$	46.5	197.9	A few cracks	Many cracks
Diethylene glycol	$HO(CH_2CH_2O)_2OH$	48.5‡	244.3	Many cracks	Broken into tiny fragments
Monoethanolamine	$HO\text{-}CH_2CH_2\text{-}NH_2$	48.9	180	A few cracks	Many cracks
Water	$H\text{-}O\text{-}H$	72.8	100	A few cracks	Many cracks

Surface tension at *16° C, †15° C, ‡25° C.

It has been shown [3] that the bulk density, porosity and Vickers hardness of the gel are $0.604\,\mathrm{g\,cm^{-3}}$, 72.55% and $8\,\mathrm{kg\,mm^{-2}}$, respectively. The small Vickers hardness value may arise not only from high porosity but also from the weak silica skeleton of the gel.

3.2. Crack formation in the gel disc

The structural formula, surface tension at 20° C, and boiling point of the solvents, and the occurrence of cracks on exposure and subsequent immersion tests, are summarized in Table I. Fig. 2 shows the appearance

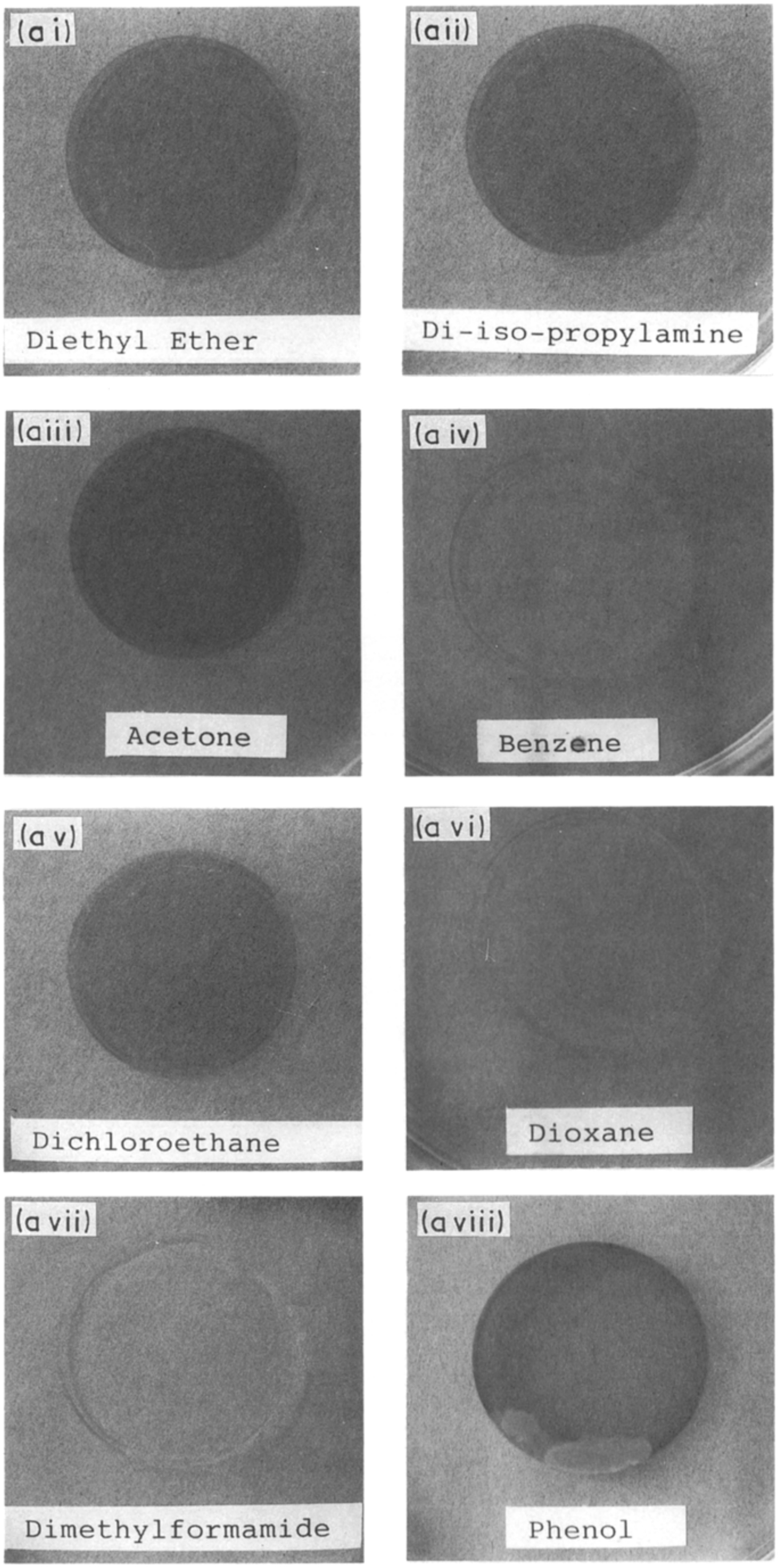


Figure 2 Photographs showing the crack formation after exposure to the vapour and subsequent immersion in the liquid.

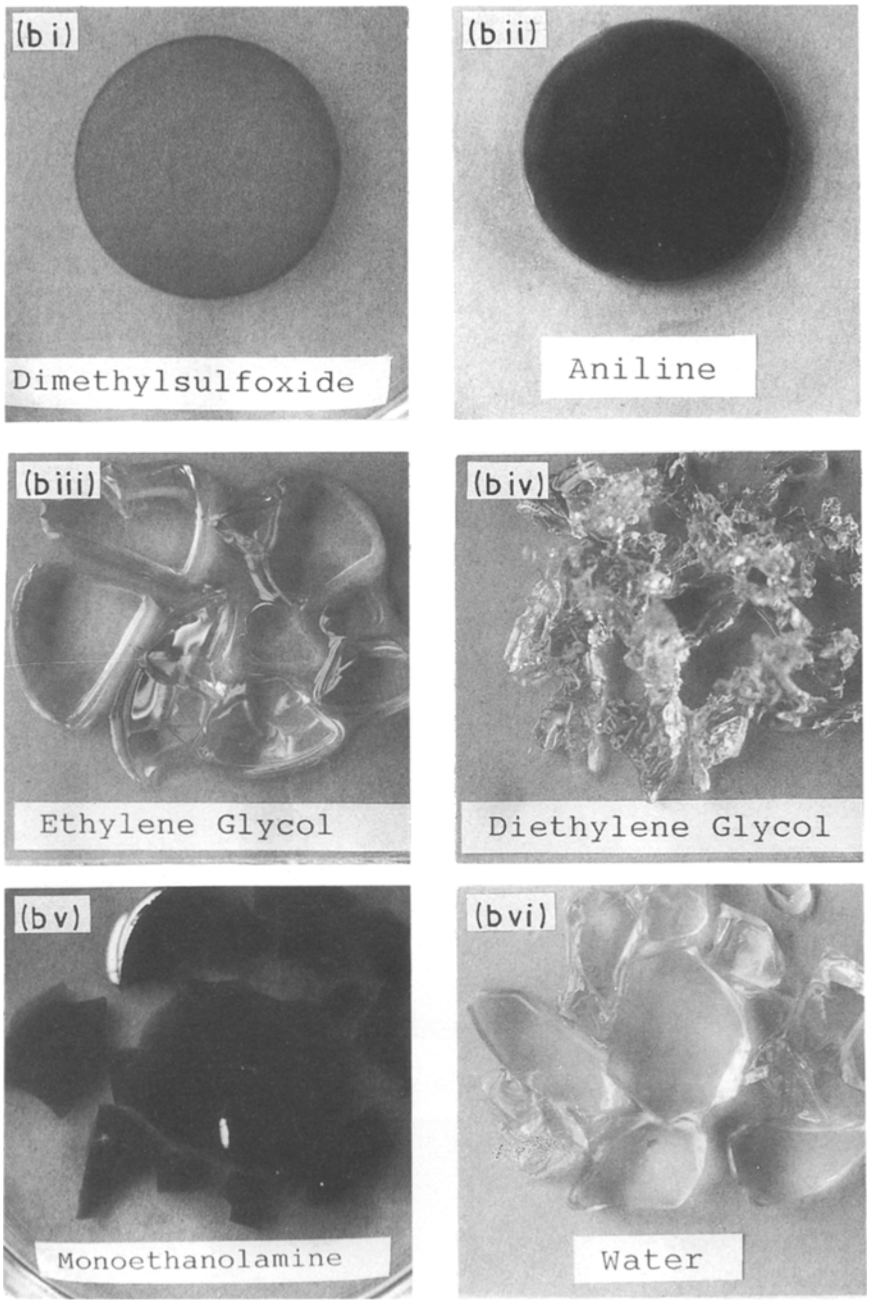


Figure 2 Continued.

of the gel which has been immersed in the solvent. The photographs were taken of the samples which had been kept in the liquid, because it is possible that cracks may newly form when the sample is removed from the liquid.

It is seen that no cracks occur on exposure to the solvent vapour when the surface tension of the solvent is $\leqslant 44.5\,\mathrm{dyn\,cm^{-1}}$, corresponding to aniline, while cracks are observed when the surface tension $\geqslant 47.7\,\mathrm{dyn\,cm^{-1}}$, corresponding to ethylene glycol. There is no exception. It is also seen that on subsequent immersion of the exposed gel in the liquid solvent, no cracks occur in the solvent which caused no cracking in the preceding exposure test, while cracks become more severe on immersion in the liquid which caused cracking in the preceding exposure test.

3.3. The appearance of the gel in the exposure test

The process of absorption of the solvent by the gel in the exposure test was observed. The gel was opalescent before exposure to the solvent vapour. After exposure to the vapour of solvents which have a surface tension equal to or smaller than that of aniline, the gel becomes opaque initially on absorbing the liquid, which partially fills the pores. However, after 48 h, the gel becomes transparent because the liquid has filled the pores completely.

On exposure to the vapour of diethylene glycol and monoethanolamine, which have high surface tensions, and thus cause cracking, the gel shows a double structure, in which the inside becomes opaque and the surface layer becomes transparent, and cracks are found in the transparent surface layer. In the case of ethylene glycol and water, the gel becomes opaque as the absorption of the liquid progresses and the whole cracked gel remains opaque after 48 h exposure. The gel retains its original disc shape after 48 h exposure to the vapour for all four solvents, even though the gel has cracked.

TABLE II Crack formation in the gel on direct immersion in liquid solvent

Solvent	Surface tension (dyn cm^{-1})	Crack formation	
		Disc, 32 mm × 20 mm	Rectangular plate, 35 mm × 25 mm × 5 mm
Diethyl ether	17.1	No crack	No crack
Methanol	22.6	No crack	Cracks
Dimethylformamide	36.8	Cracks	Cracks

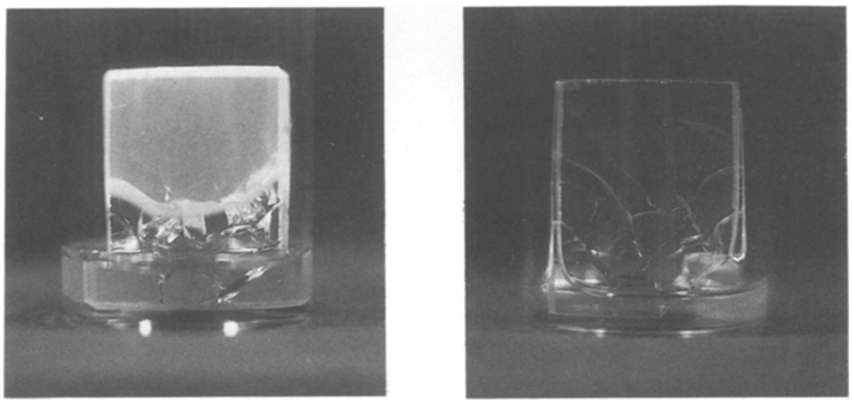
The gel was coloured brown at the last stage of the exposure test for dimethylsulphoxide, aniline and monoethanolamine, probably due to their slow decompoosition at the high temperature (120° C).

3.4. Crack formation on direct immersion in liquid solvents

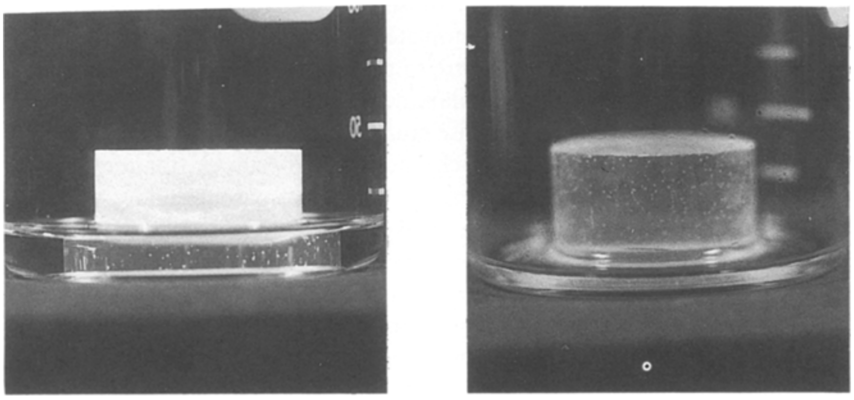
Observations made of crack formation on the direct immersion of a gel monolith in liquid solvents are shown in Table II and Fig. 3. It is seen in Fig. 3 that the liquid is absorbed by the gel in the immersed part, and the appearance of the gel changes from opalescent to transparent as the liquid front moves up. No cracking is seen in the case of diethyl ether (Fig. 3a), but cracks are formed around the liquid front in methanol, which has a higher surface tension, for the rectangular plate (Fig. 3b). It is seen in Fig. 3c, however, that no cracks occur when the gel cylinder is immersed in methanol.

As can be seen from Table I, the occurrence of

(a) Just after immersion Middle stage Final stage



(b) Just after immersion Final stage



(c) Just after immersion Final stage

Figure 3 Photographs showing the crack formation in the direct immersion test. Immersion in (a) diethyl ether (rectangular plate), (b) methanol (rectangular plate), (c) methanol (cylinder).

cracks depends on the shape of the gel as well as the surface tension of the liquid. When the surface tension of the liquid is very small (at 17.1 dyn cm^{-1} for diethyl ether) no cracking occurs in either discs or rectangular plates. When the surface tension of the liquid is larger (at 36.8 dyn cm^{-1} for dimethylformamide), direct immersion in the liquid causes cracking in both shapes. In methanol which has an intermediate surface tension (22.6 dyn cm^{-1}), no cracks are generated in the disc, but cracks are formed in the rectangular sample.

4. Discussion

4.1. Occurrence of cracking in the exposure and immersion tests

The occurrence of cracks in the dried porous gel on exposure to the solvent vapour and after immersion in the liquid solvent is attributed to the tensile stress produced by the capillary force based on the surface tension of the liquid entering the micropores. Assuming that micropores in the gel are represented by capillary tubes of diameter D, the capillary force, ΔP, acting on the capillary walls of the silica skeleton at the menisci, is expressed by

$$\Delta P = \frac{4\gamma \cos \theta}{D} \qquad (1)$$

where γ is the surface tension of the liquid filling the micropores, θ is the contact angle between the liquid and the wall of the micropores, and D is the pore diameter, which is constant in this study. If it is assumed that the contact angle θ is constant, ΔP increases in proportion to the surface tension of the solvent, γ [4, 5]. It is assumed that the capillary force in Equation 1 acts to pull the capillary wall towards the liquid [4, 5]. Because forces emanating from many capillaries are summed, the layer in which a liquid is incorporated tends to shrink and undergoes a tensile stress from the dry region, i.e. that part of the gel which is not reached by the liquid. This will result in the occurrence of cracks when the surface tension of the liquid is large enough for the tensile stress to exceed the strength of the gel. The capillary force, ΔP, may reach 10^7 N m^{-2} (Pa) for a liquid of $\gamma = 40$ dyn cm^{-1}, if it is assumed that $D = 16$ nm and $\theta = 0$. Because there are pores of diameter smaller than D, the capillary force, D, may be higher than that value.

This explains the above result where on exposure to a vapour of a liquid of higher surface tension, cracks occur in the gel disc of 32 mm diameter and 8 mm thick. In the exposure test, the vapour will be adsorbed by the pore walls, making a liquid film on the walls. It is assumed that as the exposure time increases the quantity of adsorbed solvent becomes sufficient to fill some pores with liquid solvent, which induces the tensile stress and causes cracking, if the surface tension of the liquid is large. No cracks will be formed if the surface tension is low.

It has been shown that the immersion in the liquid solvent after exposure to the vapour causes additional heavy cracking in the gel disc of 8 mm thick and 32 mm diameter, which leads to the complete fragmentation of the gel disc (Table I, Fig. 2). This means that additional stress is caused by the subsequent immersion test. It may be possible that the additional stress is created because, on immersion, the liquid fills all the remaining micropores which have not been filled in the exposure test, and the stress produced in the filled layer as a sum of capillary forces in the individual micropores becomes much larger than that produced in the previous exposure test.

It has been shown that direct immersion in the liquid solvent without previous exposure tends to lower the threshold of the surface tension of the liquid for crack formation. In Table II it is seen that direct immersion of the gel cylinder in dimethylformamide causes cracking in the gel cylinder. Immersion after exposure did not produce cracks in the gel disc, as seen in Table I. It is assumed that direct immersion may produce a large stress on the layer rapidly filled with the liquid, which does not allow the stress in the gel to be partially relaxed. When the gel is subjected to previous exposure, the stress thus produced may be partially relaxed and accordingly, the total stress produced on subsequent immersion might be smaller than that produced upon being directly immersed into the liquid.

Table II also shows that the occurrence of cracks depends on the shape of the sample tested. This is shown by the test with methanol which has an intermediate surface tension, in which no cracks are observed in the disc sample, but cracks are formed in the rectangular plate sample. Immersion in diethyl ether does not cause cracks in either shape because of the lower surface tension of the liquid, and immersion in dimethylformamide causes cracks in both shapes because the surface tension of the liquid is much higher. At present we can offer no quantitative explanation on the effect of the shape of the sample or the crack formation, but it is assumed that the total stress in the gel produced by the capillary force may be different for different shapes.

4.2. Significance of the present results in the crack-free formation of gel monolith

We have shown [1, 2] that the addition of dimethylformamide to the starting tetramethoxysilane solution is effective in drying wet gel monoliths of cylindrical shape without causing cracks. The present results on crack formation in the dried gel may explain the reasons for this, because they clearly suggest that the cracks are caused by the stress produced at the interface between the wet and dry parts of the gel. The stress arises from the capillary force based on the surface tension of the liquid when the gel is partially wet with the liquid filling the micropores.

It is assumed that the presence of dimethylformamide in the wet gel reduces the stress caused by the capillary force which might otherwise produce cracks in the gel during drying. The starting solution used for producing crack-free dried gel mainly consists of methanol, water and dimethylformamide. In the initial stage of drying, most of the methanol (with the low boiling point) evaporates from the wet gel at temperatures lower than 100° C. When the wet gel is heated at temperatures higher than 100° C, water, which has a very high surface tension of 72.8 dyn cm^{-1} also evaporates from the wet gel, leaving dimethylformamide behind. Accordingly, the remaining liquid consists mostly of dimethylformamide, which has a much lower surface tension than water, in the last stage around 150° C, where the menisci enter the gel and the capillary force may cause a stress at the menisci, i.e. at the interface between the wet inner part and the dried surface layer of the gel. Because the surface tension of dimethylformamide is not large, the stress may be small, which results in the formation of a crack-free dried gel.

We have found experimentally [6] that cracks occur in the gel during the drying process when the temperature is kept lower than 100° C until the gel is completely dried. The reason for this may be found in the surface tension of the liquid filling the micropores. It is possible that the liquid contains much water and has a higher surface tension in the last stage of drying if the temperature is kept low. This liquid would produce a larger stress.

5. Conclusions

The formation of cracks on exposure to vapour and subsequent immersion in liquid and on direct immersion in liquid has been examined with solvents of various surface tensions, for a dried silica gel monolith made by the sol–gel method. The following conclusions were drawn.

1. There is a distinct threshold of surface tension of the solvent in causing cracks in the gel on exposure to the solvent vapour.
2. The immersion of the gel in liquid solvent after exposure to vapour produces more severe cracking in the exposure test.
3. Direct immersion of the gel in liquid solvent shifts the threshold of the surface tension towards a much lower value.
4. The surface tension threshold in crack formation depends on the shape of the gel sample tested; cracks are formed in rectangular plates with a liquid solvent of lower surface tension than in the gel cylinder.
5. The formation of cracks can be explained by the occurrence of a stress caused by the capillary forces based on the surface tension of the solvent.

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