

# Solvent effect on ageing of silica gels

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The structure of silica gels derived from tetraethoxysilane (TEOS) with molar compositions of  $\text{TEOS}:\text{H}_2\text{O}:\text{HNO}_3 = 1:10:0.4$  and then aged in various solvents, was studied. The effect of various solvents having different physical properties on the gel structure, as well as the relationship between the solvent properties and the dried gel structure, were investigated. The density, surface area and pore-size distribution were measured. The results of the pore structure and SEM showed the aged gels to have a slit-shaped micropore, narrow pore-size distribution, and homogeneous microstructure. The density, surface area, pore size and pore volume of dried gels changed as the gels were subjected to ageing in various solvents. The surface area could be related to the polarity parameter of the ageing solvent.

## 1. Introduction

Sol-gel synthesis can be conducted in various solvents. However, the solvent greatly affects the sol-gel reactions and hence the structure of the resulting gel. The solvent can also react with the starting precursor of metal alkoxide and change each reaction of hydrolysis and the subsequent polycondensation in the process [1, 2]. In the sol-gel process for bulk ceramics, several steps are included: hydrolysis, gelation, ageing and firing.

A number of researchers have investigated solvent effects mainly in the context of drying control chemical additives (DCCAs) used as co-solvents with alcohol [3–5]. In addition, some attempts have been made to use different solvents as ageing media to modify the gel structures of the wet gels, and thus the dried gels [6–9]. Mizuno *et al.* [6] improved the strength of the gel by ageing silica gels in  $\text{NH}_4\text{OH}$  media which replaced OR with OH on the surface and hence increased Si–O–Si bonds. Smith *et al.* [8] obtained a narrower pore-size distribution by repeated ethanol washing for the base-catalysed gel. Davis *et al.* [9] studied the effect of pore fluids on gel structures by ageing the wet gel in a series of alcohol and water baths. They found that the surface area increased as the gel was aged in alcohol, and decreased in water. Alcohol ageing also resulted in small pore-size distribution. However, little effort has been made to relate the changes in gel structures to the physical properties of the solvents. The study of Quinson *et al.* [7] showed that the pore volume increased with an increase in polarizability of solvents for titania gels. The pore volume was measured by thermoporometer when the titania gel was aged in solvent.

The present study was undertaken to examine the effect of various solvents for hydrolysis or ageing on the gel structure and to relate the solvent properties to the dried gel structure.

## 2. Experimental procedure

### 2.1. Preparation of gels

Silica gels were prepared from high-acid hydrolysis of a mixture of tetraethoxysilane (TEOS) with water without the addition of mutual solvents. The sol was prepared by mixing in a molar ratio of  $\text{TEOS}:\text{H}_2\text{O}:\text{HNO}_3 = 1:10:0.4$  at room temperature. To study the effect of solvents on gelling time, an additional 10 ml of the desired solvent was mixed with TEOS before the hydrolysis took place. Gelation of the sol was carried out at 60 °C and the wet gels were then aged in ethanol for one day prior to further ageing in various other solvents. The solvents used as ageing media were water ( $\text{H}_2\text{O}$ ), ethanol (EtOH), 2-propanol (PrOH), acetone, acetonitrile (MeCN), tetrahydrofuran (THF), toluene, and carbon tetrachloride ( $\text{CCl}_4$ ). The aged gels were later subjected to drying in the same ageing media under open conditions at 60 °C. In the case of ageing in alcohol, the ageing media were mixed with ethanol in a ratio of 50:50 by volume. The aged gels were later dried at 80 °C under open conditions.

### 2.2. Gel characterization

Experiments to determine the surface area and pore volume were carried out on a nitrogen adsorbing analyser (Quantachrome's Quantasorb). The surface areas were calculated using the BET method, and pore volumes were determined by assuming a cylindrical model for the Kelvin equation. The samples were dried at 140 °C and degassed under a nitrogen flow before analysis.

The density was measured directly from the weight and the volume of the cylindrical dried gels using a vernier caliper and a balance. The changes in gel structures were followed by infrared diffuse reflectance using a Perkin-Elmer Model 1600 Fourier transform

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infrared spectrophotometer (FTIR). Scanning electron micrographs of the dried gel fractured surfaces were obtained with a Jeol 848 electron microscope.

In the course of gelation, the viscosity of the sol increased gradually into a solid gel. The gelling time, therefore, was defined as the time period from the pouring of a sol into mould to the moment when no more fluidity of the sol was observed by tilting of the mould.

### 2.3. Characteristics of solvents

The solvents used in this study can be classified as polar and protic. Polar solvents have a dielectric constant of 20 or greater, protic solvents act as hydrogen bond donors [10]. The classification and physical properties of various solvents are listed in Table I [10, 11].  $E^N$  is an empirical parameter of solvent polarity which characterizes the polarity more completely than  $\epsilon$  and  $\mu$ . A higher  $E^N$  value corresponds to a higher solvent polarity [12]. The solvent polarity parameters can be changed by mixing the solvents and water. Balakrishnan and Eastal [13] attributed the change in polarity to replacement of the uncoordinated water molecules by the solvents, because the uncoordinated water molecules would be considerably more polar than coordinated molecules.

## 3. Results

### 3.1. Gelling time

The effect of the addition of solvents to the sols on the gelling time is shown in Table II. It is seen that the

gelling times when acetone and tetrahydrofuran were added to sols were longer than those with ethanol and 2-propanol.

### 3.2. Density, volume shrinkage and surface area

The variations of density and volume shrinkage, with addition of different solvents to the sol as well as the drying methods, are given in Table II. The results showed that drying under open conditions resulted in the gels having a higher volume shrinkage, independent of different solvents, and hence a higher bulk density than that by slow drying. However, both density and volume shrinkage changed with the different solvents used.

The relationship between bulk density and surface area is shown in Fig. 1. A general correlation between them is observed. The dried gel with a low bulk density had a high surface area. An attempt was made to relate the change in the structure of the silica gel to physical properties of the ageing solvents by their polarity parameters. The dependence of the surface area of a gel on the polarity parameter is shown in Fig. 2. It is found that the lower the polarity parameter of the ageing solvent for the wet gel, the greater the surface area of the dried gel. That is, the changes in the structure of silica gels can be related to the physical constants of the ageing solvents, although some scattering is observed.

However, for gels aged in mixtures of aliphatic alcohols with ethanol, a reverse relation between surface area and polarity parameter is shown in Fig. 3.

TABLE I Physical properties of ageing solvents.  $\alpha$  is the polarizability,  $\epsilon$  the dielectric constant,  $\mu$  the dipole moment,  $E^N$  the polarity parameter,  $\gamma$  the surface tension,  $V_m$  the molecular volume

Ageing media	Classification		$\alpha$ ( $\times 10^{-24}$ cm)	$\epsilon$	$\mu$	$E^N$	$\gamma$ (dyn cm <sup>-1</sup> )	$V_m$ (cm <sup>3</sup> mol <sup>-1</sup> )
	polar	protic						
Water	×	×	1.45	78.54	1.85	1.000	73.05	18.0
Ethanol	×	×	5.84	24.3	1.69	0.654	22.75	58.4
Propanol	—	×	6.97	18.3	1.66	0.546	21.70	76.5
Acetone	×	—	6.4	20.7	2.88	0.460	23.70	73.5
Acetonitrile	×	—	4.4	37.5	3.92	0.355	29.32	52.2
Tetrahydrofuran	—	—	8.2	7.3	1.63	0.207	24.60	81.8
Toluene	—	—	12.3	2.38	0.36	0.099	28.25	106.3
Carbontetrachloride	—	—	11.2	2.24	0.00	0.055	26.95	96.5

TABLE II Effect of various solvents added on gelling time, and drying methods on density of dried gels at 60°C

Solvent	Gelling time (h)	Slow drying <sup>a</sup>		Open drying <sup>b</sup>	
		Density (g cm <sup>-3</sup> )	Shrinkage (vol %)	Density (g cm <sup>-3</sup> )	Shrinkage (vol %)
Ethanol	1.57	1.02	87.55	1.10	88.22
Propanol	1.42	0.92	86.35	1.07	88.40
Acetone	1.88	0.88	85.32	1.06	87.78
Tetrahydrofuran	1.77	0.94	86.31	1.08	87.91

<sup>a</sup> During drying, the covers of containers were kept on.

<sup>b</sup> During drying, the covers of containers were taken off.

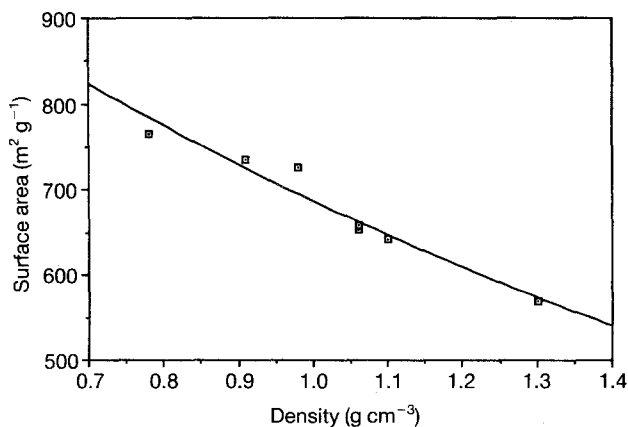


Figure 1 Relationship of surface area with density of gels aged in different solvents and dried at 60°C.

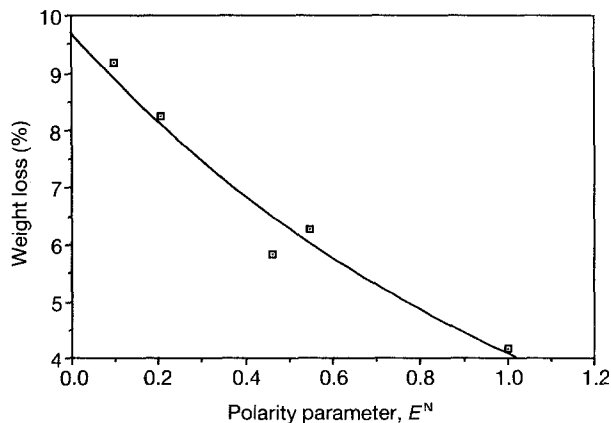


Figure 4 Changes in weight loss with polarity parameter for gels, dried at 60°C.

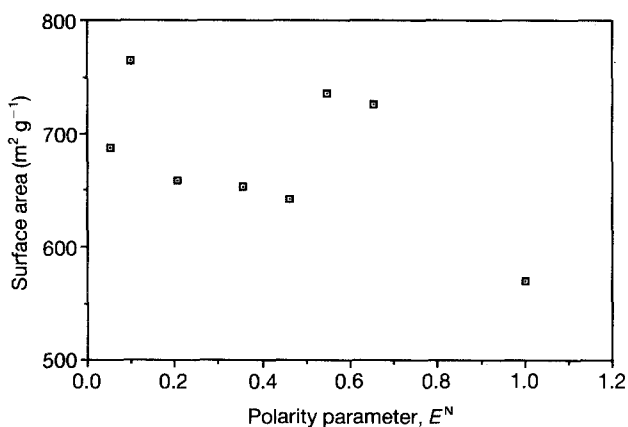


Figure 2 Changes in surface area of gels aged in various solvents and dried at 60°C.

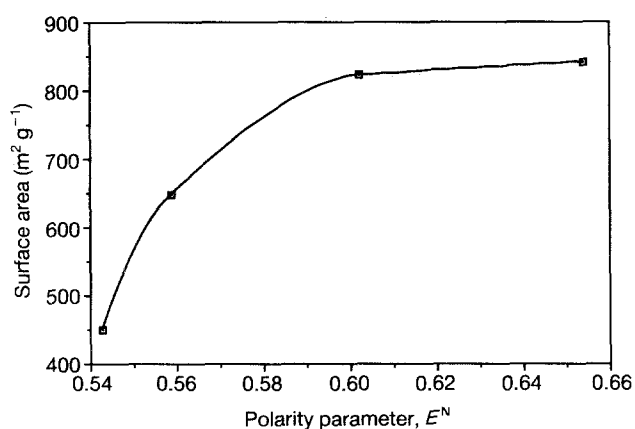


Figure 3 Changes in surface area of gels aged in different aliphatic alcohols and dried at 80°C.

The surface areas of dried gels increased as polarity parameters of ageing solvents increased. It should be noted that the values of the polarity parameter shown in the figure were those of pure alcohols (ethanol 0.654, butanol 0.602, hexanol 0.559, octanol 0.543).

### 3.3. Thermogravimetric analysis

The effect of the ageing solvent on the weight loss

with respect to polarity parameter is shown in Fig. 4. The weight loss, based on the weight loss between 120 and 800°C, decreased with the increasing polarity parameter of ageing solvent.

### 3.4. Pore structure and pore-size distribution

The nitrogen adsorption isotherms for gels aged in different solvents are shown in Fig. 5. According to the Brunauer, Deming, Deming and Teller (BDDT) classification [14], type I isotherms are produced for the solvent-aged gels. A dependence on ageing solvents is apparent from the plateau heights.

Pore-size distributions of solvent-aged gels dried at 60°C are shown in Fig. 6. It appears that the gels exhibit narrow pore-size distributions and contain no pores exceeding 2.5 nm radius for the EtOH-, THF- and water-aged gels. For the CCl<sub>4</sub>-aged gel, no pores were larger than 4.0 nm radius.

A similar relationship is seen in Fig. 7, where the pore-size distribution curves for gels prepared by ageing in mixture of alcohols are given. The alcohol-aged gels contain pores as large as 6.0 nm radius compared with 4.0 nm radius as shown in Fig. 6; however, the peak height of the distribution curve

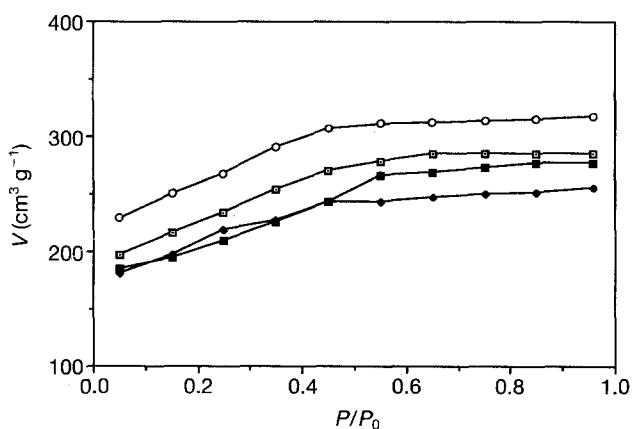


Figure 5 Nitrogen adsorption isotherms of dried gels prepared by ageing gels in various solvents and then drying them at 60°C. (□) EtOH, (◆) THF, (■) CCl<sub>4</sub>, (◇) water.

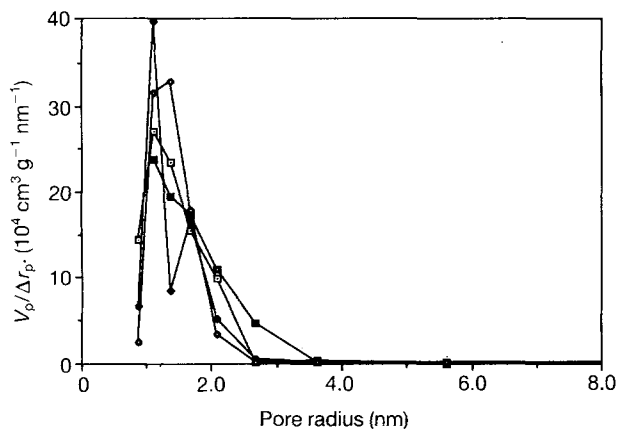


Figure 6 Pore-size distribution of gels in various solvents, dried at 60 °C. For key, see Fig. 5.

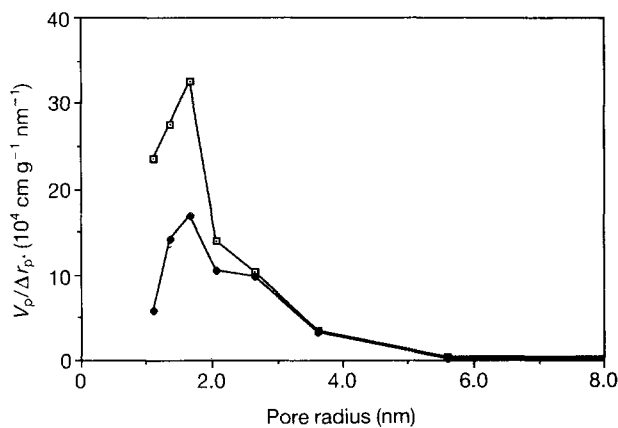


Figure 7 Pore-size distribution of dried gels after ageing gels in butanol and nonanol with an ethanol mixture of 50:50 vol %, and drying them at 80 °C. (□) BuOH, (◆) NonOH.

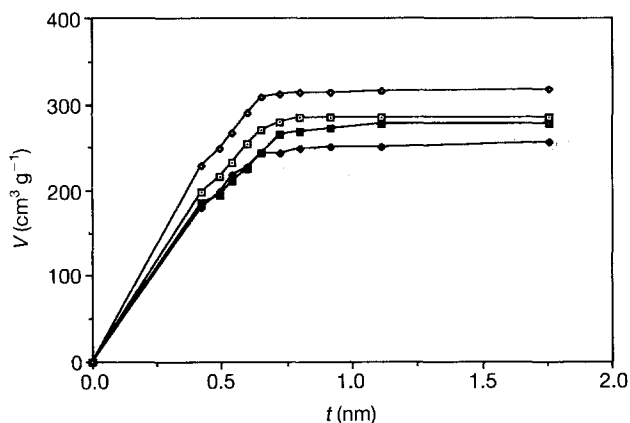


Figure 8  $V-t$  plot of gels prepared by ageing gels in various solvents and then drying them at 60 °C. For key, see Fig. 5.

decreased, which indicated the decrease in pore volume.

Fig. 8 shows the curves for the adsorption isotherms of nitrogen adsorption volume,  $V$ , versus adsorbed film thickness,  $t$ , of gels aged in various solvents. It exhibits a typical feature of the acid-catalysed gel having a straight line from the origin in the range of

low pressure and downward deviations from the straight line at higher pressure. The volume of the plateau corresponds to the micropore volume.

### 3.5. SEM observation

Scanning electron micrographs of gels aged in different solvents such as EtOH, THF and  $\text{CCl}_4$  are presented in Fig. 9. All samples show textures with uniformly distributed microstructure, but with different porosity levels. It can be seen that the gels consisted of small particles whose diameter is in a range of 20–50 nm. Compared to the surface characteristics of EtOH- and THF-aged gels, the  $\text{CCl}_4$ -aged gel has a coarser texture with slightly larger pores.

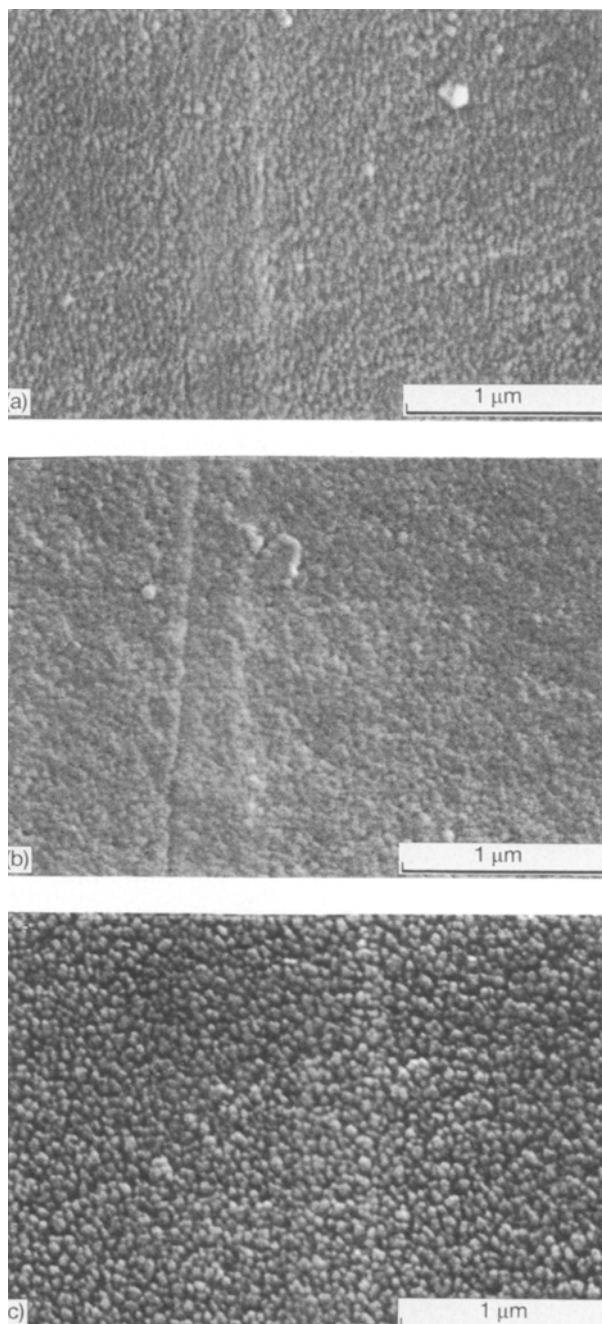


Figure 9 Scanning electron micrographs of fractured surface of gels aged in (a) EtOH, (b) THF, and (c)  $\text{CCl}_4$  and then dried at 60 °C.

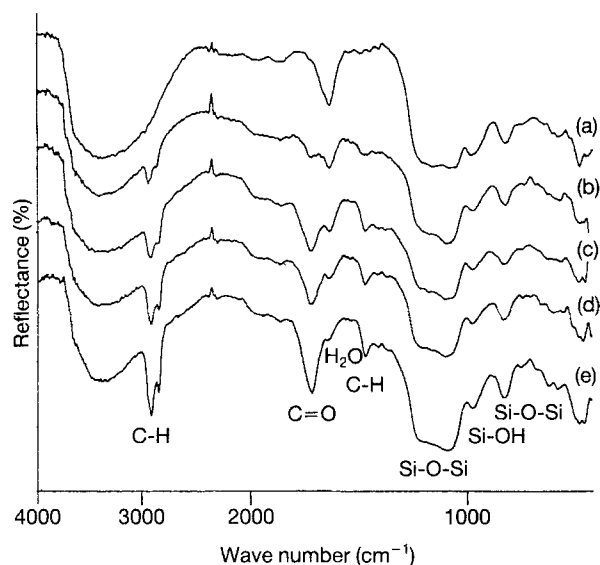


Figure 10 FTIR spectra of alcohol-aged gels in (a) ethanol, (b) butanol, (c) hexanol, (d) octanol, (e) nonanol, and dried at 80°C.

### 3.6. FTIR spectra

The structure of the skeleton in an alkoxy-derived silica gel primarily consists of a three-dimensional random network of  $\text{SiO}_4$  tetrahedra together with a large amount of SiOH covering the surface. The FTIR spectra of the alcohol-aged gels are given in Fig. 10. The absorption band due to the Si–O bonds with non-bridging oxygen, i.e. SiOH groups, appears in the vicinity of  $960\text{ cm}^{-1}$  along with the shoulder of the intense absorption peak around  $1080\text{ cm}^{-1}$ . This is assigned to the asymmetric stretching vibration of the Si–O–Si bonds with bridging oxygens. On the other hand, the symmetric stretching mode or the ring structure of tetrahedron ( $\text{SiO}_4$ ) appears in  $800\text{ cm}^{-1}$  [15, 16].

With increase in the chain length of the ageing alcohol, new bands appear at 2980, 2950, 1700 and  $1410\text{ cm}^{-1}$ ; also, the intensities of these bands are increased. The bands correspond to the C–H stretching ( $2980, 2950\text{ cm}^{-1}$ ) and C–H bending modes ( $1410\text{ cm}^{-1}$ ), while  $1700\text{ cm}^{-1}$  is associated with C=O bond [17]. The intensity of the C=O peak also increases accompanying a decrease in intensity of the  $1620\text{ cm}^{-1}$  peak due to water molecule.

## 4. Discussion

### 4.1. Gelation time

Gelation time is an indicative of the rate of the hydrolytic polycondensation reaction [18]. The effects of various solvents on the gelling time of TEOS are shown in Table II. From the table, acetone and THF exhibit longer gelling time relative to EtOH and PrOH. This is because acetone and THF are relatively basic while EtOH and PrOH are acidic solvents, by Lewis definition. Silica has an acidic surface; therefore, there would be greater acid–base interaction between the acidic silica surface and acetone and THF. This interaction reduces further condensation reaction, retarding gelation.

### 4.2. Density, volume shrinkage and surface area

In Table II, the results show that the method of drying the gel influences the physical properties to a significant extent. In open drying conditions; fast vaporization of water and ethanol may enhance the polycondensation reaction, which causes a growth of the particles. In addition, the solvents with higher surface tension have higher degree of condensation because the surface tension forces the surface groups on the gel closer. Therefore, a considerable effect on the packing of the primary particles can be expected. This therefore affects the volume shrinkage, surface area and density of the gels.

The growth of particles is controlled by the polycondensation reaction [18]. Solvents with higher polarity parameters happens to be more acidic in general and less interactive with the acidic silica surface [9]. Solvents with higher polarities enhance the condensation reaction and the growth of the primary particles, leading to a decrease in surface area (Fig. 2), thus an increase in density (Fig. 1). A decreasing weight loss with an increasing polarity parameter of the solvent in Fig. 4 indicates fewer alkoxy and hydroxy groups on the surface for the gels aged in the higher polarity solvents. These weight loss data support the surface area data in that both sets of data show an enhancement of the condensation reaction.

In Fig. 2, the scattering of the surface area for the EtOH ( $E^N = 0.7$ )- and PrOH ( $E^N = 0.6$ )-aged gels with respect to the polarity parameter may be due to the kinetics of the reverse reaction (re-esterification). Re-esterification leads to a decrease in the condensation in varying degrees. The deviation of the surface area for the toluene ( $E^N = 0.1$ )-aged gel may be due to toluene adsorbing on to the gel in a greater degree than  $\text{CCl}_4$ . This adsorption is probably due to the acid–base interaction between basic toluene and acidic silica surface when  $\text{CCl}_4$  is neutral relative to the silica surface.

In the case of alcohol ageing shown in Fig. 3, a lower polarity parameter lowers the surface area. At 80°C drying, more residual alcohols from higher aliphatic alcohols remained in the gel as indicated in Fig. 10. This suggests that another mechanism is taking place. The adsorption of a longer alkyl chain of alcohol with a lower dielectric constant decreases the charge on the particle surface reducing the electrostatic repulsive forces. Because an aggregation of particles takes place, the remaining alcohol is entrapped among the particles. This kind of aggregation results in an increase of granule size with reduced surface area.

### 4.3. Thermogravimetric analysis

To study the effect of ageing liquids on the sol–gel reactions, thermogravimetric analysis was conducted. Brinker *et al.* [19] pointed out that at temperatures above 150°C, all the weight loss is due either to SiOR or SiOH being originally present in the dried gel. In Fig. 4, the decreasing weight losses illustrate that the gels aged in solvents, shown in Table I, with higher

polarity parameters, contain less adsorbed species, alkoxy and hydroxy residuals. This implies that the high polarity promotes hydrolysis and condensation reactions.

#### 4.4. Pore structure and pore-size distribution

The type I isotherm is generally observed with the microporous compact solids [20]. This indicates that gels aged in various solvents have a large number of fine pores.

As indicated in Fig. 6, the EtOH- and THF-aged gels has relatively smaller pores than the CCl<sub>4</sub>-aged gel. This is in accordance with SEM results shown in Fig. 8. This will be explained in the next section of SEM microstructure.

A decrease in pore volume after drying for gels aged in longer chain alcohols is shown in Fig. 7. The decreased pore volume is related to the ageing solvent being a larger molecule with a higher boiling point. The adsorbed long-chain alcohol molecules on the surface of the gel probably interact with hydroxyl groups on the gel surface. Thus, the alcohol molecule remaining in the pore after drying reduces the pore volume in the gel. The adsorbed alcohol molecules in the gel are evinced by FTIR spectra shown in Fig. 10.

By plotting the volume of adsorbed nitrogen,  $V$ , as a function of the layer thickness,  $t$ , Lippens and deBore [21] classified  $V-t$  curves into three types and explained them as follows.

1. For the straight line with a constant slope, the surface is freely accessible up to high relative pressure; the multilayer can be formed unhindered on all parts of the surface in the absence of any pore filling.

2. For an upward deviation from a straight line, the material takes up more adsorbate than the corresponding volume of the multilayer. This means that at a certain pressure, capillary condensation will occur in larger pores of cylindrical shape.

3. For a downward deviation from a straight line, no capillary condensation can occur in slit-shaped pores. At a certain relative pressure the pores may be completely filled by the adsorbed layers on both parallel walls, thereby reducing the available surface for continued adsorption.

As can be seen from  $V-t$  curves in Fig. 8, the gels, regardless of the different ageing solvents, are of the third type according to the Lippens and deBore model. This implies that the gel prepared under acidic conditions appears to be slit-shaped pores.

#### 4.5. Gel microstructure

Organic solvents added to the sol affect the condensation process by changing the nature and magnitude of the electrostatic and hydrogen bonding interactions in the sol-gel system [1, 2]. Artaki *et al.* [1, 2] pointed out that these interactions, in turn, affect the degree of particle coalescence and compactness of the resulting gel.

As shown in Fig. 8, the CCl<sub>4</sub>-aged gel has relatively larger pores than EtOH- and THF-aged gels. This is in agreement with the pore-size distributions shown in

Fig. 6. This is probably due to the neutral nature of CCl<sub>4</sub> relative to the acidic silica surface. CCl<sub>4</sub> is also a non-polar solvent which makes it unable to stabilize the reactants with respect to the activated complex as explained by Brinker and Scherer [18]. Therefore, CCl<sub>4</sub> can hasten the condensation process and increase coalescence by lowering the zeta potential which should increase the pore size.

#### 4.6. FTIR spectra

For alcohol-aged gels, the presence of characteristic bands at 2980, 2950, 1700 and 1410 cm<sup>-1</sup> suggests the formation of aliphatic aldehydes formed by the decomposition of alcohol [17, 22]. The new molecule is probably linked to the surface of the gel. The decrease in the absorption band of molecular water at 1620 cm<sup>-1</sup> indicates that the gel is strongly hydrophobic. This is because the alcohol generally turns the gel from a hydrophilic to hydrophobic surface as the size of the alkyl group increases due to the decreased contribution of the hydroxyl group in the molecule.

### 5. Conclusions

1. The density of the dried gel after solvent ageing is closely related to the surface area of the gel and tends to decrease as the surface area increases.

2. The results of the pore structure and SEM show the aged gels having a slit-shaped micropore, narrow pore-size distribution, and homogeneous microstructure.

3. The surface area can be related to the polarity parameter of the ageing solvent.

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