

# Role of solvents in the gelation process: can light scattering studies shed some *light*?

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**Abstract** Sol–gel reactions continue to be of interest for the preparation of nanostructured materials. Two chemical reactions that are important in the sol–gel process are the hydrolysis and condensation reactions. The rate of these two reactions are affected by a number of factors such as reaction pH, temperature, humidity, amount of water, type of alkoxide, molar ratio of alkoxide to water, and nature of solvent. Moreover, there is a physical process, that of particle aggregation that is also important in the overall gelation process. The role of solvents in these chemical and physical processes is still not very clear. In order to clarify the role of solvents in the gelation process, small angle light scattering studies (SALS) were carried out. A model system chosen was a colloidal silica solution that contained preformed silica particles of 10–15 nm in diameter. SALS studies indicate that gelation times are independent of the nature of solvent.

**Keywords** Sol–gel · Solvent · Gelation time · Small angle light scattering · Dielectric constant

## 1 Introduction

Sol–gel chemistry has been the subject of research for the preparation of a variety of forms of oxide materials such as fibers, monoliths, powders and thin films [1–5]. The ease of preparation, the use of lower processing temperatures (as compared to conventional methods such as solid state) and the promise of obtaining homogeneity at the “molecular” level has made the sol–gel process a versatile and popular choice for the preparation of nanostructured oxides.

The two most important chemical reactions in the sol–gel process are hydrolysis and condensation. However, the physical aggregation of particles formed by these chemical reactions is also important in the overall gelation kinetics. Thus, the entire transformation from the sol to the gel to the final processed material (powder, fiber, monolith etc.) is certainly complicated and not yet fully understood. The rates of hydrolysis and condensation reactions are influenced by many factors such as type of alkoxide, amount of water, molar ratio of alkoxide to water, reaction pH, humidity, temperature, and nature of solvent [3]. By careful control of the above mentioned factors, various shapes (monoliths, fibers, powder) etc. can be obtained.

In particular the role of solvents is not very clear. Several solvents such as methanol, ethanol, propanol, butanol, acetone, acetonitrile, dioxane, formamide, glycerol, and *N,N*-dimethylformamide have been used in the sol–gel process and their effect on the final textural properties of the material examined [6–10]. Most of the studies pertain to the hydrolysis and condensation of  $\text{Si}(\text{OR})_4$  and several reviews and books pertaining to the chemistry of silica have been published. The widely studied solvents have been drying control chemical additives (DCCA) [11–22]. Thus, the literature contains a scattered amount of data with no clear picture that can comprehensively describe the role of solvents in these reactions.

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We developed a procedure to prepare MgO based on sol–gel chemistry [23, 24]. Sol–gel reactions carried out in presence of toluene usually led to powders being more porous and having high surface areas. It has been suggested that toluene affects both the hydrolysis and condensation reactions, and reduces surface tension at the pore walls [25–28]. In recent studies, we found that addition of increasing amounts of toluene to a  $\text{Mg}(\text{OCH}_3)_2$ –methanol solution, led to an increase in the rate of hydrolysis and condensation reactions and a lowering in the gelation time [29, 30]. The beneficial effect of toluene was attributed to its ability to change the kinetics of the gelation process from a reaction limited to a diffusion limited one. It was not possible to sort out if the “toluene effect” was important in the chemistry (hydrolysis and condensation rates), or if the physical aggregation was being affected.

Hence, there exists a need to use a simple system to clarify the role of the solvents in the gelation process. A simple system one can envisage is one that already contains preformed stable particles. Thus, a model system for studying such solvent effects is a silica suspension that contains preformed colloidal silica particles dispersed in an organic solvent. This system would allow one to understand the role of solvent in the gelation process better since the physical and chemical factors affecting the gelation process can be delineated.

In the present study, small angle light scattering (SALS) has been employed to investigate the role of solvents in the gelation of silica, (commercial colloidal silica solution). SALS is a powerful tool for the characterization of the gelation process and gives information of the gelation time [31, 32].

## 2 Experimental section

### 2.1 Materials

Commercially available silica MT–ST ( $\text{SiO}_2$ , 30 wt% in methanol, Nissan Chemical America Corporation), methanol (Fisher A.C.S. certified), ethanol (AAPER, 200 proof), iso-propanol (Aldrich, 99.5+ %, HPLC grade), iso-butanol (Fisher A.C.S. certified), chloroform (Fisher A.C.S. certified), toluene (Aldrich, 99.8 %, anhydrous), potassium hydroxide (Fisher A.C.S. certified), and sodium hydroxide (Fisher A.C.S. certified) were used as received. Deionized water was used throughout the experiments.

### 2.2 Gel preparation

SALS experiments were performed with commercially available silica spheres with a diameter of 10–15 nm. Sodium hydroxide or potassium hydroxide was used to

screen the Coulombic potential of the initially charge stabilized silica colloids, and thus induce aggregation. In all experiments, the initial molarity of the NaOH–methanol solution varied between 10 and 200 mM while that of KOH–methanol varied between 10 and 50 mM, and the final volume fraction of the silica particles were in the range  $2.1 \times 10^{-3}$  to  $1.7 \times 10^{-2}$ . We chose a sodium hydroxide (or potassium hydroxide) concentration large enough to ensure that the aggregation kinetics was controlled via diffusion limited cluster–cluster aggregation (DLCA) kinetics. Equal volumes (50  $\mu\text{L}$ ) of the silica suspension (Commercially available silica MT–ST ( $\text{SiO}_2$ , 30 wt% in methanol) and NaOH (KOH)–methanol solution containing different volume/volume (v/v) ratios were used to prepare the samples for light scattering studies. The two solutions were simultaneously injected into the cell (as described below) through holes in the viton O-ring with 50  $\mu\text{L}$  syringes. The mixing time ( $<5$  s) was negligible compared to the gel time, which ensured that mixing would not disturb the aggregation kinetics. The cell was made of one viton O-ring sandwiched between two 23 mm-diameter quartz windows. The quartz plates were in turn sandwiched between two metal sample holders, which could be hand tightened by screws to hold the O-ring and the quartz windows. The spacing between the windows and hence, the optical path length of the cell, was 2 mm.

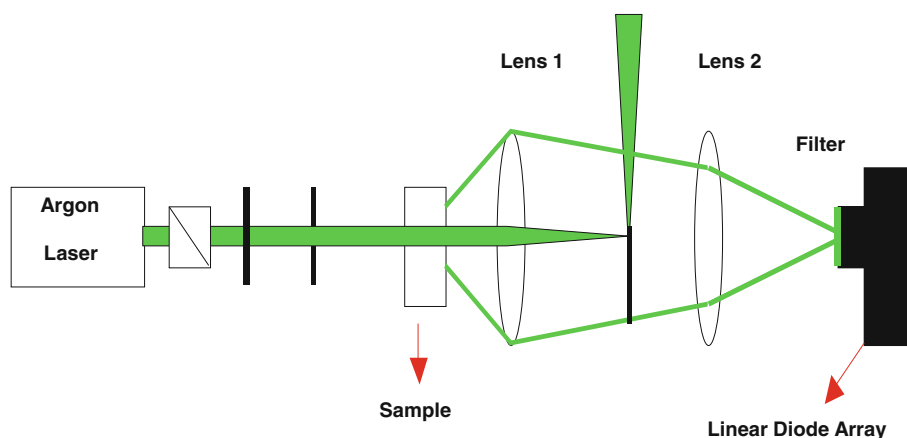
### 2.3 Instrumental methods

The small angle light scattering experiments were performed with a vertically polarized argon-ion laser (Spectra Physics, model 165) operating at a wavelength of  $\lambda = 488$  nm [33]. The scattered light intensity  $I$  was measured versus the scattered angle  $\theta$ . The range of the scattering angles was  $0.18^\circ \leq \theta \leq 13.4^\circ$  corresponding to scattering wave vectors  $q$  of  $4 \times 10^2 \text{ cm}^{-1} \leq q \leq 3 \times 10^4 \text{ cm}^{-1}$ , where  $q = 4\pi/\lambda \sin(\theta/2)$ . The background intensity was measured immediately after placing the sample on the sample holder, i.e., before any aggregation. The background intensity was then subtracted from subsequent light scattering measurements. Figure 1 shows a typical set-up used for the SALS experiment.

## 3 Results and discussion

Preliminary experiments to optimize the conditions and to get an idea of the gelation times were done by the traditional method of “tipping”. In this method, test tubes containing 1 mL of silica ( $f_v = 1.7 \times 10^{-2}$ , where  $f_v$  is the volume fraction of silica in the sol) were rapidly added to test tubes containing 1 mL of 200 mM of NaOH solution having different (v/v) ratios of toluene/methanol and set

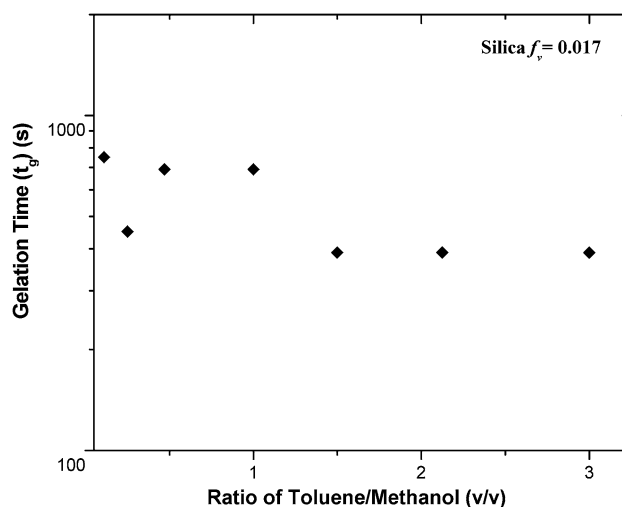
**Fig. 1** Description of the set-up used for the small angle light scattering (SALS) experiments



aside. The test tubes (at least 4 identical samples) were then gently tipped periodically to see if the solution has gelled and the gelation time was determined to be the time when the solution turned viscous and the contents refused to pour out. The silica sol consists of 10–15 nm sized silica particles that have pH of 2–4. On increasing the pH to 9–10 the colloidal silica aggregate, becomes viscous and gels. It was necessary to add NaOH to destabilize the sol and cause its aggregation. Figure 2 shows the variation in the gel time determined by the tipping method versus the amount of toluene in the NaOH–methanol solution. From Fig. 2 it is observed that the gelation time does not depend on the amount of toluene in the NaOH–methanol solution. An accurate determination of the gelation time was not possible because the silica gels are soft and flexible and hence on slight disturbance, they undergo restructuring. Hence, we determined that the tipping experiments could not be completely relied upon although it gives us some idea of the gelation times. Thus, in order to study the effect of solvents, and get a reliable estimate of the gelation times, we decided to pursue SALS experiments.

In recent years, SALS has been widely used by colloidal chemists and in particular by sol–gel chemists for investigating structural transformations occurring during the gelation process [34–37]. In a SALS experiment, the scattered intensity  $I(q)$  is measured as a function of the scattering angle ( $\theta$ ) to the incident beam. The complexity of the plot is reduced when the scattered intensity  $I(q)$  is plotted against the scattering wave vector  $q$ , in a log–log scale. The time at which the value of  $I(q)$  was found to be constant was designated as the gelation time ( $t_g$ ).

The preliminary SALS experiments were done with concentrations of NaOH (200 mM) and silica ( $f_v = 1.7 \times 10^{-2}$ ) similar to that used in the tipping experiment. However, under these experimental conditions multiple scattering was observed and the gels obtained were found to be inhomogeneous and non-uniform. Lowering the concentration of silica volume fraction ( $f_v$ ) to  $2.1 \times 10^{-3}$  and use of KOH led to reproducible results. Consistent and reproducible results



**Fig. 2** Plot of gelation time ( $t_g$ ) and ratio of toluene/methanol (v/v) for silica–MT–ST ( $\text{SiO}_2$ , 30 wt%). In this experiment, 1 mL of silica MT–ST ( $f_v = 0.017$ ) was added to 1 mL of 200 mM NaOH solution containing different v/v ratios of toluene/methanol. The gelation times were determined by the tipping method when the gel became viscous and refused to pour out

were obtained for SALS experiments using KOH instead of NaOH and hence subsequent studies were carried out using KOH–methanol solution.

Table 1 shows the variation in the gelation time as a function of mole fraction of toluene in the KOH–methanol solution obtained from SALS studies. As is evident from Table 1, the gelation times varied between 4 and 9 min and no dependence of the gelation time on the amount of toluene in the KOH–methanol solution is seen. It was not possible to perform SALS experiments under similar conditions as the tipping experiments since multiple scattering was observed. The gelation times are usually much longer in the tipping experiments because one waits until the gel becomes viscous and the contents refuse to flow. In contrast, in the SALS experiments, the intensity of light scattered by the aggregated silica particles is monitored. The

gelation times are determined to be the time about which the scattered light intensity remains constant. This may be a more accurate and true representation of the aggregation process. The differences in the gelation time deduced from the tipping and light scattering experiments may also be attributed to the different concentrations of the salt solution and volume fraction of silica. The tipping experiments were done at initial NaOH concentrations of 200 mM and volume fraction ( $f_v$ ) of silica =  $1.7 \times 10^{-2}$  whereas the SALS experiments were done at initial concentration of KOH of 50 mM and the initial volume fraction ( $f_v$ ) of silica =  $2.1 \times 10^{-3}$ .

In order to understand the influence of solvent, 50 mM KOH–methanol solutions containing different solvents (toluene, chloroform, ethanol, and iso-propanol) were prepared and the gelation times determined from SALS experiments. Table 2 shows the gelation times obtained for the four sets of solvents. The gelation times seem to hardly vary with change in the solvent. Figure 3 shows a typical plot of  $I_q$  versus the scattering wave vector  $q$ , (log–log scale) as a function of time. The gelation time ( $t_g$ ) was deduced from the plots by noting the time at which  $I_q$  remains constant. From Fig. 3 we can see that the slope in this power law regime is 1.8 and consistent with the value known to occur for aggregation kinetics via Diffusion Limited Cluster Aggregation (DLCA) process. The formation of gels is possible through two processes; condensation of polymers or through aggregation of particles. In both these cases, the growing clusters collide to produce larger clusters, i.e. gels. The two growth processes have been explained by kinetic models [12, 38]. Under DLCA

conditions, the sticking probability is close to unity whereas under Reaction Limited Cluster Aggregation (RLCA) conditions, the sticking probability is much lower than unity. Indeed, all SALS experiments indicated a slope close to 1.8 clearly suggesting that the gelation processes follow the DLCA mechanism of aggregation irrespective of the nature of the solvent.

A very important factor that profoundly affected the gelation time was the “age” of the KOH solution containing various co-solvents. During our investigation, we realized that the gelation times were found to be different if the KOH solution containing different co-solvents were prepared at different times. However, since we are interested in relative trends in the gelation time among a series of solvents rather than the absolute value of the gelation times, meaningful comparisons can be made as long as the entire set of experiments are done under similar conditions using the same “age” of KOH solution. To illustrate this point, Table 3 shows the variation in the gel times using freshly prepared and “old” KOH solutions. It has to be pointed out that the results shown in Tables 1 and 2 were obtained using KOH solutions prepared under identical conditions. In order to get reproducible data using “old” solutions, the concentration of KOH had to be further lowered to 10 from 50 mM in the KOH–methanol solution. It is clear from Table 3 that the fresh solutions took longer time for gelation compared to old solutions. For example, the gelation time was found to be 11 min. for a fresh solution containing ethanol whereas the gelation time was found to be  $\sim 5$  min. when experiments were done using the aged ethanol solution. However, one can still notice that the gelation time does not vary much on changing the solvent. In the case of iso-butanol, the gelation times were found to vary between 6 and 11 min. under identical conditions. From Table 3 one can conclude that aged solutions exhibit shorter gelation times compared to fresh solutions and that the gelation

**Table 1** Effect of toluene in the gelation time of silica

Mole fraction of toluene in KOH–methanol solution	Gelation time ( $t_g$ ) [min]	Dielectric constant of KOH–methanol solution ( $\epsilon$ )
0.0	$8 \pm 1$	32.6
0.013	$5 \pm 1$	32.2
0.019	$6 \pm 1$	31.9
0.030	$9 \pm 1$	31.7
0.040	$7 \pm 1$	31.4
0.052	$4 \pm 1$	31.0
0.075	$4 \pm 1$	30.3
0.087	$4 \pm 1$	29.9
0.203	$5 \pm 1$	26.5

The gel times were determined from small angle light scattering (SALS) studies. The initial concentration of KOH–methanol solution containing different amounts of toluene is 50 mM and the initial volume fraction ( $f_v$ ) of silica =  $2.1 \times 10^{-3}$ . Experiments were done in triplicate and the KOH containing solutions were prepared under identical conditions before SALS experiments

**Table 2** Effect of Co-solvent in the gelation time of silica

Co-solvent	Ratios of co-solvent/methanol (v/v)	Gelation time ( $t_g$ ) [min]
Toluene	0.23	$14 \pm 1$
Chloroform	0.23	$15 \pm 2$
Ethanol	0.23	$15 \pm 3$
Iso-propanol	0.23	$20 \pm 4$

The gelation times were determined from small angle light scattering (SALS) studies. The initial concentration of KOH–methanol solution containing different co-solvents is 50 mM and the initial volume fraction ( $f_v$ ) of silica =  $2.1 \times 10^{-3}$ . Experiments were done in triplicate and the KOH containing solutions were prepared under identical conditions before SALS experiments

**Table 3** Effect of Co-solvent in the gelation time of silica

Co-solvent	Mole fraction of co-solvent	$t_g$ (min) fresh solution	$t_g$ (min) old solution	Dielectric constant of KOH–methanol solution containing different co-solvents ( $\epsilon$ )
Methanol	1.0	$10 \pm 1$	$8 \pm 1^a$	32.40
Ethanol	0.276	$11 \pm 1$	$5 \pm 1^b$	30.17
Iso-propanol	0.276	$12 \pm 1$	$5 \pm 1^b$	28.51
Iso-butanol	0.276	$11 \pm 1$	$6 \pm 1^b$	27.82
Toluene	0.276	$11 \pm 1$	$5 \pm 1^b$	24.13
Water	0.276	$9 \pm 1$	$5 \pm 1^a$	45.52

The gel times were determined from small angle light scattering (SALS) studies. The initial concentration of KOH–methanol solution containing different co-solvents is 10 mM and the initial volume fraction ( $f_v$ ) of silica =  $4.25 \times 10^{-3}$ . Experiments were done in triplicate and the KOH containing solutions were prepared under identical conditions before SALS experiments

Fresh solution denotes KOH–methanol solution containing different co-solvents prepared just before start of SALS experiments

<sup>a</sup> KOH–methanol solution containing different co-solvents prepared 2 days prior to start of SALS experiments

<sup>b</sup> KOH–methanol solution containing different co-solvents prepared 1 day prior to start of SALS experiments

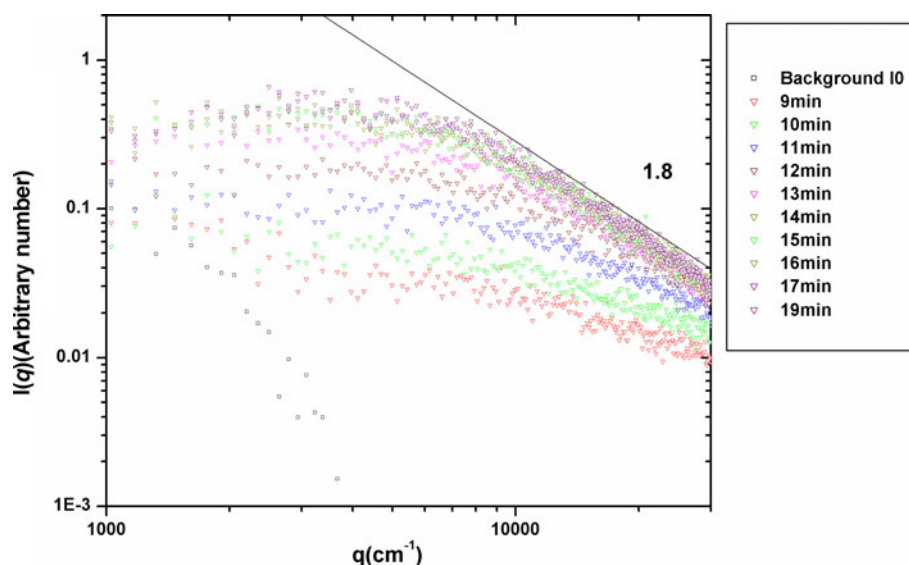
times for solutions containing toluene and iso-butanol range from anywhere between  $5 \pm 1$  and  $11 \pm 1$  min.

Figure 4 shows a plot of the dielectric constant of the solvent and the gelation times obtained from SALS experiments. We can conclude that for the silica–KOH–solvent–methanol system that the solvents employed in the study do not have any influence in the gelation process. Thus, we see that when we have preformed silica particles, the driving force for the gelation to occur is the presence of KOH in the solution, which destabilizes the sol and causes the aggregation of the silica particles.

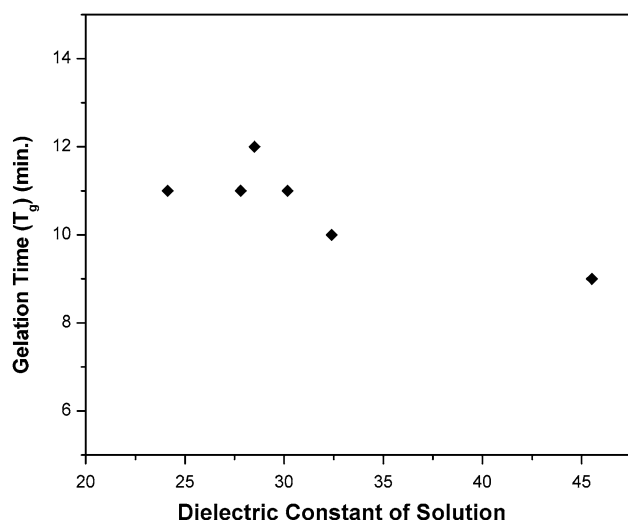
At this point, it is worthwhile to put the results obtained in this study in perspective and a detailed discussion is warranted. The results obtained in the present study are in contrast to a previous study reported by us, wherein we

observed a correlation between the dielectric constant of the solvent and the gelation times for the  $\text{Mg}(\text{OCH}_3)_2$ – $\text{H}_2\text{O}$ –solvent–methanol system [30]. In that study, the gelation time was found to increase with increase in the dielectric constant of the solvent as shown in Fig. 5. This suggests that in the hydrolysis of  $\text{Mg}(\text{OCH}_3)_2$ , the degree of solvation of the alkoxide is different for different solvents and increases with increasing dielectric constant of the solvent system. Such an argument has also been proposed by Fukuoka and Makishima [22] for the gelation of silica using different alcohols as the solvent. They also proposed that degree of solvation increases with increasing dielectric constant and alcoholic solvents of higher dielectric constant were found to increase the gelation time. Thus, one may argue that when solvents having higher dielectric constants are used, stronger

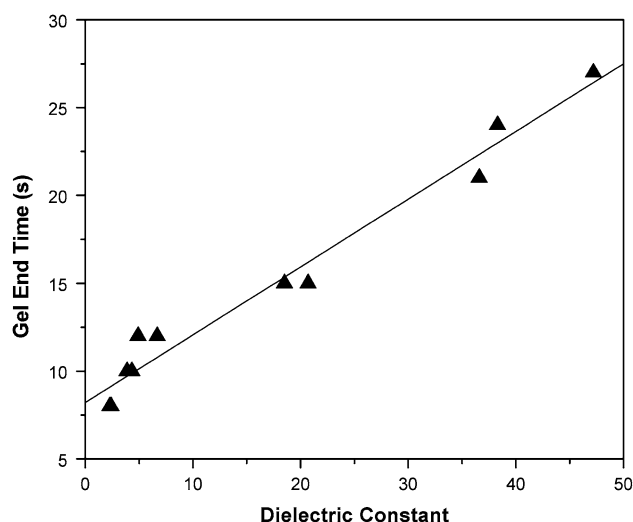
**Fig. 3** Plot of scattered intensity  $I_q$  against the scattering wave vector  $q$ . The initial concentration of KOH solution containing v/v ratio of ethanol/methanol = 0.23 is 50 mM and the initial volume fraction ( $f_v$ ) of silica =  $2.1 \times 10^{-3}$







**Fig. 4** Plot of the gel time versus the dielectric constant of solution. The gel times were determined from small angle light scattering (SALS) studies. The initial concentration of KOH–methanol solution containing different co-solvents is 10 mM and the initial volume fraction ( $f_v$ ) of silica =  $4.25 \times 10^{-3}$



**Fig. 5** Plot of gelation time and dielectric constant of solvent for the  $\text{Mg}(\text{OCH}_3)_2$ – $\text{H}_2\text{O}$ –solvent–methanol system. Reprinted (adapted) with permission from Ranjit and Klabunde [30]. Copyright (2005) American Chemical Society

solvation of the alkoxides could result in the formation of  $\text{Mg}(\text{OCH}_3)_2$  solvent solvates. Stable  $\text{M}(\text{OR})_4$  solvent solvates have indeed been isolated for several metal alkoxides such as  $\text{Ce}(\text{OPr}^i)_4$ ,  $\text{Ti}(\text{OEt})_4$  and  $\text{Zr}(\text{OPr}^i)_4$  [39, 40]. Because of solvate formation, they would be more stable toward hydrolysis and hence the gelation times would be longer when such solvents are used. Similarly, Hu et al. [41] reported that the dielectric property of the mixed alcohol–water solvent was an important factor that influenced the precipitation kinetics and the nucleation and growth of zirconia particles. In contrast, Zerda and Hoang have proposed that specific solvent effects and the spatial charge distribution are more important than dielectric constants for the hydrolysis of  $\text{Si}(\text{OCH}_3)_4$  [10]. Their results were that the gelation times were slower for dioxane and faster for formamide; their findings were consistent with earlier reports of Artaki et al. [6, 19] and Orcel et al. [20]. Table 4 summarizes the results obtained by Artaki et al. for the hydrolysis of silica and by us for the hydrolysis of magnesium methoxide. The results obtained by us are opposite to that obtained by Artaki et al.

In bimolecular nucleophilic substitution reactions such as hydrolysis and condensation of metal alkoxides, electrostatic interactions between the nucleophile and the solvent and hydrogen bonding effects are important. The solvents studied can be classified into three categories, (1) polar protic solvents such as methanol (2) dipolar aprotic solvents such as acetonitrile and *N,N*-dimethyl formamide and (3) non-polar aprotic solvents such as dioxane and toluene. Polar protic solvents can decelerate the condensation rate by deactivating the nucleophile through hydrogen bonding interactions and because of their strong dipole moments they can further stabilize the charges on the reactants to a greater extent. This would cause further deceleration in the rates of the hydrolysis and condensation reactions and hence the gelation times would be longer when solvents such as methanol or formamide are used. Indeed, we have observed that the when methanol is used as the solvent for the hydrolysis of  $\text{Mg}(\text{OCH}_3)_2$ , the gelation times are the longest. Dipolar aprotic solvents such as acetonitrile and *N,N*-dimethylformamide cannot hydrogen bond to the nucleophile but because of the high dielectric constant, stronger

**Table 4** Comparison of the effect of solvents in the hydrolysis of  $\text{Si}(\text{OCH}_3)_4$  and  $\text{Mg}(\text{OCH}_3)_2$

Co-solvent	Property	Dielectric constant	Dipole moment	Gelation time ( $t_g$ )	
				$\text{SiO}_2^a$	$\text{Mg}(\text{OH})_2^b$
Dioxane	Non-polar aprotic	2.2	0.45	41 h	NA
Toluene	Non-polar aprotic	2.4	0.38	NA	<5 s
Methanol	Polar protic	32.4	1.70	6 h	35 s
Acetonitrile	Dipolar aprotic	35.9	3.24	48 h	19 s
<i>N,N</i> -DMF	Dipolar aprotic	36.7	3.53	37 h	24 s
Formamide	Polar protic	111	3.37	8 h	NA

<sup>a</sup> Values reported from Artaki et al. [8]

<sup>b</sup> Values reported from Ranjit and Klabunde [30]

NA not available

solvation of the alkoxides could result in the formation of  $\text{Mg}(\text{OCH}_3)_2$  solvent solvates. This would slow down the hydrolysis reaction to slightly and hence the gelation times obtained using solvents having high dielectric constant would be slightly lower when compared with polar protic solvents such as methanol. We have observed previously that the gelation times for acetonitrile and *N,N*-dimethylformamide are 19 and 24 s; this is shorter than 35 s obtained when methanol was used as the solvent for the hydrolysis of  $\text{Mg}(\text{OCH}_3)_2$ . The hydrolysis and condensation reactions are most efficient in non-polar aprotic solvents such as toluene, benzene etc. which lack the ability to electrostatically interact with the nucleophile and form hydrogen bonds with the reactants. Further, the dipole moments of the non-polar aprotic solvents are negligible (toluene,  $\mu = 0.38$ ) or zero (benzene,  $\mu = 0$ ). Thus, replacing methanol with solvents such as benzene or toluene should accelerate the hydrolysis and condensation reactions and hence the gelation times should be very short. Indeed we have observed that using benzene and toluene in the hydrolysis of  $\text{Mg}(\text{OCH}_3)_2$  led to the formation of gels in  $<5$  s. Thus, the kinetics of the hydrolysis and condensation reactions and the gelation times are affected by the nature of the solvent when a metal alkoxide is hydrolyzed to produce an oxide material.

However, as this study illustrates, when pre-formed silica particles are used, solvents do not play an important role in the aggregation process. Thus, this study clearly demonstrates that when there is a purely physical process involving particle aggregation, the nature of the solvents does not influence the overall gelation process.

#### 4 Conclusion

SALS studies indicate that preformed silica particles aggregate primarily based on the destabilization of the surface charges and solvents do not play an important role in their physical aggregation to form gels. When a metal alkoxide is hydrolyzed in the presence of non-polar solvents such as toluene and benzene lack protons capable of deactivating the nucleophile and hence cause enhancement in hydrolysis and/or condensation reactions. Solvents having high dielectric constants can behave as Lewis bases and react with metal alkoxides (Lewis acids) leading to metal alkoxide solvent solvates thus slowing down the hydrolysis reactions. Highly polar protic solvents such as methanol deactivate the nucleophile through hydrogen bonding and hence cause longer gelation times. However, no solvent effects are discernible when the gelation process is purely a physical process.

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#### References

- Lu Z, Lindner E, Mayer HA (2002) *Chem Rev* 102:3543–3578
- Shea KJ, Loy DA (2001) *Acc Chem Res* 34:707–716
- Avnir D (1995) *Acc Chem Res* 28:328–334
- Collinson MM (2007) *Acc Chem Res* 40:777–783
- Mohanan JL, Arachchige IU, Brock SL (2005) *Science* 307:397–401
- Artaki I, Zerda TW, Jonas J (1985) *Mater Lett* 3:493–496
- Artaki I, Bradley M, Zerda TW, Jonas J (1985) *J Phys Chem* 89:4399–4404
- Artaki I, Zerda TW, Jonas J (1986) *J Non-Cryst Solids* 81:381–395
- Zerda TW, Artaki I, Jonas J (1986) *J Non-Cryst Solids* 81:361–379
- Zerda TW, Hoang G (1990) *Chem Mater* 2:372–376
- Iler RK (1979) *The chemistry of silica*. Wiley, New York
- Brinker CJ, Scherer GW (1990) *Sol-gel science. The physics and chemistry of sol-gel processing*. Academic Press, New York
- Hench LL, West JK (1990) *Chem Rev* 90:33–72
- Pajonk GM (1995) *Heterog Chem Rev* 2:129–141
- Pierre AC (1998) *Introduction to sol-gel processing*. Kluwer, Boston
- Hench LL, Ortel G, Nogues JL (1986) In: Brinker CJ, Clark DE, Ulrich DR (eds) *Better ceramics through chemistry II*. Mater Res Soc, Pittsburgh
- Boonstra AH, Bernards TNM, Smit JJT (1989) *J Non-Cryst Solids* 109:141–152
- Grimmer AR, Rosenberger H, Burger H, Vogel W (1988) *J Non-Cryst Solids* 99:371–378
- Jonas J (1986) In: Hench LL, Ulrich DR (eds) *Science of ceramic chemical processing*. Wiley, New York
- Ortel G, Hench LL (1986) *J Non-Cryst Solids* 79:177–194
- Chen KC, Tsuchiya T, Mackenzie JD (1986) *J Non-Cryst Solids* 81:227–237
- Fukuoka M, Makishima A (2003) *J Ceram Soc Jpn* 111:83–86
- Utamapanya S, Klabunde KJ, Schlup JR (1991) *Chem Mater* 3:175–181
- Koper OB, Lagadic I, Volodin A, Klabunde KJ (1997) *Chem Mater* 9:2468–2480
- Li YX, Koper O, Ateya M, Klabunde KJ (1992) *Chem Mater* 4:323–330
- Khaleel A, Kapoor PN, Klabunde KJ (1999) *Nanostruct Mater* 12:463–466
- Rajagopalan S, Koper O, Decker S, Klabunde KJ (2002) *Chem Eur J* 8:2602–2607
- Choudary BM, Mulukutla RS, Klabunde KJ (2003) *J Am Chem Soc* 125:2020–2021
- Diao Y, Walawander WP, Sorensen CM, Klabunde KJ, Rieker T (2002) *Chem Mater* 14:362–368
- Ranjit KT, Klabunde KJ (2005) *Chem Mater* 17:65–73
- Brown W (1993) *Dynamic light scattering*. Clarendon, Oxford
- Martin JE, Wilcoxon JP (1988) *Phys Rev Lett* 61:373–376
- Ferri F (1997) *Rev Sci Instrum* 68:2265–2274
- Rodríguez R, Arroyo R, Salinas P (1993) *J Non-Cryst Solids* 159:73–79
- Lin HL, Liu YF, Yu TL, Liu WH, Rwei SP (2005) *Polymer* 46:5541–5549
- Kjønksen AL, Hiorth M, Nyström B (2004) *Eur Polym J* 40:2427–2435
- Yamamoto T, Mukai SR, Endo A, Nakaiwa M, Tamon H (2003) *J Colloid Interface Sci* 264:532–537
- Znaldi L, Chhor K, Pommier C (1996) *Mater Res Bull* 31:1527–1535
- Livage J, Henry M (1988) In: Mackenzie JD, Ulrich DR (eds) *Ultrastructure processing of advanced ceramics*. Wiley, New York
- Bradley DC, Garter DG (1962) *Can J Chem* 40:15–21
- Hu MZC, Payzant EA, Byers CH (2000) *J Colloid Interface Sci* 222:20–36