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Influence of Several Metal Ions on the Gelation Activation Energy of Silicon Tetraethoxide

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GELATION ACTIVATION ENERGY OF SILICON TETRAETHOXIDE

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SUMMARY

The effects of nine metal cations (Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cu^{2+}, Al^{3+}, La^{3+}, and Y^{3+}) on silica gel formation has been investigated by studying the hydrolysis and polycondensation of silicon tetraethoxide (TEOS) in the presence of metal nitrates. The influence of water:TEOS mole ratio, metal ion concentration, and the reaction temperature has been investigated. The overall activation energy for gel formation has been determined from the temperature dependence of the time of gelation for each system. The activation energy for $-Si-O-Si-$ network formation is found to be 54.5 kJ/mol. The gel formation time as well as the activation energy sharply increase in the presence of Cu^{2+}, Al^{3+}, La^{3+} and Y^{3+}. In contrast, the presence of Li^+, Na^+, Mg^{2+}, Ca^{2+}, or, Sr^{2+} lowers the gelation time, but has no appreciable effect on the activation energy. This difference may be attributed to the participation or non-participation of the metal ions in the formation of the three dimensional polymeric network during the polycondensation step. The concentration of metal ion (Mg^{2+}, Ca^{2+}, Y^{3+}) or the water:TEOS mole ratio had no appreciable effect on the gelation activation energy. A simple test has been proposed to determine whether a metal ion would act as a network intermediate or modifier in silica and other glassy networks.

I. INTRODUCTION

Sol-gel processing of glasses and ceramics is important both from scientific and technological points of view. The sol-gel method has several advantages such as high purity, ultrahomogeneity, lower processing temperatures, and most significantly the possibility of making glasses of new compositions. The potential to form new materials which are structurally unstable at high temperatures also exists. The sol-gel technique[1,2] has become quite popular during the past few years. A number of papers[3-5] concerning the kinetics and mechanism of the sol-gel process have appeared.

The sol-gel process is influenced by various experimental parameters such as temperature, pH, chemical nature of the alkoxides and other reactants, water to alkoxide ratio, presence of a catalyst, concentration of the reactants, and nature of the solvent. Temperature has an appreciable effect on the kinetics of the reactions occurring during the sol-gel process. Surprisingly, very few studies have been reported[6-10] concerning the effect of temperature on the sol-gel

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process. The activation energy of gel formation of silicon alkoxides has been evaluated from the Arrhenius equation. The present author[10] recently reported a value of 58.7 kJ/mol for the gelation activation energy of 10MgO-90SiO$_2$* in the temperature range 2 - 68°C for a water:TEOS mole ratio of 7.5. However, to this author's knowledge, no work has been reported on the effect of various metal ions on the gelation activation energy. To bridge this gap, a systematic study of the influence of nine metal cations on the gelation kinetics of silicon tetraethoxide (TEOS) has been carried out and the results are being presented in this paper. The effects of metal-ion concentration, water:TEOS mole ratio, and temperature have been investigated. The gelation activation energy in the presence of various metal ions has been evaluated. The effects of the metal ion on the kinetics of gel formation and the gelation activation energy is discussed. A simple test is being proposed to decide whether a metal ion would behave as a network intermediate or modifier in silica and other glass networks.

II. EXPERIMENTAL PROCEDURE

Metal nitrates were used as the source of various metal ions. NaNO$_3$, Mg(NO$_3$)$_2$.6H$_2$O, Ca(NO$_3$)$_2$.4H$_2$O, and Sr(NO$_3$)$_2$ of analytical reagent grade from Mallinckrodt, LiNO$_3$.3H$_2$O, and Cu(NO$_3$)$_2$.3H$_2$O certified reagents from Fisher, and Al(NO$_3$)$_3$.9H$_2$O, La(NO$_3$)$_3$.6H$_2$O, Y(NO$_3$)$_3$.6H$_2$O, and TEOS from Alfa Products were used as received. Absolute ethyl alcohol was employed as the mutual solvent for TEOS and water which are immiscible with each other.

The method of gel synthesis was essentially the same as described[10] earlier. An alcoholic solution of metal nitrate was prepared and mixed under vigorous stirring with TEOS which had been diluted with alcohol. The required amount of water was then slowly added dropwise with constant stirring. A clear homogeneous solution resulted (except in case of copper probably due to the formation of copper(II) trihydroxy nitrate Cu(NO$_3$)$_2$.3Cu(OH)$_2$) which was divided in a number of parts, sealed with parafilm, and stored at various temperatures between 1 and 70°C in constant temperature baths for hydrolysis and polycondensation. The time taken for gel formation varied from about an hour to several months depending upon the reaction temperature, water:TEOS mole ratio, and the nature and concentration of the metal ions. Clear, transparent gels were obtained in almost all cases. The gels were colorless except in the presence of copper where it was blue.

III. EXPERIMENTAL RESULTS

The influence of nine metal ions on gelation of TEOS has been

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* All compositions are in mol%.

studied as a function of metal ion concentration, water:TEOS mole ratio(r), and temperature. Table 1 gives the values of gelation time for $10MgO-90SiO_2$ and $10CaO-90SiO_2$ systems for r = 4, 6, and 7.5 at various temperatures. For comparison the data for TEOS at r = 6 are also given. It may be noted that gelation time, t_{gel}, decreases with increasing value of r or temperature. Also, the presence of Mg^{2+} or Ca^{2+} greatly lowers the time taken for gel formation in comparison to TEOS.

All further investigations were carried out using a water:TEOS mole ratio of 6. Table 2 shows the effect of Mg^{2+} and Ca^{2+} ion concentration on gelation times at various temperatures for r = 6. By the addition of just 2 mol% of Mg^{2+} or Ca^{2+}, gelation time is greatly reduced. At any temperature, the time taken for gel formation decreases with increasing metal ion concentration. This effect is more pronounced at low concentrations and seems to level off at higher concentrations of Mg^{2+} or Ca^{2+}.

The data showing the influence of Y^{3+} ion concentration on the gelation times of TEOS for r = 6 at various temperatures are given in Table 3. The presence of Y^{3+} ions greatly increases the time of gel formation. Also, t_{gel} increases with increase in Y^{3+} ion concentration.

Data showing the influence of 5 mol% concentration of nine different metal ions on times of gel formation of TEOS for r = 6 at various temperatures are given in Table 4. It may be noted that Li^+, Na^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} lower the gelation time whereas the presence of La^{3+}, Al^{3+}, or Y^{3+} results in longer times of gel formation. Gelation times are longest in the presence of Al^{3+} followed by La^{3+} and Y^{3+}. The solution containing Al^{3+} and stored at $1^{\circ}C$ did not gel even after 15 months. Results for Cu^{2+} are somewhat mixed; at low temperatures (1 and $23^{\circ}C$), t_{gel} is increased whereas the opposite is true at higher temperatures.

IV. DISCUSSION

Gel formation is a chemical process involving hydrolysis and condensation reactions. When water is added to TEOS solution, hydrolysis takes place:

$$-\overset{|}{\underset{|}{Si}}-OEt \quad + \quad H_2O \quad \longrightarrow \quad -\overset{|}{\underset{|}{Si}}-OH \quad + \quad EtOH \quad (1)$$
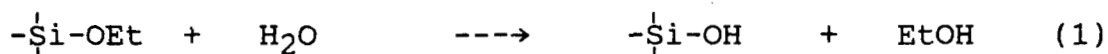
where Et is the C_2H_5 group. Condensation which results in the formation of $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ network can occur by a dehydration reaction between two hydrolyzed TEOS molecules or through a dealcoholation reaction between a hydrolyzed and an unhydrolyzed TEOS molecule:

$$-\overset{|}{\underset{|}{Si}}-OH \quad + \quad HO-\overset{|}{\underset{|}{Si}}- \quad \longrightarrow \quad -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- \quad + \quad H_2O \quad (2A)$$

$$-\overset{|}{\underset{|}{Si}}-OH \quad + \quad EtO-\overset{|}{\underset{|}{Si}}- \quad \longrightarrow \quad -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- \quad + \quad EtOH \quad (2B)$$

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This leads to the formation of oligomers in solution which upon further condensation results in the formation of a three -dimensional glass-like network. The system changes into a gel when polymerization is extensive. The water molecule regenerated during the condensation step can be further utilized for hydrolysis of another alkoxy group. Theoretically, only two moles of water/mole of TEOS are required for the complete hydrolysis and polymerization. Hydrolysis is a fast process and condensation is the rate determining step[1]. It is difficult to separate hydrolysis from condensation. However, it may be assumed that hydrolysis has been practically completed[11] shortly after the addition of water as long as enough water to complete hydrolysis is present.

Gel formation being a chemical process, temperature dependence of the rate of gelation may be expressed by an Arrhenius equation:

$$k = A \exp[-E^*/RT] \qquad (3)$$

where k is the reaction rate constant, A the temperature independent pre-exponential term or the frequency factor, E^* the apparent activation energy for the overall gelation process, R the gas constant, and T the reaction temperature in Kelvin. The time of gel formation, t_{gel}, over which the solution viscosity increases from ~10^{-1} to $10^4 P$ may be taken as the average rate of reaction. Thus, k may be replaced by $1/t_{gel}$ (or $k = 1/t_{gel}$) in Eq.(3) resulting in the following relation:

$$1/t_{gel} = A' \exp[-E^*/RT] \qquad (4)$$

Taking the logarithm of Eq.(4) gives:

$$\log(t_{gel}) = -\log A' + E^*/(2.3026RT) \qquad (5)$$

According to Eq.(5), a plot of $\log(t_{gel})$ vs. 1/T should be linear with a slope of $(E^*/2.3026R)$. The values of E^* and A' can be obtained from the slope and the intercept, respectively.

Plots of $\log(t_{gel})$ vs. 1/T for the gelation of $10MgO-90SiO_2$ composition at three different water:TEOS mole ratios are presented in Fig.1. The solid lines in this and all subsequent figures are from linear least-squares fitting of the experimental data to Eq.(5). In all cases the value of the correlation coefficient exceeded 0.99. Similar plots for the $10CaO-90SiO_2$ system at r = 4, 6, and 7.5 are shown in Fig.2. Values of the parameters E^* and A', evaluated from linear least-squares fitting of the experimental data, for $10MgO-90SiO_2$ and $10CaO-90SiO_2$ systems are listed in Table 1. The presence of Mg^{2+} or Ca^{2+} ions has virtually no effect on the gelation activation energy E^*. Also, the water:TEOS mole ratio has no appreciable influence on E^*.

Figure 3 shows the plots of $\log(t_{gel})$ vs. 1/T for three compositions in the $MgO-SiO_2$ system at the same value of r = 6. Similar plots for the $CaO-SiO_2$ system are presented in Fig.4. Also shown for comparison is the plot for SiO_2. All the plots are seen to

be linear. Values of the Arrhenius parameters obtained from linear least-squares fitting of the experimental data are listed in Table 2. Again the concentrations of Mg^{2+} or Ca^{2+} ions had virtually no effect on the value of E^*.

The linear plots of $\log(t_{gel})$ vs. $1/T$ for two Y_2O_3-SiO_2 compositions at $r = 6$ are presented in Fig. 5. Values of E^* and A' evaluated from linear least-squares fitting of the experimental data are given in Table 3. Values of both E^* and A' are much higher in the presence of Y^{3+}. This is in contrast to the results for systems containing Mg^{2+} and Ca^{2+} where E^* was unaffected by the presence of the metal ions. Also, within the experimental precision the Y^{3+} ion concentration has no effect on the activation energy.

Figure 6 shows the plots of $\log(t_{gel})$ vs. $1/T$ for various systems containing 5 mol% of metal oxides for water:TEOS mole ratio of 6. A plot for SiO_2 is also included for comparison. Values of the Arrhenius parameters, E^* and A', evaluated from linear leastsquares fitting of the experimental data for different systems are given in Table 4. It may be noted that E^* is virtually unaffected by Li^+, Na^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} ions and remains about the same as for TEOS. On the other hand Cu^{2+}, La^{3+}, Al^{3+}, and Y^{3+} ions greatly increase the value of E^*. The frequency factor A' is lowest for TEOS and increases in the presence of the metal ions. Values of E^* and A' are highest in the presence of Al^{3+} followed by Cu^{2+}, La^{3+}, and Y^{3+} in that order.

In the absence of a catalyst, polycondensation is not the rate determining[8] process. Aelion et al.[11] and Vekhov et al.[12,13] reported values of 26.4 and 28.4 kJ/mole, respectively, for the hydrolysis activation energy of TEOS. Colby et al. attributed[8] a value of 19.4 kJ/mole to the activation energy of hydrolysis rather than polycondensation for the TEOS system at $r = 4$ in the absence of a catalyst. These values are much lower than the value of 54.5 kJ/mole obtained in the present study for TEOS at $r = 6$ in the absence of a catalyst. Values of 61.1 and 55.2 kJ/mole have been reported[8,9] for gelation activation energy of TEOS using water:TEOS mole ratio of 4 in the presence of HF and HCl catalysts, respectively. For the HCl-catalyzed TEOS system, Bechtold et al.[6,7] reported values of 40 to 70 kJ/mol depending on water concentration. The gelation activation energy seems to be related[8,9] to the transport of the condensing species during the polymerization process and not to the Si-O bond energies.

According to Colby et al[8]., if hydrolysis is the rate controlling step, the gelation time should decrease with increase in water:TEOS mole ratio even after sufficient water for hydrolysis is present. Also, the activation energy should decrease with increase in r, if the hydrolysis was not complete. For the acid-catalyzed TEOS system, Colby et al[8]. showed that the gelation time did not decrease with increase in water concentration when enough water was present. But in the absence of sufficient water to complete hydrolysis, the activation energy systematically increased when r was changed from 4 to 3.5 to 3. This increase in activation energy was attributed[8] to the steric hinderance offered by the non-hydrolyzed alkoxy groups still attached to silicon. For $10MgO$-$90SiO_2$ and $10CaO$-$90SiO_2$ systems, t_{gel}

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systematically decreased when r was increased from 4 to 7.5. However, the activation energy was more or less independent of the water concentration. Thus, these results do not support the viewpoint put forward by Colby et al[8].

To understand the effect of metal ions on the gelation activation energy, plots of E^* against the metal cation charge density, q/d, as well as the ionic field strength, q/d^2, are shown in Fig. 7. Here q and d are respectively the charge and radius of the metal cation. The value of E^* is seen to increase linearly with increase in the charge density or the ionic field strength of the metal cation. However, Li^+, Na^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} ions seem to behave differently than Cu^{2+}, La^{3+}, Y^{3+}, and Al^{3+}.

Based on the results of this study, the metal ions may be classified into two categories. Metal ions of type I, such as Li^+, Na^+, Mg^{2+}, Ca^{2+}, and Sr^{2+}, lower the gelation time, probably do not participate in either the hydrolysis or the subsequent polymerization reactions of TEOS, can be introduced only in limited amounts into the gel structure (starting with inorganic metal salts) and have no appreciable effect on the activation energy of gel formation. These metal ions are only weakly bonded to the silica gel network and would still be mobile in the gel and would have a tendency to crystallize out as metal salts during drying when the solution in the gel becomes saturated with respect to the salt. During sol-gel syntheis of $MgO-SiO_2$ and $CaO-SiO_2$ glasses[10,14] from TEOS and the metal nitrates, it was not possible to introduce more than ~15 mol% of the metal oxide without crystallization of the metal nitrate during drying of the gel.

Metal ions such as Cu^{2+}, La^{3+}, Y^{3+}, and Al^{3+} belong to type II. These metal ions become part of the gel network by participating in the condensation polymerization reaction and can be incorporated in large concentration into the polymer network. This results in very long times needed for gel formation and also high gelation activation energy compared to TEOS. As these metal ions become part of the polymer network, they are not mobile anymore and have no tendency to crystallize out during slow drying of the gel. A clear homogeneous monophasic gel of mullite (60 mol% Al_2O_3-40 mol% SiO_2) composition has been prepared[15] from aluminum nitrate and TEOS. This gel showed[15] a very sharp exothermic peak at ~980°C in differential thermal analysis (DTA) due to formation of mullite indicating that Si-O-Al bonds were formed during gelation eliminating the need for long-scale diffusion and bond rearrangement during crystallization. In contrast, a diphasic gel of mullite composition prepared from colloidal silica (Ludox) and boehmite (AlOOH) did not show the formation of mullite phase until ~1350°C.

From infrared (IR) studies, all the absorption bands present in calcium silicate and magnesium silicate gels could be assigned[10,14] to the silica network indicating the formation of no M-O-Si bonds in these gels. However, the presence of IR absorption bands due to Al-O-Si and Y-O-Si bonds has been confirmed in $Al_2O_3-SiO_2$ and $Y_2O_3-SiO_2$ gels, respectively. Edney et al.[16] have reported the presence of Si-O-Y bonds in their studies of the $Y_2O_3-SiO_2$ gels by IR and Raman spectroscopy. The solid state ^{27}Al and ^{29}Si magic angle
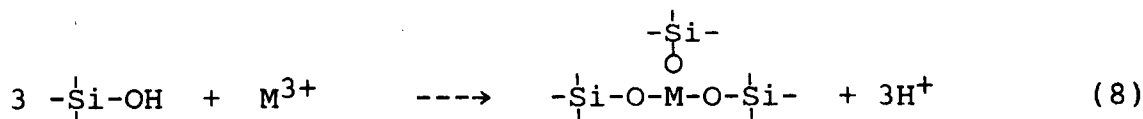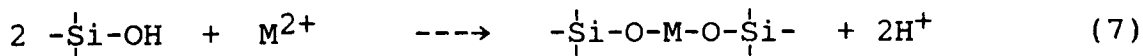
spinning nuclear magnetic resonance spectroscopy of the Al_2O_3-SiO_2 monophasic gels prepared from aluminum nitrate and TEOS showed[17] the presence of Al in the immediate vicinity of Si. From the study of glass formation in BaO-$YO_{1.5}$-SiO_2 and BaO-$LaO_{1.5}$-SiO_2 systems, Li et al[18]. have concluded that Y^{3+} and La^{3+} ions behave as network intermediates in the structure and strengthen the glass network. Replacement of BaO by $YO_{1.5}$ or $LaO_{1.5}$ decreased the thermal expansion coefficient, and increased the glass transition and softening temperatures, Vickers hardness, and packing density of the glasses. Y^{3+} was found to have a larger effect on strengthening the network because of its larger ionic field strength. In contrast, in the present work the effect of Y^{3+} on E^* is smaller than La^{3+}.

In melted glasses copper is known[19] to exist in both the divalent and monovalent states and with increasing temperature the equilibrium $Cu^{2+} \rightleftharpoons Cu^+$ is shifted to the right. However, in copper silicate glasses prepared[20,21] by the sol-gel method, copper exists predominantly in the Cu^{2+} state, at least at low temperatures. Copper silicate glasses containing 0.25 to 10 mol% CuO have been synthesized[20] by the sol-gel approach using TEOS and copper nitrate. From spectroscopic analysis, copper was found to be completely incorporated in the glass structure as Cu^{2+}.

The metal ions of type I are probably introduced into the silica gel network by a cation exchange reaction between the metal cation (M^{n+}) and the weakly acidic silanol (-Si-OH) group:

$$M^{n+} + m \text{ -Si-OH} \longrightarrow M\text{--}(\text{--O-Si-})^{n-m} + mH^+ \qquad (6)$$
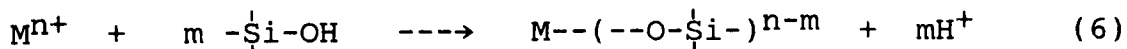
The metal ions are only loosely bonded and are still mobile. On the other hand, metal ions of the second type are locked up in the gel network through the formation of M-O-Si bonds:

$$2 \text{ -Si-OH} + M^{2+} \longrightarrow \text{-Si-O-M-O-Si-} + 2H^+ \qquad (7)$$

$$3 \text{ -Si-OH} + M^{3+} \longrightarrow \text{-Si-O-M-O-Si-} + 3H^+ \qquad (8)$$

Using the standard glass terminology, metal ions of type I are known as the network modifiers which are introduced in the voids of the silica network through the formation of non-bridging oxygens. The presence of non-bridging oxygens in heat treated Na_2O-SiO_2 gels has been confirmed[22] by X-ray photoelectron spectroscopy. On the other hand, metal ions of type II are the network intermediates. It is well known that Al^{3+} can substitute for Si^{4+} in the silica glass network, thus forming AlO_4 tetrahedra by coordinating with four oxygens. Hence, the difference in behavior of the metal ions on gelation of TEOS is determined by whether the metal oxide is a network modifier or intermediate in the silica glass network.

It is tempting to propose that a simple gelation experiment may be used to decide whether a metal ion would act as network modifier or

intermediate in the formation of silicate glass. More importantly, this would probably also be applicable to non-silicate glasses such as borates, germanates, niobates, tantalates, etc. Further work is needed to establish this point with certainty.

V. SUMMARY AND CONCLUSIONS

The effects of nine metal ions on the gelation of TEOS has been studied as a function of water:TEOS mole ratio, metal ion concentration, and temperature. Gelation activation energy(E^*) was determined from the temperature dependence of gelation time using an Arrhenius equation. The value of E^* is independent of the metal ion concentration and water:TEOS mole ratio. Based on the results of this study, the metal ions may be classified into two categories. Metal cations of type I, such as Li^+, Na^+, Mg^{2+}, Ca^{2+}, and Sr^{2+}, lower the gelation time, probably do not participate in either the hydrolysis of TEOS or the subsequent polymerization reaction, can be introduced only in limited amounts (as metal salts) into the gel structure, and have no appreciable effect on E^* of TEOS. Metal ions of the second type, such as Al^{3+}, La^{3+}, and Y^{3+}, greatly increase the time of gel formation, become part of the gel network by participating in the polymerization reaction, can be incorporated in large concentrations into the silica gel network, and increase value of E^*. This difference in behavior is determined by whether the metal cation acts as network modifier or intermediate in the silica glass network. Thus, it is proposed that the gelation kinetics may be used as a simple test to decide whether a metal ion would behave as a network intermediate or modifier in silica and, more importantly, in other glass networks.

ACKNOWLEDGMENTS

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Table I. – Influence of Water: TEOS Mole Ratio on Gelation of $10MgO-90SiO_2$ and $10CaO-90SiO_2$ Systems at Various Temperatures

System, mole %	H_2O: TEOS mole ratio	Gelling time (hr) at temperature (°C)					Arrhenius parameters of Eq. (5)	
		1	23	40.5	58	68	E^*, kJ/mole	A', s^{-1}
SiO_2	6	---	156	38.5	15.3	7.9	54.5	7.8×10^3
$10MgO-90SiO_2$	4	413	68	15.6	5[a]	3.2	56.9	4.7×10^4
	6	---	25[b]	7.5	2.4	1.3	57.8	1.6×10^5
	7.5	146[c]	25	6	2.0	1.1	58.7	2.6×10^5
$10CaO-90SiO_2$	4	---	40[d]	12	4.3[e]	2.4	52.9	1.5×10^4
	6	---	23[b]	7.5	2.5	1.3	55.8	7.4×10^4
	7.5	130[c]	23.5	6	2.1	1.1[f]	56.9	1.3×10^5

[a]At 60 °C.
[b]At 25 °C.
[c]At 2 °C.
[d]At 23.5 °C.
[e]At 57.5 °C.
[f]At 67 °C.

Table II. – Influence of Mg^{2+} and Ca^{2+} Concentration on Gelation of TEOS at Various Temperatures; Water: TEOS Mole Ratio = 6

System, mole %	Gelling time (hr) at temperature (°C)					Arrhenius parameters of Eq. (5)	
	1	23	40.5	58	68	E^*, kJ/mole	A', s^{-1}
SiO_2	---	156	38.5	15.3	7.9	54.5	7.8×10^3
$2MgO-98SiO_2$	269	42	10	3.9	2.3	55.5	4.2×10^4
$5MgO-95SiO_2$	---	27.5[a]	8.5	2.8	1.6	56.3	7.5×10^4
$10MgO-90SiO_2$	---	25[a]	7.5	2.4	1.3	57.8	1.6×10^5
$2CaO-98SiO_2$	260	44	10.3	4	2.6[b]	54.7	3.0×10^4
$5CaO-95SiO_2$	---	27[a]	8.5	3	1.6	55.2	4.9×10^4
$10CaO-90SiO_2$	---	23[a]	7.5	2.5	1.3	55.8	7.3×10^4

[a]At 25 °C.
[b]At 67 °C.

Table III. – Influence of Y^{3+} Concentration on Gelation of TEOS at Various Temperatures; Water: TEOS Mole Ratio = 6

System, mole %	Gelling time (hr) at temperature (°C)					Arrhenius parameters	
	2	22	40.5	58	68	E^*, kJ/mole	A', s^{-1}
SiO_2	----	156[a]	38.5	15.3	7.9	54.5	7.8×10^3
$5Y_2O_3-95SiO_2$	2540	384	60	17	8.8	67.8	8.2×10^5
$10Y_2O_3-90SiO_2$	3408	436	67	18.5	9.8	69.9	1.6×10^6

[a]At 23 °C.

Table IV. – Influence of Various Metal Ions on Gelation of TEOS at Different
Temperatures; Water: TEOS Mole Ratio = 6

System, mole %	Gelling time (hr) at temperature (°C)					Parameters of Eq. (5)	
	1	23	40.5	58	68	E^*, kJ/mole	A', s^{-1}
$5Li_2O-95SiO_2$	218^a	38	13.5	4	2.5	52.8	1.4×10^4
$5Na_2O-95SiO_2$	175	27.5^b	10.5	3.3	1.8	52.5	1.6×10^4
$5MgO-95SiO_2$	----	27.5^c	8.5	2.8	1.6	56.3	7.5×10^4
$5CaO-95SiO_2$	----	27^c	8.5	3	1.6	55.2	4.9×10^4
$5SrO-95SiO_2$	----	36^d	11.5	4	2.3	51.7	1.0×10^4
SiO_2	----	156	38.5	15.3	7.9	54.5	7.8×10^3
$5CuO-95SiO_2$	1896^a	218^e	23.5	6.5	2.8	77.5	7.8×10^7
$5La_2O_3-95SiO_2$	4224^a	486^e	65	16	7.5	75.4	1.4×10^7
$5Al_2O_3-95SiO_2$	----	1080	85.5	20.5	8.3	89.2	1.7×10^9
$5Y_2O_3-95SiO_2$	2544^a	384^e	60	17	8.8	67.8	8.2×10^5

[a] At 2 °C.
[b] At 24 °C.
[c] At 25 °C.
[d] At 23.5 °C.
[e] At 22 °C.
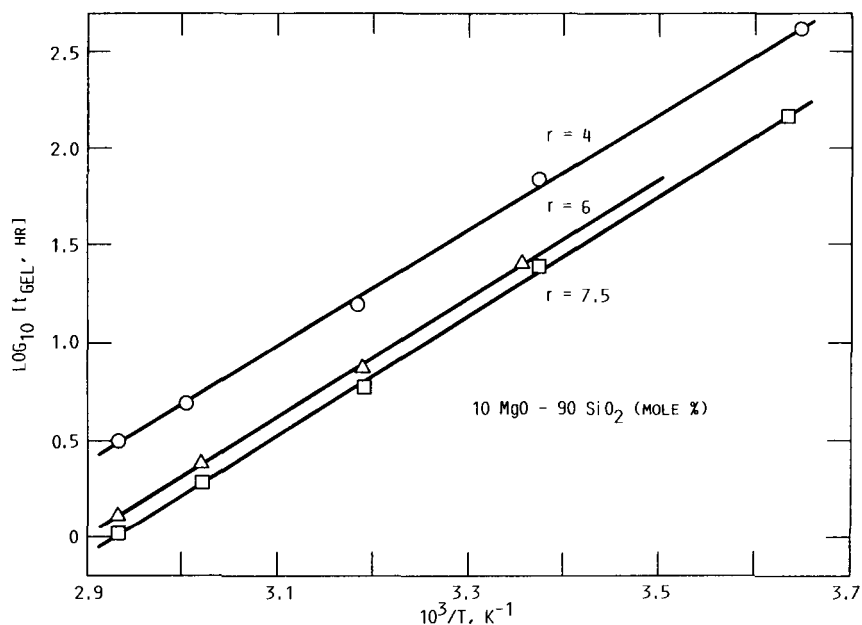
FIGURE 1. – TEMPERATURE DEPENDENCE OF GELLING TIME FOR 10MgO-90SiO$_2$, MOL %
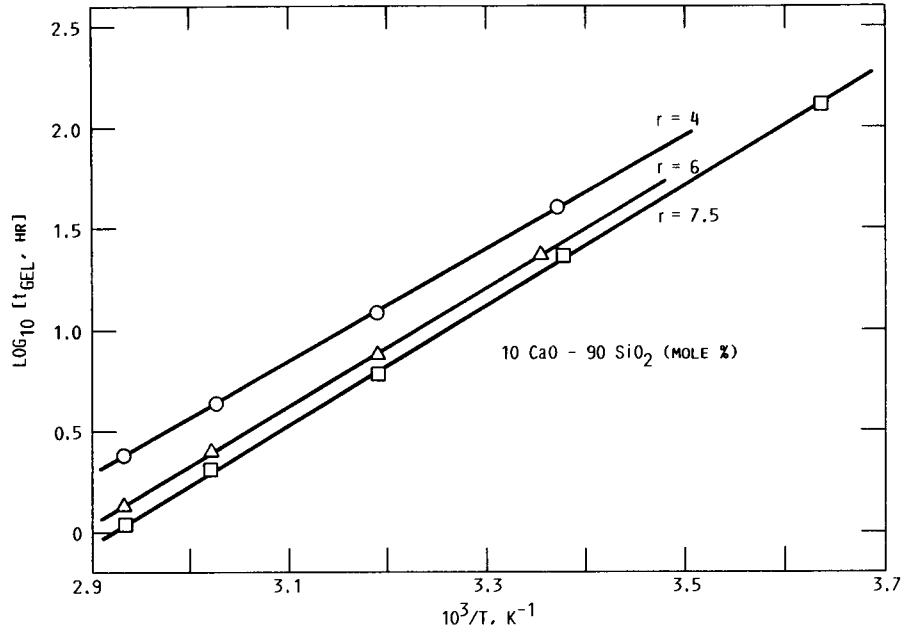COMPOSITION AT DIFFERENT WATER: TEOS MOLE RATIOS (r).

FIGURE 2. - TEMPERATURE DEPENDENCE OF TIME OF GEL FORMATION FOR 10CaO-90SiO$_2$ (MOL %) SYSTEM AT VARIOUS WATER: TEOS MOLE RATIOS (r).
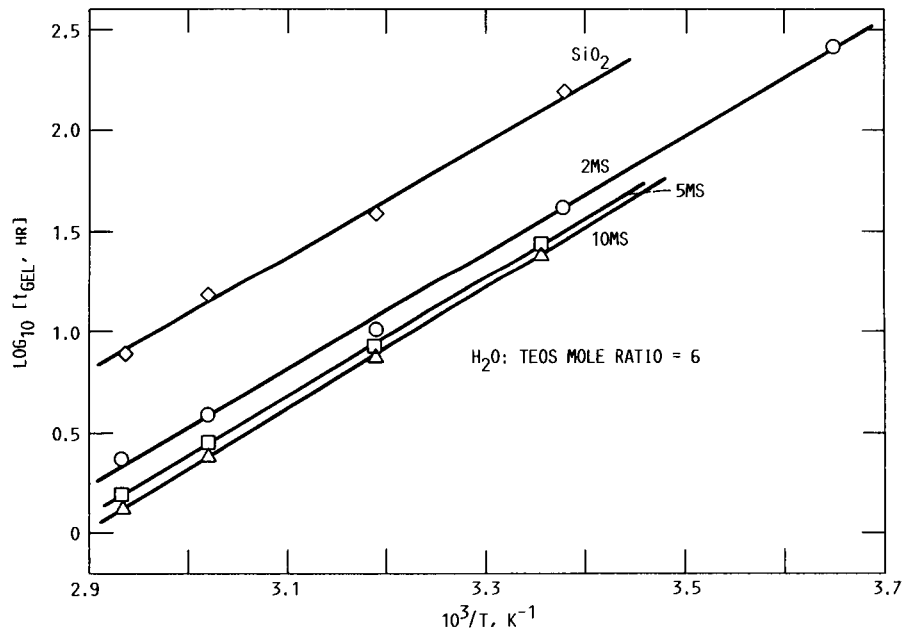

FIGURE 3. - PLOTS OF TEMPERATURE DEPENDENCE OF GELATION TIME FOR MgO-SiO$_2$ SYSTEM CONTAINING 2, 5, AND 10 MOL % MgO. PLOT FOR SiO$_2$ IS ALSO SHOWN FOR COMPARISON.
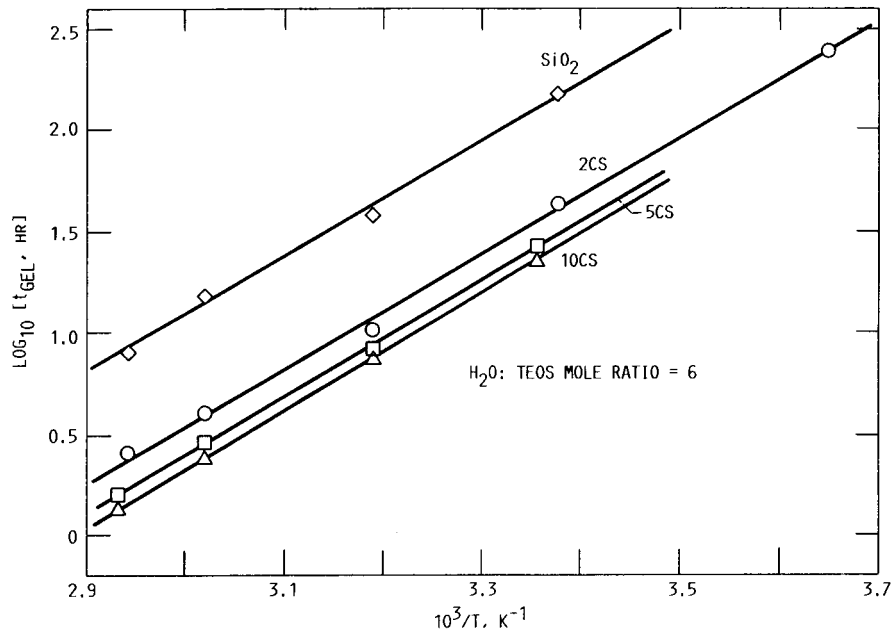
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FIGURE 4. – PLOTS OF TEMPERATURE DEPENDENCE OF GELATION TIME FOR CaO-SiO$_2$ COMPOSI-
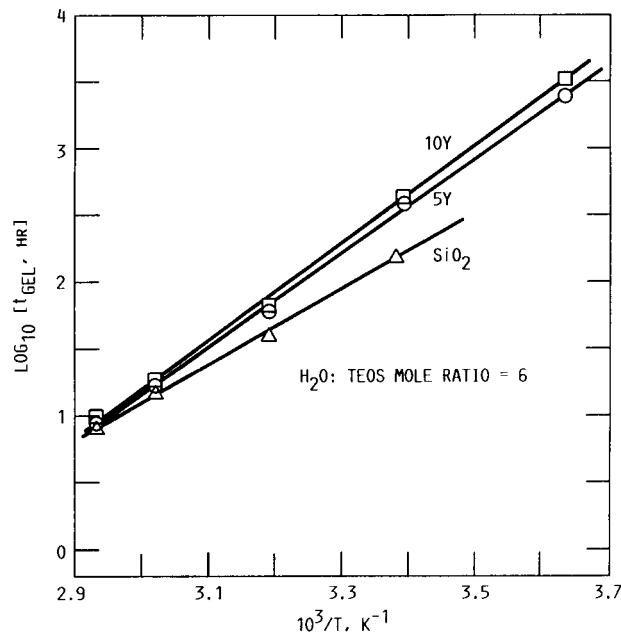TIONS CONTAINING 2, 5, AND 10 MOL % CaO. DATA FOR SiO$_2$ IS ALSO SHOWN.

FIGURE 5. – TEMPERATURE DEPENDENCE OF GELLING TIME FOR
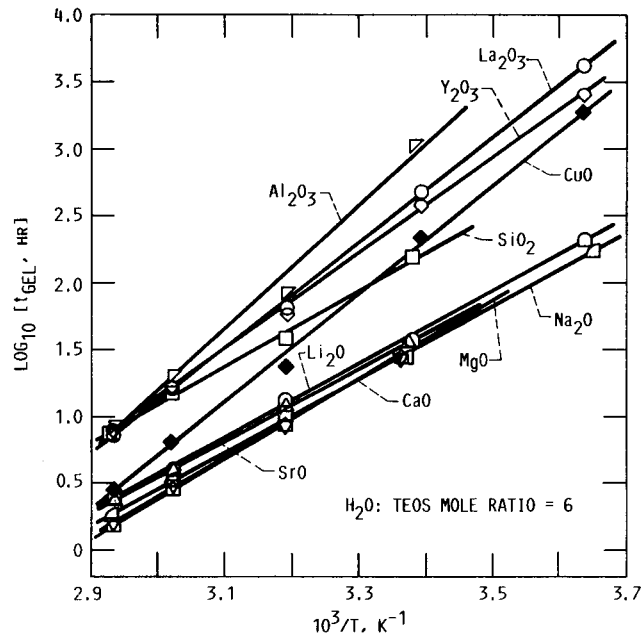Y$_2$O$_3$-SiO$_2$ SYSTEMS CONTAINING 5 AND 10 MOL % Y$_2$O$_3$.

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FIGURE 6. – TEMPERATURE DEPENDENCE OF GELLING TIME FOR
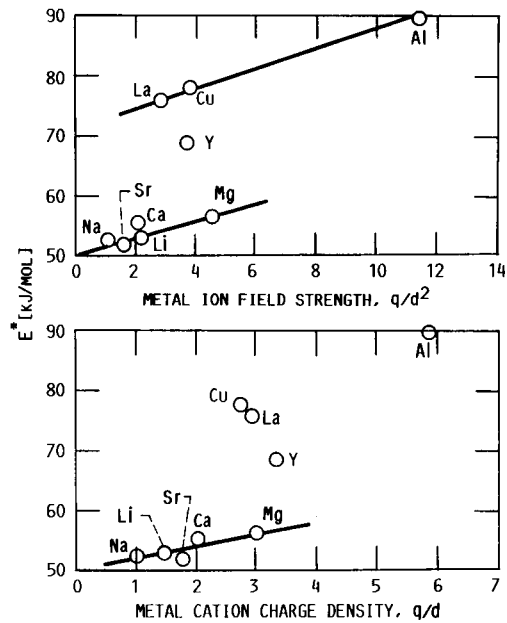VARIOUS SILICATE SYSTEMS CONTAINING 5 MOL % OF METAL
OXIDES.

FIGURE 7. – PLOTS SHOWING THE INFLUENCE
OF METAL CATION CHARGE DENSITY AND METAL
ION FIELD STRENGTH ON THE GELATION ACTI-
VATION ENERGY OF TEOS IN THE PRESENCE OF
5 MOL % OF METAL OXIDE; WATER: TEOS MOLE
RATIO = 6.

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16. Abstract

The effects of nine metal cations (Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cu^{2+}, Al^{3+}, La^{3+}, and Y^{3+}) on silica gel
formation has been investigated by studying the hydrolysis and polycondensation of silicon tetraethoxide (TEOS)
in the presence of metal nitrates. The influence of water:TEOS mole ratio, metal ion concentration, and the
reaction temperature has been investigated. The overall activation energy for gel formation has been determined
from the temperature dependence of the time of gelation for each system. The activation energy for $-Si-O-Si-$
network formation is found to be 54.5 kJ/mol. The gel formation time as well as the activation energy sharply
increase in the presence of Cu^{2+}, Al^{3+}, La^{3+} and Y^{3+}. In contrast, the presence of Li^+, Na^+, Mg^{2+}, Ca^{2+}, or,
Sr^{2+} lowers the gelation time, but has no appreciable effect on the activation energy. This difference may be
attributed to the participation or nonparticipation of the metal ions in the formation of the three dimensional
polymeric network during the polycondensation step. The concentration of metal ion (Mg^{2+}, Ca^{2+}, Y^{3+}) or the
water:TEOS mole ratio had no appreciable effect on the gelation activation energy. A simple test has been
proposed to determine whether a metal ion would act as a network intermediate or modifier in silica and other
glassy networks.

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