

Role of dopant cations in the gelation behaviour of silica sols

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Abstract. Gelation times of tetraethyl orthosilicate-derived sols containing selected di- to tetravalent cations as dopants were noted at different temperatures (15°–50°C). An analysis of these data, in conjunction with relevant published information, led to the tentative conclusions that (i) unhydrolyzed cations in bare form linked negatively charged silicate polymers in sols, thereby accelerating gelation and (ii) hydrolyzed cations retarded the process by offering molecular size-related hindrance and competition for the available water for hydrolysis.

Keywords. Silica sol; sol-gel transition; dopant cations.

1. Introduction

The phenomenon of gelation of silica sols in presence of dopant cations has been attracting the attention of researchers from the early part of this century (Dienert and Wandenbulcke 1924; Hurd *et al* 1958) till date (Bansal 1990; Patra and Ganguli 1992a,b). The common approach followed in most of these investigations was to find out if and how the process of aggregation of silicate species in a sol (reflected by, among others, the gelation time) was accelerated or retarded by a dopant cation. The issue has gained importance in recent times because of the current interest in doped silica gel-glass optics (e.g. Moreshead *et al* 1990; Thomas *et al* 1992), special glasses (Aizawa *et al* 1994) and silicate catalysts (e.g. Lopez *et al* 1991) including zeolite precursors (McCormick *et al* 1987, 1989) of tailor-made specifications, and the expected influence of the dopants on the gel structures (Ganguli 1988; Murakata *et al* 1992). Gelation time is also an indicator of the workability of a sol and therefore, is of great practical significance in sol-gel processing.

Effects of various cations on the gelation behaviour of alkali silicate or alkoxide-derived sols have been studied (discussed in detail later). However, no general picture of the effect seems to have emerged. In addition, parallel investigations have sometimes led to conflicting conclusions, demanding further study. The present work attempts to re-examine the above phenomenon in the light of existing data and new information on gelation (used as a broad term to include condensation and aggregation of polymeric units) of alkoxide-derived silica sols in presence of selected di- to tetravalent cations.

2. Experimental

All the sols were prepared at 25°–27°C from alcohol-free (initially) alkoxide-water-acid systems. Tetraethyl orthosilicate (TEOS) of purum grade was used as the source of silica with H₂O : TEOS : H⁺ molar ratio at 14 : 1 : 0.01. Cations in required proportions were added via inorganic compounds (Pb-, Zn- and La-nitrates, ammonium

ceric nitrate, Al-chloride, Zr-oxychloride and boric acid) dissolved in deionized water. HNO₃ (for nitrates) or HCl (for other compounds) was used as catalyst. The temperature of the hazy two-phase system thus obtained increased to 70°–80°C with formation of a clear sol, but came back to ambient conditions within about 15 min. The pH was adjusted to 3.5 by addition of dilute NH₄OH solution. All the chemicals were of AR or equivalent grade.

Sol-gel transition was studied at different temperatures (15°–50°C) in a constant temperature bath ($\pm 1^\circ\text{C}$). Sols of 15 ml volume in closed containers were used. Gelation times at 25°C and higher temperatures were repeated for check under similar conditions; the differences were found to be reasonably small for the present purpose. However, mean values (2–3 experiments) were used in this work.

3. Results

Tables 1–5 present information on the gelling time of silica sols doped with B³⁺, Al³⁺, La³⁺, Zr⁴⁺ and Ce⁴⁺ at different temperatures. Similar data for Pb²⁺ and Zn²⁺ have been reported earlier (Patra and Ganguli 1992a,b) and will not be presented here in full. The data for 40°C (not given in tables 1–5) for all the seven cations have been pictorially presented in figure 1 for a ready comparison of relative trends of gelation. Note that all the sols were cast at a final pH of 3.5, requiring similar additions of NH₄OH; the effect of NH₄⁺ has therefore been considered to be similar in all cases.

4. Discussion

4.1 Earlier observations on gelation of doped silica sols

The earliest experiments (e.g. Hurd *et al* 1958) on gelation, coagulation or aggregation

Table 1. Gelling times of boron-doped silica sols.

Equivalent mol% B ₂ O ₃	Gelling time (h)			
	15°C	25°C	30°C	50°C
0.5	27.38	8.91	4.95	0.55
1.5	33.08	9.38	5.16	0.58
2.5	40.00	10.83	7.08	1.00
5.0	45.00	15.58	8.33	1.13

Table 2. Gelling times of aluminium-doped silica sols.

Equivalent mol% Al ₂ O ₃	Gelling time (h)		
	15°C	30°C	50°C
0.2	22.00	5.33	0.75
0.5	39.81	7.00	1.08
1.0	92.00	13.75	2.17

Table 3. Gelling times of lanthanum-doped silica sols.

Equivalent mol% La ₂ O ₃	Gelling time (h)		
	15°C	25°C	50°C
0.5	18.62	4.57	0.45
1.0	12.30	3.16	0.35
3.0	6.30	1.99	0.29
5.0	3.01	0.80	0.17

Table 4. Gelling times of zirconium-doped silica sols.

Equivalent mol% ZrO ₂	Gelling time (h)		
	15°C	25°C	50°C
0.5	26.92	10.59	1.99
1.0	47.86	17.58	1.83
3.0	63.00	21.88	1.92
5.0	5.50	3.02	0.78

Table 5. Gelling times of tetravalent cerium-doped silica sols.

Equivalent mol% CeO ₂	Gelling time (h)		
	15°C	30°C	50°C
1.0	23.00	5.89	1.12
3.0	19.49	5.25	0.92
5.0	15.14	4.07	0.80

(taken to be synonymous here) in silica sols as a function of the type of electrolyte present in the system showed monovalent cations to accelerate the process in the order $K^+ > NH_4^+ > Na^+ > Li^+$ at pH = 4.8. Recent work of Bansal (1990) confirmed the accelerating action of Li^+ and Na^+ ; a similar behaviour was also noted for all the alkali cations and tetramethyl ammonium, $(CH_3)_4N^+$ (Wijnen *et al* 1993) by measuring fractal aggregate size as a function of time at pH = 4.0.

Among the divalent ions, Mg^{2+} , Ca^{2+} , Sr^{2+} , Pb^{2+} and Zn^{2+} have been shown to accelerate gelation (Bansal 1990; Patra and Ganguli 1992a,b) at pH values ranging between 3.5 and 4.3. Wijnen *et al* (1993), on the other hand, found the initial silicate aggregate growth to be very slow in presence of Mg^{2+} at pH = 4.0 and considered it to be a retarding process. Divalent copper was shown by Bansal (1990) to retard gelation.

Al^{3+} , Y^{3+} and La^{3+} have been reported to hinder gelation (Bansal 1990); boron is known to behave similarly (Woignier *et al* 1984), though no detailed information is on print. Large amounts (10–50 wt%) of ZrO_2 in SiO_2 sols have been shown to increase the gelling time drastically (Klein 1987).

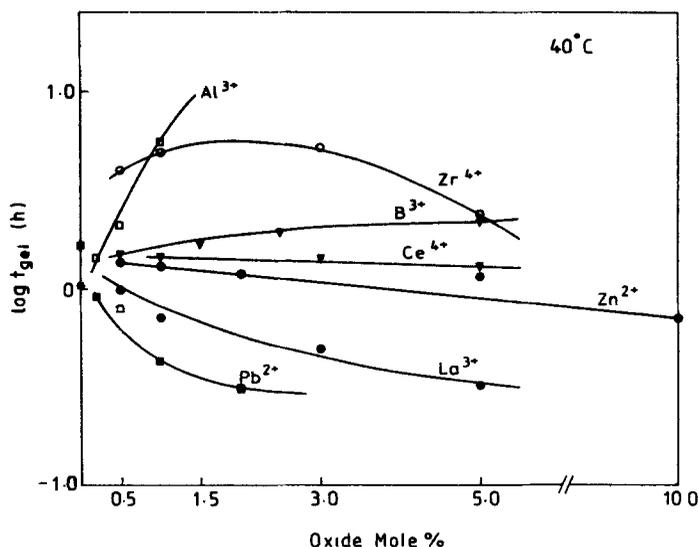


Figure 1. Gelation times at 40°C of some bi- to tetravalent cation doped silica sols (derived from TEOS) prepared at a final sol pH of 3.5. The curves are only visual aids, and do not have any other significance. The asterisk on the Y-axis indicates the gelling time of a pure silica sol catalyzed with HCl; the filled box on the Y-axis indicates the same, catalyzed with HNO₃.

4.2 The past and present results and their interpretation

A comparison of the results presented in tables 1–5 and figure 1 with the published information assembled in §4.1 gives a first hand indication of a general trend of the role of cations in the gelation of a silica sol: (i) Monovalent ions in general accelerate gelation; (ii) divalent ions mostly accelerate gelation (except Cu²⁺); and (iii) small trivalent and tetravalent ions hinder gelation, and ions with radius ~ 1 Å may do so under suitable conditions.

Under the conditions of this work (i.e. alcohol-free solution) the first major interaction of the cations would be with water molecules, i.e. *hydration or hydrolysis*. Even when alcohol was present in the original solution, monovalent cations have been shown to be solvated by water rather than ethanol (Sanchez and McCormick 1991). This indicates a clear relationship between hydrated dopant cations and quick gelation. Considering the fact that cations with small size and high formal charge hydrolyze easily in aqueous solutions of suitable pH (Baes and Messmer 1976; Ramsay 1994), it was thought proper to examine the present data in this light.

Figure 2, re-assembled from Baes and Messmer (1976), indicates that at pH = 3.5, cations which clearly accelerated gelation in this work, i.e. Pb²⁺, Zn²⁺, La³⁺ also remained predominantly hydrated; B³⁺ and Zr⁴⁺ which hindered gelation (except for 5 mol% ZrO₂) were hydrolyzed. Boron always remains hydrolyzed in aqueous solution and the reaction steps indicated by Irwin *et al* (1987) clearly show how it hinders hydrolysis-condensation of Si-alkoxy group. Zirconium forms a cyclic tetramer, [Zr₄(OH)₈(H₂O)₈]⁸⁺ in oxychloride solutions (Clearfield and Vaughan 1956). Al³⁺ also hindered gelation, though figure 2 is not clear about its hydrolyzability at pH = 3.5. Recently, Klopogge *et al* (1993) used NMR data to show that AlOH²⁺ started

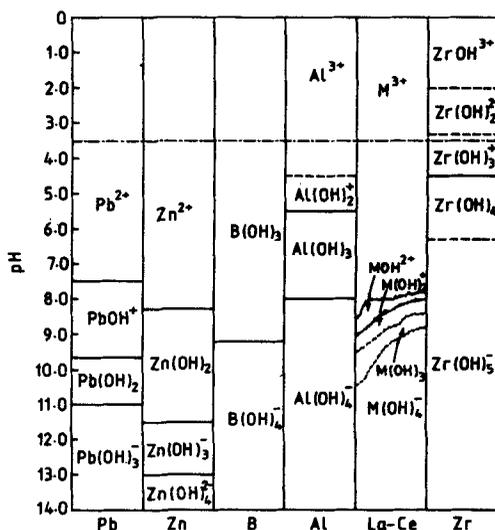


Figure 2. Predominance diagrams for hydration/hydrolysis of cations related to the present work in aqueous solutions of different pH values. Reassembled from Baes and Messmer (1976).

forming at pH 3–3.7 in $AlCl_3$ or $Al(NO_3)_3$ solutions. Bottero *et al* (1982) identified $Al_2(OH)_2^{4+}$ species at pH 3 at the expense of at least 10% of monomers. A rise in temperature during sol preparation (see §2) can be of assistance in the formation of larger polynuclear species. This is also valid for boron and zirconium.

Tetravalent cerium is expected to take part in complexation in most low-pH aqueous solutions. However, it is also a strong oxidizing agent and can be reduced, at least in part, by water (Moeller 1973; Greenwood and Earnshaw 1984) or species present in aqueous solutions to form hydrated (at pH = 3.5) Ce^{3+} , promoting gelation in silica sols.

Sanchez and McCormick (1991) suggested formation of ion-pair complexes between alkali cations and negatively charged silicate groups in TEOS sols to explain enhanced condensation. Patra and Ganguli (1992a) suggested formation of transition state bonds between O^- (of silicate polymers) and M^{2+} cations to accelerate gelation. In both cases, facile shedding of hydration shells (thinner for larger ions) has been assumed. This generalized approach has been found to fit satisfactorily in most cases of relatively quick gelation of cation-doped silica sols.

A simple correlation between a hydrolyzed dopant cation and retardation of gelation of a silica sol seems difficult because of the wide differences among the nature and products of hydrolysis (and eventually, polymerization) of different cations under a given set of experimental conditions (e.g. solution pH, temperature, water/cation ratio). It is, however, noted that even the smallest product of hydrolysis of a cation is sufficiently larger than the corresponding bare cation, and due to this enhanced size, can offer geometrical hindrance to small silicate polymers in approaching each other; this is expected to retard their already slow rate of condensation (shown by the very slow increase in viscosity of TEOS-derived sols). Another factor involved in this process is the competition between silicon and the dopant cation for the available water for hydrolysis; this is also known to retard the hydrolysis of TEOS (Boilot *et al* 1988; Patra 1992; Fukui *et al* 1992).

5. Conclusion

Based on the previous and present information, it can probably be commented that broadly speaking (i) a hydrated cation assists gelation of a silica sol by shedding the hydration shell and cross-linking silicate polymers; and (ii) a hydrolyzed cation hinders gelation by growing in molecular size and offering size-related hindrance in the cross-linking process. This has direct bearing on predicting and manipulating the workability of a sol (i.e. time available for casting, coating etc before gelation) and thus, is of significant practical utility.

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