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Effects of organic acids on sol–gel transition of silicic acid—A rheological study

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The sol–gel transition in the silica system is dependent upon the degree of hydrolysis and polymerization reaction in the system [1]. The polymerization reaction for the formation of the gel network occurs in different stages, i.e. polymerization of monomer to form particles, growth of particles and finally linking of particles into chains and the formation of the network which extends throughout the liquid medium. The structural evolution through the growth of silicate polymers from the genesis to the gel point has been well established by various *in-situ* methods such as NMR, vibrational spectroscopy and small-angle scattering. However, a rheological study can be an important tool to characterize sols and sol–gel transition and can give a qualitative information on the structure at the time of gelation.

Many processing parameters, such as the presence of a catalyst, H_2O:Si ratio, type of solvent, pH, temperature, steric and inductive factors, etc. effect the mechanisms of hydrolysis and condensation of silicon alkoxide [1, 2]. For the hydrolysis and condensation rate of silicon alkoxide, the effect of a catalyst was investigated by Pope and Mackenzie [3], and the dependence of gel time on H_2O:Si ratio was observed by Klein [4]. Artaki *et al.* [5] showed the effect of different solvents on the condensation rate of silicon alkoxide. Colby *et al.* [6] reported the effects of temperatures on the gelation of silicon alkoxide and the pH dependence on the hydrolysis and condensation of the same system is also well known [1, 2]. Voronkov *et al.* [7] pointed out that steric and inductive factors influenced the condensation rate of silicon alkoxides.

In the present work, a rheological study, i.e. the determination of gelling time t_g, the dynamic flow behaviour, the viscoelastic property of the sols and gels and its relation to relaxation exponent n and fractal dimension d_f in a three-dimensional space during hydrolysis and condensation of tetraethyl orthosilicate (TEOS), in the presence of different organic acids, i.e. oxalic acid, citric acid and succinic acid was carried out at the same pH, temperature and H_2O:Si ratio in the system.

Silicic acid sols were prepared by using (initially) alcohol-free TEOS (Fluka Chemica, Purum grade), deionized water and different organic acids, i.e. oxalic acid, citric acid and succinic acid (AR grade, S. D. Fine Chem. Pvt. Ltd.) in the molar ratio of 14:1:0.2 respectively at 32 ± 1 °C. The system was stirred magnetically and the temperature was increased to 70–80 °C. After stirring for about 15 min, a clear sol was obtained [8]. The pH of each sol was adjusted to 3.5 by addition of dilute NH_3 (25 wt%, G. R. grade, E. Merck, India).

The rheological measurements of the sols were carried out by using a Haake rheometer (Rotovisco, model: RT20) at 30 °C. The instrument was connected to a computer, loaded with Haake software (Version V3). A cone and plate sensor (c60/1°) was used for all measurements. Steady shear flow measurements of the samples in controlled rate (CR) mode were carried out by increasing the shear rate from 0 to 200 s^{-1} over 30 s followed by an immediate decrease in the shear rate from 200 s^{-1} back to zero in another 30 s. The dynamic flow behavior, i.e. loss modulus (G'') and storage modulus (G') of the sols and gels was determined using oscillatory flow with varying radial frequency (ω) i.e., 0.924, 1.985, 4.279 and 19.855 rad s^{-1}. Loss tangent ($\tan\delta$) can be obtained as,

$$\tan\delta = G''/G' \quad (1)$$

where, δ is the phase displacement angle between applied stress and resulting deformation [9]. The value of δ, is a measure of the viscoelastic property of a sol and it is proportional to the relaxation exponent n as [10],

$$\delta = n\pi/2 \quad (2)$$

The relaxation exponent n, is related to the fractal dimension in three-dimensional space as [11, 12],

$$n = 3(5 - 2d_f)/2(5 - d_f) \quad (3)$$

Fig. 1 shows the change of viscosity of silicic acid sols in the presence of three different organic acids, i.e. oxalic acid, citric acid and succinic acid at different time intervals. It reveals that viscosity (at the shear rate of 50 s^{-1}) did not change markedly during the initial stage of ageing; however, after a certain time of ageing, it increased sharply. A steep change of viscosity was found after about 300 min of ageing for the sol in oxalic acid system while in the presence of citric acid and succinic acid, sharp changes of viscosity were obtained after about 400 min of ageing of the sols. The sharp change of viscosity indicated qualitatively the gel point of the corresponding sol. A more precise determination of gel points of silicic acid sol was obtained from Figs 2–4 for oxalic acid, citric acid and succinic acid respectively. At the gel point, $\tan\delta$ is independent of frequency [13], and the curves passed through a single point for all the frequencies, i.e. 0.924, 1.985, 4.279 and

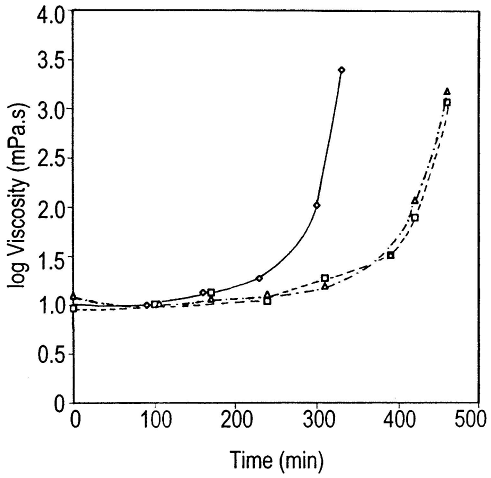


Figure 1 Change of viscosity of silicic acid sols in presence of three different organic acid with ageing time. ◇: Oxalic acid, △: Citric acid, □: Succinic acid.

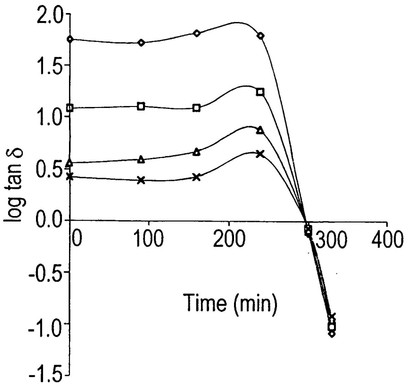


Figure 2 Change of tan δ of silicic acid sols in presence of oxalic acid with ageing time at different frequencies. ◇: 0.924 rad s^{-1}, □: 1.985 rad s^{-1}, △: 4.279 rad s^{-1}, ×: 19.855 rad s^{-1}.

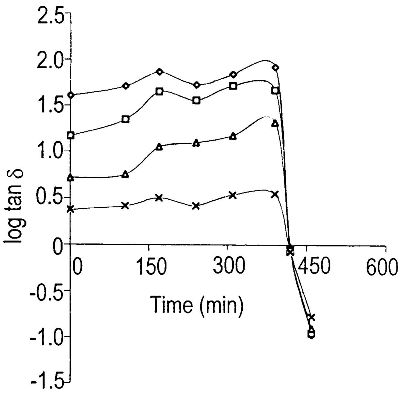


Figure 3 Change of tan δ of silicic acid sols in presence of citric acid with ageing time at different frequencies. ◇: 0.924 rad s^{-1}, □: 1.985 rad s^{-1}, △: 4.279 rad s^{-1}, ×: 19.855 rad s^{-1}.

19.855 rad s^{-1}. It was found that the gel point of silicic acid sol in the presence of oxalic acid was 300 min becoming 420 min in the presence of citric and succinic acids. At the gel point of silicic acid sol, the relaxation exponents n, calculated from Equation 2 were found to be 0.43, 0.46 and 0.48 for oxalic, citric and succinic acids respectively; and the fractal dimensions d_f, for the above systems calculated from Equation 3 were observed as 2.08, 2.04 and 2.01, respectively.

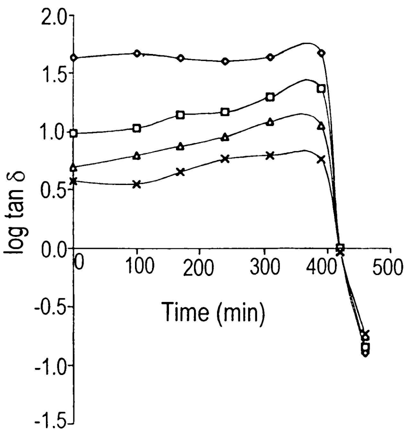
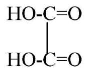
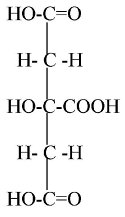
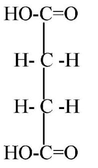


Figure 4 Change of tan δ of silicic acid sols in presence of succinic acid with ageing time at different frequencies. ◇: 0.924 rad s^{-1}, □: 1.985 rad s^{-1}, △: 4.279 rad s^{-1}, ×: 19.855 rad s^{-1}.

As the rheological studies of silicic acid sol for the three systems, oxalic, citric and succinic acids were carried out at the same pH, i.e. 3.5 and temperature, i.e. 32 °C, the difference in gelling time was due to the presence of different organic acids and their structures. In this case, the steric (spatial) and inductive effects of three different acids played an important role in the sol–gel transition of silicic acid sol. The structures of the three different acids are:

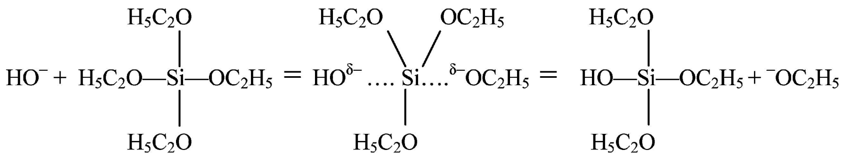

(Oxalic acid)


(Citric acid)


(Succinic acid)

During the hydrolysis and condensation reactions, the counter ions of the different acids, i.e. oxalate, citrate and succinate interacted with the silica network of the silicic acid sol through hydrogen bonding or weak forces like van der Waals's interaction etc. The steric crowding (bulkiness) of oxalic acid is less than that of citric acid and succinic acid. The greater the steric crowding in succinic and citric acids, the greater will be the retardation of the condensation reaction, i.e. increased gelling time as compared to oxalic acid in which steric crowding is less leading to reduced gelling time. Comparing the two acids, i.e. citric and succinic acids, the gelling time for the former should be greater as the former is somewhat more bulky than the latter. However, in actual practice, the gelling time for citric and succinic acids was the same. It was due to the fact that at pH 3.5, i.e. above the isoelectric point (IEP) of silica (pH = 2.7), the base-catalyzed hydrolysis of TEOS took place via the following mechanism [2].

The carboxyl group (—COOH) in different organic acids is an electron withdrawing group (-I effect) which stabilized the negatively charged cloud of silicon in step II through the interaction of hydrogen bonding, van der Waals forces, etc. causing the enhancement of



hydrolysis of TEOS and also the condensation reaction [1]. The electron withdrawing ability in citric acid facilitated the hydrolysis and condensation reaction of TEOS to a slightly greater extent than that with succinic acid. Therefore, for citric acid, though the steric bulkiness is higher decreasing the hydrolysis and condensation rates, the presence of the extra electron withdrawing effects of the carboxylic acid in it keep the hydrolysis and condensation reaction rate almost the same as succinic acid. It is to be noted that the steric bulkiness and electron withdrawing ability in succinic acid are slightly lower than those of citric acid.

It is concluded that above the IEP of silica, in the presence of different organic acids, the rate of hydrolysis and condensation of TEOS enhanced with the less steric crowding and increased electron withdrawing ability in the organic acids, leading to decrease in gelling time. Qualitative structural information at the gelling time was obtained from the relaxation exponent n and fractal dimension d_f. At the gel point, the relaxation exponent for all the systems, i.e. oxalic, citric and succinic acids in TEOS is close to 0.5 and fractal dimensions for the same system are almost 2; the values of n and d_f are theoretical predicted values. However, for the three systems, it was observed that the values of n and d_f were very much closer to their corresponding theoretical predicted values in the presence of succinic and citric acids than in case of oxalic acid in the system.

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References

1. C. F. BRINKER and G. W. SCHERER, in "Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing" (Academic Press, San Diego, 1990).
2. R. K. ILER, in "The Chemistry of Silica" (Wiley-Interscience Publication, John? Wiley & Sons, New York, 1979).
3. E. J. A. POPE and J. D. MACKENZIE, *J. Non-Cryst. Solids* **87** (1986) 185.
4. L. C. KLEIN, *Ann. Rev. Mater. Sci.* **15** (1985) 227.
5. I. ARTAKI, T. W. ZERDA and J. JONAS, *J. Non-Cryst. Solids* **81** (1986) 381.
6. M. W. COLBY, A. OSAKA and J. D. MACKENZIE, *ibid.* **99** (1988) 129.
7. M. G. VORONKOV, V. P. MILESHKEVICH and Y. A. YUZHELEVSKI, in "The Siloxane Bond" (Consultants Bureau, New York, 1978).
8. M. K. NASKAR, M. CHATTERJEE and D. GANGULI, *Trans. Ind. Ceram. Soc.* **61** (2002) 12.
9. V. G. SCHRAMM in "Haake Rheometer: Introduction to Rheometry (Gebruder Haake GmbH, Karlsruhe, Germany, 1995)
10. A. IZUKA, H. H. WINTER and T. HASHIMOTO, *Macromolecules* **25** (1992) 2422.
11. M. MUTHUKUMAR, *ibid.* **22** (1989) 4656.
12. A. PONTON, S. WARLUS and P. GRIESMAR, *J. Colloid Interface Sci.* **249** (2002) 209.
13. M. E. DE ROSA and H. H. WINTER, *Rheologica Acta* **33** (1994) 220.

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