LIGHT SCATTERING STUDY ON SOL-GEL TRANSFORMATION OF SiO$_2$ COLLOID AT EXTREMELY HIGH CONCENTRATIONS

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Abstract—Ludox SiO$_2$ sols with a reasonably uniform size of 12 nm and in the high concentration of 10 to 40 wt% were transformed to gels by lowering the pH. The process from sol to gel, followed by light scattering, did not show a sign of fractal growth within the length scale of observation ($>$40 nm). Rather, a density fluctuation due to a dynamic (non-equilibrium) disorder was apparent. Together with the results of viscosity measurements, it was concluded that the process consists of 3 stages: 1) A dynamic (non-equilibrium) density fluctuation grows rapidly. 2) Such density fluctuation acquires some order. 3) The entire bulk loses fluidity and becomes a macroscopic gel.

Key Words—Light Scattering Study, SiO$_2$ Colloids, Sol-gel Transformation.

INTRODUCTION

The sol-gel processes have been widely used in various materials preparations (Hench and West 1990; Spanhel and Anderson 1991; Zhang et al. 1992) in spite of a lack of fundamental understanding. Recently, however, complicated processes have been clearly delineated, particularly for SiO$_2$ colloids (Martin and Keefer 1986; Martin et al. 1987; Martin and Wilcoxon 1989; Winter et al. 1990; Martin et al. 1991). A comprehensive review is available (Martin and Adolf 1991). At the early stage of the process, a predominantly cluster–cluster aggregation in the presence of tetraalcoxysilicate monomer molecules proceeds either by reaction-limited (Schaefer et al. 1984; Aubert and Cannell 1986; Martin 1987; Winter et al. 1990) or by the diffusion-limited growth (Martin et al. 1990), depending on the conditions. At higher pH and lower salt conditions, the reaction-limited process prevails, and vice versa. Each process is characterized by the appropriate fractal dimension of growing aggregates. When the aggregates become large to fill the entire bulk, the gelation occurs, which is understood in terms of percolation theory as the divergence of the bond connectivity rather than the spatial correlation. Hence, no drastic change in "structure" was found at the gelation threshold (Winter et al. 1990). In all of these studies, tetraalcoxysilicate monomers seem to remain in the solution even at the gelation point. For example, Winter et al. (1990) showed that the monomer concentration was about 10% at the gel point in the mixture of tetramethoxysilicate, H$_2$O, and methanol in the mole ratio of 1:4:4. Thus a possibility of monomer–cluster aggregation still exists all through the process.

Strictly cluster–cluster aggregation leading to gelation is realized at low pH and high salt conditions starting with SiO$_2$ colloidal particles with a uniform particle size (Iler 1979). By using light scattering technique, Dietler et al. (1986) studied gelation processes for less than 10 wt% SiO$_2$ particles 7 nm in diameter (Ludox SX) in 0.45 M NaCl at pH 7.0. The scattering intensity was found almost constant in a low angle range, $K\xi < 1$, indicating a uniform, long-range structure.

$$K = 4\ \pi n\ \sin(\theta/2)/\lambda \qquad [1]$$

K is the momentum transfer of scattering where n is the refractive index of the medium, λ is the wavelength of the incident light *in vacuo* and θ the scattering angle. A similar K-independent scattering was observed for SiO$_2$ aerogel (Schaefer and Keefer 1986). For large K, $K\xi > 1$, scattering intensity showed a power law decay indicating an aggregating fractal. The value ξ is a characteristic crossover length, several tens to a few hundred nm, depending on the concentration of SiO$_2$ in the mixture. For 10 wt% SiO$_2$, the scattering intensity was constant in the range $K < 1/50$ (nm). While this value of ξ could be identified as characteristic cluster size at gelation, Dietler et al. (1986) warn themselves as ignoring the possibility of "screening" of the fluctuations associated with the large clusters by the presence of smaller clusters.

Light scattering could provide information on spatial variation of density of the medium in the size range from several tens of nm to a few hundred nm. The scattering intensity per unit scattering volume measured as a function of K, $I(K)$, is the product of the form factor, $P(K)$, and the structure factor, $S(K)$. The $P(K)$ is due to scattering from particles themselves. The SiO$_2$ particles in the present case are spherical and monodispersed with the average diameter of the order of 10 nm. Thus, $P(K)$ remains almost constant within the range of observation. The $S(K)$ is a manifestation of interparticle correlation, and if $S(K)$ decays in the following form:
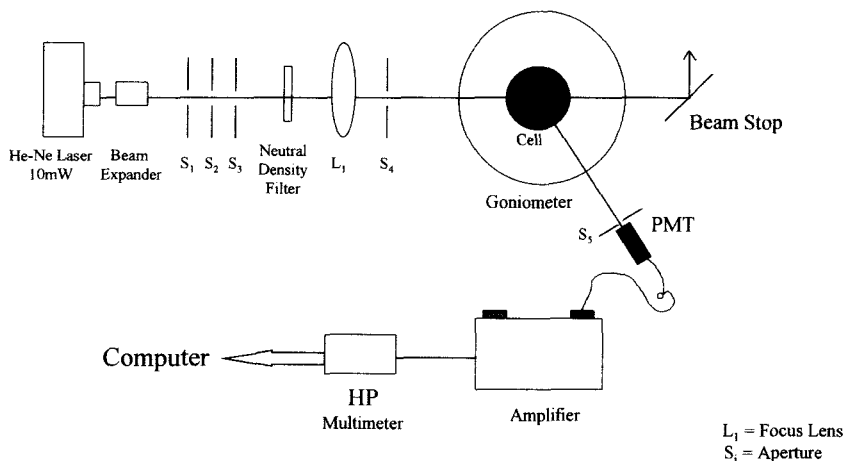
$$I(K) \sim S(K) \sim K^{-d_f} \qquad [2]$$

Figure 1.   Schematic diagram of light scattering apparatus.

then d_f is closely related to the fractal dimension of aggregates. In colloids at equilibrium, the value of $S(K)$ extrapolated to $K = 0$ is directly proportional to the number density fluctuation:

$$I(0) \sim S(0) \sim \langle (N - \langle N \rangle)^2 \rangle \qquad [3]$$

A peak in $S(K)$ is an indication of some correlation among scattering centers, and a number of interpretations are possible, 2 of which will be discussed below.

The present study starts with a stable SiO_2 sol of a reasonably monodispersed size distribution in highly concentrated conditions, 5 to 40 wt% SiO_2, and renders it transformed to a gel by changing pH. It is the case of strictly "cluster–cluster aggregation" with cluster having a reasonably uniform size in a high concentration regime. Much earlier studies of the conversion of sols with relatively uniform discrete particles to gels (Iler 1979) found that at about pH = 5, the rate of gelation became maximum, and increased hundredfolds when the concentration of SiO_2 increased from 10 to 40 wt%. We studied this sol-gel process by static light scattering and viscosity measurements. We define gelation simply as loss of fluidity of the mixture, following the general convention (Winter et al. 1990).

EXPERIMENTAL METHODS

SiO_2 sols (Ludox HS-40) were donated by Canada Colors and Chemicals Ltd. The supplier specifies 40 wt% as SiO_2, pH = 9, and the average diameter of SiO_2 particles as 12 nm. These values were confirmed by gravimetry, pH measurement and small angle X-ray scattering. The SiO_2 sols were diluted by borax buffer (0.01 M, pH = 9) and pH values adjusted by adding 6 M HCl dropwise. All the solutions used were filtered through Millipore 0.1-μm membrane filter, to remove dust particles.

The home-built light scattering apparatus is shown in Figure 1. The light source is Uniphase model 1135

He-Ne laser ($\lambda = 632.8$ nm). The vertically polarized light is focused at the center of the sample cell, a cylinder of the inner diameter of 3.96 cm from Brice Phoenix. The scattered intensity is detected by a photomultiplier and is fed to a PC via HP34401a digital multimeter. Scatterings are measured at every 2° in the range 30 to 140° by a photomultiplier tube mounted on the goniometer. This angular range is equal to 0.006 to 0.025 nm^{-1} in terms of the momentum transfer of scattering, K (Equation [1]). At each angle 30 readings are collected and the average is calculated after removing erroneous data possibly due to scattering from dust particles. At times, a polarizer is inserted in front of the photomultiplier to measure horizontally polarized scattered intensity in order to check presence of any multiple scattering (Sorensen et al. 1978). The background scattering and the angular dependence of the scattering volume are corrected, and the scattering intensity per unit scattering volume, $I(K)$, was determined. The performance of this apparatus was satisfactory. Scatterings from toluene and benzene were constant in the angular range studied within 5% and the ratio of intensities was found to be 1.2 ± 0.1, in good agreement with the literature value of 1.15 ± 0.02 (Pike et al. 1975).

Viscosity extrapolated to the zero shear was determined using a Haake model VT500 viscometer. Two kinds of cylindrical rotors were used: the NV sensor for low viscosity (sols) and the MV1 sensor for high viscosity (sols and gels).

RESULTS AND DISCUSSION

Figure 2 (Xu et al. 1996) shows the sol-gel diagram in the pH-SiO_2 concentration field, valid from 2 weeks to at least 6 mo. On changing the pH value, the sample remained as a stable sol at first, and after some induction period of hours to days, depending on the conditions, the sample lost fluidity and turned into gel
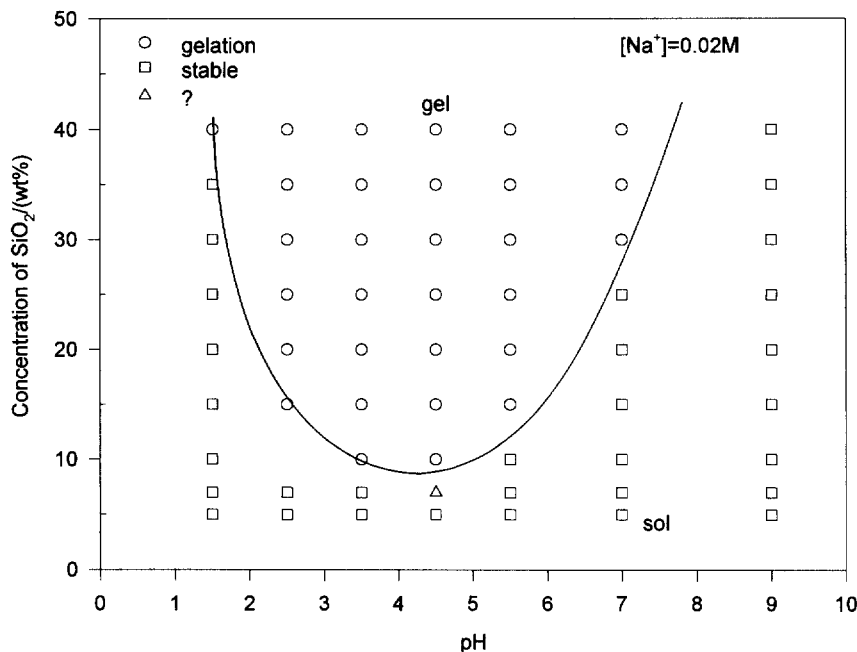
Figure 2.   Sol-gel diagram in the pH-SiO$_2$ concentration field.

rather suddenly. For most of the resulting gels, turbidities remained low except for the cases at pH = 4.5 with 7 and 10 wt%, as discussed below. This diagram is similar to the kinetic diagram by Iler (1979), in which the gelation time is the minimum and the gelation rate is the maximum at pH ≈ 5.0. As the SiO$_2$ concentration increases, the gelation time decreases rapidly. In this series of experiments, the ionic strength is virtually constant throughout. The total Na$^+$ concentration is kept at 0.02 M, and as HCl is added, borate ions, B$_4$O$_7^{2-}$ are replaced by 2 Cl$^-$ and are converted to H$_2$B$_4$O$_7$ (or actually 4 H$_3$BO$_3$ with 5 H$_2$O). Earlier, Allen and Matijevic (1969) showed that SiO$_2$ colloids are unstable and coagulate by Na$^+$ adsorption in the pH range pH > 14 with 0.02 M Na$^+$ concentration and 2 wt% of SiO$_2$. Moving boundary electrophoresis studies on 5 wt% SiO$_2$ sols confirmed that the point of zero charge occurred at pH = 2.5. Thus, gelation in the region shown in Figure 2 is triggered neither by destabilization due to Na$^+$ adsorption, nor by the zero surface charges. Iler (1979) interpreted the gelation under similar conditions. As pH increase in the low pH range, OH$^-$ catalyzes the silanol condensation between the surfaces of 2 particles, while at higher pH, the surface charges of particles prevent collision among them. We note that the salt concentration in this work, 0.02 M Na$^+$, is much lower than that in Dietler et al. (1986), 0.45 M NaCl. Hence, gelation occurred within a realistic time scale for lower concentrations of SiO$_2$ (<10 wt%) for Dietler et al. (1986) in comparison with those of ours (>10 wt%).

We followed the process from sol to gel at the pH = 4.5 by light scattering. Figure 3 shows the scattering intensity per unit scattering volume, $I(K)$, for 10 wt% SiO$_2$ colloids as a function of time. The value of pH when adjusted to 4.5 is time zero. As seen in the figure, almost K-independent scattering increased as time progresses, and a broad peak with a maximum at 0.015 nm^{-1} appeared at about 4822 min and developed clearly after 10,200 min. Gelation occurred at 15,800 min, and the sample became very turbid (transmission less than 0.4) with a clear indication of multiple scattering. Up to this point, however, multiple scattering did not occur. The transmission remained at about 0.8. While there may be a rapid decay for $K > 0.025$ nm^{-1}, no clear fractal behavior is apparent in the range accessible to the present observation, $K < 0.025$ nm^{-1}, or $\xi > 40$ nm. As time progresses, the scattering increases by several times and a broad peak gradually develops. This contrasts with the data of Dietler et al. (1986), in which the intensity increased a hundredfold at least for 2.4 wt%, and no peak was apparent in the range $K\xi > 1$. Dietler et al. hinted that the K-independent scattering in $K\xi < 1$ could be due to screening effect of filling voids among large clusters by smaller ones. For the present findings, however, we present an alternative interpretation based on a dynamic disorder (Ratje and Ruland 1976; Roe 1983; Roe and Curro 1983). Such explanation leads naturally to interpretation of a broad peak observed here.

The process from sol to gel is kinetic, and hence the value of $S(K)$ extrapolated to $K = 0$, $S(0)$, is not
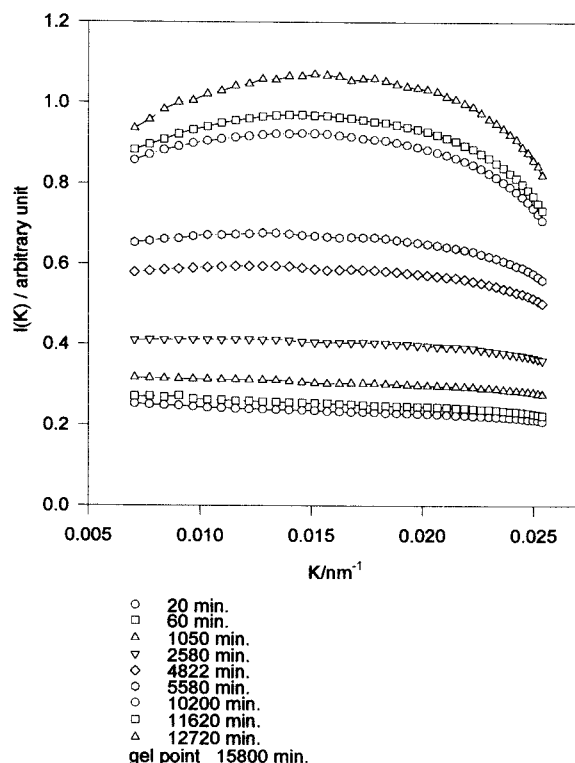
Figure 3.   Light scattering intensity per unit scattering volume, $I(K)$ vs. K, at various times, 10 wt% SiO_2 and pH = 4.5.

Figure 4.   Extrapolation of $I(K)$ to $K = 0$, by $1/I(K)$ vs. K^2 plots, 10 wt% SiO_2 and pH = 4.5.

entirely due to the equilibrium number density fluctuation, Equation [3]. Rather it will have a contribution from the fluctuation due to a dynamic disorder (Ratje and Ruland 1976; Roe 1983; Roe and Curro 1983), in addition to the equilibrium thermal fluctuation. The rapid increase in scattering intensity shown in Figure 3 must be due to the contribution from this dynamic (non-equilibrium) disorder.

In order to extrapolate $I(K)$ to $K \rightarrow 0$, we use the Ornstein–Zernike approximation (Stanley 1971):

$$I(K) \sim S(K) \sim (K^2 + a^2)^{-1} \qquad [4]$$

where a is the correlation length. This approximation is valid only for the thermal fluctuation and not applicable for a dynamic disorder. Indeed, at the later stages shown in Figure 3, $I(K)$ increases with K rather than decreases as Equation [4] would indicate. Nevertheless, in the absence of an appropriate description, the plots of $1/I(K)$ against K^2 are useful for extrapolation purpose only. Figure 4 shows such plots. The extrapolated values of $I(0)$, which are proportional to $S(0)$, are plotted in Figure 5a for 10 wt% SiO_2. As is evident from the figure, $I(0)$ grows rapidly at first, but there is the break point at which the rate of growth changes. This break point seems to correspond where a broad peak becomes apparent. For the cases of 20, and 30 wt% SiO_2 at pH 4.5, the transmission of the sample
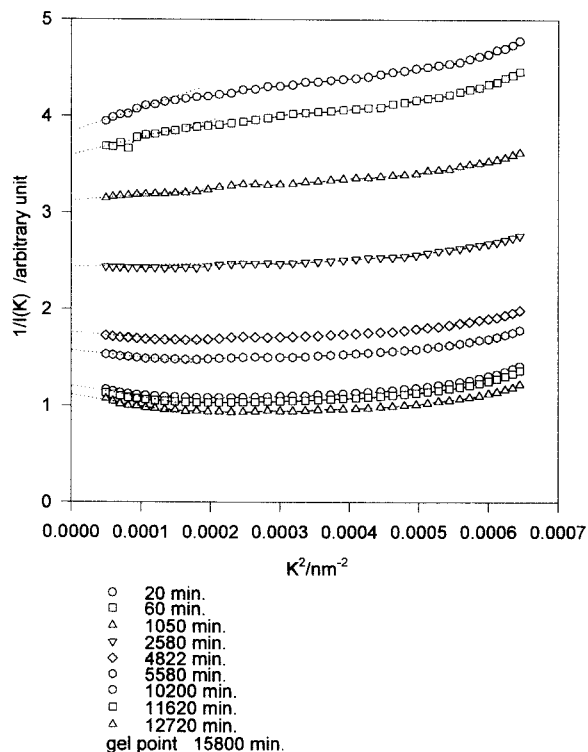
remained high (about 0.8) even after gelation occurred. Hence, the scattering data were taken even after gelation. They showed similar shapes with broad peaks (the maximum at about 0.015 nm^{-1}) as those of 10 wt% before gelation but after the break point. Figures 5b and 5c show the plots of $I(0)$ against time for 20 and 30 wt% SiO_2.

A peak in the scattering curve could be interpreted as the system acquiring a paracrystalline order (Matsuoka et al. 1987 and 1988) out of dynamic disorder, or as aggregates inducing depleted regions in particle density concentrically around them (Guinier and Fournet 1955; Carpineti et al. 1995). The difference in these 2 interpretations lies on the difference in emphasis of the point of view. The former emphasizes the behavior of $S(K)$ with $P(K)$ being the form factor of actual particles, while the latter considers the growing aggregates as the scattering centers. In the present case of highly concentrated SiO_2 particles, either interpretation may describe the reality only partially. To acquire some order in the mode of collective aggregation, regions of high particle density and those of depleted density must arrange themselves in a orderly manner. Thus, the apparent difference between these interpretations is only marginal. We suggest, therefore, that the process from sol to gel in the present case of extremely high particle concentrations may be regard-
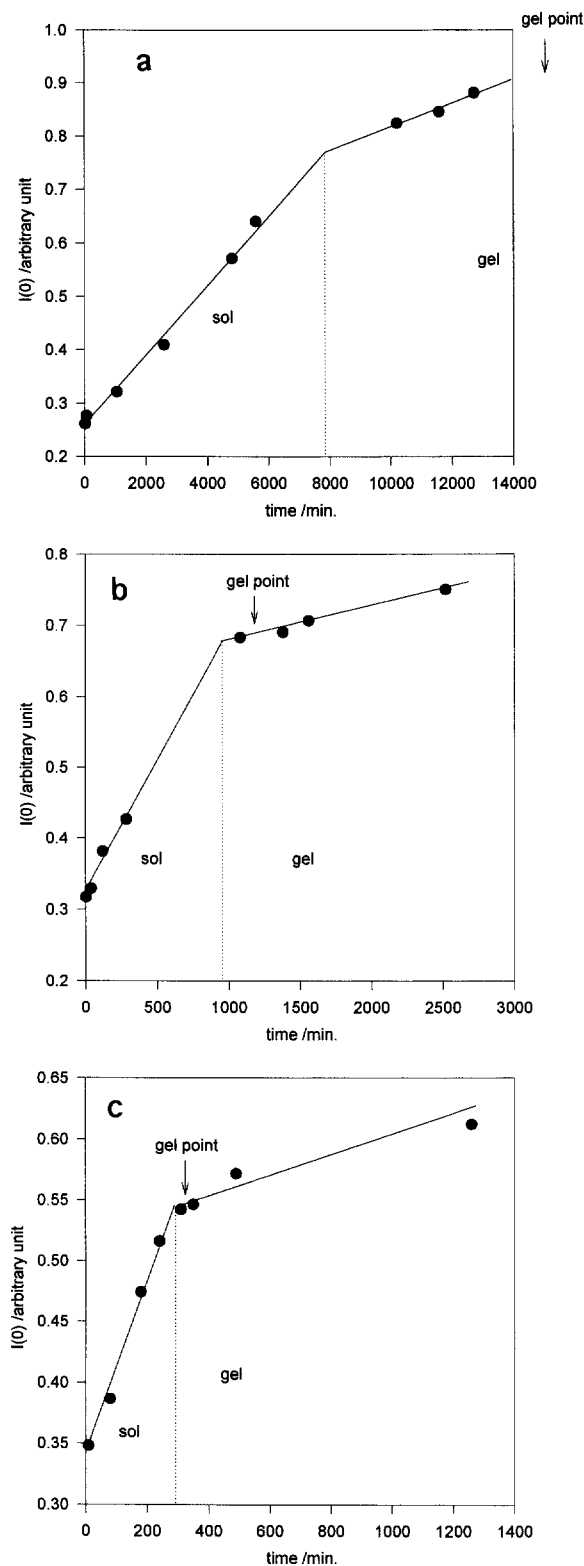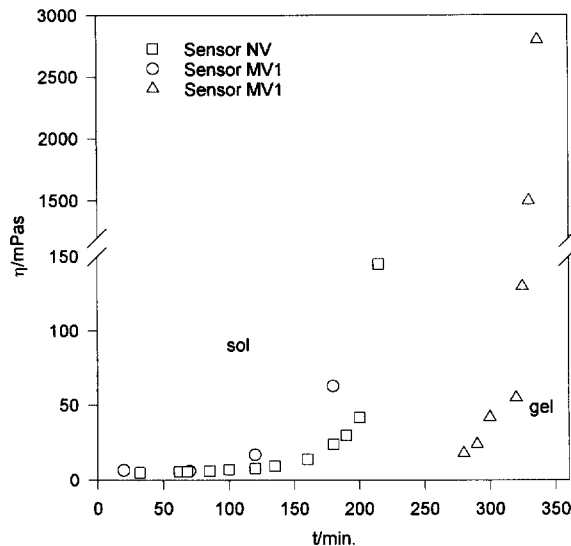
Figure 6. Viscosity at zero shear, η, measured by rotating coaxial cylinders, vs. time, 30 wt% SiO_2 and pH = 4.5. $\triangle$: The sample was left standing for 280 min before the measurement was commenced. See text.

ed as consisting of 3 stages: 1) fluctuations due to a dynamic (non-equilibrium) disorder increase rapidly; 2) such fluctuations acquire some order, but the entire bulk has not yet lost fluidity; and 3) the entire bulk becomes gel.

Figure 6 shows the viscosity extrapolated to zero shear, η, for 30 wt% SiO_2 at pH = 4.5. Gels are characterized by a large value of viscosity, $\eta > 2000$ m Pa s, while those for sols are 2 orders of magnitude smaller. Since the sample is subjected to shear stress as measurements are made, the kinetic behavior will be different from that for the samples left standing without disturbance. While the sample was in the sol state, η was small and changed almost linearly in time. At a certain point, however, η starts to deviate from linearity somewhat, before it increases dramatically by hundredfold when the sample became gel. In one run, marked by Δ in Figure 6, the sample was left standing for 280 min, which is the break point for the same sample shown in Figure 5c, and then the measurement was commenced. The value of η started to deviate from the linear extension, increased rapidly up to about 320 min, and thereupon the sample turned into gel, as seen in Figure 6. Thus, in terms of viscosity, the process from sol to gel seems to occur in 3 stages also: 1) The value of η increases slowly and almost linearly in time; 2) the value of η starts to deviate from linear growth and increases sharply; and 3) the value of η increases dramatically. Despite lack of unequivocal evidence, these 3 stages very likely coincide with those discussed above using the results by light scattering.
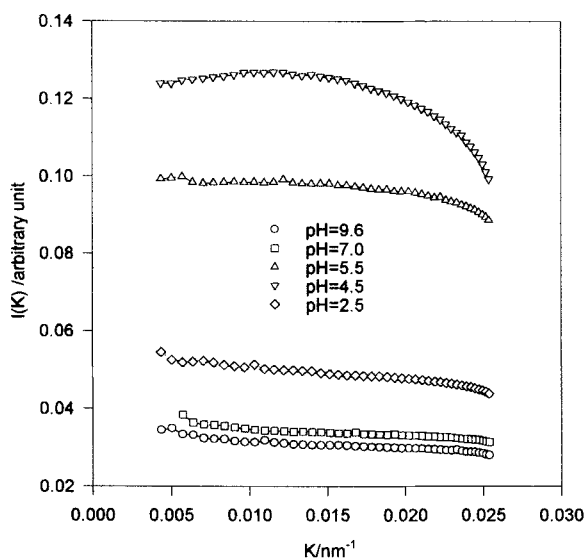
Figure 5. Zero angle scattering $I(0)$ vs. time plots. The gel point is shown by an arrow. a) 10 wt% SiO_2, b) 20 wt% SiO_2 and c) 30 wt% SiO_2, all at pH = 4.5.

Figure 7. Light scattering intensity per unit scattering volume, $I(K)$ vs. K, at various pH values for 7 wt% SiO_2, after 8 d (11520 min).

The fact that the sample became highly turbid when gel formed for 10 wt% SiO_2, while those for 20 and 30 wt% remained translucent, is reminiscent of critical opalescence with the critical point at pH 4.5 and 10 wt% SiO_2. Figure 7 shows light scatterings from 7 wt% SiO_2 at various pH values after 8 d (11,520 min). At pH 4.5, the scattering indicates some structure, suggesting "supercriticality." After 20 d, all the other samples remained the same, except for pH = 4.5, in which case the turbidity became very high (transmission ~0.2) although it did not lose fluidity. Analogy of gelation for polymer gels to a phase transition and a critical phenomenon is well known (Tanaka 1978). While the sol-gel diagram shown in Figure 2 is not an equilibrium phase diagram, we present our observations that remind us of a phase separation, or a spinodal decomposition.

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