

Thermostimulated Sol–Gel Transition in Suspensions of Sulfate–Zirconium Oxychloride

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(Received 23 July 1996; accepted 29 January 1997)

Abstract

The sol–gel transition of an aqueous solution of zirconium oxychloride modified by sulfuric acid (Zr:S 3:1) has been studied by small-angle X-ray scattering (SAXS) performed *in situ* during one cycle of heating and cooling between 298 and 358 K. The experimental SAXS curves exhibit three regions, at small, medium and high q values, characteristic of the Guinier, ‘fractal’ and Porod regimes, respectively. The value of 5.5 Å for the radii of the primary particles, obtained from the cross over of the Porod and fractal regimes, is consistent with the size of the inner core of the polynuclear $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$ molecule. These molecules aggregate as small clusters (31 Å) of fractal structure, with a dimensionality $D = 2.16$ in the sol. The value of the fractal dimensionality, which is characteristic of ideal branched polymers, decreases during heating, attaining a value of 2.0, characteristic of swollen polymers. Above the critical temperature (329 K), the average size of aggregates increases abruptly to 200 Å and the fractal dimensionality decreases to $D = 1.75$, this value being characteristic of a cluster–cluster aggregation process.

1. Introduction

Zirconia-based ceramic materials have been obtained through the sol–gel process, aiming at improving their thermomechanical, electrical, optical and catalytic properties (Bartlett, Woolfrey, Percy, Spiccia & West, 1994). Zirconia gels are prepared by hydrolysis and condensation of alkoxides such as zirconium *n*-propoxide or ethoxide. The zirconium alkoxide precursors are highly reactive and these reactions have to be controlled by modifying the precursors using complexing ligands (Chatry, Henry, In, Sanchez & Livage, 1994). There is some evidence (Henry, Jolivet & Livage, 1992) that mineral complexing ligands, like SO_4^{2-} , PO_4^{3-} and NO_3^- , can also control the condensation reactions of aqueous zirconium solutions prepared from metal halides. While studying the possibility of controlling these reactions by adding a mineral complexing ligand, we discovered that an aqueous solution of zirconium oxychloride in the presence of sulfate exhibits a thermoreversible sol–gel transition.

Thermoreversible gels are two-phase systems which acquire elastic properties under temperature changes as a result of the formation of a connected network by physical linkages (Djabourov, 1987). Thermoreversible gelation is often observed in biological systems and mixtures of synthetic polymers, but this behaviour is not usual for inorganic gels. To our knowledge, only one article reports the formation of an inorganic thermoreversible gel, namely of aluminium and sodium polyphosphate, which was attributed to the formation of a network of polycations and polyanions (Lima & Galembeck, 1994).

In this paper we present the first SAXS study concerning the thermoreversible sol–gel transition of zirconium oxychloride modified by sulfuric acid. Structural parameters, such as the fractal dimensionality and the upper and lower cut-off lengths, are determined from the SAXS results.

2. The structure function for fractals

Many investigations have clearly established that the structures of a number of gels and aerogels can be described by the concept of fractals (Chaput, Boilot, Dauger, Devreux & De Geyer, 1990; Freltoft, Kjems & Sinha, 1986; Teixeira, 1988). The structure function and the SAXS intensity, $I(q)$, which is proportional to the structure function, exhibits the following remarkably simple behaviour:

$$I(q) = Kq^{-\alpha} \quad (1)$$

where q is the modulus of the scattering vector and α and K are constants; the exponent $\alpha = D$, where D is the fractal dimensionality of the mass fractal object. The infinite q range for which (1) holds only applies to ideal fractals having extremely large size and very small basic units. In real systems, the potential dependence of $I(q)$ [(1)] is limited both at large and at small q values because of the finite size or correlation length of the aggregates, ξ , and because of the non-zero size of the elementary particles, a , respectively. The effect of these cut-offs is the appearance of two crossovers in the scattering curve: the first at $q = 1/\xi$, between the Guinier and the fractal regimes, and the second at $q = 1/a$, between the fractal and the Porod regions.

The scattering intensity function $I(q)$ is given by

$$I(q) = \varphi P(q) S(q) \quad (2)$$

where $S(q)$ is the structure function, $P(q)$ is the form factor of the elementary units and φ is the number of scattering units per unit volume.

Freltoft, Kjems & Sinha (1986) and Teixeira (1988) established the structure function for a fractal composed of elementary particles of size a having a cut-off for the correlation represented by a function $C(r) \propto \exp(-r/\xi)$. The dependence of $S(q)$ on D , ξ and a is given by

$$S(q) = C \left(1 + \left\{ \left[1/(qa)^D \right] \times \left\{ [D\Gamma(D-1)] / \left[1 + (1/q^2 \xi^2)^{(D-1)/2} \right] \right\} \times \sin[(D-1) \tan^{-1}(q\xi)] \right\} \right) \quad (3)$$

where Γ is the gamma function and C is a constant. Note that this expression becomes $S(q) \simeq q^D$ when $\xi^{-1} \ll q \ll a^{-1}$. At small q , $S(q)$ exhibits Guinier-type behaviour (Chaput, Boilot, Dager, Devreux & De Geyer, 1990). The form factor was approximated by a Gaussian function assuming spherical-shaped elementary particles:

$$P(q) \simeq \exp[-(1/5)q^2 a^2]. \quad (4)$$

Equation (3) holds for $q < 1/a$. For $q \gg 1/a$ the SAXS intensity exhibits the classical Porod asymptotic behaviour.

3. Sample preparation

The colloidal suspensions were prepared by adding an aqueous solution of $ZrOCl_2$ (0.2 mol l⁻¹, room temperature) to a hot (353 K) aqueous solution of sulfuric acid (0.2 mol l⁻¹), drop by drop under magnetic stirring. The volume of the $ZrOCl_2$ solution was adjusted to yield suspensions containing the following $Zr^{4+} : HSO_4^-$ molar ratios: 1:1, 1:2, 1:3, 2:1, 3:1 and 4:1. Aliquots of 15 ml of the suspensions were put inside acetylcellulose membrane tubing with molecular weight cut-off smaller than 14 000, and then submitted to static dialysis against 200 ml of doubly distilled water during 24 h. Dialysis was carried out in order to decrease the ionic strength of the suspensions by extracting the excess of ions; consequently, peptization of the precipitate was favoured. Peptization occurs only for samples prepared with molar ratios of 3:1 and 2:1, leading to the formation of transparent and stable suspensions, which gelify as the pH increases from 1.6 to 3.0. Elemental analysis of these samples showed that the nominal molar ratio was preserved after dialysis. We have also noted that the isocoric gelation may be obtained by increasing the temperature of the sol prepared with a molar ratio of 3:1. Moreover, the liquefaction of the system is observed as the temperature decreases to values smaller than the critical temperature. This thermoreversible behaviour is

observed if the system is kept at temperatures higher than the critical temperature for a short period of time (less than 1 h).

4. SAXS measurements

The SAXS study was performed using the D24 SAXS workstation at the synchrotron X-ray source DCI at LURE, France. The workstation is equipped with a bent silicon crystal monochromator which yields a monochromatic ($\lambda = 1.49 \text{ \AA}$) and horizontally focused beam. A set of slits defines the beam vertically. A position-sensitive X-ray detector and a multichannel analyser were used to determine the SAXS intensity $I(q)$ as a function of the modulus of the scattering vector q . Because of the small size of the incident-beam cross section at the detection plane, no mathematical desmearing of the experimental function was needed. The scattered intensity was determined as the difference between the experimental curve recorded with the sample and the parasitic scattering curve obtained with the solvent (water). An ionization chamber, placed downstream from the sample, was used to monitor the intensity decay of the transmitted beam and to determine the sample attenuation. The natural decay intensity of the incident beam was monitored also by recording the electronic current in the synchrotron source.

In situ SAXS measurements were carried out during one cycle of heating and cooling (rate 1 K min⁻¹) between 303 and 358 K. Each spectrum was recorded during 150 s, which corresponds to a temperature rise of 1.5 K. The sample was put into a cell between two thin films of Kapton, separated by 0.8 mm, placed in a Metler FP82 'hot stage' to control the thermal cycle.

5. Results and discussion

The thermoreversibility of this system was evidenced by turbidimetric measurements carried out at different rates of heating and cooling, as shown in Fig. 1, in which gelation during heating is characterized by an abrupt increase in the turbidity at the sol-gel transition temperature. During cooling, the decrease in turbidity revealed the liquefaction, the temperature of which (gel-sol transition) is always lower than the gelation temperature, resulting in a hysteresis loop. This behaviour is associated with differences in the mobilities of the small and large particles. The small particles in the sol have high mobility, favouring aggregate growth. On the other hand, in the large aggregates in the gel, the interaction forces between the clusters make liquefaction (disaggregation) more difficult. It is noteworthy that fast rates of cooling prevent the system from returning to the sol state (Fig. 1*b*). The *in situ* SAXS measurements were carried out at 1 K min⁻¹. In order to obtain complete reversibility, a much slower cooling rate is necessary.

This slow type of cycle was not tried because of the limited time available for the experimental run.

Fig. 2 shows the log-log plot of the scattered intensity $I(q)$ as a function of the modulus of scattering vector q , measured at different temperatures during sample heating (Fig. 2a) and cooling (Fig. 2b). For the region of high q ($q > 0.05 \text{ \AA}^{-1}$) the curves measured at different temperatures are approximately overlapping and two power-law regimes can be distinguished. The first one, at high q , presents a slope of -4 , in agreement with the Porod law. This behaviour is confirmed by the plot presented in Fig. 3, which shows that the product $I(q)q^4$ is a constant in the high q region, either for the sol or the gel, indicating that the primary particles have well defined surfaces. The Porod limit, which is proportional to the surface area of the interface, is nearly invariant during the sol-gel transition. This suggests that aggregation occurs by simple branching with local contacts between the primary particles and without the contribution of any density-increasing or phase-separation mechanisms, which would produce a noticeable variation in the interface area.

The second power-law regime at medium q produces a linear behaviour in the double logarithmic plots (Fig. 2). The slope is equal to -2.2 at room temperature and decreases as the temperature is raised. Moreover, the q

range of the linear region increases toward small q values for higher temperatures, indicating an increase in size of the fractal aggregates. A third regime is observed at small q values where the scattered intensity is approximately independent of q , which is characteristic of noninteracting clusters. This feature is expected for fractal clusters with finite correlation range which behave as independent objects.

Fig. 4 shows the fitting for the data displayed in Fig. 2 with the theoretical function $I(q)$ given by (2) using $S(q)$ and $P(q)$ defined by (3) and (4), respectively. The parameter a was determined from the crossover between the fractal and Porod regions. The other parameters of the theoretical function were determined by a nonlinear least-squares refinement procedure. The theoretical equation gives, as expected, a good agreement with the experimental observations only below $1/a$.

The q value of the crossover of the two power regimes remains approximately constant during the sol-gel-sol transition and corresponds to $a = 5.5 \text{ \AA}$ for the size of the primary particles. This value is in good agreement with the radius of the inner core of a molecule of $\text{Zr}_{18}\text{O}_4(\text{OH})_{38.8}(\text{SO}_4)_{12.6} \cdot 33\text{H}_2\text{O}$ (Squatrito, Rudolf & Clearfield, 1987), which is formed under conditions of synthesis similar to those used in the present study. In this structure, the inner core of the molecule is formed by

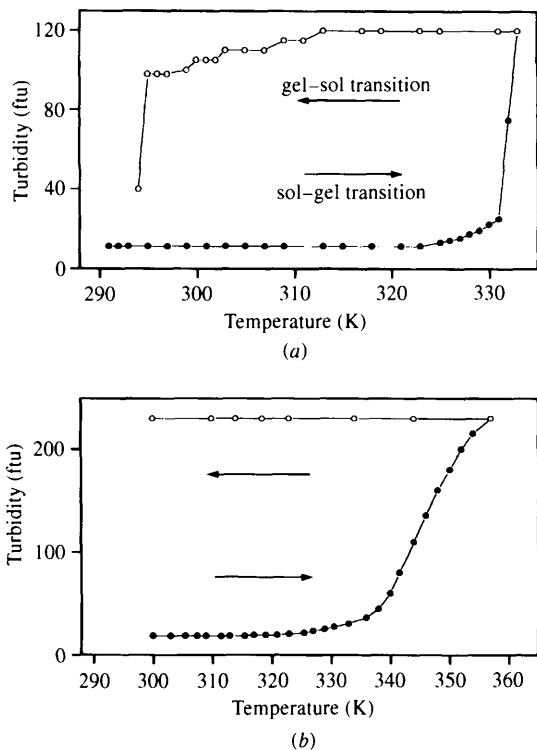


Fig. 1. Temperature evolution of the turbidity of the colloidal suspension of zirconium oxychloride modified by sulfuric acid (Zr:S 3:1 and $[\text{Zr}] = 0.15 \text{ mol l}^{-1}$) during a cycle of heating and cooling at (a) 0.01 and (b) 1 K min^{-1} .

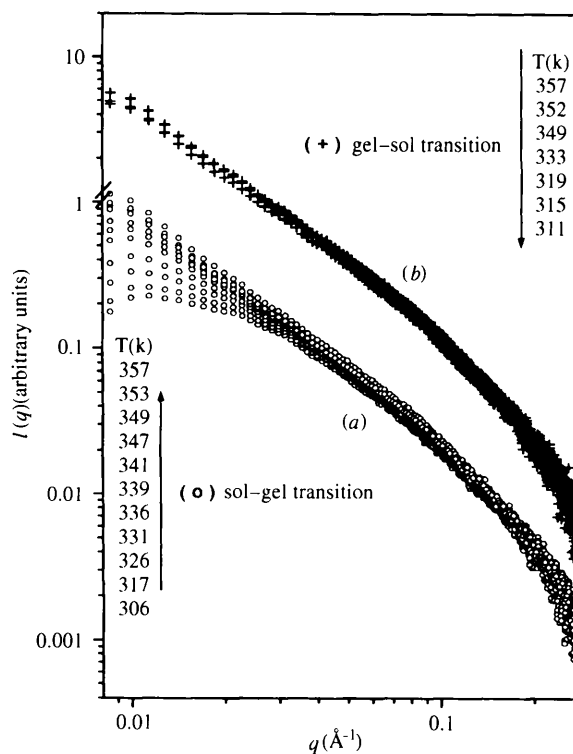


Fig. 2. Log-log plot of the experimental SAXS curves measured at different temperatures during (a) heating and (b) cooling. The set of SAXS curves corresponding to cooling are vertically displaced for clarity.

hydroxy and oxo groups bridging Zr atoms, whereas the sulfate ligands are located at the surface of the $\text{Zr}(\text{OH})_x\text{O}_y$ core. These molecules are held together by electrostatic interactions with the remaining water molecules.

Fig. 5 shows the temperature evolution of the fractal dimensionality D (Fig. 5a) and the correlation length of the aggregates ξ (Fig. 5b) during the sol–gel–sol transition. Note that, during cooling, the values of both D and ξ are not the same as during heating, indicating a strong hysteresis effect. This was expected from the turbidimetric measurements at the same heating rate.

Both sol and gel can be characterized by a fractal structure model, the dimensionality D decreasing progressively from 2.2 to about 2.0 in the sol phase and remaining constant and equal to 1.75 in the gel phase.

The value of D of 2.2 at room temperature is theoretically expected for ideal branched polymers, as is $D = 2.0$ for swollen branched polymers (Chaumont, Craievich & Zarzycki, 1992a,b, and references therein). This implies that in solution at room temperature, ideal branching occurs with monomers interlinked by a matrix formed by water, similar to the crystalline structure of $\text{Zr}_{18}\text{O}_4(\text{OH})_{38.8}(\text{SO}_4)_{12.6} \cdot 33\text{H}_2\text{O}$. In solution, these interactions relax as the temperature increases due to the diminution of the dielectric constant of water. This leads to swelling of the cluster, which produces a decrease in

the fractal dimensionality from 2.2 to 2.0 and an increase in the cluster correlation length from 31 to 46 Å as the temperature increases from 298 to 328 K. However, the change in ξ seems to be small when compared to the large relative variation in the fractal dimensionality, suggesting that relaxation involves only small and local structural modifications.

At about 333 K, the size of aggregates, ξ , increases abruptly and the fractal dimensionality decreases from 2.0 to 1.75 and remains almost constant up to 343 K. The value of D of 1.75 is close to the value expected for the mechanism of random-walk cluster–cluster aggregation (Chaumont, Craievich & Zarzycki, 1992a,b, and references therein). The enhanced mobility of the clusters and the change of the electrostatic interactions as the temperature increases may play a role in the modification of the aggregation mechanism above the gelation temperature.

The thermoreversible behaviour observed for the colloidal suspensions of zirconium oxychloride modified by sulfuric acid is qualitatively similar to that observed in some polymers in solution with lower critical solution temperature (LCST), in which phase separation and gelation occurs above a critical temperature. This behaviour is often assigned to a decrease in the

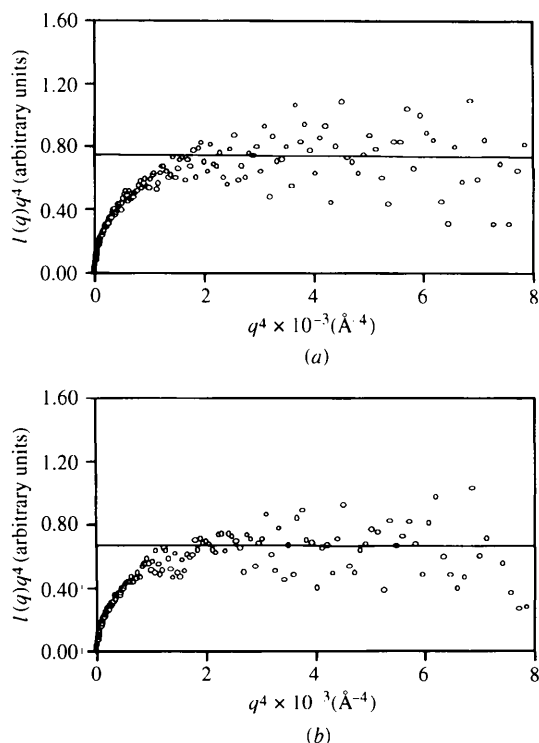


Fig. 3. Porod plots corresponding to (a) the gel phase ($T = 343$ K) and (b) the sol phase ($T = 303$ K). In spite of the large statistical errors in this q range, the Porod asymptotic behaviour seems to be obeyed for both sol and gel.

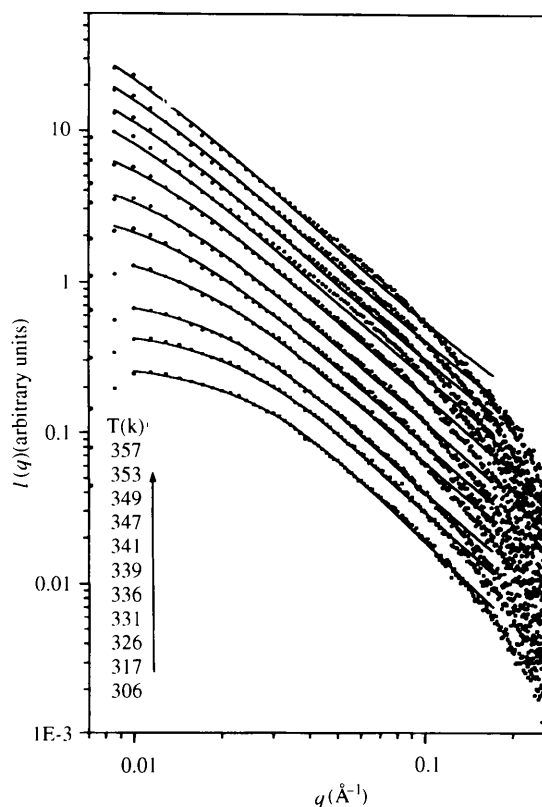


Fig. 4. Experimental points and fitting of the structure function $S(q)$ for the SAXS curves. The curves are vertically displaced for clarity.

effectiveness of the solvent, causing a decrease in the volume entropy due to the density-increase mechanism of the polymers (Sperling, 1992). Moreover, in the case of a transition from the solution to a phase-separated structure, a significant variation in the surface area is expected.

In contrast, our system shows swelling of the fractal cluster with increasing temperature, indicating that the effectiveness of the solvent increases. Moreover, the Porod limit does not indicate any variation in the surface area (Fig. 3) during the sol-gel transition. Therefore, it is difficult to explain our results from the thermodynamic concepts of LCST.

It seems more consistent to attribute the sol-gel-sol transition to a change in the affinity between the solvent and the clusters. In general, the enthalpy of hydration becomes less negative as the temperature increases. As a consequence, the solvation tends to decrease during heating, favouring the formation of more efficient electrostatic interactions between the $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}$ molecules by means of sulfate bridging.

In fact, we have observed by IR spectroscopy the presence of a bidentate SO_4 ligand in the irreversible gel,

obtained after ageing at 353 K for 3 h (Chiavacci, 1996). Therefore, the thermoreversibility seems to be a consequence of an intermediate step involving the formation of a sulfate complex, in which the short-lived nodes of the network are due to the electrostatic interaction between the clusters.

6. Conclusion

An aqueous solution of zirconium oxychloride modified by sulfuric acid exhibits a thermoreversible sol-gel transition, as evidenced by turbidimetric measurements. This SAXS study, during a cycle of heating and cooling, demonstrates that both the sol and the gel are formed by clusters or aggregates having a fractal structure. The size of the elementary structural unit is similar to that of the inner core of the $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$ molecule. The size of the basic building block does not vary along the whole heating-cooling cycle.

As temperature increases, the initial clusters of perfect branched polymers (with $D = 2.2$) in the sol phase progressively swell (with D decreasing to 2.0).

Gelation is produced by the enhanced electrostatic interaction between the clusters resulting in a network with a fractal dimensionality D of 1.75, which is consistent with the value expected for the mechanism of cluster-cluster aggregation.

This work was supported by CNPq, CAPES/COFE-CUB and FAPESP (Brazil).

References

- Bartlett, J. R., Woolfrey, J. L., Percy, M., Spiccia, L. & West, B. O. (1994). *J. Sol-Gel Sci. Technol.* **2**, 215-220.
- Chaput, F., Boilot, J. P., Dager, A., Devreux, F. & De Geyer, A. (1990). *J. Non-Cryst. Solids*, **116**, 133-139.
- Chatry, M., Henry, M., In, M., Sanchez, C. & Livage, J. (1994). *J. Sol-Gel Sci. Technol.* **1**, 233-240.
- Chaumont, D., Craievich, A. & Zarzycki, J. (1992a). *J. Non-Cryst. Solids*, **147/148**, 41-46.
- Chaumont, D., Craievich, A. & Zarzycki, J. (1992b). *J. Non-Cryst. Solids*, **147/148**, 127-134.
- Chiavacci, L. A. (1996). Masters thesis, UNESP, Brazil.
- Djabourov, M. (1987). *Rev. Gen. Therm. Fr.* **306/307**, 369-373.
- Freltoft, T., Kjems, J. K. & Sinha, S. K. (1986). *Phys. Rev. B*, **33**, 269-275.
- Henry, M., Jolivet, J. P. & Livage, J. (1992). *Structure and Bonding*, Vol. 77, edited by R. Reisfeld & C. K. Jorgensen, pp. 153-203. Berlin: Springer-Verlag.
- Lima, E. C. O. & Galembeck, F. (1994). *J. Collect. Interface Sci.* **166**, 309-315.
- Sperling, L. H. (1992). *Introduction to Physical Polymer Science*, pp. 127-130. New York: Wiley Interscience.
- Squattrito, P. J., Rudolf, P. R. & Clearfield, A. (1987). *Inorg. Chem.* **26**, 4240-4244.
- Teixeira, J. (1988). *J. Appl. Cryst.* **21**, 781-785.

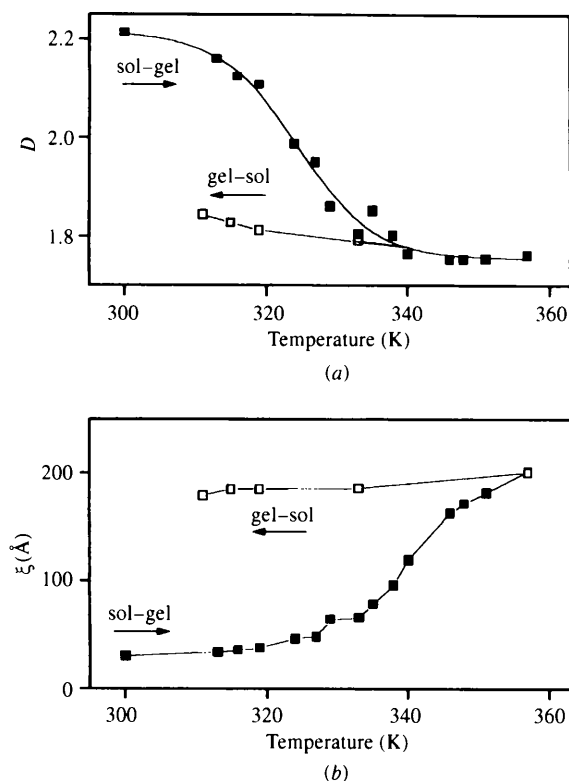


Fig. 5. Temperature dependence of (a) the fractal dimensionality D and (b) the size of aggregates ξ , obtained from the fittings using (2).