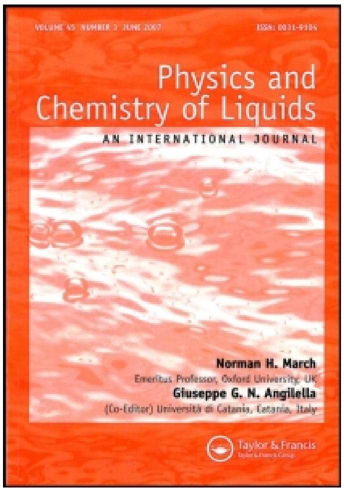

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S. D. Romano[a]; D. H. Kurlat[a]
[a] Departamento de Física, Facultad de Ingeniería, Universidad de Buenos Aires, Buenos Aires, Argentina

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RHEOLOGICAL MEASUREMENTS IN TITANIA GELS SYNTHESIZED FROM REVERSE MICELLES

S. D. ROMANO and D. H. KURLAT*

Departamento de Física, Facultad de Ingeniería, Universidad de Buenos Aires. Av. Paseo Colón 850, (1063) Buenos Aires, Argentina

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TiO_2 sol and gel systems have been synthesized by hydrolysis of titanium butoxide in microemulsions W/O. Different systems compositions were prepared at constant $W_o = [H_2O]/[AOT]$ and changing $R = [H_2O]/[Ti(BuO)_4]$. Experimental measurements show a progressive increase of the viscosity with time, characteristic of a sol-gel transition. The rheology of the transition was studied by following the behavior of viscoelastic parameters (G', G'' and η^*) as a function of time at different frequencies.

The possibility to apply standard percolation theory was discussed. The application of two alternative growth models-either "fractal growth model" or "nearly linear growth model"-has been analysed.

Keywords: TiO_2; Rheology; Sol-gel transition; Microemulsions W/O

INTRODUCTION

A very important problem, from a technological point of view, is the ability to synthesize TiO_2 nanometric particles. This oxide, is a non-toxic semiconductor which can be used in several processes, *i.e.*, as a photocatalyst for solar energy conversion, water detoxification, anti-reflective coatings, *etc.* [1].

Now, microemulsions are a very useful kind of systems in the production of nanoparticles because the droplets in solution are of the similar size as the particles to be produced and the system presents

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*Corresponding author.

thermodynamic stability. Hence, some experimental methods have been developed in order to capture the droplet microestructure, by using hydrolysis and condensation reactions inside the inverse micelles [2, 3].

On the other hand, due to the need to fix the particles onto a substrate, it is necessary to obtain a gel from the corresponding sol.

The goal of this work is to study the sol–gel transition in these systems.

EXPERIMENTAL

Materials and Methods

Reverse micelles were prepared from distilled water and AOT (sodium bis (2 ethylhexyl) sulfosuccinate, Sigma, 99%) dissolved in isooctane. Titania sols were synthesized by adding titanium butoxide ($Ti(BuO)_4$) to the microemulsion under continuous stirring. The molar relation between water and AOT ($W_o = [H_2O]/[AOT]$) was held constant ($W_o =$ 0.65 w/w) whereas $R = [H_2O]/[Ti(BuO)_4]$ was changed between 2 and 3. All chemical reactions were performed at constant temperature (25°C).

$$\begin{aligned} Ti[O(CH_2)_3CH_3]_4 + xH_2O \rightarrow {} & Ti[(OH)_x(O(CH_2)_3CH_3)_{(4-x)}] \\ & + xCH_3(CH_2)_2CH_2OH \end{aligned}$$

$$\begin{aligned} & Ti[(OH)_x(O(CH_2)_3CH_3)_{(4-x)}] + (4-x)H_2O \\ & \quad \rightarrow TiO_2 + (4-x)CH_3(CH_2)_2CH_2OH + 2H_2O \end{aligned}$$

The isooctane range concentration in the microemulsions changed between 60% and 80% (w/w), whereas the water concentration was lower than 1% (w/w) in all the cases. Immediately after the compounds are mixed, all samples are optically transparent, low viscosity solutions. As the time raises, the sol viscosity increases and the system evolves towards a white gel. The time of gelification depends on the sample composition and it was determinated at the crossing-point of G' and G'', at the lowest frequency [4].

The viscoelastic measurements have been performed in a "Rheometrics RFR 788" (Lehrstuhl für Physikalische Chemie I, Universität Bayreuth).

TABLE I Samples components concentration

Sample	AOT (%w/w)	iC_8H_{18} (%w/w)	H_2O (%w/w)	$Ti(BuO)_4$ (%w/w)	W_o $[H_2O]/[AOT]$	R $[H_2O]/[Ti(BuO)_4]$
1	34.80	55.74	0.91	8.55	0.65	2.00
2	29.10	65.37	0.76	4.77	0.65	3.00
3	19.10	76.63	0.50	3.77	0.65	2.50

Different samples components concentration are shown in Table I.

RESULTS

The different rheological parameters (G'-elastic modulus-, G''-loss modulus-and η^*-complex viscosity-) have been measured by varying either the frequencies (0.1 rad/sec < ω < 60 rad/sec) or the butoxide concentration at constant frequency (ω = 10 rad/sec).

In Figure 1a G' and G'' experimental values as a function of time (ω = 20 rad/sec) are shown. The behaviour of both physical magnitudes are typical ones [5], being $G' < G''$ at the beginning of the experience, whereas at increasing times this fact is clearly

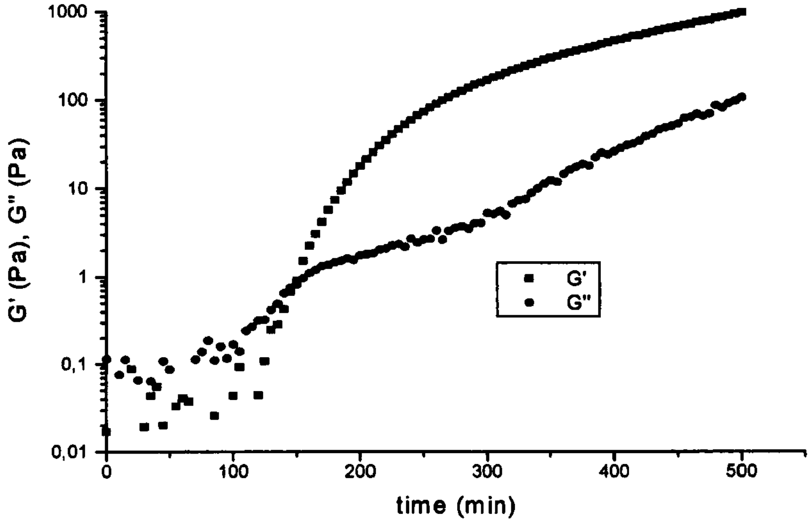

FIGURE 1a G' and G'' experimental values as a function of time (sample 1; ω = 20 rad/sec).

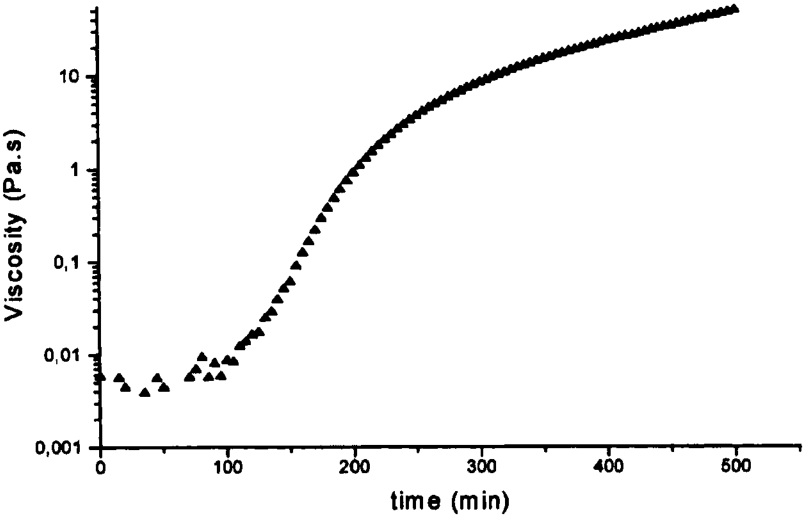

FIGURE 1b η^* experimental values as a function of time (sample 1; $\omega = 20$ rad/sec).

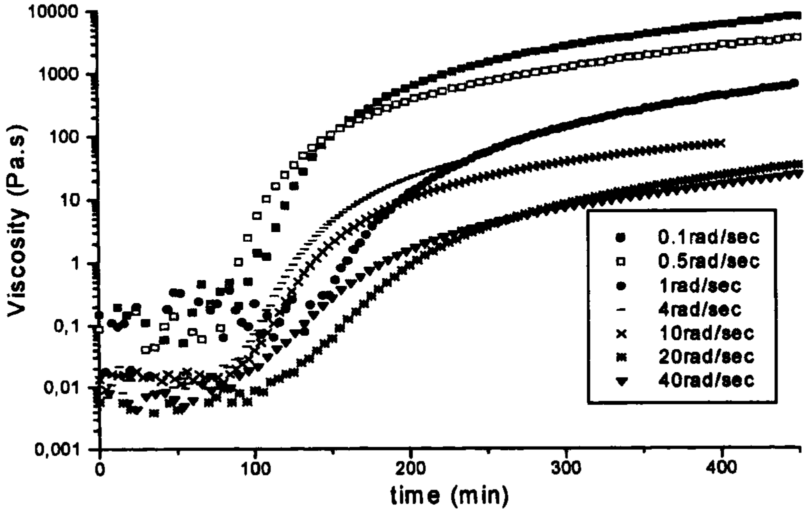

FIGURE 2 η^* experimental values as a function of time at different frequencies (sample 1).

reversed ($G' > G''$). In Figure 1b is shown a typical η^* variation curve as a function of time ($\omega = 20$ rad/sec). After a certain time η^* tends to saturation.

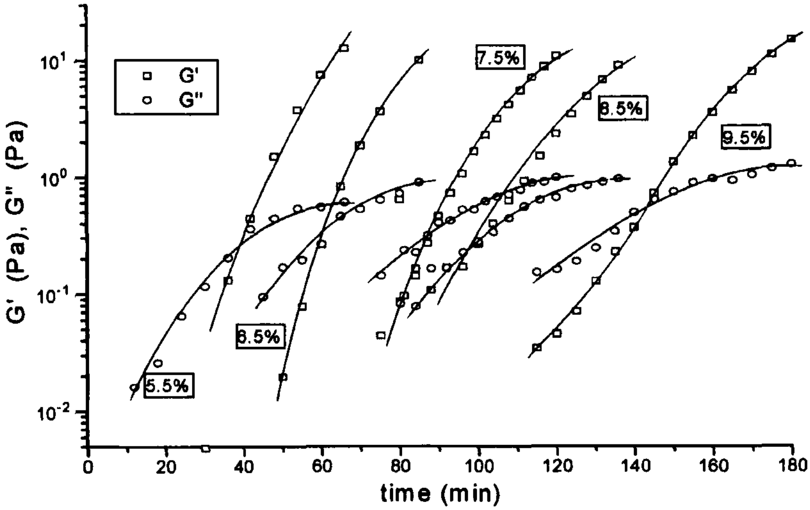

FIGURE 3 G' and G'' cross points as a function of time for different $Ti(BuO)_4$ concentrations ($\omega = 10$ rad/sec).

In Figure 2 is shown that η^* experimental values growths while frequency diminishes after the gelification time (t_{gel}) is attained.

In Figure 3 is shown the time in which occurs the intersection between G' and G'' curves for different concentrations of $Ti(BuO)_4$ ($\omega = 10$ rad/sec). The composition of the microemulsion is the same than in sample 1. $Ti(BuO)_4$ concentration was changed between 5 and 10%. The necessary time in which the condition $G' = G''$ is hold increases with the concentration of $Ti(BuO)_4$ in the sample.

DISCUSSION

The theoretical basis of scaling expressions [6, 7] is the analogy first proposed by De Gennes between the A. C. conductivity of a resistor-capacitor random mixture and the viscoelastic modulus.

Later experimental works [8, 9] supported the above mentioned proposal.

According to the scaling theory [10]

$$\delta^* = \frac{\pi(1-\Delta)}{2} = \frac{\pi}{2}\left(\frac{k}{f+k}\right) \tag{1}$$

being

$$\Delta = \frac{f}{f+k} \quad \begin{cases} f = 1.94 \\ k = 0.75 \end{cases} \Rightarrow \Delta = 0.72 \tag{2}$$

Now, Δ is the critical exponent which rules the behaviour of G' and G'' near the t_{gel}, according to the following expression:

$$G' \cong G'' \cong \omega^{\Delta} \tag{3}$$

This approach is still an open question [10], being Δ values under controversy.

When we represent $\log G'$ *versus* $\log \omega$ at different times, it is clearly observed that there is not possible to adjust the experimental data points by means of a linear representation. On the other hand, the behaviour of $\log G''$ *versus* $\log \omega$ at different times is linear, being the slope $0.48 < \Delta < 0.54$ (Fig. 4).

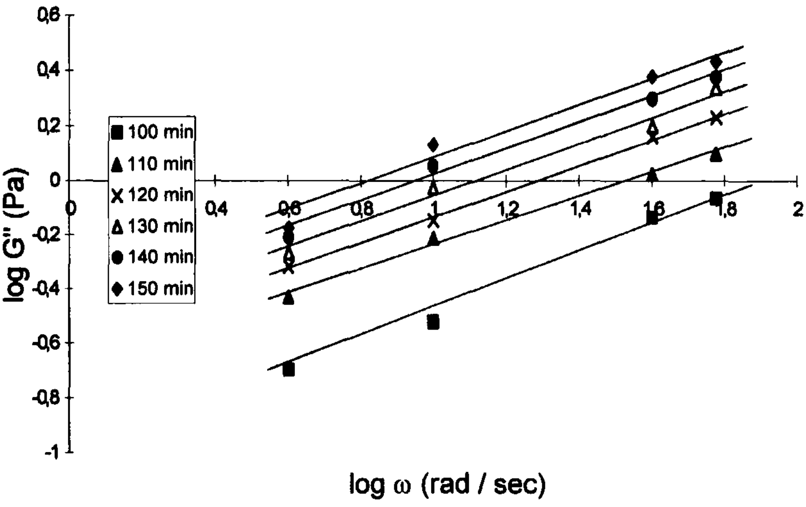

FIGURE 4 Log G'' *versus* $\log \omega$ (sample 1).

Pope and Mackenzie [11] have proposed two alternative theoretical models to describe the viscosity-time relations. These are the "nearly linear growth model" and the "fractal growth model". The first one is applied to linear or nearly linear gel structures. In these kind of systems the degree of cross-linking may be neglected. The second is able to describe the evolution of a system in which a high degree of cross-linking has occurred. It is natural to consider the latter case as a typical fractal theory problem. Both models predict the viscosity-time behaviour, as a linear relation. Hence, in principle it is possible to distinguish between a linear from a branched growth, by plotting the viscosity *versus* time curve.

In both models the well-known Einstein's equation for the viscosity of a suspension of particles in a fluid is applied

$$\eta^* = \eta_o(1 + LC) \tag{4}$$

η_o: viscosity of the pure fluid,
C: volume concentration of particles,
L: a geometrical shape constant.

The specific viscosity (η_s) is defined as:

$$\eta_s = \frac{\eta^* - \eta_o}{\eta_o} \tag{5}$$

The growth in molecular weight or in mass [12] of a fractal object varies with its radius (r) as

$$M = Ar^D \tag{6}$$

where D is the fractal dimension.

On the other hand, Cannel and Aubert [13] have proposed that the particle radius (r) increases exponentially as:

$$\frac{r}{r_o} = e^{q_r t} \tag{7}$$

r_o: core radius,
q_r: radius exponential rate constant.

After a little algebraic calculation

$$\ln \eta_s = \ln(QL/\rho_o) + (3 - D)q_r t \tag{8}$$

Q: mass concentration of monomer in solution,
ρ_o: fractal core density.

Hence a plot of $\ln \eta_s$ as a function of time should show a linear behaviour in the case of fractal growth regime.

In Figure 5 a curve of $\ln \eta_s$ *versus* t/t_{gel} ($\omega = 10$ rad/sec) show a linear behaviour for $0.6 < t/t_{\text{gel}} < 0.8$.

In Table II the corresponding correlation coefficients for all the samples are shown.

The nearly linear growth model [13] proposes the following relationship:

$$\ln \eta^* = \ln A + m \ln \Omega + m \ln\left(\frac{\alpha}{1-\alpha}\right) \tag{9}$$

where

$$\Omega = \frac{2M_o}{\beta},$$

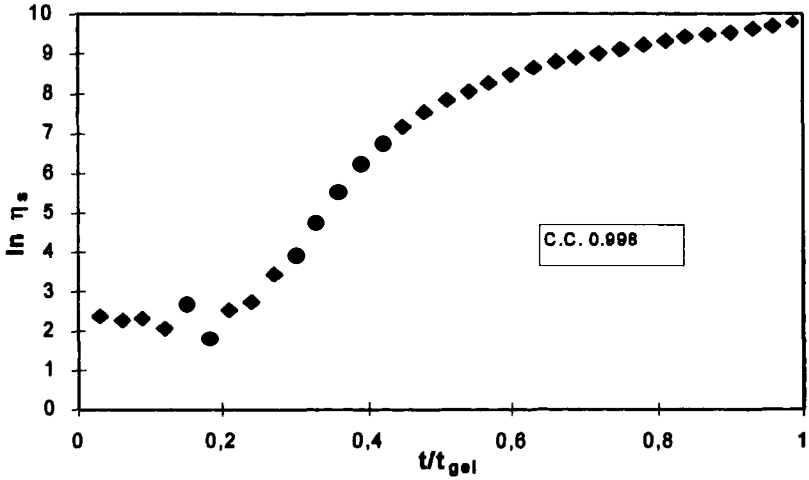

FIGURE 5 $\text{Ln}\,\eta_s$ as a function of t/t_{gel} (sample 2; $\omega = 10$ rad/sec).

TABLE II Correlation coefficients

Frequencies (rad/sec)	*Correlation coefficient (Sample* 1)	*Correlation coefficient (Sample* 2)	*Correlation coefficient (Sample* 3)
0.1	0.996	0.997	0.998
0.5	0.995	–	0.998
1	0.998	0.997	0.991
4	0.997	$\cong 1$	$\cong 1$
7	0.993	0.996	$\cong 1$
10	0.998	0.998	0.998
20	0.998	0.998	0.998
40	0.997	$\cong 1$	–
60	$\cong 1$	$\cong 1$	$\cong 1$

M_o: initial molecular weight of monomer;
β: $f-2$ (f: functionality) and

$$\alpha = \frac{t}{t_{\text{gel}}}.$$

This equation is clearly different from the (8). In order to test the validity of this model we have represented $\ln \eta^*$ *vs.* $\ln(\alpha/(1-\alpha))$. The curves are not linear.

We can conclude that the growth process can be described by the fractal growth model.

CONCLUSIONS

Sols containing TiO_2 nanoparticles evolve with time towards a gel system.

Rheological measurements were performed in these systems in order to study the sol-gel transition. Viscoelastic parameters (G', G'' and η^*) were measured as a function of time at different frequencies. The gelification point depends on the ratios $[H_2O]/[AOT]$ and $[H_2O]/[Ti(BuO)_4]$.

From the representation of viscoelastic parameters as a function of the frequency, it is not possible to validate the scaling hypothesis.

On the other hand, two different growth models have been analysed. Both of them predict the evolution of the viscosity as a linear function of time. The fractal growth model equation gives a better adjustment than the other one.

Acknowledgements

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