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KERR EFFECT IN SYSTEMS CONTAINING TiO₂ NANOPARTICLES

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Kerr effect measurements as a function of the relation [water]/[alkoxide] concentration (h) were performed. These systems were prepared from water/AOT/isooctane microemulsions by adding titanium (IV) butoxide. From a certain h value it was observed that Kerr constant values change abruptly. This behaviour is indicative of the beginning of the sol–gel transition. The influence of the overall alkoxide concentration is discussed.

Keywords: Kerr effect; titanium dioxide; sol–gel transition; polymerized microemulsions

INTRODUCTION

Nowadays, there is an increasing interest in order to obtain metallic, semiconductor or metallic halides nanoparticles [1, 2]. Among these systems, those which contain TiO₂ outstand due to their important technological applications [3]. Different authors have developed a process in which ultrafine particles are formed [4, 5]. The main idea was to “capture” the microemulsion size by hydrolysis and condensation reactions which take place inside the inverse micelle. On the other hand, for specific applications it is convenient to fix the particles onto an adequate substrate. A possible way to fulfil this requirement is by forming a gel. Hence, the analysis of the sol–gel transition is

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particularly suitable. Different experimental techniques (SANS [6], SAXS [7], DLS [8], visible-ultraviolet absorption [9]) have been applied to the study of this problem.

In this work, we present experimental results related to the sol–gel transition which have been obtained by using static Kerr effect technique.

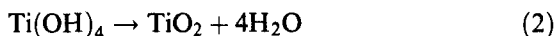
EXPERIMENTAL

Samples Preparation

Reverse (W/O) microemulsions were prepared by mixing water (double distilled), AOT (sodium, bis 2 ethylhexyl sulfosuccinate – Sigma 99%) and isooctane (Fluka, HLPC grade). By adding titanium (IV) butoxide (Fluka) to each microemulsion either sols and gels of titania were prepared. The overall hydrolysis reaction may be described by the following [4, 5]:



Titanium dioxide is obtained by condensation:



There are three relevant parameters [7] which are W_o (mol/mol), h (mol/mol) and m (mol/kg of solution), where are $W_o = [\text{H}_2\text{O}]/[\text{SURFACTANT}]$, $h = [\text{H}_2\text{O}]/[\text{ALCOXYDE}]$ and $m = [\text{ALCOXYDE}]$. The size and number of the micelles is controlled by W_o whereas h controls the hydrolysis rate.

In Table I components concentration of each microemulsion and the W_o parameter are shown. In Table II the percent of $\text{Ti}(\text{BuO})_4$

TABLE I Microemulsions components concentration and W_o parameter

	<i>Isooctane</i> % (w/w)	<i>Water</i> % (w/w)	<i>AOT</i> % (w/w)	W_o
Microemulsion I	79.47	0.53	20.00	0.65
Microemulsion II	68.25	0.82	30.93	0.65

TABLE II Titanium (IV) butoxide percent (weight $Ti(BuO)_4$ /weight of solution) added to microemulsion I (serie I), to microemulsion II (serie II) and m and h parameters

Serie I			Serie II		
% $Ti(BuO)_4$	m	h	% $Ti(BuO)_4$	m	h
11.093	0.326	0.80	11.402	0.335	1.20
9.983	0.293	0.90	10.618	0.312	1.30
9.076	0.267	1.00	9.935	0.292	1.40
8.319	0.244	1.10	9.625	0.283	1.45
7.861	0.231	1.17	9.335	0.274	1.50
7.679	0.226	1.20	8.802	0.259	1.60
			8.328	0.245	1.70
			8.109	0.238	1.75

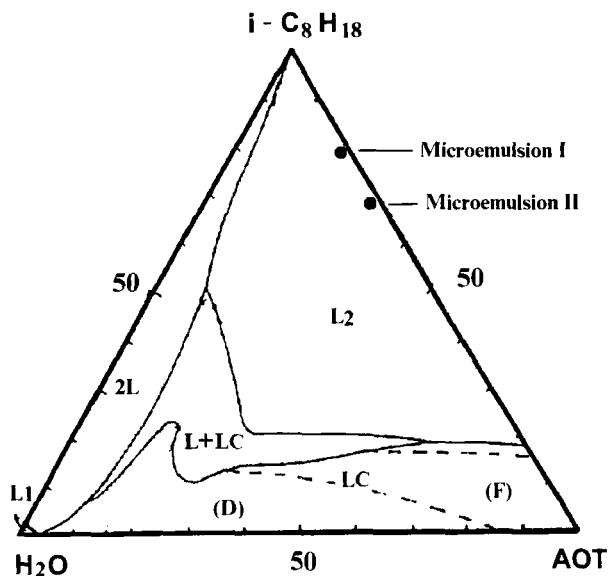


FIGURE 1 Location of initial microemulsions compositions in the ternary phase diagram AOT/water/isooctane. L_1 means aqueous micellar solution, 2L emulsion, L_2 reversed micellar solution, LC liquid crystal whose structure being divided into lamellar (D) and hexagonal (F) types and LC the phase region where liquid crystal exists in equilibrium with solution.

(weight/weight) which was added to each microemulsion and m and h parameters are shown. Both initial microemulsions composition have been indicated in the ternary phase diagram [10] (Fig. 1).

Kerr Effect Technique

The apparatus used to study the Kerr effect is similar to those described in the literature dealing with this subject [11]. A laser beam ($\lambda = 632.8$ nm) polarized by means of a Glan–Thomson type polarizer, passes through a cell where the liquid sample is placed. The cell is composed of an optical cuvette (Hellma QS 500; $L = 50$ mm) and two electrodes separated by a 2.0 mm distance. Both electrodes are connected to a pulsed high voltage (up to 2.5 kV) source. The rise-time of the source is < 100 ns. The cell is immersed in a thermostatic bath. On leaving the cell, the beam goes through a second polarizer (analyser). The optical axes of the first and second polarizer are at 45° and 135° respectively from the direction of the electric field. A quarter-wave plate is placed between the cell and the analyser. The polarizer extinction coefficient is of the order of 10^{-5} . The light signal is detected by a photodiode (THORLABS PDA 155). The light intensity detected in the photodetector is related to the expression

$$\Delta n = n_p - n_t = \lambda B E^2 \quad (3)$$

where n_p and n_t are parallel and perpendicular refractive indices in respect of the field direction, E is the orientation field strength, λ the laser vacuum wavelength and B the Kerr constant.

All measurements were performed (at 298 K) after one hour of each sample preparation in order to normalise the results. By visual inspection we have observed that all samples were transparent, isotropic and with high fluidity at the beginning of the experience.

EXPERIMENTAL RESULTS AND DISCUSSION

Kerr experimental values as a function of h are represented in Figures 2a and 2b. For serie I, the Kerr constant increases abruptly for $1.10 \leq h \leq 1.20$ whereas for $h < 1.10$, it remains nearly constant. A similar qualitative behaviour was observed for serie II (B remains nearly constant for $h < 1.45$ and it increases abruptly for $h > 1.50$). For $h > 1.20$ (serie I) and $h > 1.75$ (serie II), B values fluctuate because the gel is not stabilised. For both series, it was observed that the abrupt change in B value is coincident with a greater light dispersion and a

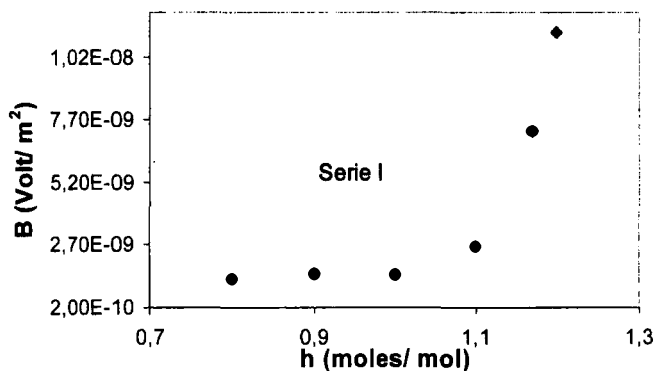


FIGURE 2a Kerr constant as a function of [water]/[alkoxide] relation (serie I).

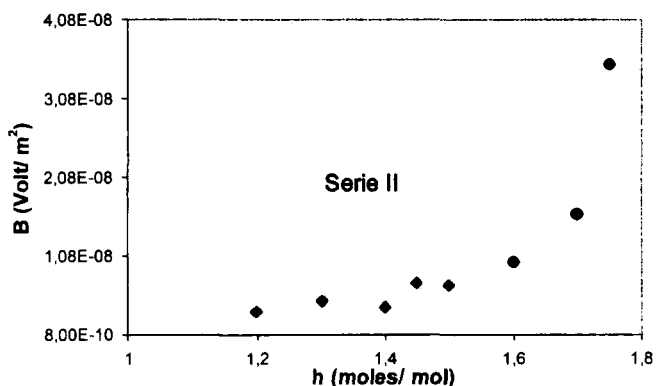
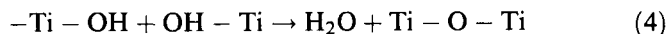


FIGURE 2b Kerr constant as a function of [water]/[alkoxide] relation (serie II).

pronounced lower fluidity. This behaviour corresponds to the sol-gel transition and the zone change regime is very narrow. It must be pointed out that, in our case, the smaller the quantity of titanium (IV) butoxide, the greater the gelification rate. Now, the gelification mechanism explanation in these systems is an open question.

Generally, it is accepted that the gel formation is linked to the TiO_2 synthesis. Subsequently, hydrolysed monomers stick together and form the polymer backbone ("polymeric microemulsions" [12]):



Some authors, by using different experimental techniques, have determined the fractal structure of these systems [6]. Unfortunately, as it has been pointed out [13], there is no satisfactory Kerr constant theory for dispersions of particles of arbitrary shape and size. It is not clearly established neither the relative position of surfactant molecules nor the alkoxyde after the chemical reaction was produced. Two different models have been suggested:

- (i) The surfactant and (eventually) the alcohol surround TiO_2 nanoparticles and a progressive branching of these new entities generates the gel.
- (ii) Both, surfactant and alcohol, are dispersed in the continuous medium and a progressive bonding of oxide particles takes place. Auvray [14] has claimed that the latter hypothesis is the correct one.

Following the Table II on composition data, we can see that our m interval values are:

$$0.226 \leq m \leq 0.326 \text{ (serie I)}$$

$$0.238 \leq m \leq 0.335 \text{ (serie II)}$$

Now, it must be pointed out that the gel formation depends on the [water]/[alkoxyde] relation (see Eqs. (1) and (2)). W_o values are indicative that each droplet has a little water content. Hence, the possibility of formation of a stable network is difficult.

In spite of the absence of a straightforward interpretation, Kerr effect has proved to be a useful tool to detect the beginning of the sol–gel transition.

CONCLUSIONS

The main purpose of this work was to follow the Kerr constant behaviour in systems containing TiO_2 nanoparticles as a function of the initial [water]/[titanium (IV) butoxide] relation. We have observed that:

- The Kerr constant behaviour is clearly different in two h intervals. It can be inferred that this is a consequence of the sol–gel transition.
- The capacity of gelification does not depend only on the overall titanium (IV) butoxide concentration but also the [water]/[titanium (IV) butoxide] relation.

The Kerr effect as other optical techniques is very sensitive to the gel initial stage formation.

References

- [1] Desai, S. D., Gordon, R. D., Gronda, A. M. and Cussier, E. L., Polymerized Microemulsions In: *Current Opinion in Colloid and Interface Science*, Vol. 1, No. 4 (August 1996). Eds. Kaler, E. W. and Robinson, B. H.
- [2] Sager, W. F. C. (1998). *Current Opinion in Colloid and Interface Science*, **3**, 276–288.
- [3] Balfour, J. G., Titanium Dioxide Pigments in Technological Applications of Dispersions: *Surfactant Science Series*, Vol. 52, 1994, Ed. McKay, R. B.
- [4] Joselevich, E. and Willner, I. (1994). *J. Phys. Chem.*, **98**, 7628–7635.
- [5] Chhabra, V., Pillai, V., Mishra, B. K., Morrone, A. and Shah, D. O. (1995). *Langmuir*, **11**, 3307–3311.
- [6] Marignan, J., Guizard, C. and Larbot, A. (1989). *Europhysics Lett.*, **8**(7), 691–696.
- [7] Lebon, S., Marignan, J. and Appell, J. (1992). *J. of Non-Cryst. Solids*, **147 & 148**, 92–96.
- [8] Barthez, J. M., Ayrat, A., Hovnanian, H., Guizard, C., Cot, L. and Marignan, J. (1994). *J. of Sol–Gel Sc. Tech.*, **2**, 283–287.
- [9] Hirai, T., Sato, H. and Komasaawa, I. (1993). *Ind. Eng. Chem. Res.*, **32**, 3014–3019.
- [10] Tamamushi, B. and Watanabe, N. (1980). *Coll. & Polym. Sci.*, **258**, 174–178.
- [11] Fredericq, E. and Houssier, C., “*Electric dichroism and electric birefringence*” (Clarendon Press, Oxford 1973).
- [12] Candau, F., “*Polymerization in Microemulsions*” in Polymerization in Organized Media. Gordon and Breach Science Publishers, Ed. Paleos, C. M., 1992.
- [13] Mantegazza, F., Giardini, M. E., Degiorgio, V., Asnaghi, D. and Giglio, M. (1995). *J. of Coll. and Interf. Sc.*, **170**, 50–56.
- [14] Auvray, L., Ayrat, A., Cot, L., Dabadie, T., Guizard, C. and Ramsay, J. (1994). *J. of Sol–Gel Sc. and Tech.*, **2**, 205–209.