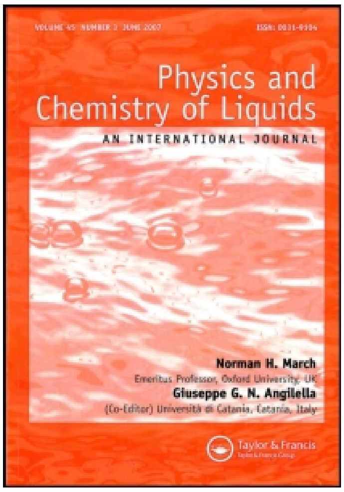

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KERR EFFECT OF XANTHAN/DTAB AQUEOUS SOLUTIONS

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The Kerr effect of the Xanthan (charged polyelectrolyte; 113 ppm)/DTAB (surfactant) mixture in aqueous solution was studied. The static Kerr constant (B) and mean relaxation times (τ) values as a function of surfactant concentration (C_{DTAB}) were determined. The observed birefringence (Δn) is not a linear function of the electric applied field (E^2). For small E values Δn grows with E^2 and at a certain field value the birefringence tends to saturate. The addition of small quantities of DTAB lowers B values with respect to the Kerr constant of Xanthan (113 ppm) aqueous solution. The relaxation time of the mixtures is linearly dependent on the applied field and it decreases when DTAB concentration increases. The importance of the equivalent point is signalled. It is supposed that the initial rigidity of the polyelectrolite decreases because of the surfactant addition. Conductivity (σ) values as a function of surfactant concentration are presented.

Keywords: Kerr effect; Polymer surfactant systems

Physical Abstract Classification: 78.20; 82.70

INTRODUCTION

Polymer–surfactants water soluble mixtures are very interesting for their technological applications. These systems present a broad range of properties such as emulsification, flocculation, rheological control etc. Typical examples are paints, detergents, cosmetics, personal care products etc.

On the other hand, to understand their physical-chemical properties from a basic point of view presents a challenge [1].

It is well known that at low surfactant concentrations, the presence of a polymer may or may not lower the surface tensión which is due to the surfactant alone. This is dependent on the polymer–surfactant interaction and the polymer surface activity. When the surfactant concentration rises, the surface tension (γ) curve shows a break and a γ constant value (plateau) is attained. The usual interpretation of this behaviour is as follows: the plateau starting is related to the onset of association of surfactant to the polymer. This characteristic concentration is coined as "critical aggregation

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concentration'' or CAC [2]. It is a matter of controversy to accept whether the presence of the plateau and the corresponding CAC is a general feature of these systems.

When the polymer is saturated and the surfactant concentration is increased, the surface tensión decreases again until the concentration reaches the CMC. Some experimental techniques-spectroscopic analysis, self-diffusion, surfactant selective electrodes or equilibrium dialysis – have sustained this description [1,2].

In a previous paper, the influence of polymer backbone rigidity on polyelectrolite–surfactant complexes surface behaviour was studied by applying surface tension and X-ray reflectivity [3]. A very important question is to relate surface and bulk properties. In order to achieve this goal we have performed static and dynamic Kerr effect measurements.

EXPERIMENTAL

Materials

We have used mixtures of dodecyltrimethil ammonium bromide (DTAB)(surfactant) and Xanthan (polyelectrolyte).

The DTAB is a cationic surfactant and was obtained by Sigma (99%) and used without further purification. Xanthan is an extracellular polysacharide produced by fermentation of the microorganism *Xanthomonas campestris*. It consists of a linear 1–4 linked D-glucan chain substituted on every glucose residue by a tyrisaccharide side chain. It was provided by the ''Institute Français de Petrole''. The DTAB concentration range varied between 0.01 and 1.0 mM. The Xanthan has the following characteristics:

Molecular weight of the polyelectrolyte (M_R) = 1.8.10^6 g/mol.
Molecular weight of each monomer = 930 g/mol.
Number of monomeric units = 2000.
Charge = 1.5 elementary negative charge per monomer.

METHODS

Kerr Effect

Under the action of an external electric field (E) a sample, originally isotropic, becomes birefringent. This process is called Kerr effect.

The experimental procedure to measure this effect has been described in some previous papers [4].

Static Kerr Effect

A laser beam ($\lambda = 632.8$ nm) is polarised by means of a Glan-Thomson type polariser. The beam passes through an optical cuvette (Hellma QS 500; 50 mm in length) where the liquid sample is placed. Inside the cuvette there are two stainless steel plates (electrodes) separated by a 2.0 mm distance. Both electrodes are connected to a pulsed high voltage source (up to 2.5 kV) with a rise time less than 100 ns. On leaving the cuvette the laser beam goes through a second polariser (''analyser''). Optical axes of polariser and analyser are at 45° and 135° respectively from the E direction. In order to measure the

Kerr constant sign a quarter wave plate is placed between cuvette and analyser. The light intensity is related to the expression

$$\Delta n = n_p - n_t = \lambda B \cdot E^2.$$

where n_p and n_t are parallel and perpendicular refractive indices with respect to E direction, and B, the Kerr constant. All measurements were performed at 298 K. The maximum field strength used in our experience was 20 kV/cm.

Dynamic Kerr Effect

The relaxation time is obtained by the analysis of the decay curves under field-free conditions [5]. We have calculated the average relaxation time defined as:

$$\tau = \int_0^t \frac{\Delta n(t)\, dt}{\Delta n_0}$$

where $\Delta n(t)$ is the decay curve and Δn_0 the birefringence at the steady state.

The electronic relaxation time is 3 μs.

Conductivity

We have used an A.C bridge and a standard cell of conductance.

EXPERIMENTAL RESULTS

Conductivity

Conductivity measurements (σ) of the Xanthan (113 ppm)/DTAB aqueous solution systems as a function of the DTAB concentration (C_{DTAB}) or the DTAB concentration square root (C_{DTAB} 1/2) are shown in Figs. 1A and B respectively. It can be seen (Fig. 1A) that at $C_{DTAB} \equiv 0.2$ mM conductivity attains a maximum. For higher concentrations a solute precipitation is observed.

Static Kerr Effect

In Figs. 2A, B and C induced birefringence (Δn) experimental results as function of the square of the external applied field (E^2) are shown. In Fig. 2A the Xanthan (113 ppm) in aqueous solution birefringence is represented. Figure 2B is presented as a particular example of the general behaviour of these systems. In Fig. 2C the ensemble of results is shown. It can clearly be seen that Δn is not a linear function of E^2 (for small E values). In every case the qualitative behaviour is very similar, namely it grows with E^2 and at certain field square value, Δn tends to saturate. Because of this non-linear behaviour, a polynomial in powers of E^2 was fitted to the Δn experimental values [6]. The coefficient of the first term of this expansion is the Kerr constant. The coefficients of the higher order terms depend on the type of orientation mechanism.

In Fig. 3 the Kerr constant(B) variation of the mixture Xanthan (113 ppm) as a function of surfactant concentration is represented. The addition of small DTAB quantities

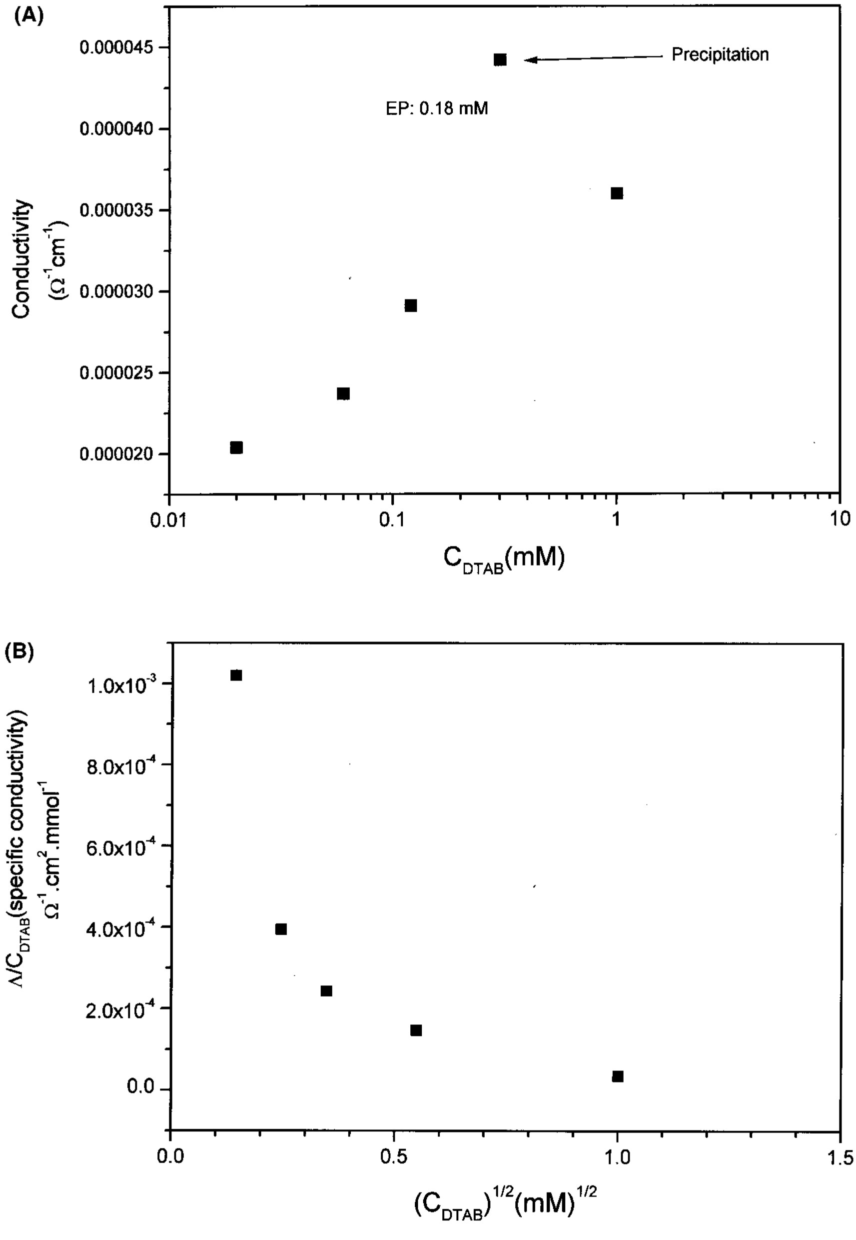

FIGURE 1 (A) Conductivity (σ) as a function of DTAB concentration (C_{DTAB}); (B) Specific conductivity (Λ/C_{DTAB}) as function of $(C_{DTAB})^{1/2}$.

lowers the Kerr constant values of the mixture with respect to pure Xanthan (113 ppm) aqueous solution. As DTAB concentration is increased, the Kerr constant values increase, becoming greater than the Kerr of pure Xanthan in water. It must be pointed out that for a DTAB concentration greater than ≈0.18 mM a two phase formation starts. It can be appreciated by visual inspection that there is a gel-like phase which is immersed into the liquid phase.

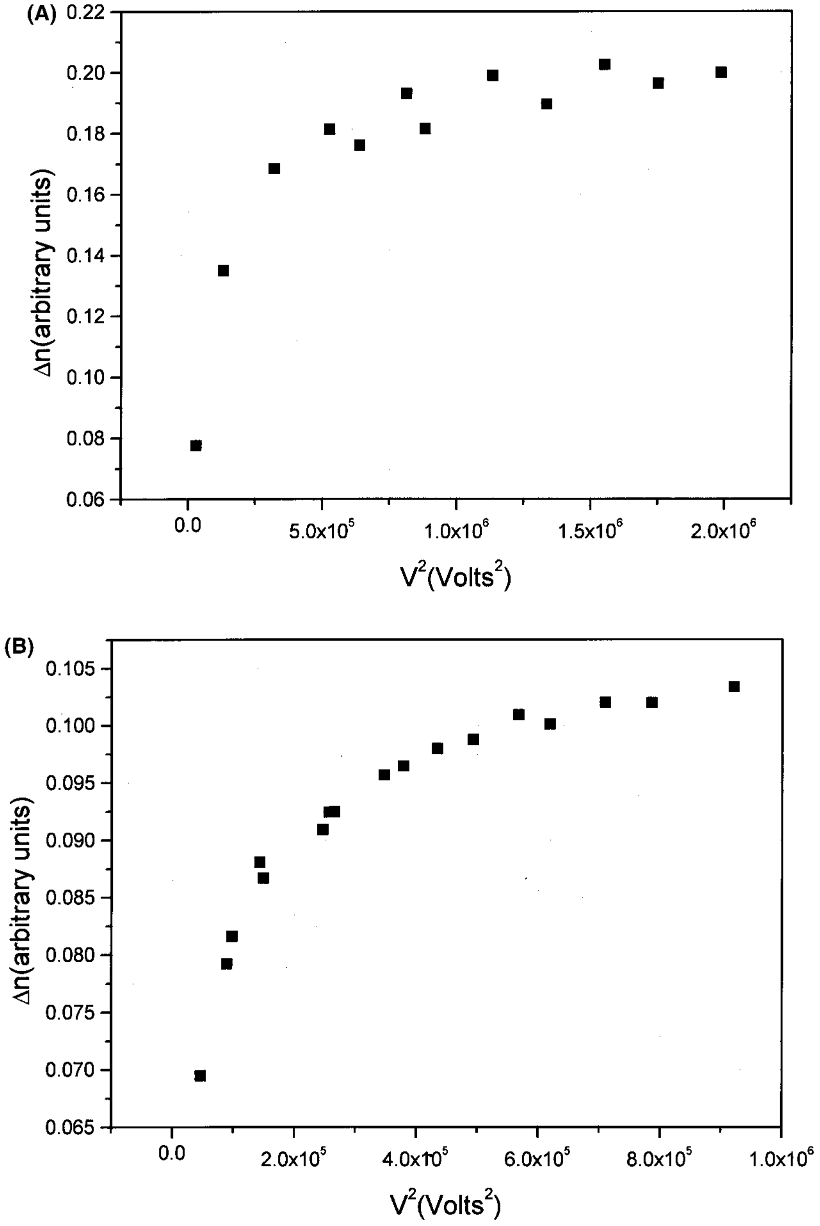

FIGURE 2 (A) Birefringence (Δn) of the Xanthan (113 ppm) aqueous solution as a function of the square of the applied voltage (V^2); (B) Birefringence (Δn) of the Xanthan (113)/DTAB (0.02 mM) aqueous solution as a function of the square of the applied voltage (V^2); (C) Birefringence (Δn) of the Xanthan/DTAB aqueous solution for different DTAB concentrations as a function of the square of the applied voltage (V^2).

Dynamic Kerr Effect

Relaxation time values (τ) are represented in Figs. 4A, B and C. A very interesting feature in the time relaxation behaviour, which is shown in Figs. 4A and B is

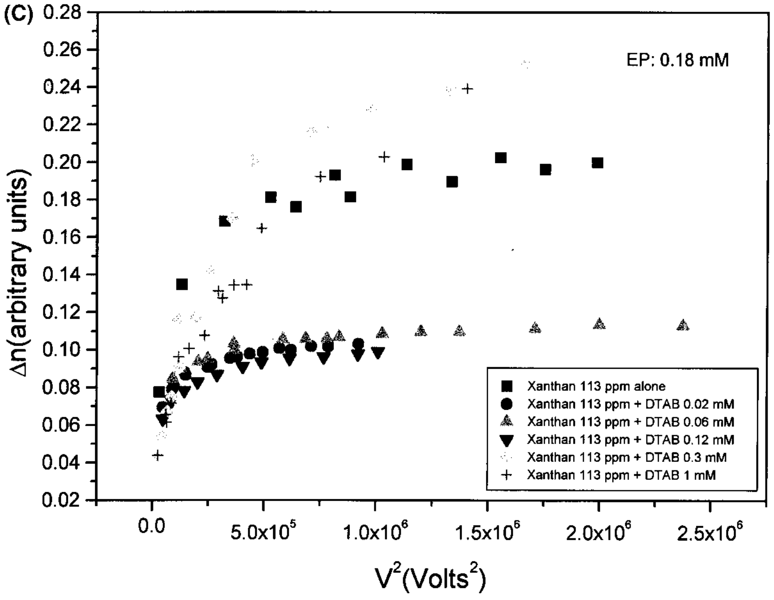

FIGURE 2 (Continued).

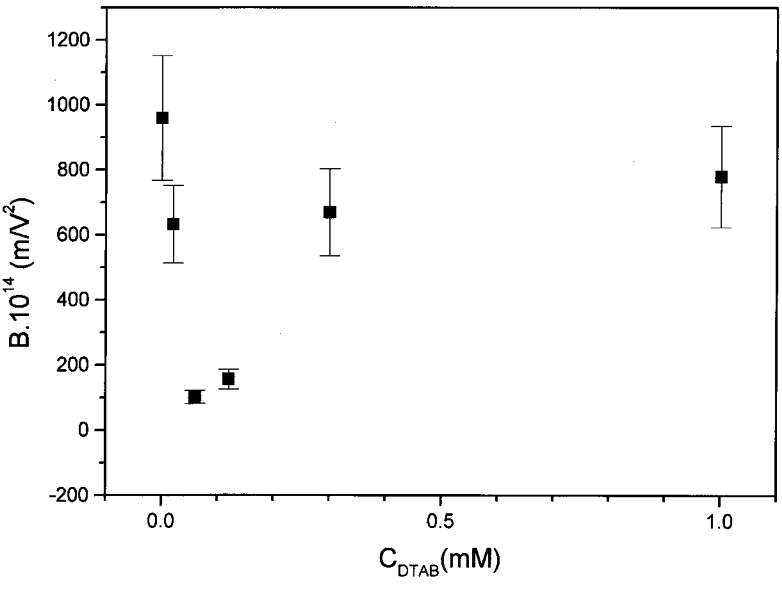

FIGURE 3 Kerr constant (B) of Xanthan (113 ppm)/DTAB mixture in aqueous solution as a function of DTAB concentration (C_{DTAB}).

that τ depends in a linear way on the electric field which is applied before being turned off.

Xanthan (113 ppm) in aqueous solution relaxation time is 50 ms approximately. This value is not dependent on the applied external field. When the DTAB is added τ

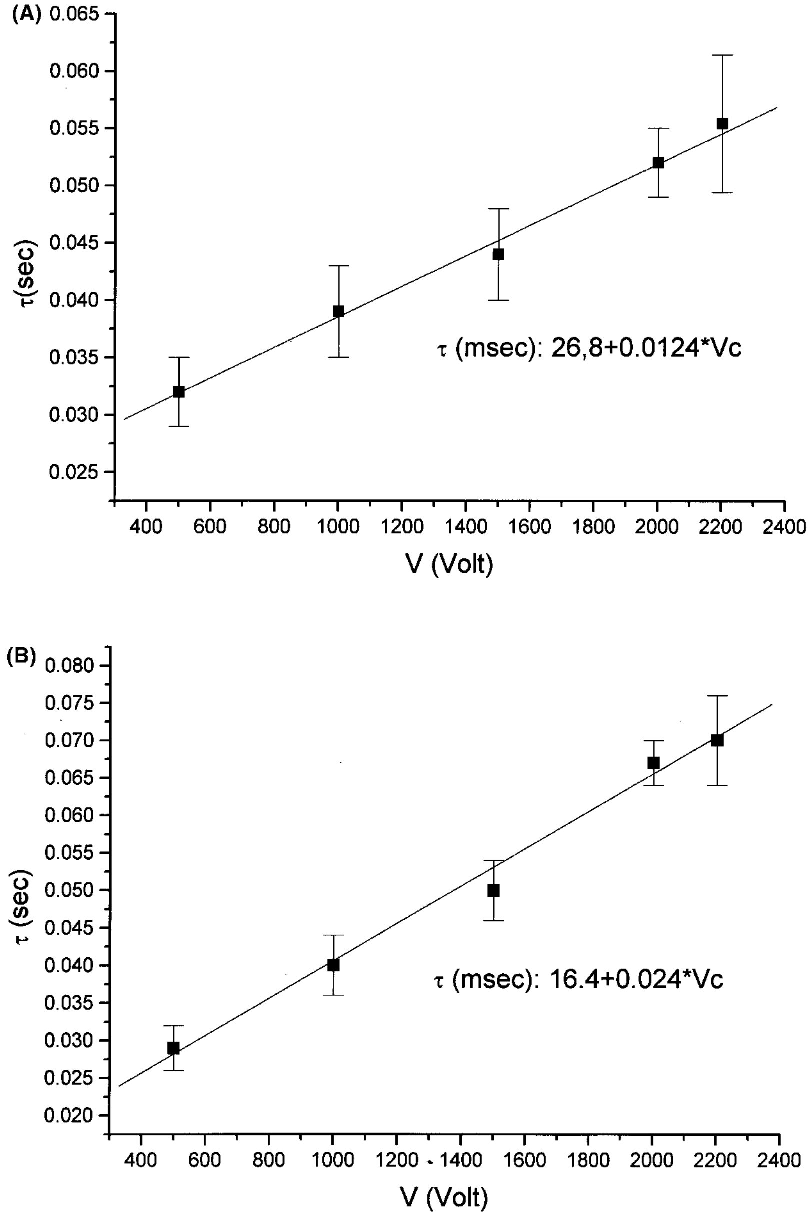

FIGURE 4 (A) Relaxation time (τ) of the Xanthan (113 ppm/DTAB(0.06) mixture in aqueous solution as a function of the applied voltage (V); (B) Relaxation time (τ) of the Xanthan (113 ppm/DTAB (0.3 mM) mixture in aqueous solution as a function of the applied voltage (V); (C) Relaxation time (τ) of the Xanthan (113 ppm)/DTAB mixture in aqueous solution as a function of the DTAB concentration (C_{DTAB}).

decreases to 0.15 ms approximately and afterwards it remains nearly constant. Relaxation time values are calculated by extrapolating the curve τ (E) to zero electric field. It is shown that the addition of surfactant decreases the relaxation as compared to Xanthan (113 ppm) in aqueous solution. All the experimental measurements were performed at constant temperature (298 K).

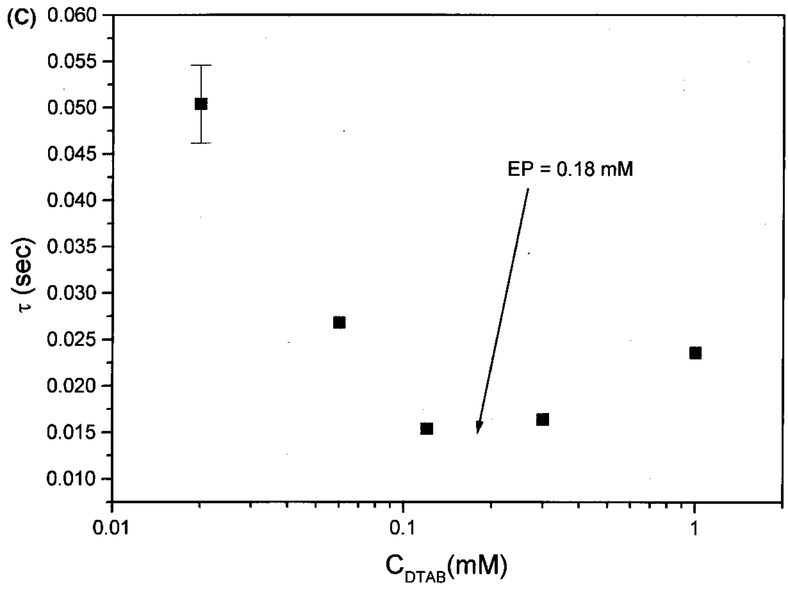

FIGURE 4 (Continued).

DISCUSSION AND CONCLUSIONS

It must be remembered that the Kerr constant of pure water is very low ($B \approx 3.10^{-4}\,m\,V^{-2}$) as compared with Xanthan in water or Xanthan–DTAB mixed systems.

On the other hand, Kerr constant of DTAB–water solution is close to pure water. The situation is similar for the respective relaxation times.

Hence, it is evident that the principal contribution to the induced birefringence is due to the Xanthan.

Generally speaking in the case of pure polymers case, there are satisfactory theories for the Kerr effect for two cases

(i) rigid polymers without interactions in solution [7]

$$B = \frac{C(n+2/3)^2 2\pi N_{AV}\Delta\alpha^0(\Delta\alpha^e + \mu^2/kT)}{nM_{\mathrm{mono}}15k_BTN}$$

where C is the concentration in grams/unit volume, N_{AV} is the Avogadro's number, M the molar mass of a monomeric unit, N is the number of monomerics number per molecule and k_{Bt} the Boltzmann's constant.

The optical anisotropy per monomeric unity is defined as $\Delta\alpha^0/N = \Delta\alpha^0_{\mathrm{mon}}$. In the case of charged macromolecules it is assumed that the distribution counterion polarisation is more important that other contributions (permanent dipole moments and atomic or electronic polarisability).

(ii) Nagai *et al.* [8] have proposed a modified expression for the case of non-interacting deformable molecules where an average over all conformations of the macromolecule in a fixed molecular co-ordinate frame in the absence of electric field is carried out. Afterwards, a more elaborate theory was presented [9,10]. Now, it is difficult to know whether those models describe our systems in an appropriate way.

In principle pure Xanthan can be described as a rigid polyelectrolite but it is evident that the addition of DTAB changes this condition considerably. As far as we know there are no theoretical models which can explain the induced birefringence for these systems. So we can only suggest a qualitative explanation.

First of all we shall calculate the equivalent point.

$$\text{Equivalent Point (EP)} = \frac{0.113\,\text{gr/L}}{930\,\text{g/mol}}\,1.5\,\text{e/monomer} \cdot 1000$$

$$\text{Charge concentration} = \text{Equivalent point} = 0.18\,\text{mM}.$$

When the DTAB concentration attains a value $\approx 0.18\,\text{mM}$ a clear distinction in Kerr static behaviour may be established. Between $0 \leq C_{\text{DTAB}} \leq 0.18\,\text{mM}$ the addition of the surfactant causes the Kerr constant decrease of the mixture with respect to the pure Xanthan in an aqueous solution.

Before the EP it is supposed that when DTAB molecules concentration increases they are binding progressively with polyelectrolite molecules. This would produce a double competitive effect.

(i) The dipolar moments (either induced or permanent) of the Xanthan molecule diminishes (B decreases)
(ii) Also, the initial rigidity of the polyelectrolite molecule decreases and the complex becomes more flexible. (τ decreases).

Immediately after the EP there is a two phase formation in solution and for greater concentrations a precipitation is observed. It must be pointed out that for concentrations close to the surfactant cmc both Xanthan and DTAB are soluble in water. Hence the precipitation is due either to the great complex weight or to the lack of electrostatic equilibrium forces.

Now, for $C_{\text{DTAB}} \geq 0.18\,\text{mM}$ B values are greater than B_{XANTHAN} but this case must not be taken into account because of the previously mentioned reasons, so the comparison between concentrations before and after EP has no meaning. Finally, in the conductivity values measurements (Fig. 1) the maximum is observed close to the EP. In principle before the EP concentration two competitive factors are present.

(i) the formation of aggregates decreases the mobility and consequently this would reduce the conductivity.
(ii) Inversely, because of the aggregate formation, there are Na^+ and Br^- free ions in the solution.

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