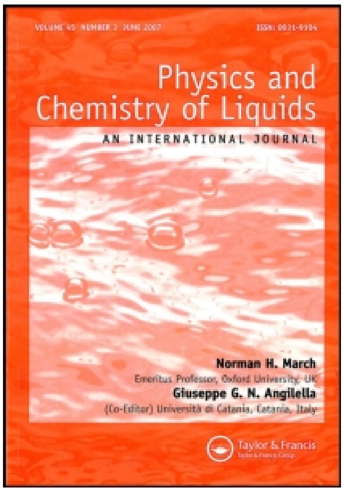

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KERR EFFECT OF PAMPS/DTAB AQUEOUS SOLUTIONS

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The Kerr effect of polyelectrolyte/surfactant mixtures in aqueous solutions has been measured. Investigated materials are: PAMPS (Polymer) and DTAB (surfactant). Two kinds of polymer were employed to assemble the studied systems: one of them (“System I”) contains 10% (mol) charged monomer whereas the other one (“System II”) contains 25% (mol).

Kerr constants (B) and mean relaxation times $\langle\tau\rangle$ as a function of the surfactant concentration (C_{DTAB}) were determined. B_{I} is always positive whereas B_{II} values are negative before the equivalent, point null in its vicinity and grows with positive values after it. A relationship with tension surface measurements is analysed. System II relaxation times are greater than System I. The influence of the flexibility is taken into account.

Electrical conductance measurements are also presented.

Keywords: Kerr effect; Polymer surfactant systems

Physical Abstract Classification: 78.20.J; 82.70

INTRODUCTION

During the last few years, mixtures of polymers and surfactants have been actively studied. From the point of view of technological applications these systems were used in pharmaceutical formulation as paints

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and coatings, industrial detergents, etc. [1,2]. On the other hand, the knowledge of basic properties raises a challenge because the complexity of the interactions which are to be taken into account. In order to solve this problem a great number of experimental techniques has been used such as viscosity, conductance, thermochemical and volumetric parameters, surfactant binding isotherms, phase diagrams etc. The modelling at a microscopic level of polymer–surfactant aqueous mixtures was improved by the use of more sophisticated experimental techniques such as NMR or fluorescence.

The behaviour of polyelectrolyte in a solution is ruled by the balance of hydrophobic and hydrophilic interactions of the polymeric segment either between themselves or with the solvent. In a similar way, surfactant aggregates in solution are ruled by hydrophilic, hydrophobic or ionic interactions. Hence, aqueous solutions which contain polymer/surfactant mixtures present a great diversity of molecular structures.

It must be pointed out that whole number of appointed studies of charged polymers/surfactants is lower than neutral polymers/surfactants ones.

As regards surface tension measurements it has been found that many polymer/surfactant systems act in a co-operative way in the interface solution/air [3–5]. The result is a decrease in the surface tension, which is greater than expected whether the polymer or the surfactant is in aqueous solution alone.

This "synergic" effect is particularly interesting, its explanation being of great importance. We shall see this problem in the section "Discussion" again.

The relationship between surface and bulk properties is still an open question.

Although there exist numerous investigations on the induced birefringence by an external electric field (Kerr effect) either on polymers or in surfactants, there are no systematic studies on the combinations of both simultaneously. The Kerr effect provides information on bulk properties of the studies liquid systems.

The aim of this paper is to present the obtained results when applying this technique to study DTAB (surfactant)/PAMPS (polyelectrolite) in aqueous solution and its relationship with surface properties. This study is completed with electrical conductivity measurements.

EXPERIMENTAL SECTION

Materials

The PAMPS is a statistical copolymer of acrylamide (AM) neutral monomers and charged acrylamidomethylpropanesulfonate (AMPS) monomers.

This material was provided by the "Laboratoire de Physique des Solides", Universite Paris Sud and elaborated by Institut Français du Petrole.

Two kinds of polymers were used. One of them contains 10% (mol) charges monomer (PAMPS 10%) and the other one 25% (mol) (PAMPS 25%). Molecular weights (M_w) of both polymers, the mean molecular weights (M_{MONOMER}) and the polymerisation degree (N) are:

PAMPS (10%): $M_w = 4 \times 10^5$ g/mol; $M_{\mathrm{MONOMER}} = 85$; $N = 4800$
PAMPS (25%): $M_w = 2.8 \times 10^6$ g/mol; $M_{\mathrm{MONOMER}} = 121$;
$N = 23{,}140$.

The chosen tensioactive was the dodecyltrimethylamoniumbromide (DTAB) which is a cationic surfactant and it was used as provided by Sigma (99%) without further purification.

The polyelectrolyte/surfactant systems of opposed charges are labelled as:

System I: PAMPS (10%) 108 ppm/DTAB (0.05–20 mM) in aqueous solution.

System II: PAMPS (25%) 109 ppm/DTAB (0.05–3 mM) in aqueous solution.

METHODS

Kerr Effect [6]

A laser beam ($\lambda = 632.8$ nm) polarized by means of a Glan-Thomson type polarizer passes through a cell where a liquid sample is placed. The cell is composed of an optical cuvette (Hellma Q-S-500; $L = 50$ mm) and two electrodes separated by a distance of 2.0 mm.

Both electrodes are connected to a pulsed high voltage source (up to 2.5 kV). The rise time of the source is < 100 ns. The cell is immersed in a thermostatic bath (298 K): on leaving the cell the bean goes through a second polarizer ("analyser"). The optical axes of the first and second polarizers are of 45 and 135°, respectively from the direction of the electric field. A quarter-wave plate is placed between the cell and the analyser. The extinction coefficient is of the order of 10^{-5}. The light is detected by a photomultiplier or a photodiode. The light intensity detected in the photomultiplier (or photodiode) is related to the expression:

$$\Delta n = n_{\mathrm{P}} - n_{\mathrm{t}} = \lambda \cdot B \cdot E^2,$$

where n_P and n_t are parallel and perpendicular refractive indices with respect to the field direction.

We have calculated the mean relaxation time defined as:

$$\langle \tau \rangle = \int \frac{\Delta n_{\mathrm{D}}(t) \cdot dt}{\Delta n_0},$$

where Δn_{D} is the decay time curve and Δn_0 is the birefringence at the steady-state.

CONDUCTIVITY

Measurements were made by means on a ac bridge and a standard conductance cell.

EXPERIMENTAL RESULTS

Conductivity

Specific conductivity in aqueous solutions of surfactant (κ_{DTAB}), polymer ($\kappa_{\mathrm{PAMPS\text{-}10\%}}$ and $\kappa_{\mathrm{PAMPS\text{-}25\%}}$) and both polymer/surfactant mixtures (κ_{I}, System I) and (κ_{II}, System II) have been measured.

The experimental results are shown in Fig. 1 where these different conductivity values are represented as a function of the surfactant concentration C_{DTAB}.

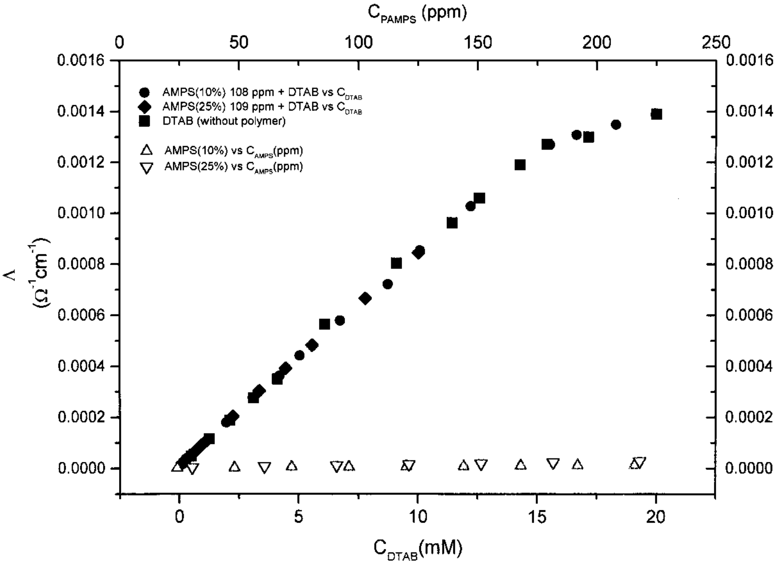

FIGURE 1 Equivalent conductance as a function of DTAB concentration.

It can be seen that the addition of the polymer in both cases, either in System I and in System II, is negligible when compared to the surfactant contribution to the whole mixture conductivity.

It must be pointed out that in this type of representation $\kappa = f(C_{DTAB})$ show a linear behaviour in the conductivity and there are no break points, except for the surfactant concentration value which corresponds to the surfactant critical micelle concentration ($C_{DTAB} = 16\,mM$).

Kerr Effect

The Kerr constant (B) and the mean relaxation times ($\langle \tau \rangle$) of the different investigated systems have been measured in the surfactant concentration interval, $0.1 < C_{DTAB} < 10\,mM$. At higher concentrations samples become very conductive and it has not been possible to measure the Kerr effect. In Figs. 2(a–c) Kerr constants for aqueous solution of DTAB (B_{DTAB}) and Systems I and II (B_I and B_{II}) are represented. In Figs. 2a and b results for Systems I and II as a function of C_{DTAB} are shown respectively. In Fig. 2c

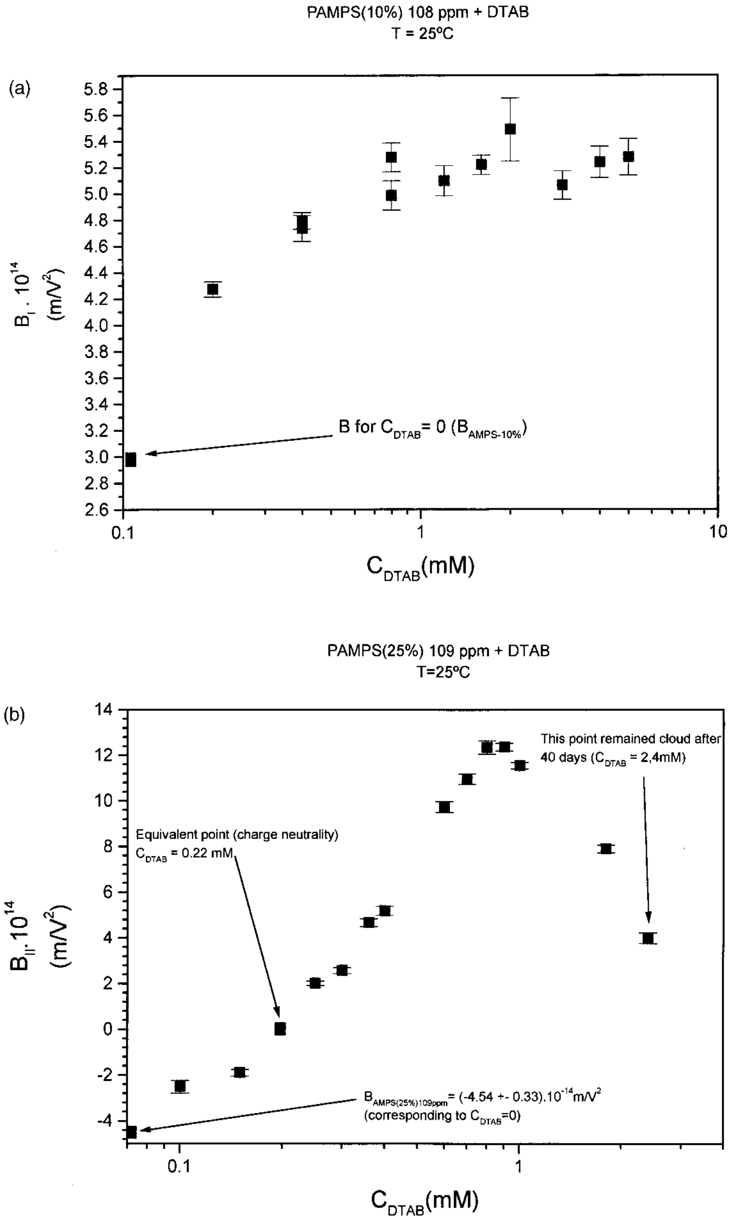

FIGURE 2 Kerr constant as a function of DTAB concentration. (a) System I: PAMPS-10% 108 ppm + DTAB. (b) System II: PAMPS-25% 109 ppm + DTAB. (c) Kerr constant for all systems as a function of DTAB concentration.

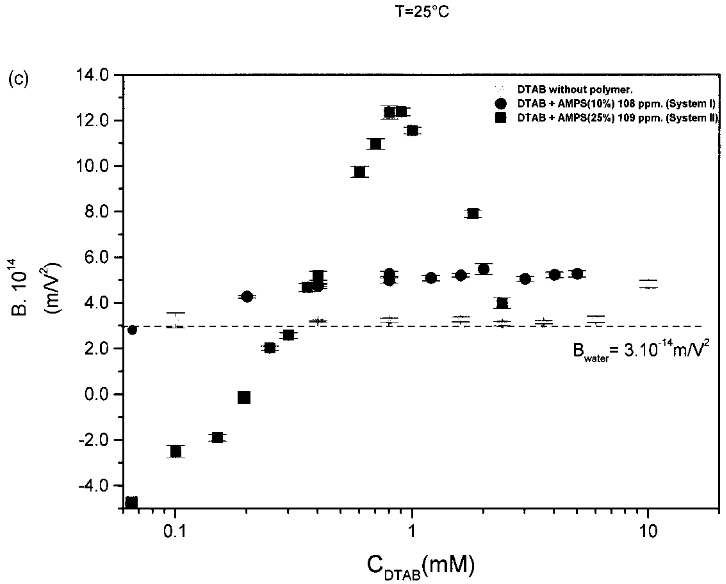

FIGURE 2 (Continued).

both mixed system values are compared with those of the system without polymer (B_{DTAB}).

In Fig. 2c it can seen that B_{DTAB} is small and has practically the same value as the pure water Kerr constant ($2.7 \times 10^{-14}\,\mathrm{mV}^{-2} < B_{\mathrm{WATER}} < 3 \times 10^{-14}\,\mathrm{mV}^{-2}$).

Likewise Kerr constant, values of both polymers in an aqueous solution have been determined. We have found that $B_{\mathrm{PAMPS\text{-}10\%}} = 3 \times 10^{-14}\,\mathrm{mV}^{-2}$ and $B_{\mathrm{PAMPS\text{-}25\%}} = -4.54 \times 10^{14}\,\mathrm{mV}^{-2}$.

In Fig. 2b it is shown that the induced birefringence of the System II is rather different from the DTAB solution (without polymer). For surfactant concentration low values ($C_{\mathrm{DTAB}} \cong 0.1\,\mathrm{mM}$) it can be seen that the B_{II} remain negative. Whereas, C_{DTAB} increases B_{II} values diminishes (in modulus) up to $C_{\mathrm{DTAB}} = 0.25\,\mathrm{mM}$ approximately, where $B_{\mathrm{II}} = 0$. Afterwards it increases for increasing C_{DTAB} values and reaches a relative maximum at $0.8\,\mathrm{mM} < C_{\mathrm{DTAB}} < 0.9\,\mathrm{mM}$ approximately. Then it begins to decrease again. When $C_{\mathrm{DTAB}} \cong 2\,\mathrm{mM}$ the system becomes permanently turbid (at least after 40 days). A somewhat different behaviour is shown for the System I (Fig. 2a).

It begins with a positive Kerr constant value and slightly increases with C_{DTAB} up to 0.9 mM.

In Fig. 3a, the relaxation time variation of the pure surfactant solution, $\langle \tau_{DTAB} \rangle$, and of the System I, $\langle \tau_I \rangle$, are represented as a function of C_{DTAB}. Surfactant relaxation times (without polymer) are very small and in the limits of the experimental device fiability. System I relaxation times are nearly constant (10 μs) up to $C_{DTAB} \cong$ 1.2 mM. Then $\langle \tau_I \rangle$, decreases down to the experimental device limit of fiability ($\cong$ 3 μs). In Fig. 3b relaxation times as a function of surfactant concentration for System II are represented. The observed behaviour is, here, rather different. At low concentrations $\langle \tau_{II} \rangle$ is relatively great (140–150 μs) and decreases down to the experimental limit, the concentration at which this value is attained is 0.2 mM approximately. In the Fig. 3c the relaxation time behaviour for the System II is represented for the $0.2 < C_{DTAB} < 3$ mM interval in an amplified scale. One can see that after $C_{DTAB} = 0.2$ mM $\langle \tau_{II} \rangle$ increases until $C_{DTAB} \cong 0.4$ mM, then remain constant (20 μs) and, at

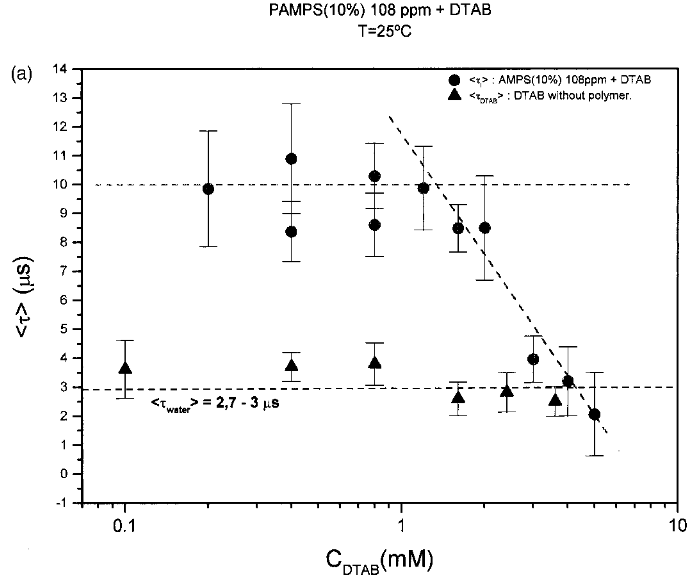

FIGURE 3 (a) Relaxation time as a function of DTAB concentration. (b) Relaxation time as a function of DTAB concentration. System II. (c) Relaxation time as a function of DTAB concentration. Amplified scale. System II.

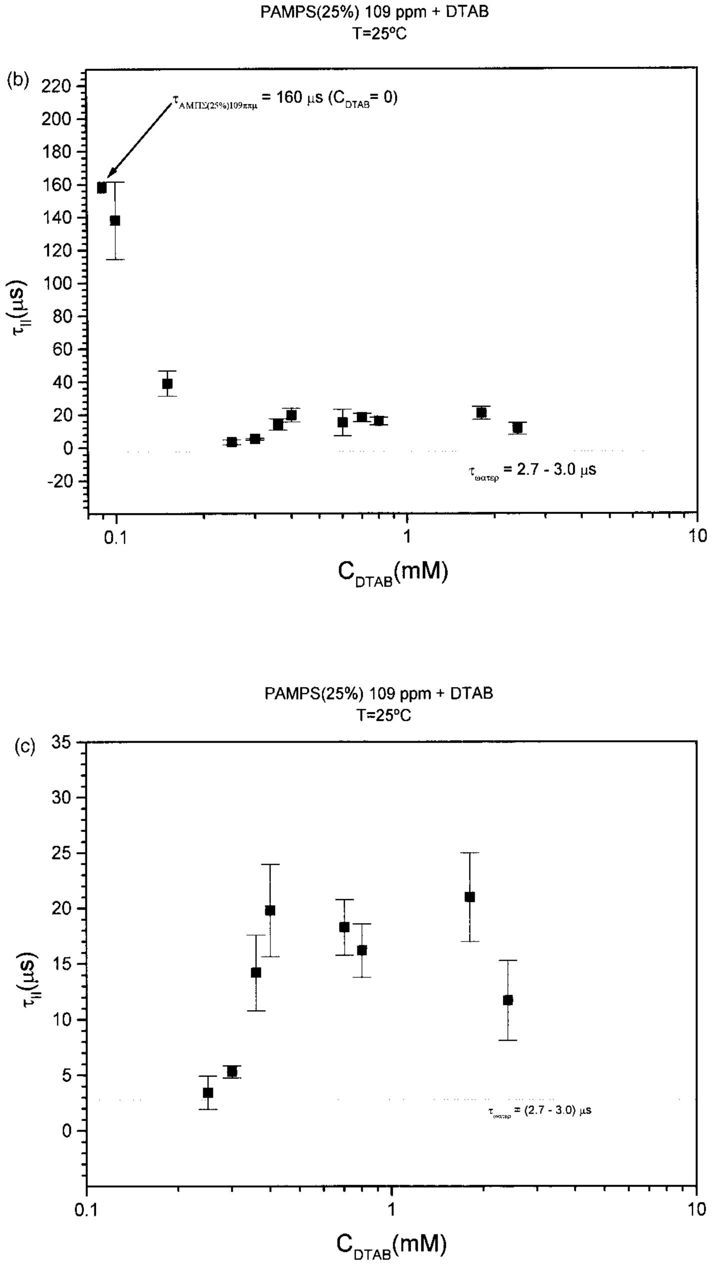

FIGURE 3 (Continued).

$C_{\mathrm{DTAB}} \cong 2\,\mathrm{mM}$, begin to decrease again (this last behaviour is similar to the System I).

DISCUSSION

Conductivity

We have represented in Fig. 4 the molar conductivity, $\Lambda = \kappa / C_{\mathrm{DTAB}}$, as a function of the square root of the surfactant concentration, $\Lambda = f(C_{\mathrm{DTAB}})^{1/2}$. It can be appreciated that for a concentration between $C_{\mathrm{DTAB}} \cong 0.4$ and $1\,\mathrm{mM}$ there is a Λ slope change for Systems I and II but there is no for DTAB solutions. All three systems present a second change for $C_{\mathrm{DTAB}} \cong 16\,\mathrm{mM}$ which in turn correspond to the c.m.c. of the surfactant aqueous solution.

Kerr Effect

Equivalent Point

The so called "equivalent point" is defined [2] as the concentration of surfactant cations equal to the concentration of ionizable groups

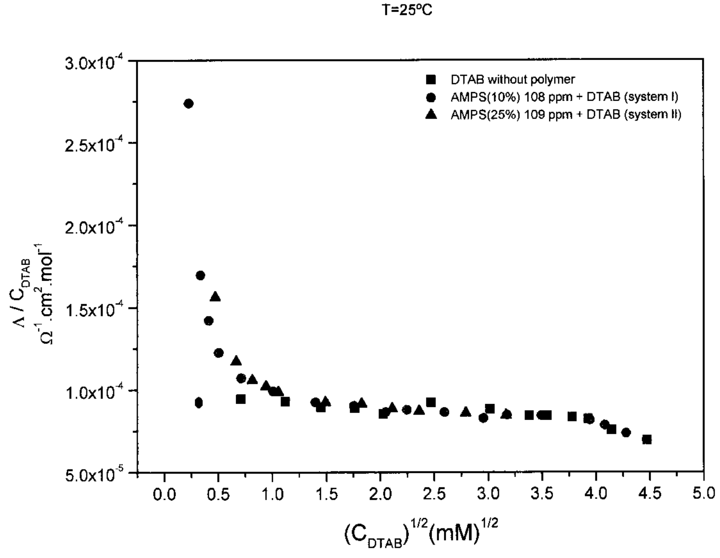

FIGURE 4 $\Lambda / C_{\mathrm{DTAB}}$ as a function of square root of DTAB concentration.

on the polyion. In one of the systems studied by Kogej and Skerjanc [2] a change in the slope of the molar conductivity as a function of the concentration root square was attributed to this particular concentration. Now, an elementary calculation allows to estimate this concentration in our systems.

$$\begin{aligned}\text{Equivalent Point} = \{&(\text{Polymerisation degree}) \\ &\times (\text{fraction of charged monomers})/ \\ &(\text{polymer molecular weight})\} \\ &\times (\text{Polymer Concentration})\end{aligned}$$

$$\text{EP (mM)} = \frac{N \times \%q/100}{M_{\mathrm{W}}} \times c_{\mathrm{poly}}$$

For the System II the equivalent point concentration is

$$\text{EP}_{\text{II}} = \frac{23140 \times (25\%/100)}{2.8 \times 10^6} \times 0.108\,\text{g/l} = 0.22\,\text{mM}$$

and for System I is $\text{EP}_{\text{I}} = 0.127\,\text{mM}$.

As we have indicated, no appreciable change in Λ for these concentrations was observed. The System II Kerr constant (B_{II}) vanishes for $C_{\text{DTAB}} \cong 0.25\,\text{mM}$.

In the System I, B_{I} is always positive. This is a predictable result because in this case all Kerr constants are both positive and it is unlikely to obtain a null value for the Kerr constant.

Critical Aggregation Concentration (c.a.c.)

The polymer/surfactant aggregation process is produced by ionic exchange between both of them and its corresponding counterions. An accumulation on non-polar parts of the surfactants molecules in the vicinity of the polymer arises. An important experimental facts is that the surfactant concentration in which this process takes place is very inferior to the critical micelle concentration (CMC). This concentration is called "critical aggregation concentration" (c.a.c.) [7].

Kogej and Skerjanc [2] explains that different experimental methods predicts c.a.c. different values, which makes very difficult to specify it accurately. There is an additional problem because the surfactant concentration is very small at the beginning of the cooperative binding. Generally, its value depends on the hydrocarbonated chain length, the ionic strength and the polymer flexibility. A parameter which characterises the flexibility is persistence length which in turn depends on the spontaneous rigidity of the polymeric chain and on its charge degree.

Wallin and Linse [8] have simulated the complexation of a charged micelle (surfactant aggregate) and a polyelectrolite of opposed charge by using the Monte Carlo method.

The authors calculate the c.a.c./cmc rate by means of the following expression

$$\frac{\mathrm{CAC}}{\mathrm{CMC}} = e^{\frac{\Delta A_{\mathrm{PE}}}{NkT}}$$

where ΔA_{PE} is the change in the free energy of the complexation between one micelle with corresponding counterions and polyelectrolite with its corresponding counterions, T is the absolute temperature and k the Boltzman constant. In the model the Gibbs free energy is equivalent to the Helmholtz one.

Wallin and Linse have demonstrated that the relationship c.a.c./cmc grows with the polymer rigidity. The estimated relation values are in good qualitative agreement with those which have experimentally been found (in the concentration interval $-001 <$ [c.a.c.]/[cmc] < 0.1).

In a later paper [9] the authors have changed the charge density by changing the distance bead/bead all the beads being charged. Likewise, the latter case the c.a.c. increases with rigidity which in turn increases with linear charge. Hence, it is the polymer rigidity (or flexibility) a fundamental parameter in the complexation process.

System I is less rigid than System II. Now, the parameter which is associated with rigidity is persistence length (L_t) which depends on an intrinsic part (L_B) and an electrostatic part (L_E).

$$L_t = L_B + L_E$$

The quantitative analysis of the Kerr constant in polyelectrolites presents the difficulty that it is not possible to describe them by means of a regular geometric form, due to the their fractal structure. By the using scaling elements theory it has been proposed [10,11] that $B \propto (L)^S$, where the scaling s exponent depends on the kind of polyelectrolite. Therefore, it is evident that the rigidity plays a key role and it goes inversely to the charge content.

Stubenrauch *et al.* [5] have measured the interfacial tension (γ) of the System II in the surfactant concentration range $10^{-3}\,\text{mM} < C_{\text{DTAB}} <$ 15 mM. It is very interesting to compare the results obtained with both of them experimental techniques, in spite that one describes processes in the liquid surface and the other processes in bulk. For γ_{II} measurements between $0.7 < C_{\text{DTAB}} < 1.1\,\text{mM}$ a plateau is observed. The beginning of this plateau is considered as the c.a.c. and it is similar to the concentration in which the maximum in the Kerr constant is observed. Although, this correlation between both experimental technique results may be attractive, due to the lack of systematic experimental data it is not possible to affirm conclusively that the Kerr effect is an useful technique to determine the c.a.c. region.

It is interesting to relate this surface process with the corresponding one in bulk.

The description of the System II behaviour may be as follows:

- For the surfactant concentration interval, $0 < C_{\text{DTAB}} <$ [c.a.c.] a gradual complexation should be produced. When C_{DTAB} increases an ionic exchange between the polyion or the surfactant and its corresponding counterions is produced. This process is favoured by an entropy increase due to the Br^- and Na^+ ions liberation. Hence, there is an increasing neutralization of the charged polymer and a progressive flexibilization of the polymeric chain. Consequently, a coiling process is carried out. The relative influence of the polymer decreases and the Kerr constant diminishes down to the equivalent point. For larger C_{DTAB} the corresponding B_{II} increase with positive values may be explained by the fact that the surfactant addition either enlarges each complex polymer/surfactant or creates new structures with the same size or both together. This process continues up to a maximum. It could be inferred that this is a zone which corresponds to a maximum in the molecular aggregation and it is in correspondence with the plateau starting. As we explained before (Section "Experimental") for $C_{DTAB} > 2\,mM$ turbidity is observed. The increase of each size aggregate may be the reason of the precipitation.

The behaviour of the System I is rather different from the previous one. The persistence length of System II is greater than the System I, because it is more charged. So, its rigidity is larger. Hence it would be expected to have a more stretched structure and for this reason its relaxation time is greater than the System I relaxation time $\langle \tau_I \rangle$.

Generally, the System I behaviour analyse is not straightforward. It must be pointed out that in this case, the c.a.c. determination is not so clear as in the System II [12].

CONCLUSIONS

The behaviour of Kerr constants is different. B_I is always positive regardless of surfactant concentration. In turn, the B_{II} evolves from negative values for low surfactant concentrations and becomes null for a surfactant concentration in the neighbourhood of the equivalent point. For greater C values B is positive. It reaches a relative maximum in the vicinity of the c.a.c.

Relaxation changes of the System II are greater than those of System I.

In System II when surfactant concentration increases, a progressive growth of aggregates formation is produced. This process reaches a maximum for concentrations near the c.a.c. Starting at this point, a gradual precipitation is observed. This aggregation process takes place simultaneously with a gradual coiling of the polyelectrolite chains which are wrapped around the micelles.

This coiling process is more important in System II than in System I because the first is more charged than the second one. Hence, flexibility plays a key role.

Due to lack of a satisfactory theory of induced birefringence in these systems, only a qualitative explanation of the experimental results may be presented.

Another aspect to be analysed in a future work is the relationship between surface and bulk process. This problem is very interesting due to the synergic effects which are produced by the addition of slight quantities of a polymer.

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