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Studies of Surfactant/Water Systems Near the Critical Micellar Concentration Using Thermal Lens Spectroscopy

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Abstract. A novel application of photothermal spectroscopy to the study of surfactant-water systems near the critical micellar concentration is reported. The thermal lens signal was induced by a slightly soluble dye and was measured with a dual-beam thermal lens spectrometer.

For the two surfactants considered: nonyl phenol and Triton X-100, sharp variations of the thermal lens signal were observed at the critical micellar concentration (CMC), namely an increase for nonyl phenol and a decrease for triton X-100. These effects are arguably related to micelle formation.

Our work serves as an initial assessment of the potential of the technique for the study of disperse systems of a higher complexity or dark systems where conventional techniques are impossible to apply.

Key words: thermal lens spectroscopy, micellar solutions, surfactant CMC.

When a laser beam is focused on a sample of an absorbing solution and a non-absorbing solvent, a temperature gradient is produced by nonradiative relaxation. Since the refractive index of the media changes with temperature, a lens-like optical element is formed (thermal lens). If a second Gaussian beam (probe beam), which is not absorbed by the medium, is passed through the illuminated sample area, it progressively diverges. By monitoring the intensity at the center of the probe beam, the magnitude of the divergence can be measured. This signal is called the thermal lens signal (S) and it depends on the thermooptical properties of the sample [1–4].

Amphiphilic molecules such as surfactants may associate in aqueous media to form dynamic micellar aggregates. Micelle formation occurs at a characteristic value of surfactant concentration called the critical micellar concentration (CMC). This phenomenon can be monitored by following changes in several physical properties of the solution with increasing concentration of the amphiphile. Among those properties are absorbance maxima, surface tension, conductance, etc. [5–8]

The CMC value is of practical importance as it defines the minimal concentration of surfactant, which is required to solubilize a hydrophobic molecule. The peculiar properties exhibited by micellar solutions may sometimes be very useful in analytical research [7, 9, 10, 11]. The most important of these properties is the ability of micelles to solubilize, within their microstructure regions, compounds which are insoluble or sparingly soluble in water. The liquid-like non-polar micellar core acts as solvent for non-polar species.

Several authors report on the applications of these properties of the micelles in different analytical techniques: UV-visible molecular absorption, fluorescence, luminescence, etc [7, 9]. In photothermal spectroscopy the non-radiative relaxation processes responsible for the induced heating are dependent on the local chemical environment around the absorbing molecule. In particular, the formation of micelles changes the thermal properties of the medium. One should then expect variations in the relaxation processes of excited species trapped in the micellar core, as compared to species in the bulk. To our

knowledge, little work has been previously done in applications of photothermal spectroscopy to surfactant/water systems in the CMC regions.

Specially relevant to the present work are the investigations of Mermet and Georges, and those of Franko and Tran [9–13]. Both groups found by different methodologies, that working with micellar solutions produces an enhancement in the thermal lens signal, for surfactant concentrations well above CMC. They attribute this change not to micelle formation but to changes in the thermooptical properties of the bulk, the argument being that organic systems are known to exhibit a higher variation of the refraction index with temperature than water.

In this article we report our investigation on the behavior of two surfactant-water systems near CMC. All the concentrations considered here are significantly lower (at least two order of magnitude) than those employed by other authors [6, 10, 11]. We observe both enhancement and reduction of the experimental signal, depending on the surfactant and the effect is clearly related to micelle formation. We interpreted these results as due to changes in the physical thermooptical properties of the local environment around the absorber induced by micellization, which in turn determines the characteristic time for heat propagation and relaxation of the thermal lens signal.

In a dual-beam configuration the thermal lens effect can be conveniently monitored in the far field by measuring the changes in the intensity at the center of a probe beam. In Fig. 1 a typical waveform is shown; the upper plot shows the pump beam intensity, whereas the lower one shows the intensity of the probe beam at the center as a function of time. As the pump beam illuminates the sample, the thermally induced defocusing produces a decrease in the probe beam intensity and when the pump beam is blocked, the probe beam intensity returns to its initial value.

The thermal lens signal (S) is generally measured as a relative change intensity at the probe beam center in the far field [1, 2, 3, 14]:

$$S = \frac{I_{t=0} - I_{t=\infty}}{I_{t=\infty}} = \frac{\Delta I}{I} = -\frac{2.3P(dn/dT)}{\lambda\kappa}A \qquad (1)$$

where ΔI is the intensity change at the beam center. It reflects the relative change in the spot size of the probe beam at times zero ($I_{t=0}$) and in steady state conditions ($I_{t=\infty}$); P (W) is the laser power, dn/dT (K^{-1}) is the variation of the refractive index of the

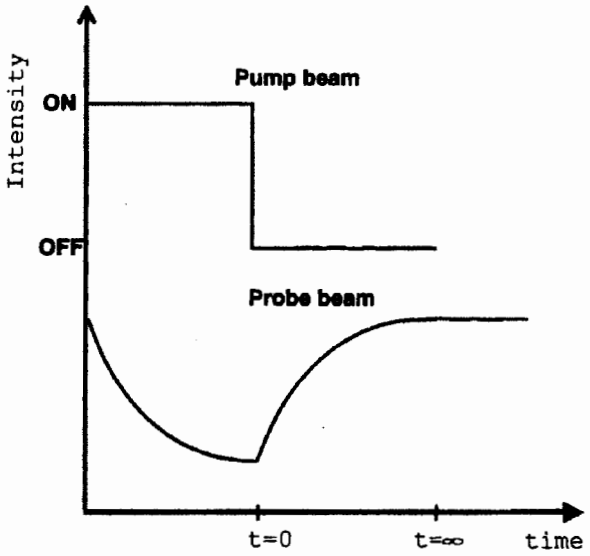

Fig. 1. Time dependence of a CW thermal lens signal

solution with the temperature, λ(cm) is the wavelength of the radiation; κ ($W\,cm^{-1}K^{-1}$) is the thermal conductivity and A is the absorbance of the solution. This expression assumes that all absorbed radiation is converted to heat [2, 3]. The rate of approach of the time-dependent thermal lens signal to its steady state value is determined by a characteristic relaxation time t_c [1, 2, 3, 14] as:

$$S(t) = S(0)\,(1 + 2t/t_c)^{-2} \qquad (2)$$

The important parameter $t_c(s)$ is related to the rate of buildup or decay of the thermal lens and can be expressed in terms of the physical constants characterizing the thermal properties of the medium and the geometrical radius of the pump beam. Explicitly,

$$t_c = \frac{\omega^2\rho C_p}{4\kappa} = \frac{\omega^2}{4D} \qquad (3)$$

where $\omega(\mu m)$ is the beam radius, $\rho(g\,cm^{-3})$ the density of the medium, $C_p(Jg^{-1}K^{-1})$ the heat capacity, and κ is the thermal conductivity entering in eq. (1). The property D in eq. (3) includes all the relevant thermal information about the medium and is called the thermal diffusivity.

Experimental

We have used a thermal lens spectrometer with a collinear dual-beam configuration, of which a schematic diagram is shown in Fig. 2. A Coherent Innova 300 argon ion laser was used as pump beam operating in a single line mode (514 nm) and used an average

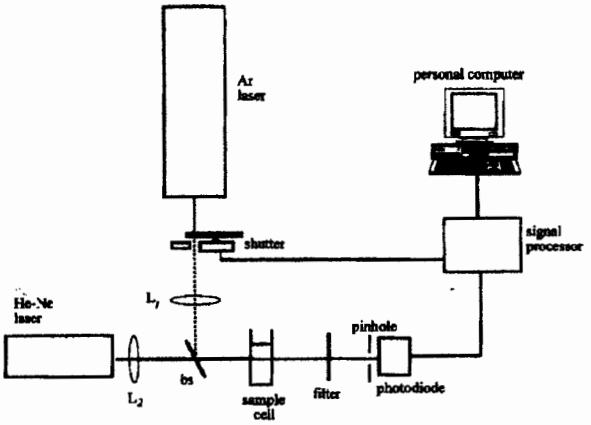

Fig. 2. Schematic diagram of a dual-beam collinear spectrometer

power onto the sample of 100 mW. The excitation beam, which was amplitude modulated by a mechanical Copper (10 Hz) was focused onto the sample cells with a lens *L*1 (200 mm focal length). A 5 mW He-Ne laser (Melles Griot 05-LHR-151, 632.8 nm) was used to produce a probe beam and this was focused with the lens *L*2 (200 mm focal lens). A 50% beam splitter was used to direct collinearly the excitation and probe beam through the sample cell. In order to enhance the sensitivity, a mode-mismatched configuration was used for sample cell positioning. This means that the waist positions of the pump and probe beams did not coincide. The probe beam focus was situated 6 cm before the sample cell. The signal (*S*) was obtained by sampling the intensity at the center of the probe beam with a precision pinhole (20 μm) and a silicon photodiode (Melles Griot LM2). The detector-pinhole system was mounted on a XYZ translator in order to localize the laster beam center. The photocurrent is amplified by a trans impedance amplifier (Melles Griot 13-AMP-003). The amplified photocurrent was transduced to a PC (AT 386) with an ADC/DAC board (Lab-PC card, National Instruments). A sampling rate of 2000 samples/seconds was used. In order to measure the intensity variation of the probe beam ($I_{t=0} - I_{t=\infty}$), the DC level was subtracted from the signal using a differential amplifier.

The experiments were performed with two different surfactants: P-T-Octyl benzene/oxyothylene/9 (Triton X-100) and benzene oxyethylene 10 alcohol (nonyl phenol). A small amount (in the range of 100 nM) of an organic dye was added to the water-surfactant solutions to induce the thermal lens signal. Coumarine 440 and 1-xylylazo-2-naphthol (non-fluorescent dye) were selected because both dyes are sparingly soluble in water and their solubilities are considerably increased in the presence of the surfactant, which indicates the greater affinity of the dye for the surfactant.

Coumarine-440 dissolves easily in Triton X-100 micellar solution but is not appreciably soluble in the presence of nonyl phenol. 1-Xylylazo-2-naphthol dissolves easily in nonyl phenol but is not soluble in Triton X-100 micellar solution. Due to this fact, thermal lens signal studies with Triton X-100 were performed with coumarine while nonyl phenol studies were performed with 1-xylylazo-2-naphthol.

Two different experimental methods were used. In the first method, different micellar solutions were prepared with a constant surfactant to dye concentration ratio. In the second method, the dye concentration was kept constant while the surfactant's was varied. This strategy was intended to observe changes in *S* due to micelle formation only.

Stock solutions of 1 mM of each dye in the surfactant were prepared by dissolving the exact amount of dye in a known weight of the corresponding surfactant. For the first experimental method the solutions were prepared by dissolving the desired weight of the stock solution in the appropriate amount of distilled water, so as to obtain the required surfactant concentration. For solutions with constant dye concentration the following procedure was used: a constant amount of the stock solution was used for all solutions and a known amount of the pure surfactant was added so as to obtain the final desired surfactant concentration. Finally, the appropriate amount of distilled water was added. All the micellar solutions were kept in an ultrasonic bath for 5 minutes at 25 °C before using them.

The signal (*S*) was measured in different water surfactant solutions with a surfactant concentration going from premicellar passing through critical micellar concentration to up to 1000 times the CMC. The average reported [15] CMC value are $(1.5\pm0.5) \times 10^{-2}$% w/v and $(4.0\pm0.5)\times10^{-3}$% w/v for Triton X-100 and nonyl phenol respectively. At least eighteen different solutions were prepared in the selected concentration range and especially significant for us were points near the CMC of each surfactant. All the experimental data reported in this work are the average of at least 5 replicate measures. In general a relative standard deviation less than 3% were obtained for replicates of the thermal lens signal.

Results

In Fig. 3 the variation of *S* as a function of nonyl phenol concentration is shown for the set of experiments where the ratio of dye to surfactant concentration was held constant. The blown-up portion of the

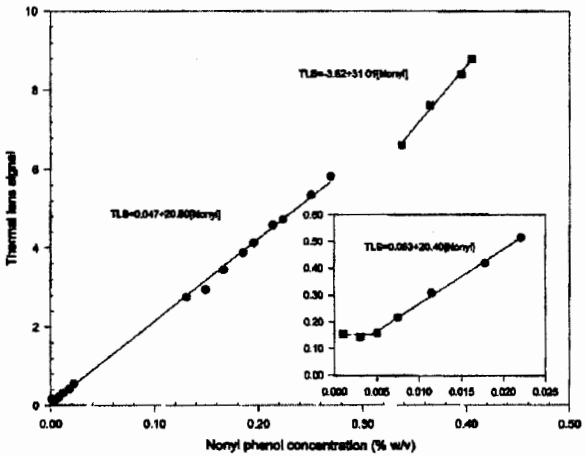

Fig. 3. Variation of the thermal lens signal as a function of the nonyl phenol concentration for a constant ratio of dye and surfactant concentrations. Inset: detail of the plot corresponding to concentrations below 0.025%

plot displayed in the inset shows, that for concentrations below 0.005% w/v there is no appreciable change in the signal and thereafter it increases linearly with concentration up to a break point located around 0.30% w/v, above which the rate of increase in the signal is much faster and linear. In the two zone where the slope changes (break points, a) low reproducibility in S is observed. The constant S values observed below CMC could be attributed to the extremely low solubility of the selected dye in water and it is not appreciably increased for a nonyl concentration below the CMC.

The first break point appears near the value of the CMC for nonyl phenol reported in the literature [15], $(4.0\pm0.5)\times10^{-3}$% w/v. It is clear that the increase in the signal occurs for quite a low surfactant concentration it cannot be attributed to the change in thermooptical properties of the solution due to the massive incorporation of surfactant molecules with thermooptical properties differing very much from those for water. Therefore it should be attributed to a local change in the chemical environment of the absorber induced by the micellization. Changes in the thermooptical bulk properties of the solution as the result of a large concentration (30 times CMC) of surfactant were reported by Franko and Tran [11] for different surfactants. These authors did not report any change in S at the CMC, which is probably due to the fact that they considered only two concentration values in the neighbourhood of the CMC.

The second break point occurs at a much higher concentration of surfactant and it could be interpreted to be due to a structural transition of the micelles of the kind reported in reference [16], to changes on dn/dT as reported in reference [11], or to a combination of both factors. We shall not consider this point any further in this article.

Focusing our attention on the region around the first break point, we performed a second series of experiments where the concentration of dye was kept constant. The idea was to discriminate between the effects of the dye and the surfactant itself. In the absence of surfactant, S increases linearly with the concentration and this effect is the basis for a quantitative determination of the absorbing species. For a constant concentration of the absorber, S should also remain constant. The slope of the signal versus concentration line however, is determined by the physical properties of the solution and it is its variation that we are trying to relate to micelle

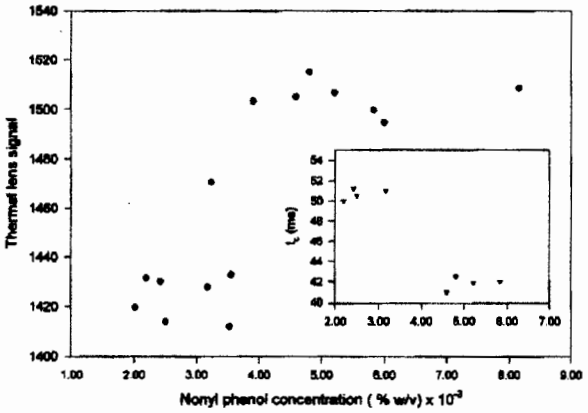

Fig. 4. Variation of the thermal lens signal as a function of the nonyl phenol concentration for constant concentrations of the absorber. Inset: characteristic time (t_c), calculated from equation (3) as a function of the nonyl phenol concentration

formation. In Fig. 4 the results of these experiments are shown. As expected from our previous argument, the response curve now has the form of a step-function with two nearly constant segments and a significant increase in the thermal lens signal could be observed when the concentration of surfactant exceeds CMC.

In Figs. 5 and 6 the results of the two sets of experiments with Triton X-100 as surfactant are shown. Although an overall linear behavior of S with surfactant concentration is preserved in the set of experiments, where the ratio of dye to surfactant was held constant (Fig. 5) there is a striking difference at

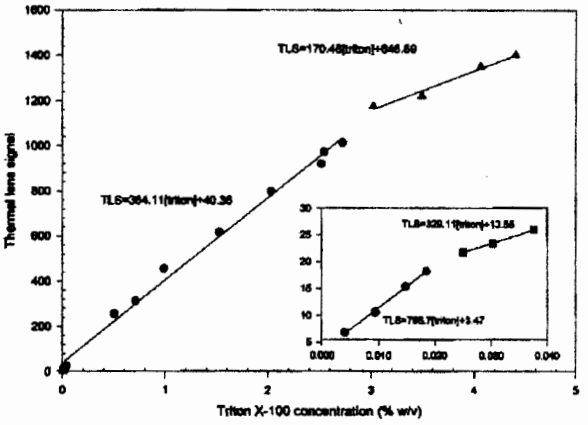

Fig. 5. Variation of the thermal lens signal as a function of the Triton X-100 concentration for a constant ratio of the dye and surfactant concentrations. Inset: detail of the plot corresponding to concentrations below 0.04%

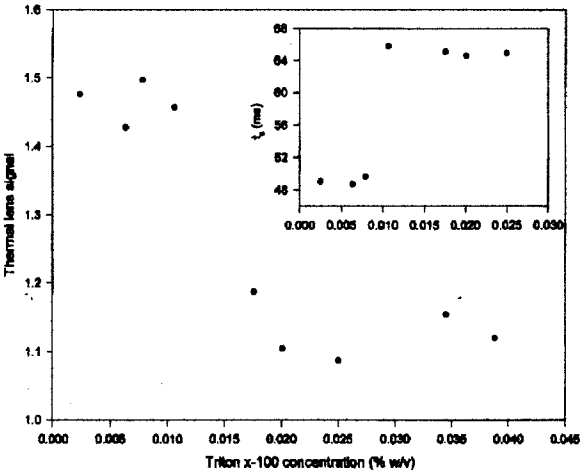

Fig. 6. Variation of the thermal lens signal as a function of the Triton X-100 concentration for a constant concentration of the absorber. Inset: characteristic time (t_c), calculated from equation (3), as a function of the Triton X-100 concentration

the CMC, where a decrease rather than an increase in the signal is observed. As obtained for the nonyl phenol, the first break point appears close to the CMC reported in the literature [15], namely $(1.5\pm0.5)\times 10^{-2}$% w/v, whereas the second one is observed at higher surfactant concentration. The results for the experiment with constant absorber concentration experiments for Triton X-100 (Fig. 6) shows a similar behavior as that obtained for nonyl phenol, namely two nearly constant segments with a appreciable change (decrease) for surfactant concentration, above the CMC value. However, the micellization process in the Triton X-100 affects the thermal lens signal negatively, i.e. the thermal lens signal is diminished. This depressing effect is stronger than the enhancement effect observed with nonyl phenol.

In order to rule out the possibility that a variation in the properties of the absorber as a consequence of micellization could be responsible for the observed change in S, we took conventional absorption spectra for the same surfactant dye solutions used in our thermal lens experiments. These spectra showed no variation in the shape and position of the absorption band for both surfactants, and although molar absorptivity is a global property of the dye in solution and not locally induced as the photothermal signal, this result supports the evidence that the variation in the S indeed is due to micelle formation.

In view of the experimental evidence and the theoretical relationship between the characteristic time t_c and the thermal diffusivity D, we interpret our results as due to changes in the heat transport properties of the medium, arising from micelle formation, which in turn translate into changes in the characteristic times. We have computed the t_c values by fitting the experimental signals to equation 2. As the signal amplitude is not the same for all sample solutions, all the signal curves were normalized by plotting $[S(t)/S(0)]^{-1/2}$ as a function of time. These plots are straight lines with slopes equal to $2/t_c$, from which we can evaluate the characteristic time. The inset in Figs. 4 and 6 shows t_c as a function of the concentration for each surfactant. For nonylphenol solutions we obtained an average value for t_c of (50.3 ± 0.6) ms and (41.7 ± 0.7)ms for regions below and above the CMC. The corresponding values for Triton X-100 were (49.3 ± 0.7) ms and (65.0 ± 0.8) ms. For pure water using a pump laser beam with a waist of 166 μm and a value of thermal diffusivity (D) of 14.58 cm^2s^{-1} [4], we obtain a value of 47.8 ms for t_c from equation (3).

For solutions with a surfactant concentration below CMC the values of t_c are close to those obtained for water, indicating that the presence of the surfactant does not substantially modify the heat transport properties. For solutions with surfactant concentrations above the CMC, t_c appreciably differs from its value for water, indicating that micellization produces a pronounced change in the thermal properties of the medium around the dye molecules.

It is clear from our results, that there exists a direct connection between changes in t_c and the behavior of S near CMC. An enhancement (reduction) in S corresponds to a shorter (longer) t_c. This agrees with what could be predicted directly from equation 2, since t_c is a measure of the time required to achieve the maximum signal amplitude.

The reduction of S for Triton X-100 solutions had been conjectured but not observed by other authors [11]. The reason for the absence of experimental confirmation lies in the fact that for surfactant concentrations well above the CMC it is the variation in dn/dT rather than the one in t_c, that dominates the response of the solution.

Conclusions

A careful study of the surfactant concentration dependence of the photothermal signal for water-surfactant solutions near the CMC has revealed a

more complex behavior than could be anticipated on the basis of previous studies at concentrations well above the CMC. We have found both enhancement and reduction of the thermal lens signal as a consequence of micelle formation. We interpret these results as due to variations in the energy transport properties of the microenvironment around the absorber, which in the conventional theory of photothermal spectroscopy are condensed in the single parameter t_c of equation 2. Our results indicate that micelles formed with nonyl phenol as surfactant reduce the rate of heat transfer thereby slowing down the thermalization process and enhancing S. Micelles formed with Triton X-100 exhibit the opposite behavior. It would be of interest to correlate these differences in behavior with microscopic and structural properties of the micelles. This is a complex task and we are in the process of constructing simple models for this effect. Another interesting result is the observation of a second breakpoint in the curves of S versus the surfactant concentration. Such transitions have been reported in other contexts in the literature.

The observation of a sharp variation in the thermal lens signal at the CMC can be used to develop a powerful tool to study complex disperse systems for which other techniques are difficult to use, e.g. asphaltenes solutions. Work in this direction is currently under progress.

Acknowledgments

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