

Study of Adsorption of Nonionic Surfactants at the Liquid–Solid Interface by FTIR/CIR

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ABSTRACT: Fourier transform infrared spectroscopy (FTIR), using the attenuated total reflectance (ATR) method, can be used to characterize the interface of a system. We investigated the adsorption at the liquid–solid interface of nonionic surfactant aqueous solutions with or without a hydrotropic agent. We studied monofunctional diblock copolymers of poly(ethylene oxide-propylene oxide) (PEO–PPO) as nonionic surfactants and sodium *p*-toluenesulfonate (NaPTS) as hydrotropic agent. The samples were analyzed by FTIR technique using the circular internal reflectance (CIR) accessory, which confirmed that the hydrotrope shifts the surfactant from the liquid–solid interface. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1668–1676, 2001

Key words: block copolymers; hydrotrope; adsorption; PEO–PPO; nonionic surfactant

INTRODUCTION

Fourier transform infrared spectroscopy (FTIR), using the attenuated total reflectance (ATR) method, can be used to characterize the surface of a compound.^{1–5} By the methods already developed,^{6,7} it is possible to obtain spectra that characterize the physicochemical nature of the surface without interference of the composition and the structure of the bulk of the sample. The penetration depth of the analysis is around 0.3–3.0 μm . This method is not appropriated for the characterization of the entire sample composition; however, it is useful, for example, to characterize the migration or diffusion of the additives to the surface, or to compare the content of one of the component mixtures on the surface and in the bulk of the sample.

The ATR technique is based on the phenomenon of total reflection of the radiation in the material's interface with different refraction indices. The radiation beam through the sample, which is placed in contact with a crystal of high refraction index, penetrates the crystal and is reflected on the sample surface. The incident angle is slightly greater than the critical angle, to provide total reflection. Part of the energy is absorbed (attenuated radiation) and can be detected. The multiple internal reflectance (MIR) can be used to analyze liquid and solid samples, although the circular internal reflectance (CIR) can be used only for liquids. Figure 1 shows the schematic representation of the CIR technique accessory.⁸

In the CIR technique, the radiation penetrates and goes through a crystal cylinder (e.g., ZnSe) for cylindrical internal reflections, about 10 in all, at 45°. The crystal is selected so that its refraction index is greater than that of the analyzed sample. The effective penetration depth d_p depends on the wavelength, the beam angle, and the refraction indices of the sample and the crystal.⁸

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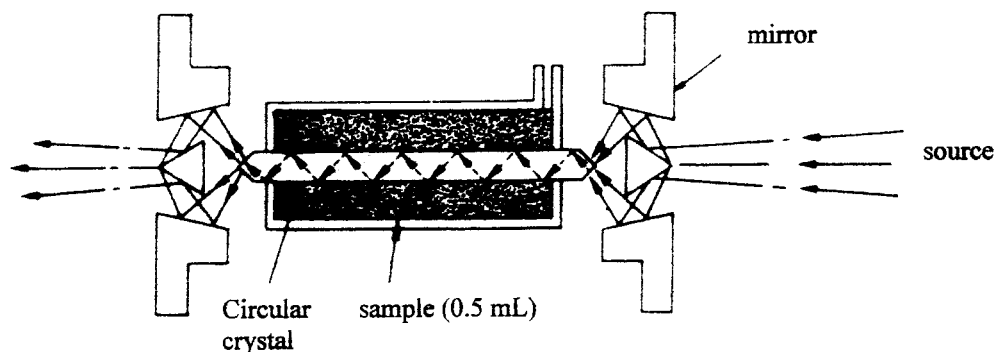


Figure 1 Schematic representation of the circular internal reflectance (CIR) accessory.⁸

$$d_p = \frac{\lambda_c^-}{\sqrt{2\pi[\sin^2\theta - (\eta_s/\eta_c)^2]}} \quad (1)$$

where λ_c is the wavelength in the crystal (λ/η_c), θ is the incident angle, and η_s and η_c are the refraction indices of the sample and the crystal, respectively.

The aim of this work was to study the adsorption of the aqueous nonionic surfactant solutions with or without a hydrotropic agent, sodium *p*-toluenesulfonate (NaPTS), at the interface. We studied monofunctional diblock copolymers (R-PEO-PPO-OH and R-PPO-PEO-OH, where R is linear C₄ and C₁₂₋₁₄). In spite of the extensive literature about nonionic surfactants, no study was found that used FTIR/CIR to analyze its solution behavior.

The work is very important because both PEO-PPO copolymer surfactants and NaPTS hydrotrope exhibit surface activity. As shown in previous works,⁹⁻¹¹ the presence of this hydrotrope in the aqueous solutions changes the behavior of the PEO-PPO copolymers. Our intended aim in using FTIR/CIR in this study was to elucidate the behavior suggested from the results obtained by surface tension measurements of the aqueous solutions,^{9,10} as well as to use a new technique in the study of aqueous PEO-PPO copolymer solutions.

The behavior of copolymers in aqueous solutions used in this work was already studied in our laboratory and it was observed that these copolymers exhibit phase separation with increasing temperature. The temperature at which phase separation occurs is known as cloud temperature or cloud point.⁹ Before they exhibit a phase separation, these surfactants can manifest solubility in water not as unimers but as aggregates that

are known as micelles. The critical micelle concentration (CMC) is the concentration at which the micelles start to form.^{10,11}

EXPERIMENTAL

Materials

Monofunctional diblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) (R-PEO-PPO-OH and R-PPO-PEO-OH, where R = linear C₄) were obtained from Grupo Ultra-Divisão Química (São Paulo, Brazil). Monofunctional diblock copolymer of C₁₂₋₁₄-PEO-PPO-OH was obtained from Henkel S.A. Indústrias Químicas (São Paulo, Brazil).

The aqueous solution of the hydrotropic agent sodium *p*-toluenesulfonate (NaPTS, 2.10M) was obtained from COEMA S.A. (São Paulo, Brazil).

Characterization data of PEO-PPO copolymers are summarized in Table I.⁹⁻¹¹

Methods

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analyses were carried out using a Perkin-Elmer FTIR 1720x spectrometer, controlled by digital computer DEC station, 320sx, IR Data Manager (IRDM; Perkin Elmer Cetus Instruments, Norwalk, CT). For ATR analyses, the circular internal reflectance (CIR) accessory with ZnSe crystal was used.

For transmission analysis, PEO-PPO copolymers (liquid samples) were cast onto a NaCl cell and the film was covered with another NaCl cell (capillary film technique).

Table I Characterization Data of the PEO-PPO Block Copolymers⁹⁻¹¹

Structure	\bar{M}_n^a	\bar{M}_w/\bar{M}_n^b	EO/PO Ratio ^c	CMC ^d (%)
C ₄ -(EO) ₄ -(PO) ₁₁ -OH	920	1.24	0.36	2.70
C ₄ -(PO) ₁₀ -(EO) ₆ -OH	900	1.23	0.60	1.45
C ₁₂₋₁₄ -(EO) ₉ -(PO) ₆ -OH	910	1.12	1.50	0.007

^a Determined by vapor pressure osmometry (VPO).

^b Determined by gel-permeation chromatography (GPC).

^c Determined by nuclear magnetic resonance of hydrogen (¹H-NMR).

^d Determined by surface tension measurements of the aqueous copolymer solutions at 30°C.

The spectra were obtained at a 2 cm⁻¹ resolution, 100 scans, and processed by an IRDM.

Refraction Index Measurements

The refraction index measurements were obtained using a Bausch & Lomb refractometer (Bausch & Lomb, Rochester, NY) at 25°C.

RESULTS AND DISCUSSION

Aqueous Solutions of PEO-PPO Copolymers

Surface Tension Measurements

As shown in previous works,^{10,11} the surface tension curves (as a function of the surfactant concentration in aqueous solutions) show that the surface tension decreases as the surfactant concentration increases. This behavior identifies the surface adsorption process by the surfactant until the surface tension becomes almost constant, even after adding more surfactant. In this step, the surfactant adsorption at the surface is no longer observed and the solubility takes place by the surfactant aggregation in the solution. The adsorption occurs not only at the surface but also at the liquid-solid interface.

By the surface tension technique, it was possible to determine the CMC values, in addition to the surface activity of the PEO-PPO copolymers. The results obtained showed that these parameters were dependent on the structure of the copolymers.^{10,11}

FTIR/Transmission Analyses

The monofunctional diblock copolymers of PEO-PPO were analyzed by FTIR/transmission to identify the groups present in its chains by the absorption bands. The spectrum obtained, shown

in Figure 2, presents the characteristic absorption bands, in agreement with those presented in the literature¹²: at 3486 cm⁻¹, absorption of axial deformation of the OH group; at 2971 cm⁻¹, absorption of asymmetric axial deformation of the CH₃ and CH₂ groups; at 2872 cm⁻¹, absorption of symmetrical axial deformation of the CH₂ and CH groups; at 1458 cm⁻¹, absorption of asymmetric angular deformation of the CH₃ group; at 1345 cm⁻¹, absorption of angular deformation of the OH group; at 1094 cm⁻¹, absorption of asymmetric axial deformation of the C—O—C group; at 1014 cm⁻¹, absorption of axial deformation of the C—O group; and at 867 cm⁻¹, angular deformation of the CH₂ group.

FTIR/CIR Analyses

To study the interface of the aqueous copolymer solutions, we chose the absorption band at 1094 cm⁻¹, relative to the C—O—C group absorption, because the water does not present any absorption bands in this area (see the spectrum in Fig. 3).

The crystal used in the CIR accessory was ZnSe, which is water insoluble and exhibits a high refraction index (from 2.31 to 2.44, in the wavelength interval from 667 to 3636 cm⁻¹). The refraction index of the samples was measured and the solutions manifested values in the range of 1.2–1.4. Therefore, this crystal can be used because its refraction index is higher than that of the sample. The penetration depth changes as a function of the wavelength, calculated by using eq. (1), to be around 2.3 mm for the wavelength of 1094 cm⁻¹. To investigate whether such penetration depth is in agreement with our objective (to analyze the adsorption at the liquid-solid interface) we analyzed the PEO-PPO copolymer solutions before and after CMC.

Figure 4 presents the enlarged spectrum obtained for the C₄-(PO)₁₀-(EO)₆-OH copolymer,

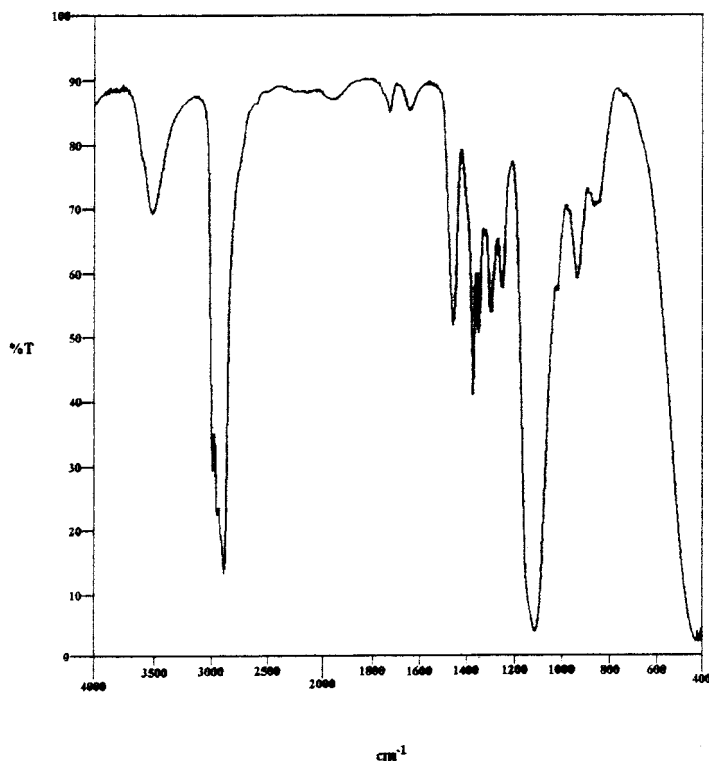


Figure 2 FTIR/transmission spectrum of $C_4-(PO)_{10}-(EO)_6-OH$ copolymer.

showing the C—O—C group absorption band. The other copolymers studied presented similar spectra.

As shown previously,¹⁰ after the formation of micelles, the aqueous solution surface is already saturated. Thus, graphs of absorption variation as a function of surfactant concentration, before and after CMC, were plotted. Before CMC, the absorbance relative to the molecules present at the interface layer increases, given that the surface is not yet saturated with surfactant. After CMC, this absorbance should be practically constant because the surface is already saturated. However, it is observed (Fig. 5) that the absorbance increases as the surfactant concentration increases, even after CMC (1.45 wt %). The results show that the radiation penetration depth in the analysis allowed us to observe beyond the surfactant monolayer.

Aqueous Copolymer Solutions Containing the Hydrotrope

Surface Tension Measurements

Hydrotropes or hydrotropic agents are organic compounds that enhance the aqueous solubility of

poorly soluble organic compounds. These agents form associated structures at a certain concentration and temperature, and their ability to increase the solubility of organic compounds seems to depend on the formation of these structures.^{13,14}

By surface tension analyses of aqueous NaPTS solutions, its aggregation point was determined at 0.5M concentration.^{9,10}

To study the influence of the hydrotrope on the copolymer interfacial adsorption, the surface tension were measured as a function of NaPTS concentration, containing 1 wt % of the copolymer in the aqueous solutions.¹⁰ At this copolymer concentration, the results obtained showed that as the NaPTS concentration increases, the surface tension remains constant up to the NaPTS aggregation concentration. Beyond this NaPTS concentration, the surface tension increases. Therefore, the first portion of these curves is related to the adsorption of copolymers at the air/water interface and NaPTS molecules in solution can be associated with micelles of the copolymers, given that the interface is saturated. After NaPTS aggregation in solution, an increase of the surface tension values (second portion of these curves) is

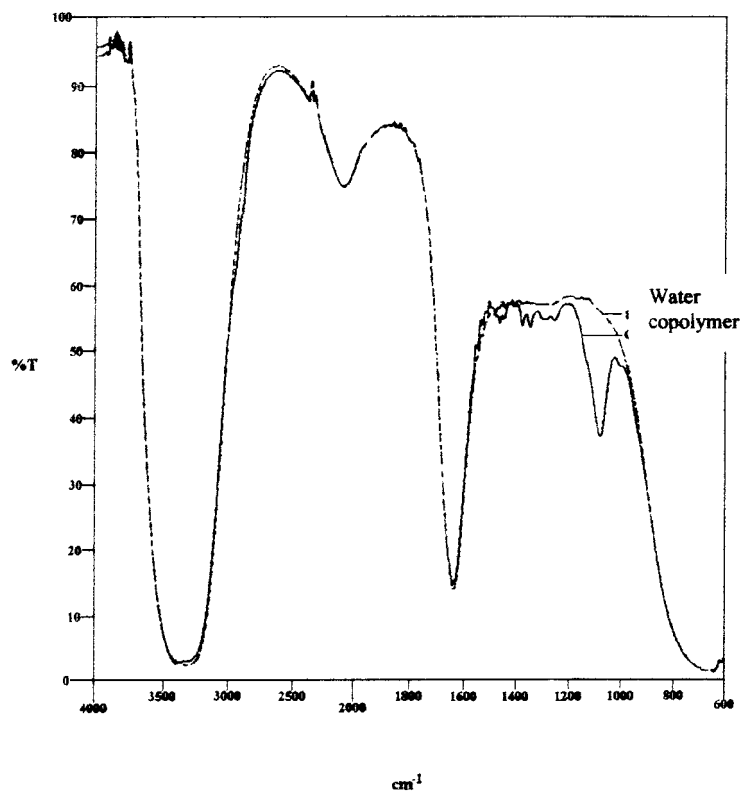


Figure 3 FTIR/CIR spectra: water and $C_4-(PO)_{10}-(EO)_6-OH$ copolymer in aqueous solution (concentration = 8 wt %).

observed, suggesting a displacement of the copolymers from the air/water interface to the bulk solution. To confirm this suggested phenomenon, additional measurements of the same solutions by FTIR/CIR were carried out.

FTIR/Transmission Analyses

The aqueous NaPTS solution was also analyzed by FTIR/transmission. Figure 6 shows the spectrum obtained. The characteristic absorption bands were observed, in agreement with those presented in the literature¹²: at 1180 cm^{-1} , absorption of symmetrical axial deformation of the $S(=O)_2$ group; at 1035 cm^{-1} , absorption of axial deformation of the $S-O-C$ group; and at 1012 cm^{-1} , absorption of axial deformation of the $S-O-C$ group.

FTIR/CIR Analyses

The behavior of the aqueous copolymer solutions containing NaPTS was evaluated using two different conditions. In the first condition, the copolymer concentrations were changed and the

NaPTS concentration remained constant; in the second condition, the NaPTS concentrations were changed and the copolymer concentration remained constant.

Study of the Aqueous Copolymer Solutions Containing NaPTS at Constant Concentration, at Different Copolymer Concentrations. Figure 7 presents the spectra of the aqueous NaPTS solutions at different concentrations and the aqueous copolymer solutions [$C_4-(PO)_{10}-(EO)_6-OH$] containing NaPTS at $0.75M$. These spectra show the characteristic absorption bands,¹² already mentioned. It can be observed that the absorption band at 1180 cm^{-1} (A_{1180}), relative to NaPTS, it is the only one that is not overlapped with the absorption band of the copolymer [1094 cm^{-1} (A_{1094})]. For this reason, the graphs of the absorption band ratio of the copolymer and NaPTS as a function of the copolymer concentration were plotted using A_{1094}/A_{1180} (Fig. 8).

By these plots, it is observed that the A_{1094}/A_{1180} ratio increases as the copolymer concentration increases, for the three NaPTS concen-

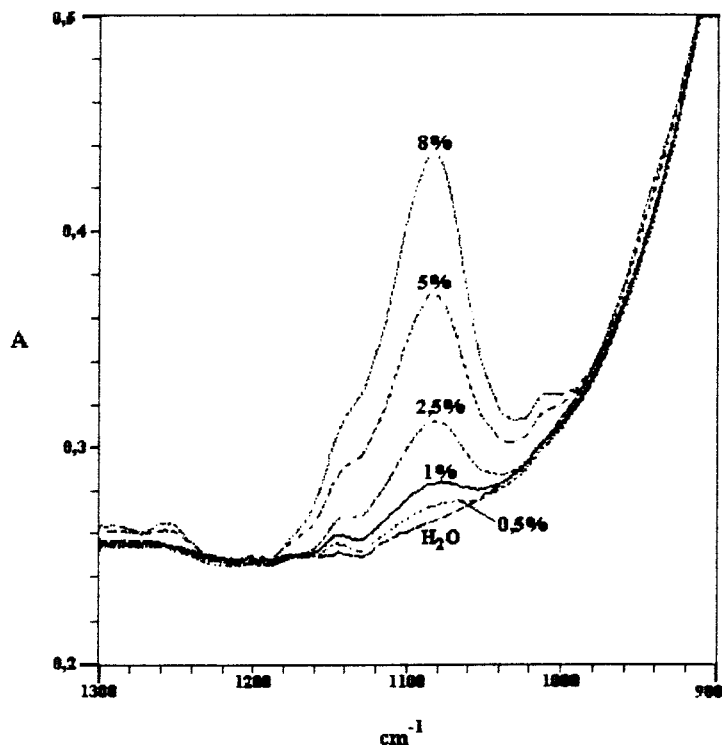


Figure 4 Enlarged FTIR/CIR spectrum for the $C_4-(PO)_{10}-(EO)_6-OH$ copolymer showing the C—O—C group absorption band of these copolymer in aqueous solution.

trations studied. The same behavior was observed when analyzing the aqueous copolymer solutions without NaPTS. The copolymer adsorption at the liquid–solid interface increased

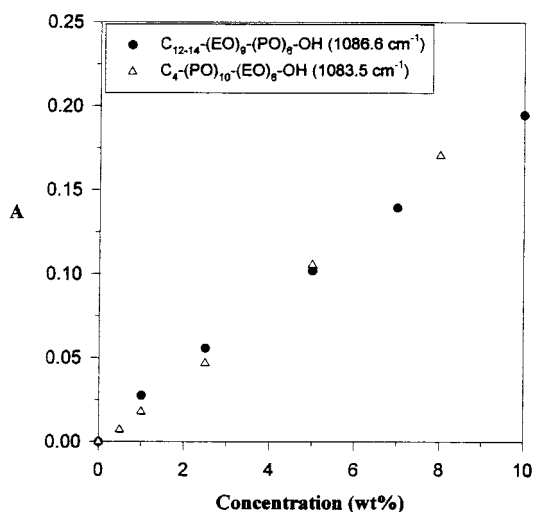


Figure 5 Graph of absorption variation as a function of surfactant concentration in aqueous solution, both before and after copolymer CMC.

even at concentrations above CMC. However, the straight-line slope obtained for the aqueous copolymer solutions containing NaPTS, at the concentration below its aggregation point ($0.25M$), is greater than that obtained for these solutions using NaPTS concentrations above its aggregation point (0.5 and $0.75M$). This behavior indicates a decrease of the copolymer concentration at the liquid–solid interface as the NaPTS concentration increases, which means there is a displacement of the copolymer molecules from the interface to the bulk as a result of the solubility increase caused by the presence of the NaPTS aggregates. The results are in agreement with the temperature versus concentration phase diagrams shown in the previous study,⁹ which show that the increase of these copolymers' solubility is caused by NaPTS. Moreover, this behavior at the liquid–solid interface can be extended to the liquid–air interface and the increase of surface tension as the NaPTS concentration increases above the aggregation point can be attributed to the copolymers' displacement from the surface to the bulk.¹⁰

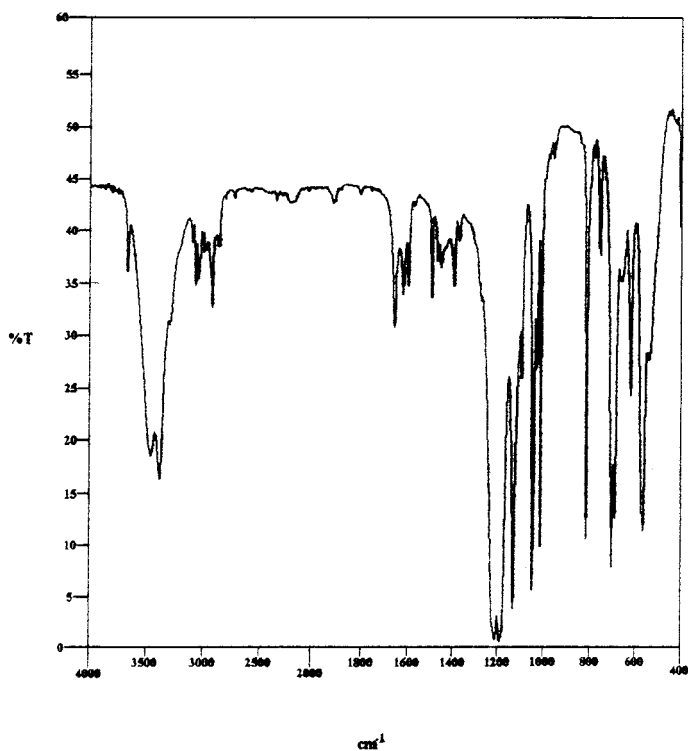


Figure 6 FTIR/transmission spectrum of aqueous NaPTS solution.

Study of Aqueous NaPTS Solutions, at Different Concentrations, Containing Copolymer at Constant Concentration. The spectra of the aqueous NaPTS solutions, for different concentrations,

containing the PEO-PPO copolymer (5 wt %) are shown in Figure 9. The plot of A_{1094}/A_{1180} as a function of NaPTS concentration is presented in Figure 10.

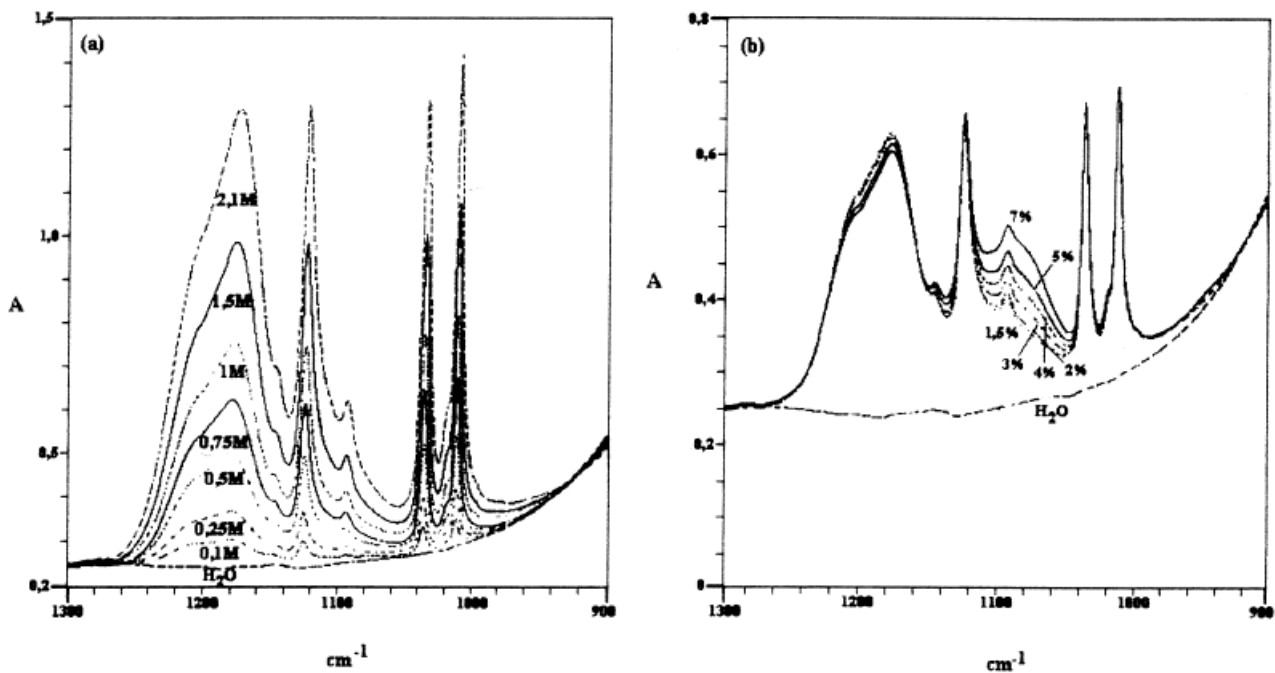


Figure 7 FTIR/CIR spectra: (a) aqueous NaPTS solutions at different concentrations; (b) aqueous copolymer solutions $[C_4-(PO)_{10}-(EO)_6-OH]$ containing NaPTS at 0.75M.

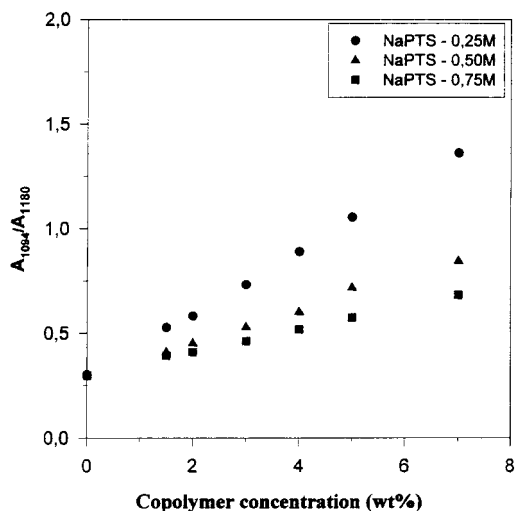


Figure 8 Graph of ratio of absorption bands A_{1094}/A_{1180} as a function of PEO-PPO *block*-copolymer concentration in aqueous solution containing NaPTS.

By analyzing the plot, it is observed that the relation between the absorption bands of the copolymer and NaPTS decreases as the NaPTS concentration increases, up to a concentration of 1.0M, at which level this relation becomes practi-

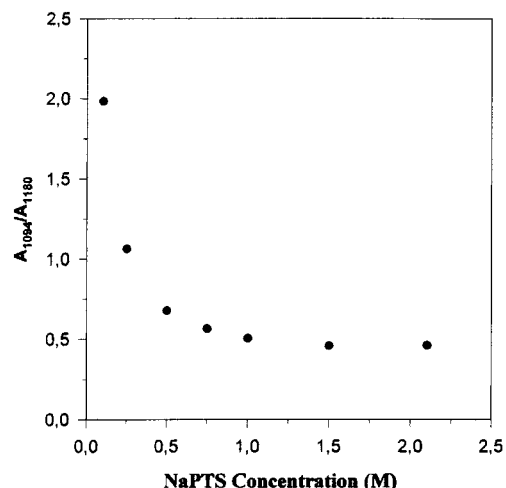


Figure 10 Graph of ratio of absorption bands A_{1094}/A_{1180} as a function of NaPTS concentration in aqueous solution containing the PEO-PPO copolymer (5 wt %).

cally constant. This behavior confirms the previous observations: the decrease of the copolymer adsorption at the liquid-solid interface and also the saturation of the solution layer closer to the liquid-solid interface, at NaPTS concentrations above 1.0M.

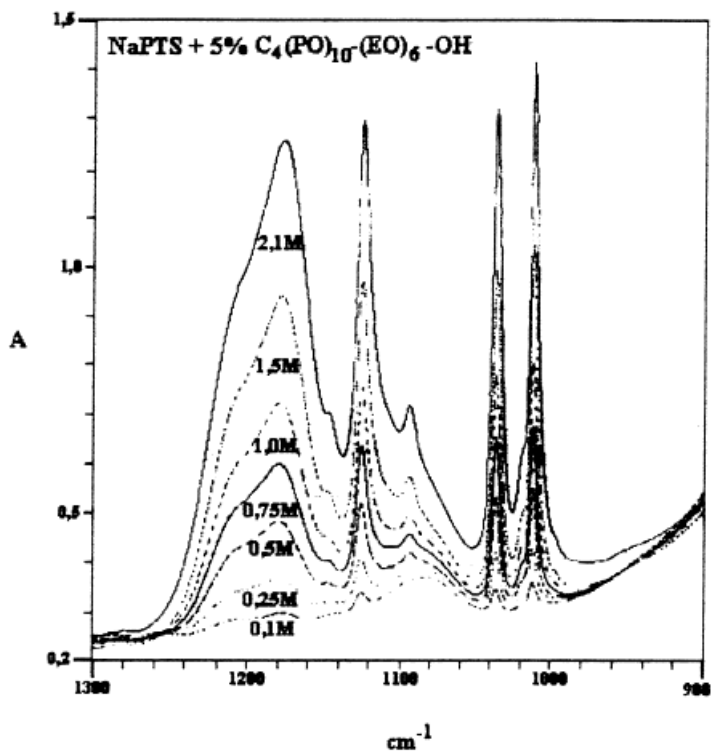


Figure 9 FTIR/CIR spectrum of the aqueous NaPTS solutions, for different concentrations, containing the PEO-PPO $C_4-(PO)_{10}-(EO)_6-OH$ copolymer (5 wt %).

CONCLUSIONS

Analyses by Fourier transform infrared spectroscopy, using the CIR accessory, were obtained for the first time and the results showed that it is possible to determine the behavior the aqueous copolymer solutions at the liquid–solid interface. Although it was possible to obtain the spectra of these solutions using the CIR technique, the radiation penetration allowed us to observe beyond the surfactant monolayer.

Moreover, the study of aqueous copolymer solutions containing NaPTS is very important, given that this hydrotrope has its own surface activity and changes the behavior inside the solutions. Observations confirmed that the NaPTS aggregates cause a decrease of the PEO–PPO copolymer's absorption at the liquid–solid interface and an increase of the PEO–PPO copolymer's solubility. The surfactant displacement by NaPTS from the interface to the bulk was observed by FTIR/CIR, which explains the increase of surface tension observed previously.^{10,11}

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