Behavior of Aqueous Solutions of Poly(ethylene oxide-*b*-propylene oxide) Copolymers Containing a Hydrotropic Agent

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ABSTRACT: The effect of the hydrotropic agent, sodium *p*-toluenesulfonate (NaPTS), was evaluated on the micelle formation process and on phase behavior of aqueous solutions containing poly(ethylene oxide-*b*-propylene oxide)(PEO–PPO) copolymers. We have studied monofunctional diblock copolymers coupled with hydrocarbons groups (R—PEO—PPO—OH and R—PPO—PEO—OH, where *R* length is linear C_4 and C_{12-14}). The critical micelle concentration (CMC) and critical micelle temperature (CMT) values of the aqueous copolymers solutions were obtained from both surface tension versus concentration plots and the dye solubilization method. The influence of the hydrocarbons groups length and PPO segment position in the structure of the copolymers were also analyzed. The same measures were obtained for the aqueous solutions of hydrotropic agent which, in turn, also presented molecular aggregation. The presence of the hydrotropic agent in the aqueous copolymers solutions altered the surface tension of these solutions and the occupied molecular area per copolymer molecule at air–water interface and CMC and CMT values of the copolymers. On the other hand, the aggregation points and the surface tension of the NaPTS solutions were dependent on the copolymer structure and composition. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2459–2468, 1998

Key words: copolymers; surface tension; dye solubilization; hydrotropy

INTRODUCTION

Block copolymers of poly(ethylene oxide)(PEO) and poly(propylene oxide)(PPO) have long been known as nonionic surfactants.[1] Although PPO and PEO have a similar structure, the former is not water-soluble under usual conditions and is the hydrophobic portion of the surfactant.[2] In aqueous solutions, these copolymers undergo phase separation as a function of temperature, and such temperature is known as the cloud point. Below this temperature, such copolymers can remain in solution, not as unimers, but in the form of aggregates, called micelles. Experimentally, the micelle formation region can be determined by the measurements of some physical and spectroscopic properties that change with the micelle formation as a function of the surfactant concentration or the surfactant temperature in the aqueous solutions. Such properties include surface tension, density, and osmotic pressure.[3] The critical micelle concentration (CMC) and the critical micelle temperature (CMT) are the concentration

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and temperature at which the micelles start forming, respectively.[4] The micelle formation of the difunctional triblock copolymers (HO—PEO—PPO—PEO—OH), the widely known series of commercial products, PLURONIC polyols, was extensively studied because of the importance of these systems in several industrial applications.[1,5] These spherical micelles are composed of a central core of dense PPO and an outer corona of hydrated EO units.[6] Micellar systems enhance the solubility of water-insoluble compounds because the core of the micelles provides a suitable microenvironment for solubilization.[7] The more important parameters studied are the concentration at which the micelles start forming, fraction of the copolymers molecules in the micellar form, and the size and number of the micelle aggregates.[8–13]

We have studied the phase behavior of aqueous solutions of monofunctional diblock copolymers (R—PEO—PPO—OH and R—PPO—PEO—OH, where R length is linear C_4 and $C_{12–14}$).[14] We have also studied the influence of the hydrotrope, sodium p-toluenesulfonate (NaPTS), in these copolymers solutions, and an increase of the copolymer solubility in the aqueous solutions was observed. The copolymers' phase diagrams depended on the copolymer structure.

The literature[15,16] has shown that the hydrotropes or hydrotropic agents are organic compounds that enhance the aqueous solubility of poorly soluble organic compounds. The molecular mechanism of hydrotropic solubilization has not yet been explained, but it seems clear that hydrotropy differs from micellar solubilization and from the salting-in effect by some inorganic salts. It has also been shown that the hydrotropes can solubilize molecules that do not necessarily form crystal phases, like dyes or drugs.

The purpose of this work is to verify the micelle formation of ethylene oxide–propylene oxide (EO–PO) block copolymers in aqueous solutions by the surface tension measurements, dye solubilization method, and differential scanning calorimetry (DSC) analysis; the latter also showed the phase behavior of these copolymers solutions. The copolymers used were the same as analyzed in previous work,[14] monofunctional diblock copolymers (R—PEO—PPO—OH and R—PPO—PEO—OH, where R length is linear C_4 and $C_{12–14}$). Moreover, the effect of sodium p-toluenesulfonate (NaPTS), used as the hydrotrope, on the aqueous copolymers solutions was studied. The influence of the length of the hydrocarbon groups and PPO segment posi-

tion in the PEO–PPO chains, and the interaction between the copolymers and NaPTS was also analyzed.

EXPERIMENTAL

Materials

Monofunctional diblock copolymers of EO and PO (R—PEO—PPO—OH and R—PPO—PEO—OH; R length = linear C_4) and C_{12}—(EO)$_6$—OH were obtained from OXITENO (Grupo Ultra-Divisão Química). Monofunctional diblock copolymers of EO–PO (R—PEO—PPO—OH and R—PPO—PEO—OH; R length = linear $C_{12–14}$) were obtained from Henkel S.A. Indústrias Químicas.

NaPTS and the dye 1,4-bis(isopropylamino) anthraquinone were obtained from COEMA S.A. and ZENECA Brasil S.A., respectively. Copolymers characterization data are summarized in Table I.[14,17]

Methods

Surface Tension Measurements

The surface tension was measured using a Krüss tensiometer equipped with a platinum ring (Krüss instruments, K-10 model, digital tensiometer), at 30°C, controlled by a circulation water thermostatic bath (Ophterm, ECV model, 088179 serial), which was connected to the surface tension cell. For each copolymer solution, a surface tension (mM/m) versus copolymer concentration (wt %) plot was built at a range of 3–0.0001 wt % in order to determine CMC values. CMT values were determined using a surface tension as a function of copolymer solution temperature (copolymer concentrations at 1 and 10 wt %), in the temperature range of 8–40°C. The calibration curve of the water was constructed using the same range of the copolymers solutions temperature.

The measurements using NaPTS were obtained by the same method described above. First of all, surface tension measurements of aqueous solutions as a function of NaPTS concentration in the range of 0.05–2.10M were analyzed. After this, surface tension measurements of the copolymers solutions, at 1 wt %, containing NaPTS concentrations in the range of 0.05–2.10M and surface tension measurements of the NaPTS solutions, at 0.25, 0.50, and 0.75M, containing copolymers concentrations in the range of 3–0.0001 wt %, were analyzed. All analyses were

Table I   Characterization of EO–PO Block Copolymers

Copolymer	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]	EO/PO Ratio[c]	O/C Ratio[d]
C$_4$—(EO)$_4$—(PO)$_{11}$—OH	920	1.24	0.36	0.36
C$_4$—(PO)$_{10}$—(EO)$_6$—OH	900	1.23	0.60	0.37
C$_{12-14}$—(PO)$_4$—(EO)$_5$—OH	600	1.15	1.25	0.29
C$_{12-14}$—(EO)$_6$—(PO)$_5$—OH	720	1.15	1.20	0.30
C$_{12-14}$—(EO)$_9$—(PO)$_6$—OH	910	1.12	1.50	0.33

[a] By vapor pressure osmometry (VPO).
[b] By gel permeation chromatograph (GPC).
[c] By ^{1}H nuclear magnetic resonance spectroscopy (^{1}H-NMR)
[d] O/C means oxygen-to-carbon atoms ratio.

obtained at 30°C. The reliability of results is ±0.5 dynes/cm.

Dye Solubilization Method

The dye solubilization method[11] was used in order to verify CMC and CMT values of the aqueous copolymers solutions. The hydrophobic dye used was 1,4-bis(isopropylamino) anthraquinone. The dye solution in methanol was analyzed in the ultraviolet (UV) visible equipment (CAMSPEC spectrofotometer, model M330) to determine the wavelength at which the dye absorption is maximum. Methanol was used to prepare the dye solution since this solvent, at low concentrations, has little influence on CMT values of the aqueous nonionic surfactants solutions.[11]

The aqueous copolymers solutions were prepared in the concentration range of 0.1–4.5 wt %. The dye concentration in methanol was 0.4 mM, and 2.5 μL of this solution were added to 2.5 mL of copolymer solution so that the final copolymer solution contained 1% v/v methanol and 0.004 mM dye. The solutions were left at the temperature of the measurement to equilibrate for at least 3 h (the temperature range was 16–40°C). The UV absorption of copolymer–hydrophobic dye in methanol–water samples was recorded at the 640 nm (the maximum absorption of the dye) using a colorimeter.

CMC values of the C$_4$—(PO)$_{10}$—(EO)$_6$—OH copolymer in aqueous solutions containing NaPTS (0.13–2.10M) and aggregate formation of NaPTS was also determined through this method, using the same procedure described above.

RESULTS AND DISCUSSION

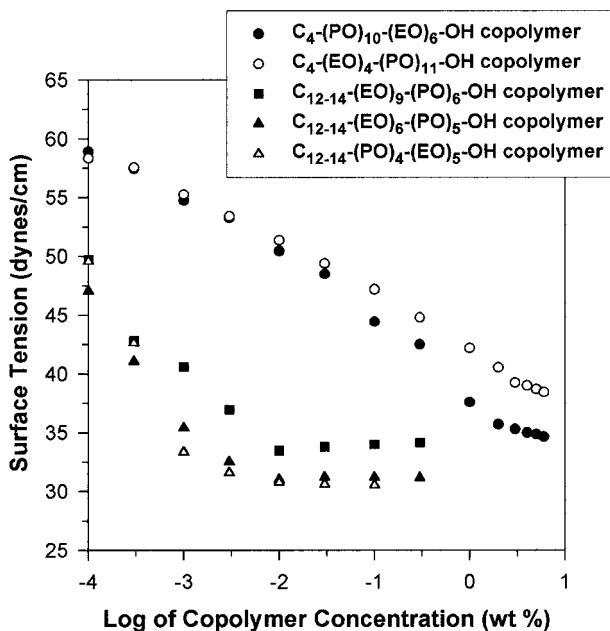### Surface Activity of Aqueous Copolymers Solutions

To study CMC of the EO–PO block copolymers, surface tension measurements as a function of aqueous copolymer solution concentration were performed. In general, surface tension versus concentration plots show a discontinuity in the slope. The first portion of the curve (at lower concentration) is related to the surfactant adsorption at the interface and the second portion of the curve (at higher concentration) is usually a straight line parallel to the concentration axis and indicates that, in this step, adsorption does not take place. The extension of both portions leads to the discontinuity average, which is related to the CMC.[18] This behavior of the surface tension plots of the copolymers solutions may be described using Gibb's adsorption equation, as follows[3,4]:

$$\Gamma = \frac{-1}{RT}\left(\frac{\partial\gamma}{\partial\ln C}\right)_{P,T} \qquad (1)$$

where γ is the surface or interfacial tension, C is the concentration of the solution, Γ is the surface excess (moles or surfactant adsorbed per unit area), R is the gas constant and T is the absolute temperature.

The surface tension (γ) curves were plotted as a function of the copolymer solution concentrations (log C). Equation (1) shows a number of features applied to the γ–log C curves. Just below CMC, γ changes linearly with log C indicating that ($\partial\gamma/\partial$ log C) is constant. This shows that in this region, saturation of the interface by the surfactant molecules must have taken place. On the other hand, above CMC, ($\partial\gamma/\partial$ log C) equals 0. Since γ remains constant in this region, the concentration of unimers must remain constant above CMC. Equation (1) can be applied to obtain Γ, from the gradient of the linear portion of the γ–log C curve just below CMC. The area per molecule can be obtained from Γ, since[3]

Figure 1 Surface tension as a function of aqueous copolymer solution concentrations, at 30°C.

$$\text{area/molecule} = \frac{1}{\Gamma N_A} \qquad (2)$$

where N_A is the Avogadro constant.

Equation (1) can also be expressed by the following equation:

$$\text{area/molecule} = -\frac{2.3RT}{N_A} \left(\frac{\Delta \log C}{\Delta \gamma} \right) \qquad (3)$$

Figure 1 shows the surface tension of the copolymers as a function of copolymers concentrations. It can be seen that the surface tension decreases (from 72 dynes/cm for water) to a limit value around 30–40 dynes/cm. The surface tension of the aqueous solutions was reduced more significantly when copolymers with R length equal to C_{12-14} were used. At lower concentrations, the copolymers with R length equal to C_4 presented lower surface activity than the copolymers with R length equal to C_{12-14}; but at higher concentrations (at CMC), the surface tension values of the solutions became closer. The copolymers with R length $= C_4$ have lower surface activity when used at low concentrations; but at higher concentrations (at CMC), these copolymers have surface tensions near to the values of the copolymers with

R length equal to C_{12-14}. Table II shows CMC and surface tension values obtained from plot 1, and the area per molecule of the copolymer at the air–water interface calculated using eq. (3).

According to Table II, the copolymers with R length equal to C_{12-14} have much lower CMC values than the copolymers with R length equal to C_4. This can be ascribed to the hydrophobic segment length. By analyzing the CMC result for the C_{12}—$(EO)_6$—OH solution, it was observed that this value was similar to that of the C_{12-14}—(EO)$_6$—$(PO)_5$—OH copolymer solutions. This behavior can be due to the hydrophobic segment length having a higher influence on the CMC values of these copolymers than the EO/PO ratio since the copolymers with R length equal to C_{12-14} have higher EO/PO ratios than the copolymers with R length equal to C_4 (Table I). The longer the hydrocarbon segments in these EO–PO chains, the easier the molecular aggregation.

By analysing CMC results (Table II) for the copolymers with R length equal to C_{12-14} solutions, C_{12-14}—$(EO)_9$—$(PO)_6$—OH has the higher CMC due to its highest EO/PO ratio (Table I). On the other hand, C_{12-14}—$(EO)_6$—$(PO)_5$—OH has a higher CMC value than C_{12-14}—$(PO)_4$—$(EO)_5$—OH, even though their EO/PO ratios were similar (Table I). The same behavior was observed for the copolymers with R length equal to C_4, where C_4—$(PO)_{10}$—$(EO)_6$—OH has a lower CMC value than C_4—$(EO)_4$—$(PO)_{11}$—OH, although the former has a higher EO/PO ratio (Table I). In our study on the phase behavior of these copolymers,[14] we showed that the copolymer in which hydrophilic (EO and OH)–hydrophobic (R and PO) segments are alternating exhibits a higher cloud point and CMC value than the copolymer constituted of adjacent segments. Such behavior was ascribed to the ease of molecular association induced by the structure for the copolymer in which hydrophilic–hydrophobic segments are adjacent. We have already proposed a model for the molecular association in both cases.

Table II also shows that the copolymers with R length equal to C_{12-14} have smaller surface areas than copolymers with R length equal to C_4. This means that the higher the hydrophobic block, the smaller the surface area occupied by the copolymer. Donbrow[19] showed that in nonionic surfactant derivatives of EO chains (hexadecanol and dodecanol), the hydrophobic group has little influence on the surface area, which is determined by the size of the hydrated EO; the hexadecanol

Table II Results Obtained from the Surface Tension Measurements for the Aqueous Copolymers' Solutions

| Copolymer	Initial Surface Tension (dyn/cm)	CMC (wt %)	Surface Tension at CMC (dyn/cm)	Final Surface Tension (dyn/cm)	Area per Molecule (A^{o2}/molecule)
C_4—$(EO)_4$—$(PO)_{11}$—OH	58.4	2.700	39.7	38.5	162.6
C_4—$(PO)_{10}$—$(EO)_6$—OH	59.0	1.450	36.0	34.4	140.0
C_{12-14}—$(PO)_4$—$(EO)_5$—OH	49.9	0.001	31.7	30.6	59.1
C_{12-14}—$(EO)_6$—$(PO)_5$—OH	46.4	0.003	31.1	31.2	96.7
C_{12-14}—$(EO)_9$—$(PO)_6$—OH	48.5	0.007	33.5	34.2	118.3
C_{12}—$(EO)_6$—OH	59.5	0.003	28.2	28.2	52.6

derivatives present smaller surface areas than the dodecanol derivatives, but the difference between these surface areas is small; the surface area increased with increasing EO chain length.

The influence of the EO chain size can be observed since C_{12-14}—$(EO)_9$—$(PO)_6$—OH, with the higher EO/PO ratio, has a higher surface area than C_{12-14}—$(EO)_6$—$(PO)_5$—OH. Unusual behavior was observed for the copolymers with adjacent hydrophobic–hydrophilic segments. They presented smaller surface areas in spite of the EO chain size; C_{12-14}—$(PO)_4$—$(EO)_5$—OH exhibited smaller surface area than C_{12-14}—$(EO)_6$—$(PO)_5$—OH, despite both having a similar EO/PO ratio. By comparing the surface area values for the C_{12-14}—$(EO)_6$—$(PO)_5$—OH and C_{12-14}—$(PO)_4$—$(EO)_5$—OH copolymers solutions and the value obtained for aqueous C_{12}—$(EO)_6$—OH solutions (Table II), it was observed that the former has a higher surface area than the others; and the C_{12-14}—$(PO)_4$—$(EO)_5$—OH copolymer and C_{12}—$(EO)_6$—OH presented similar surface area, indicating that the PO block inserted in such position in this copolymer did not alter significantly the surface area value. The behavior of the copolymers with adjacent hydrophobic–hydrophilic segments can be ascribed to the more compact packing of these copolymers molecules at the air–water interface, as was observed in the aqueous C_{12}—$(EO)_6$—OH solutions, and is shown in Figure 2.

Surface Activity of Aqueous NaPTS Solutions Containing 1 wt % of the Copolymer

The study of the surface tension as a function of concentration of aqueous NaPTS solutions showed that the NaPTS is surface active. NaPTS reduces the surface tension of water and at a concentration around $0.5M$ ($\sim$ 8.9 wt %), surface

saturation seems to have been achieved as the surface tension becomes constant around 51 dynes/cm; in any case, such a value is higher than those found for copolymer solutions (Table II). The molecular area occupied at the air–water interface by this hydrotropic molecule was estimated from eq. (3), and this value was 81.35 A^{o2}/molecule. Similar results have been reported for several hydrotropes, and it has been suggested that hydrotropes self-aggregate beyond a given concentration in water to produce noncovalent assemblies.[15] The breaks in surface tension curves of NaPTS solutions might not represent micellization but rather dimerization or stepwise association.[15]
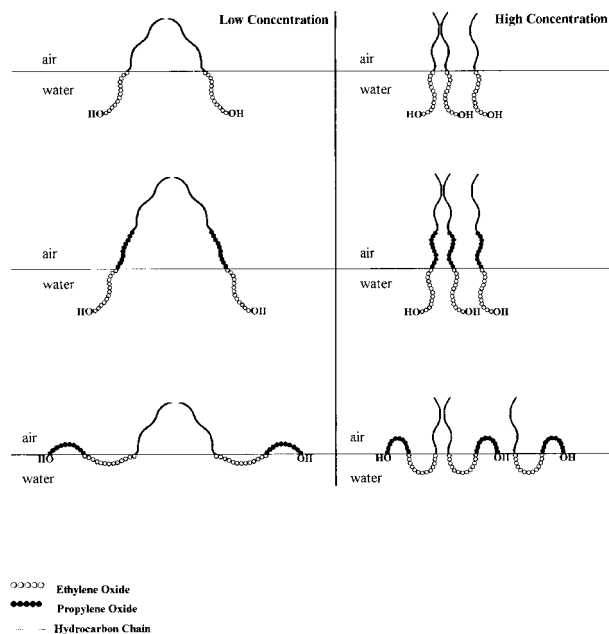
Figure 2 Schematic representation for C_{12}—$(EO)_6$—OH and EO—PO block copolymers with alternate and adjacent hydrophobic–hydrophilic segments structure at the air–water interface.

Table III   Results Obtained from the Surface Tension Measurements of the Aqueous NaPTS Solutions Containing 1 wt % of the Copolymer

Copolymers Added	Surface Tension at 0.05M (dyn/cm)	Aggregation[a] (M)	Surface Tension at CMC (dyn/cm)	Surface Tension at 2.10M (dyn/cm)
C_4—$(EO)_4$—$(PO)_{11}$—OH	40.2	0.20	41.6	43.3
C_4—$(PO)_{10}$—$(EO)_6$—OH	38.1	0.22	38.2	42.9
C_{12-14}—$(PO)_4$—$(EO)_5$—OH	31.2	0.55	30.7	33.4
C_{12-14}—$(EO)_6$—$(PO)_5$—OH	31.2	0.53	31.7	34.6
C_{12-14}—$(EO)_9$—$(PO)_6$—OH	34.3	0.50	34.5	36.3
—	64.15	0.55	51.0	51.0

[a] Aggregation of NaPTS in solution.

To study the influence of the copolymer structure on aqueous NaPTS solutions, surface tension curves as a function of NaPTS solutions containing 1 wt % of the copolymer were plotted and the results are summarized in Table III. The opposite behavior from that observed for the NaPTS solutions was found for the NaPTS solutions containing 1 wt % of copolymer: at increasing NaPTS concentration, the surface tension remained constant up to the NaPTS aggregation concentration. Beyond this concentration, surface tension increased. Through these analyses, it can be observed that the aggregation concentration of NaPTS depends on the copolymer structure and composition.

For copolymers with R length equal to C_{12-14} (Table II), 1 wt % is above the CMC. From the results, it may be observed that the micelles of these copolymers did not alter to a great extent the aggregation concentration of NaPTS in aqueous solution. The surface tension values at $0.05M$ of NaPTS (shown in Table III) were similar to the surface tension values obtained above the surface saturation, that is, at the final surface tension values presented in Table II. Therefore, the first portion of these curves is related to the copolymers adsorption at the air–water interface, and NaPTS molecules in solution can be associated to micelles of the copolymers since the interface is saturated. After NaPTS aggregation in solution, an increase of the surface tension values (second portion of these curves) is observed that may indicate a displacement of the copolymers from the air–water interface to bulk solution. This behavior can be ascribed to NaPTS aggregates, which can increase the interactions between the solvent and the solute molecules.

According to Table II, the copolymers with R length equal to C_4 did not show micelles formation at 1 wt %. These copolymers did not reduce the aggregation concentration of NaPTS in aqueous solutions (Table III). This effect may be ascribed to the presence of the unassociated surfactant molecules, which decreased the concentration of the free solvent molecules to interact with the solute. Therefore, the first portion of these curves is related to the coadsorption of the copolymers and NaPTS at the air–water interface since, in agreement with Figure 1, this interface was not yet saturated by the copolymer molecules and NaPTS molecules adsorbed at this interface have little influence on the surface tension. The second portion of the curves presents the same behavior observed for the copolymers with R length equal to C_{12-14}.

Surface Activity of Aqueous Copolymer Solutions Containing NaPTS

Since the formation of an associated structure is required for hydrotropic effect, the surface tension curves of copolymers solutions were built up using NaPTS concentrations before, after, and around the concentration at which it self-aggregates (0.25, 0.75, and $0.50M$, respectively). Figure 3 shows these curves for 2 copolymers. The other copolymers, coupled with the same hydrocarbon chains, presented the same curve profile; the results for all copolymers are summarized in Table IV.

By analyzing the results shown in Tables II and IV for the C_{12-14}—$(EO)_9$—$(PO)_6$—OH and C_{12-14}—$(EO)_6$—$(PO)_5$—OH copolymers solutions, it is observed that $0.25M$ NaPTS added to these solutions did not alter CMC values nor the area occupied per molecule at the interface. The same was not observed for the same copolymer solutions containing 0.50 and $0.75M$ NaPTS,
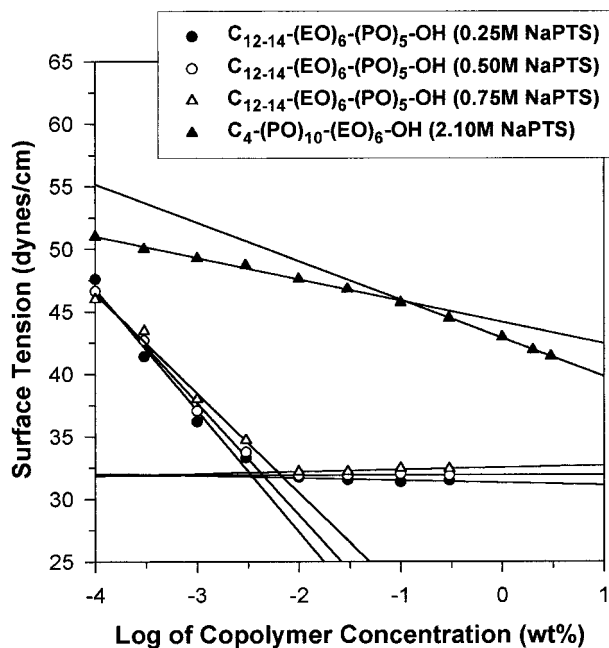
Figure 3 Surface tension as a function of aqueous copolymer solution concentrations containing NaPTS, at 30°C.

which gave CMC values and surface areas increasing significantly at increasing NaPTS concentration. C_{12-14}—$(EO)_9$—$(PO)_6$—OH and C_{12-14}—$(EO)_6$—$(PO)_5$—OH are more water-soluble than C_{12-14}—$(PO)_4$—$(EO)_5$—OH; therefore, they are less sensitive to the effect provided by NaPTS; the hydrotrope effect is only observed after the aggregation of NaPTS. The copolymers for which the water solubility is poor are more sensitive to the effects provided by NaPTS, just as is shown in our study on the phase behavior of these copolymers.[14] C_{12-14}—$(PO)_4$—$(EO)_5$—OH copolymer is poorly water-soluble so it is more sensitive to the effects provides by NaPTS. This can be observed through the higher CMC and surface area values for the copolymer solutions containing $0.25M$ NaPTS than those for the pure copolymer solutions (Table II), even though there is no NaPTS association at $0.25M$.

The copolymers with R length equal to C_4 presented unusual behavior; CMC values decreased as NaPTS concentration increased, at and above the aggregation concentration. As discussed previously, these copolymers were highly water-soluble, and their surface activities were lower than the copolymers with R length equal to C_{12-14} (Fig. 1). In this case, the nonaggregated NaPTS molecules may be interacting with the solvent mole-

cules, decreasing the free solvent molecules to interact to the copolymer molecule and decreasing CMC. After NaPTS aggregation, the behavior of the copolymer solutions can probably be ascribed to hydrotrope molecule incorporation close to the core of the copolymer micelle forming a mixed micelle.

Surface Tension of Aqueous Copolymers Solutions at Different Temperatures

Another important study is concerned with the determination of the critical micelle temperature (CMT). Figure 4 shows the curves obtained from the surface tensions of aqueous copolymers solutions, at 1 wt %, as a function of temperature and, also, the water calibration curve. The copolymer solutions curves presented a discontinuity related to CMT: below the aggregation temperature the surface tension of the copolymer solutions decreased slightly, just like the pure water curve; above the aggregation temperature, it continued to decrease, with this reduction being more pronounced. At higher temperatures, the copolymer solubility in water decreased so the copolymer molecules tend to go to the interface and self-aggregate in solution.

The CMT results agree with the CMC ones: C_4—$(PO)_{10}$—$(EO)_6$—OH was more water soluble than the 2 others, so its CMT values were higher. CMT decreased for all copolymers as the copolymer concentration increased since the copolymer solubility decreased (Table V). The concentration effect on the solubility was more evident for the C_4—$(PO)_{10}$—$(EO)_6$—OH solutions, in which CMT dropped from 30.4 to 16°C for 1 and 10 wt % copolymer solution concentrations, respectively.

Determination of CMT and CMC of Copolymers Solutions by the Dye Solubilization Method

For the dye solubilization method, 1,4-bis(isopropylamino)anthraquinone was used as a hydrophobic dye. At low temperatures, the dye absorption was not observed due to its hydrophobic character; the dye was not dispersed in solution. At high temperatures, the micelles of the EO—PO block copolymer started forming; the dye could be solubilized into the micelles, and the solution became colored, exhibiting absorption at 640 nm. The absorption intensities of aqueous copolymers solutions containing the hydrophobic dye were measured at 640 nm (the wave length where dye

Table IV   Results Obtained from the Surface Tension Measurements for the Aqueous Copolymers Solutions Containing NaPTS at 0.25, 0.50, and 0.75M Concentrations

Copolymer	Initial Surface Tension (dyn/cm)	CMC (wt %)	Surface Tension at CMC (dyn/cm)	Final Surface Tension (dyn/cm)	Area per Molecule (A^{o2}/molecule)
C_4—$(EO)_4$—$(PO)_{11}$—OH					
0.25M	45.0[a]	2.200	37.5	37.6	163.3[b]
0.50M	45.0[a]	2.100	41.2	38.7	156.8[c]
0.75M	45.1[a]	1.200	42.4	38.1	146.2[c]
C_4—$(PO)_{10}$—$(EO)_6$—OH					
0.25M	44.5[a]	1.400	37.0	35.8	150.2[b]
0.50M	44.2[a]	0.950	40.0	36.3	186.3[c]
0.75M	41.9[a]	0.500	42.2	37.0	189.7[c]
2.10M	51.0	0.160	45.6	41.4	312.0[c]
C_{12-14}—$(PO)_4$—$(EO)_5$—OH					
0.25M	47.5	0.002	32.5	30.3	78.0
0.50M	43.0	0.003	31.3	31.0	130.9
0.75M	43.2	0.006	31.3	31.4	150.5
C_{12-14}—$(EO)_6$—$(PO)_5$—OH					
0.25M	46.9	0.003	31.7	31.3	99.2
0.50M	46.8	0.005	31.9	32.0	107.6
0.75M	46.4	0.007	32.0	32.5	121.1
C_{12-14}—$(EO)_9$—$(PO)_6$—OH					
0.25M	50.0	0.007	33.8	34.5	111.8
0.50M	49.1	0.013	34.4	35.1	138.9
0.75M	48.5	0.022	34.5	35.1	161.0

[a] Initial copolymer concentration = 0.1 wt %.
[b] First slope.
[c] Second slope.

absorption was maximum). Figure 5 shows the dye absorption intensities as a function of temperature for different concentrations of aqueous
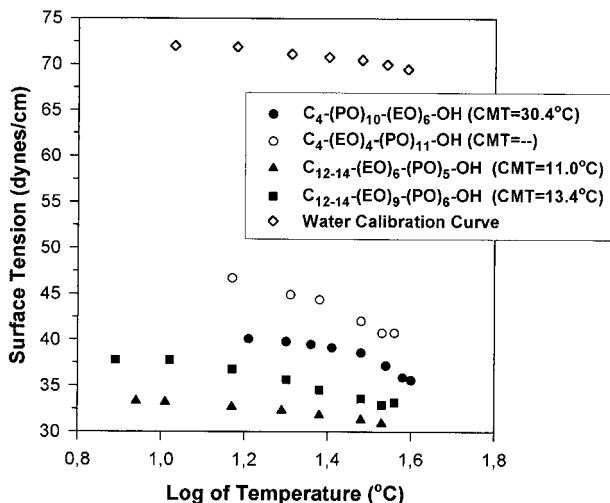
Figure 4   Surface tension versus log T plot of aqueous copolymer solutions. Concentration is 1 wt %.

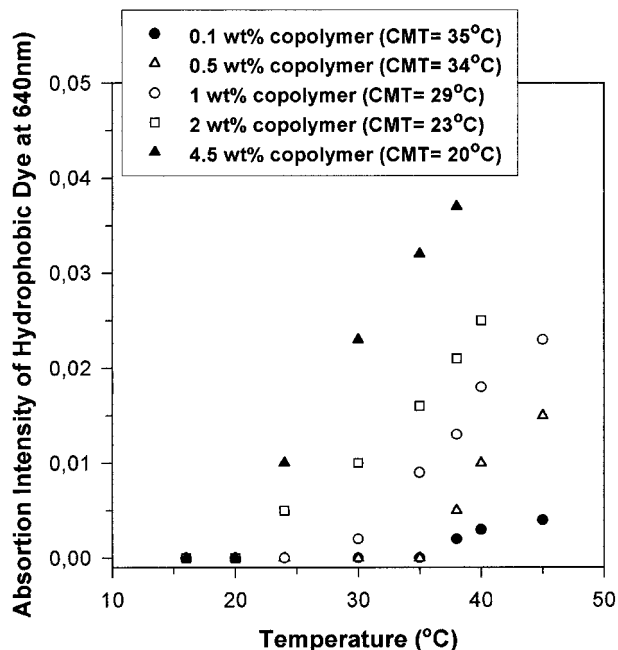C_4—$(PO)_{10}$—$(EO)_6$—OH solutions. CMT values were calculated from the curve inflection.

From Figure 5, we can see the CMT decreasing gradually at increasing copolymer concentration, just as was observed for the surface tension results. CMT values obtained from surface tension measurements and dye solubilization method are in good agreement; for C_4—$(PO)_{10}$—$(EO)_6$—OH

Table V   Results of CMT Values Obtained from the Surface Tension Measures as a Function of Temperature of Aqueous Copolymers Solutions

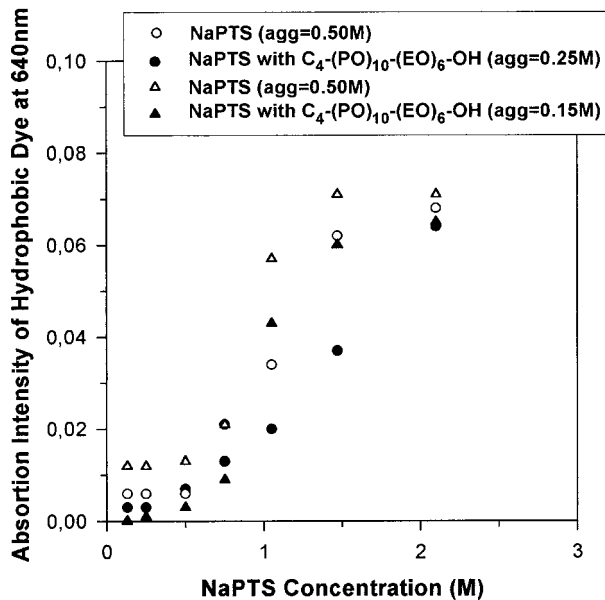| Copolymer	CMT (°C)	
	1 wt %[a]	10 wt %[a]
C_4—$(PO)_{10}$—$(EO)_6$—OH	30.4	16.0
C_{12-14}—$(EO)_6$—$(PO)_5$—OH	11.0	9.0
C_{12-14}—$(EO)_9$—$(PO)_6$—OH	13.4	12.0

[a] Copolymer concentration.

Figure 5 Absorption intensities of the hydrophobic dye at 640 nm as a function of temperature of aqueous C_4—$(PO)_{10}$—$(EO)_6$—OH solutions.

Figure 6 Absorption intensities of hydrophobic dye at 640 nm as a function of NaPTS concentration of aqueous NaPTS solutions with and without 1 wt % copolymer C_4—$(PO)_{10}$—$(EO)_6$—OH. ($\bigcirc$ = 30°C; $\triangle$ = 40°C; Agg = aggregation).

solution at 1 wt %, they were 30.4°C (Fig. 4) and 29.0°C (Fig. 5), respectively.

CMC and CMT values for all copolymers were also obtained by the dye solubilization method. CMT for 1 wt % copolymer solutions and CMC of copolymer solution at 30°C obtained for different copolymers are summarized in Table VI. Even though the dye solubilization method analyzes the bulk solution where micelles form, and the surface tension measurements determine the micelles formation through the surface adsorption, CMT (Tables VI and V) and CMC (Tables VI and II) values from the dye solubilization method and surface

tension measurements are in good agreement for all copolymers studied.

Determination of CMC by the Dye Solubilization Method of Aqueous Copolymers Solutions Containing NaPTS

Figure 6 shows the aggregation results obtained by the dye solubilization method for the aqueous copolymers solutions containing NaPTS. Such results are in agreement with those obtained by surface tension measurements. From Figure 6, it is clear that NaPTS was able to solubilize the hydrophobic dye and also that the C_4—$(PO)_{10}$—$(EO)_6$—OH copolymer reduced the aggregation concentration of NaPTS for analysis at the same temperature. The interaction between the copolymer and NaPTS aggregates caused a reduction in the solution absorption intensity; it is supposed that the NaPTS aggregates associate with the copolymer, resulting in a reduction of the volume available to dissolve the organic dye. If this is true, the NaPTS aggregates solubilize the dye 1,4-bis(isopropylamino)antraquinone better than the mixed aggregates, which are constituted of NaPTS and copolymer.

Table VI   Results Obtained by the Dye Solubilization Method of Aqueous Copolymers Solutions

	CMC (wt %)	CMT (°C)
Copolymers	30°C	1 wt %
C_4—$(EO)_4$—$(PO)_{11}$—OH	2.4	—
C_4—$(PO)_{10}$—$(EO)_6$—OH	1.0	29.0
C_{12-14}—$(EO)_6$—$(PO)_5$—OH	0.004	11.5
C_{12-14}—$(EO)_9$—$(PO)_6$—OH	0.006	13.6

CONCLUSION

These copolymers and NaPTS are surface active, though NaPTS is somewhat less active than the copolymers analyzed. The CMC results obtained for the copolymers showed that these values are dependent on the hydrophobic segment length and PPO position. The copolymers with adjacent hydrophilic–hydrophobic segments presented CMC values lower than the copolymers with alternate hydrophilic–hydrophobic segments.

With increasing NaPTS concentration in the NaPTS–copolymer solutions, the surface tension remained constant until the aggregates of NaPTS start forming; beyond this concentration, the surface tension increased. The aggregation concentration of NaPTS depends on the copolymer structure and composition. The copolymers, which are poorly water-soluble, were more sensitive to the hydrotropic effects provided by NaPTS, as shown in our study on the phase behavior.[14] The copolymers with R length equal to C_4 present an unusual behavior; CMC values decreased at increasing NaPTS concentration, at and above the aggregation concentration. This behavior was ascribed to the interaction between copolymers and NaPTS aggregates.

CMT and CMC values obtained from surface tension measurements and the dye solubilization method presented good agreement.

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