

Linear and Branched Polyoxide-Based Copolymers: Methods to Determine the CMC

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ABSTRACT: Evaluation of the physical–chemical properties of aqueous solutions of nonionic surfactants based on polyoxides can be performed by different methods. Depending on the technique used, there can be a significant variation in the critical micelle concentration (CMC) found. This is related to the sensitivity of the technique regarding the unimers and micelles present in the solution as well as the structure of the surfactant evaluated. In this work, the CMC values of aqueous solutions of linear and branched poly(ethylene oxide–polypropylene oxide) (PEO–PPO) block copolymers were determined by tensiometry, fluorescence, and particle size analysis, using copolymers having adjacent structures (that is, hydrophilic and hydrophobic segments located adjacently in the copolymer) and alternating structures. Tensiometry was used to measure

the surface tension as a function of the copolymer concentration in aqueous solution. Fluorescence was used to determine the fluorescence intensity of pyrene to plot the graphs of the I_1/I_3 and I_E/I_M relations according to the surfactant concentration. Finally, particle size analysis was used to determine the diffusion coefficient of the particles. The results showed that the fluorescence and particle size techniques provide lower (and mutually concordant) CMC values and can be considered more precise because these methods directly analyze the bulk of the solution. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 392–399, 2009

Key words: surfactants; micelles; fluorescence; light scattering

INTRODUCTION

The properties of aqueous solutions of PEO–PPO block copolymers can be studied using various physical methods.¹ The classic techniques to study micelle systems use measures of their macroscopic properties, such as surface tension and viscosity, or thermodynamic properties, determined by differential scanning calorimetry. Besides this, spectroscopic and light scattering techniques can also be used to study these aqueous solutions.²

In this work, we evaluated and compared the critical micelle concentration (CMC) values of aqueous solutions of linear and branched poly(ethylene oxide–polypropylene oxide) (PEO–PPO) block copolymers, determined by three different techniques: tensiometry, fluorescence, and light scattering.

To study the activities of PEO–PPO block copolymers at the water/air interface and determine the CMC values, measures of surface tension can be plotted as a function of the concentration of the aqueous copolymer

solution. In general, the resulting curves have a discontinuity. The behavior of the first segment shows that the solution's surface tension decreases as the surfactant concentration increases, representing its adsorption at the surface. The second segment is in general straight and parallel to the x -axis, where the variation in surface tension is minimal in relation to increasing concentration. At this stage, the surfactant is no longer adsorbed at the surface. The intersection of the extension of these two segments is the average point of the discontinuity and is related to the start of the surfactant's aggregation in solution. The concentration where this point occurs corresponds to the CMC.^{3–7}

The fluorescence method using pyrene as a marker has been employed to study aqueous PEO–PPO block copolymer solutions, due to the fact that this compound presents well resolved emission and absorption spectra. Besides this, the spectra are sensitive to the polarity of the medium where the pyrene is found, making this technique very useful in the study of the micellization of these copolymers in aqueous solution.^{8–13}

The fluorescence spectrum of polynuclear aromatic compounds, such as pyrene, changes as a function of extreme concentration conditions. At low concentrations ($\sim 10^{-5}M$), the pyrene spectrum presents five narrow bands in the region of 350–420 nm, which are differentiated by the medium's polarity. The higher the medium's polarity, the greater will be the I_1/I_3 ratio (the ratio between the intensity of band 1 and that of

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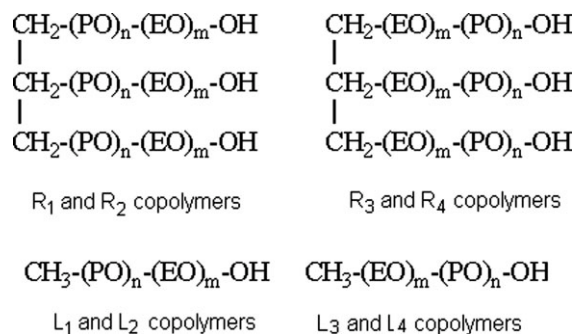


Figure 1 Structures of PEO-PPO block copolymers.

band 3, numbered from the smallest to the greatest wavelength). Generally, the I_1/I_3 ratios are monitored as a function of the surfactant concentration. At concentrations above $10^{-5}M$, a broad band also is observed at the longest wavelengths (~ 460 nm). This band is attributed to the pyrene excimer, a denomination used to designate molecular complexes involving two molecules of the same type, which forms only in the excited electronic state. Usually, these complexes are formed with the molecules oriented in a configuration where their planes are parallel, forming a sandwich structure.^{14,15}

These processes show that the formation of these species depends on concentration, and that the excimer emission is always different than the emission of isolated molecules. Besides this, their emission spectra do not present a vibrational structure and have very

broadened bands at lower energy levels than those of the emissions corresponding to the isolated species.¹⁶

Dynamic light scattering is a technique used for particle sizing of samples, typically in the submicron range. The technique measures the time-dependent fluctuations in the intensity of scattered light from a suspension of particles undergoing random Brownian motion. Analysis of these intensity fluctuations allows the determination of the diffusion coefficients, which in turn yield the particle size through the Stokes-Einstein equation.¹⁷

EXPERIMENTAL

Materials

The linear and branched poly(ethylene oxide-polypropylene oxide) (PEO-PPO) block copolymers were donated by Dow Química, São Paulo, Brazil. Figure 1 shows the structure of the copolymers used in this work.

Characterization of the copolymers

The copolymers used in this work were characterized in a previous study,¹⁸ as shown in Table I.

Methods

Tensiometry

The tensiometry analyses were carried out with a Krüss model K10ST digital tensiometer, coupled to

TABLE I
Characterization Data of PEO-PPO Block Copolymers¹⁸

Copolymers	\bar{M}_n^a	\bar{M}_w^a	\bar{M}_w/\bar{M}_n^a	EO/PO ratio ^b	Copolymer structure
R ₁	6800	7100	1.04	0.32	$\begin{array}{c} \text{CH}_2(\text{PO})_{31}(\text{EO})_{10}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{31}(\text{EO})_{10}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{31}(\text{EO})_{10}\text{OH} \end{array}$
R ₂	7900	8200	1.03	0.53	$\begin{array}{c} \text{CH}_2(\text{PO})_{31}(\text{EO})_{10}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{32}(\text{EO})_{17}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{32}(\text{EO})_{17}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{32}(\text{EO})_{17}\text{OH} \end{array}$
R ₃	7800	8000	1.02	0.54	$\begin{array}{c} \text{CH}_2(\text{EO})_{17}(\text{PO})_{31}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{17}(\text{PO})_{31}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{17}(\text{PO})_{31}\text{OH} \end{array}$
R ₄	9100	9400	1.03	0.47	$\begin{array}{c} \text{CH}_2(\text{EO})_{18}(\text{PO})_{38}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{18}(\text{PO})_{38}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{18}(\text{PO})_{38}\text{OH} \end{array}$
L ₁	2900	3300	1.14	0.36	CH ₃ -(PO) ₃₉ -(EO) ₁₄ -OH
L ₂	3300	3700	1.13	0.56	CH ₃ -(PO) ₃₉ -(EO) ₂₂ -OH
L ₃	2600	2700	1.05	0.38	CH ₃ -(EO) ₁₃ -(PO) ₃₄ -OH
L ₄	3300	3400	1.05	0.56	CH ₃ -(EO) ₂₂ -(PO) ₃₉ -OH

^a By ¹H-NMR.

^b By SEC.

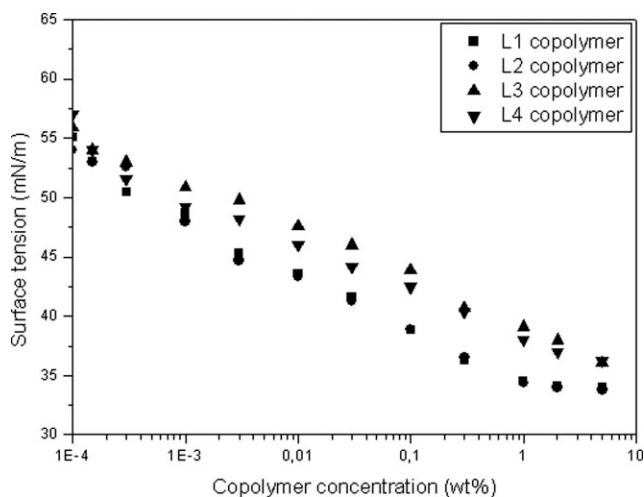


Figure 2 Surface tension of linear PEO-PPO block copolymers in aqueous solutions.

an OpTherm circulating water bath. All surface tension measurements were performed in triplicate, with the copolymers dissolved in water at 25°C. For each copolymer, a graph of the mean tension value (in mN/m) versus the logarithm of the concentration (in % p/v) was plotted. This graph was then used to determine the CMC.

Fluorescence

The analyses were carried out with a Varian Cary Eclipse spectrofluorimeter. The fluorescence emission spectra of the aqueous PEO-PPO copolymer solutions at different concentrations were obtained using pyrene as a marker, at an excitation wavelength of 335 nm and temperature of 25°C.

The copolymer samples were prepared in an aqueous solution, at a concentration interval from 0.0001 to 0.3% p/v. When all the copolymer was solubilized, the pyrene compound was added to each solution, at a concentration of $10^{-4}M$. Because the solubilization of pyrene is slow, the solutions were left at rest for 24 h, and before the start of the measurements, the solutions were placed for about 2 h in a thermostated bath with constant stirring at 25°C.

Light scattering

The aqueous solutions of nonionic surfactants were evaluated in a Zetasizer Nano ZS particle size analyzer (Malvern). This apparatus works on the typical dynamic light scattering principle, with four main components. The first is a laser, which provides the light source to illuminate the particles within the cell. The largest part of the laser beam passes straight through the sample, but another part is scattered by the particles present in the medium. A detector is used to measure the intensity of the scattered

light. Because a particle scatters light in all directions, it is possible to place a detector in any position and still detect the scattering.

In DLS, the placement of the detector at 90° from the incident beam is the traditional setup, but presents a smaller detectable band and hence can only be used for very high sample concentrations. In the apparatus used in this work, the detector was placed at 173° from the incident beam. The intensity of the scattered light must be within a specific band for the detector to be able to measure it successfully. When the quantity of detectable light was outside this band, attenuators were used to reduce the intensity of the laser light and thus the intensity of the scattered light.¹⁹

The intensity of the scattered signal to the detector is passed through a digital signal detector called a correlator. The correlator compares the scattering intensity in successive time intervals to derive the rate at which the intensity is varying. The detection optic of this device measures the scattering information near 180°. This technique is known as detection by backscattering, a patented technology called non-invasive backscattering (NIBS).

The analyses carried out in this work were done from two automatic readings from the device, in which the best attenuator, the ideal number of runs, and the analysis time were selected. Five sequential analyses were performed.

RESULTS AND DISCUSSION

Surface tension analysis of the aqueous solutions of PEO-PPO block copolymers

To study the behavior of the PEO-PPO block copolymers at the water/air interface and to determine the CMC values, we measured the surface tension as a

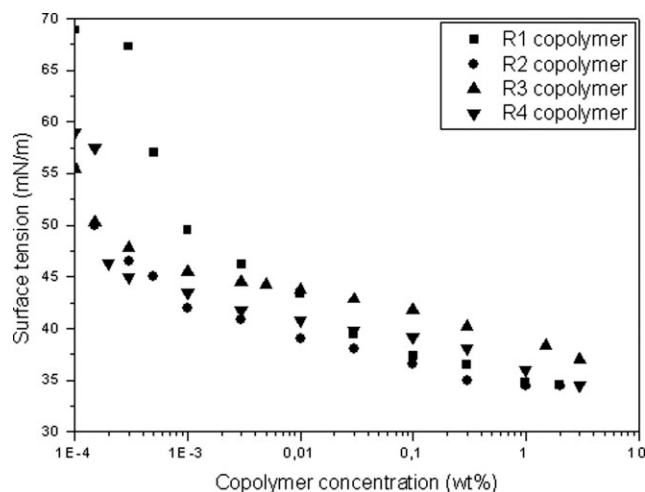


Figure 3 Surface tension of branched PEO-PPO block copolymers in aqueous solutions.

function of the copolymer's concentration in the aqueous solutions.

Figures 2 and 3 show the curves of surface tension (γ) as a function of the logarithm of the concentration of the linear and branched copolymers in aqueous solution ($\log C$), respectively. For the linear copolymers, L_1 and L_2 (Fig. 2), the surfactants behaved conventionally, that is, the surface tension decreased as the concentration increased until the tension remained constant. This discontinuity indicates the CMC of the surfactant. Copolymers L_3 and L_4 showed a linear decline in the tension with increasing concentration, and no discontinuity was detected, making it impossible to determine the CMC.

For branched copolymers, R_1 and R_2 (Fig. 3), it can be seen that at low copolymer solutions, the surface tension dropped sharply with increasing concentration until values near $10^{-3}\%$ p/v were attained, where the curves show a discontinuity.

After this point, the solution's surface tension continued to decline until reaching a concentration where the variation in surface tension was minimal (second discontinuity). Since after the CMC, the solution's surface tension should remain constant, we attributed the CMC values to the concentration where the second discontinuity occurred in these curves.

Some authors have studied the occurrence of the first discontinuity observed in surface tension curves,^{20,21} and the most recent hypothesis attributes this behavior to the change of conformation of the copolymer chains at the surface of the aqueous solution.

In contrast, branched copolymers, B_3 and B_4 (Fig. 3), showed only the first discontinuity, without any phase observed in which the surface tension remained constant, even at the highest copolymer concentrations (up to 3% p/v).

Table II shows the CMC results obtained for each aqueous copolymer solution analyzed.

The results show that the copolymers with alternating structure, that is, alternating hydrophilic (EO and OH) and hydrophobic segments (R and PO;

Samples B_3 , B_4 , L_3 , and L_4) did not present a defined CMC when evaluated up to a concentration of 3% p/v. For the copolymers that have adjacent hydrophilic-hydrophobic segments, the curves obtained showed well-defined inflections in the CMC region. This behavior can be attributed to a more suitable molecular structure of these copolymers for the occurrence of molecular association, as shown in the model presented in the literature, based on the results obtained in previous works.⁵

The CMC values obtained for the branched copolymers R_1 and R_2 and linear copolymers L_1 and L_2 agreed with the observations of a solubility analysis carried out in a previous work¹⁸: the fact that the EO/PO ratio of copolymer R_2 is greater than that of copolymer R_1 , and the EO/PO ratio of copolymer L_2 is greater than that of copolymer L_1 (Table I), explains why these copolymers are more soluble in water, causing their CMC values to be higher as well.

Using this technique, the linear copolymers showed higher CMC values than the branched copolymers. This may be due to a better chain packing of the linear copolymers at the surface of the aqueous solution, so that this surface becomes saturated at higher concentrations.

To confirm that there was no micelle formation for alternating copolymers or that this formation was not detected by tensiometry, we also used the fluorescence technique. The results are shown in the next section.

Fluorescence analysis of the aqueous solutions of PEO-PPO block copolymers

The fluorescence emission spectrum of the aqueous solutions of the PEO-PPO block copolymers at different concentrations was analyzed using pyrene as the fluorescent marker (conc. = $10^{-4}M$) to evaluate the micelle formation of the linear and branched PEO-PPO block copolymers, whose structures contain either alternating or adjacent hydrophobic and hydrophilic segments. Figures 4 and 5 show the emission spectra obtained for the aqueous solutions of two of the linear and branched copolymers containing pyrene, respectively. These spectra give the I_1 and I_3 intensities, measured from the wavelengths corresponding to the first and third pyrene vibrational bands, located near 172 and 183 nm. Besides this, for concentrations above the CMC, a band located at a wavelength of 60 nm can be observed, corresponding to the formation of a pyrene excimer. Excimer is the name given to designate complex molecules involving two molecules of the same type, which forms only in the excited electronic state. The formation of the excimer depends on the number of pyrene molecules solubilized in the micelles, which is a function of the aggregation number and surfactant concentration.

TABLE II
Critical Micelle Concentration Values of the PEO-PPO Block Copolymers Obtained by Different Methods

Copolymer	Tensiometry (wt %)	Fluorescence		Light scattering (wt %)
		I_1/I_3 ratio (wt %)	I_E/I_M ratio (wt %)	
R_1	0.04	0.02	0.02	0.03
R_2	0.05	0.04	0.05	0.05
R_3	–	0.03	0.01	0.05
R_4	–	0.03	0.03	0.05
L_1	0.50	0.03	0.07	0.05
L_2	0.70	0.07	0.07	0.10
L_3	–	0.03	0.04	0.05
L_4	–	–	–	–

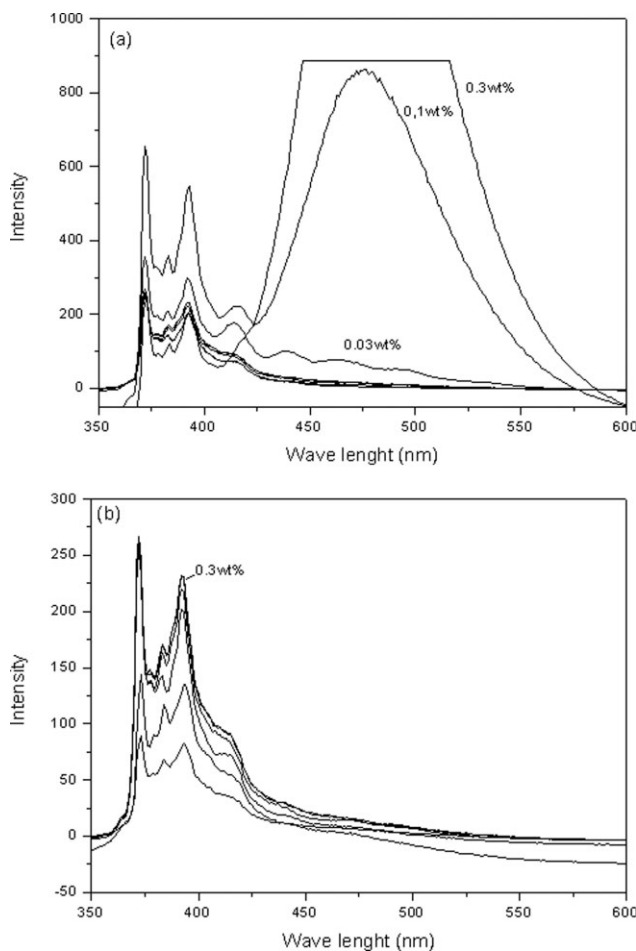


Figure 4 Emission spectra for the aqueous solutions of linear copolymers containing pyrene. Copolymer concentration: 0.0001–0.3 wt %. (a) L_2 copolymer and (b) L_3 copolymer.

The emission spectra for the aqueous solutions of alternating copolymers containing pyrene [Figs. 4(b) and 5(b)] show a lower intensity at a wavelength of 460 nm, corresponding to the excimer formation. This behavior can be attributed to a more suitable molecular structure of copolymers with adjacent structures for molecular association to occur in comparison with copolymers having alternating structures, as already proposed from the tensiometry analysis. Therefore, adjacent copolymers may be forming more stable micelles in the bulk of the solution, which favors the solubilization of the pyrene molecules in the solution's interior, leading to greater excimer formation. On the other hand, the alternating copolymers can be forming relatively unstable micelles or fewer of them in the bulk of the solution in comparison with the adjacent copolymers, leading to less intense excimer formation.

The CMC values were determined by two spectrophotometric methods, and in each the intersection of the lines obtained was calculated. In the first method, a graph was plotted of the I_1/I_3 ratio of

pyrene as a function of the copolymer concentration. This is one of the most popular procedures utilized to determine this parameter in micelle systems. The other method evaluates the I_E/I_M ratio, where I_E is the intensity of the excimer (obtained at an excitation wavelength of 460 nm) and I_M is the intensity of the monomer, corresponding to the third vibrational band (obtained at 183 nm). We also plotted a graph of this ratio as a function of the copolymer solution.

In the graphs of copolymers R_1 and L_3 shown in Figure 6, it can be seen that below the CMC, both the pyrene and copolymer molecules are solubilized in the solution, but the values of I_1/I_3 and I_E/I_M do not vary with increasing copolymer concentration. However, after the CMC and with the increasing copolymer concentration in the solution, the pyrene, because of its low solubility in water, migrates within the micelles, now finding a more hydrophobic environment. This behavior can be observed in the graphs of all the copolymers, as shown in Figure 6, from the fall in the I_1/I_3 ratios and increase in the I_E/I_M ratios. The exception is linear copolymer L_4 ,

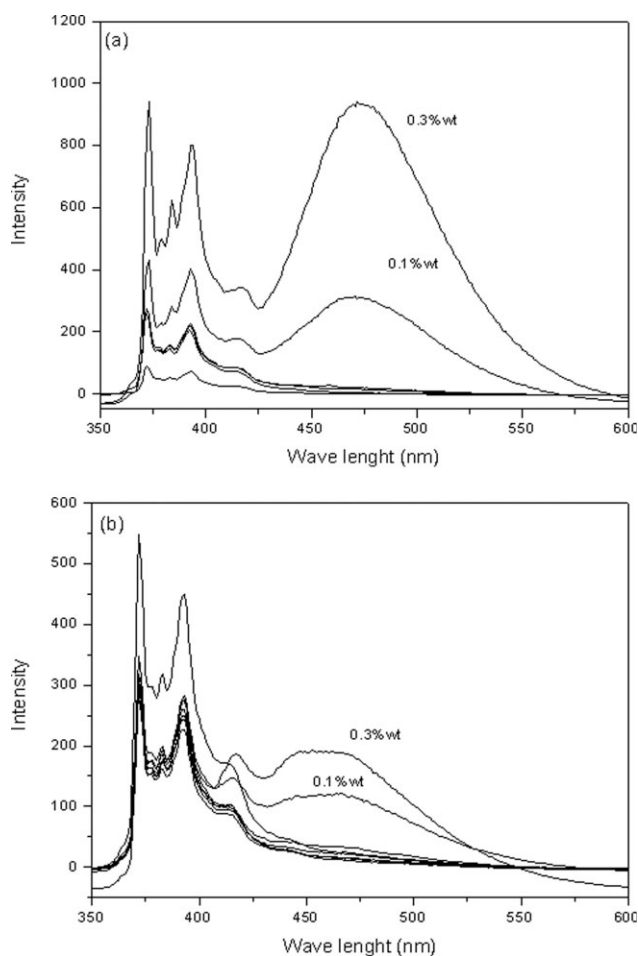


Figure 5 Emission spectra for the aqueous solutions of branched copolymers containing pyrene. Copolymer concentration: 0.0001–0.3 wt %. (a) R_1 copolymer and (b) R_4 copolymer.

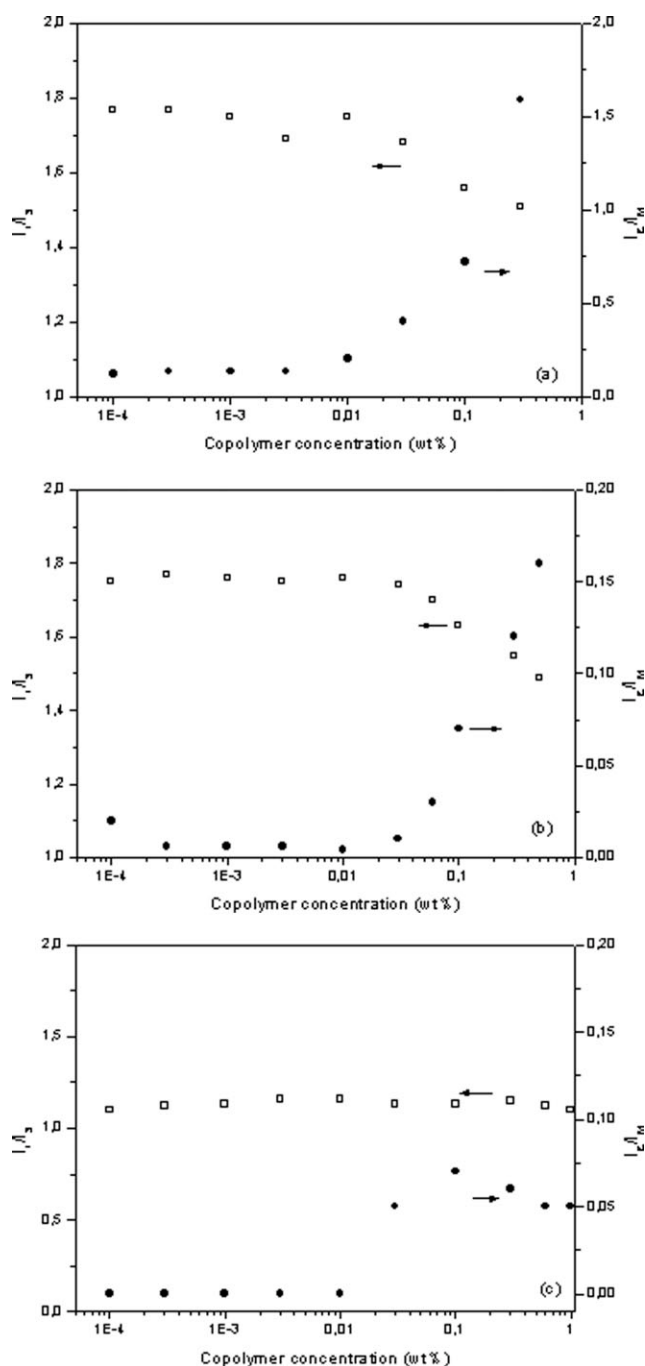


Figure 6 I_1/I_3 and I_E/I_M ratios of pyrene versus copolymer concentrations in aqueous solution: (a) R_1 ; (b) L_3 ; and (c) L_4 copolymer.

for which the curves obtained once again do not intersect, indicating that no micelles may be formed in this copolymer. This graph shows that there was a small increase in the I_E/I_M ratio at a concentration of 0.03 wt %, and then this ratio remained practically constant until the highest concentration analyzed (1 wt %). This behavior can be attributed to the increasing copolymer concentration in solution.

Table II shows that the CMC values obtained by the two methods agree for all the copolymers ana-

lyzed. The small variations observed in these results can be due to the fact that the excimer formation depends on the number of micelles formed and also on the number of pyrene molecules captured by these micelles, whereas the other method (the I_1/I_3 ratio) depends only on the formation of these micelles. Hence, the I_E/I_M method may result in a greater error in determining the CMC values.

Although there was no discontinuity in the surface tension curves of copolymers B_3 , B_4 , L_3 , and L_4 through tensiometry, these copolymers presented CMC values by the fluorescence technique, except for copolymer L_4 . This behavior can be due to the alternate position of the EO and PO groups in its chains, besides this copolymer's high molar mass.

An analysis of the CMC results obtained by the fluorescence technique, using the I_1/I_3 method, shows the same behavior discussed previously: copolymers R_2 and L_2 , because they have a greater quantity of EO in their chains than do copolymers R_1 and R_4 and L_1 and L_3 , respectively, have higher CMC values.

Among the branched copolymers, it can be seen that R_2 also had higher CMC values than R_3 , even though the EO/PO ratio and molar masses are similar (Table I). For this reason, these samples might have been expected to show similar solubilities, but the chemical structure of copolymer R_2 , with hydrophilic segments (PEO and OH) arranged adjacently and more to the outside of the molecules, facilitates interaction with the water molecules.^{5,12,18,22} Besides this, once again this can be attributed to the fact that adjacent copolymers have a more suitable molecular structure for molecular association to occur.⁵

The behavior shown by the branched copolymers can be confirmed with the results obtained for the linear copolymers L_1 and L_3 . The latter has a slightly higher molar mass than the former and also has a higher EO/PO ratio. Therefore, one would expect L_1 to have a higher CMC value because of its greater solubility in water. However, by the I_1/I_3 method, these values were equal, and by the I_E/I_M method, copolymer L_1 had a higher CMC value (Table II). In this case, the alternating structure of L_3 appears also to be affecting its behavior in aqueous solution.

The CMC values obtained by the two techniques (fluorescence and tensiometry) for the branched copolymers were in agreement, whereas for the linear copolymers, the values obtained by the fluorescence technique were lower than those by tensiometry. This behavior can be attributed to the type of measurement done in each technique. Through tensiometry, the CMC is determined by observing the saturation of the surface of the aqueous solution, whereas in the fluorescence technique, the CMC is determined by the polarity variation that occurs in the bulk of the solution. Therefore, tensiometry indirectly measures the

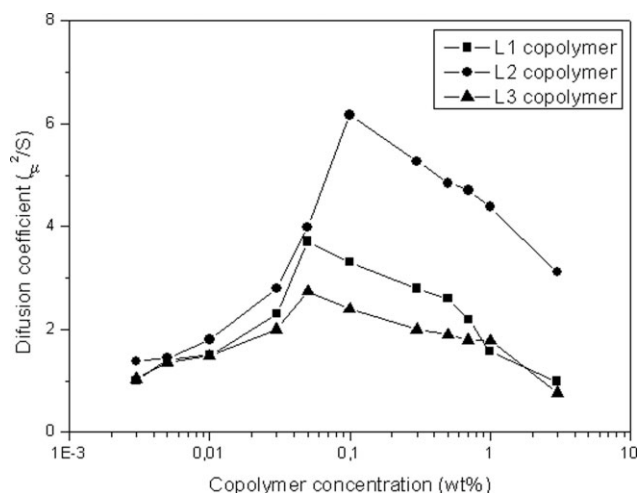


Figure 7 Diffusion coefficient as a function of aqueous solutions of linear PEO-PPO block copolymers.

molecular aggregates in the aqueous solution, which can lead to bigger errors in the CMC values. Besides this, because the fluorescence technique directly observes the solution, the CMC values are more reliable and can be determined earlier than through tensiometry.

In the case of linear copolymers, the better packing of their chains at the aqueous solution's surface might be hindering observation of the start of molecular aggregate formation within the solution, so that the surface saturation is observed at higher concentrations.

Light scattering analysis of the aqueous solutions of PEO-PPO block copolymers

Dynamic light scattering is based on photon correlation spectrometry (PCS), which consists of determining the velocity distribution of the particle movement by the dynamic measurement of the fluctuations in the intensity of the scattered light. The particles or macromolecules dispersed in a liquid medium undergo Brownian motion, which causes oscillations in the concentration of the particles. This, in turn, results in the variations in the intensity of the scattered light. The width of the peak related to the intensity of scattered light Γ (defined as the half-width at half-height) is proportional to the diffusion coefficient of the D particles [eqs. (1) and (2)] and k is the wave scattering vector^{17,23}:

$$\Gamma = Dk^2 \quad (1)$$

where

$$k = (4\pi n/\lambda)\sin(\theta/2) \quad (2)$$

where n is the medium's refractive index, λ is the laser's wavelength, and θ is the scattering angle.

Assuming that the particles are spherical and do not interact, the measurement of radius is obtained from the Stokes-Einstein equation¹⁷ as follows:

$$R = k_b T / 6\pi\eta D \quad (3)$$

where k_b is the Boltzmann constant, T is the temperature, and η is the solvent's viscosity.

We determined the CMC values by dynamic light scattering from the diffusion coefficient of the particles obtained for each solution of known copolymer concentration. To do this, we analyzed a copolymer concentration interval between 0.001 and 3% p/v. The diffusion coefficient values used to plot the graphs in function of the copolymer concentration were the median values of the five replications for each solution.

Figures 7 and 8 show the graphs obtained for the linear and branched copolymers, respectively.

It can be observed that in all cases there was initially an increase in the diffusion coefficient of the particles with increasing copolymer concentration in the aqueous solution, because the higher number of molecules in this solution was promoting greater structural contraction. The peak diffusion coefficient shown in the curve means that the molecules have attained their maximum concentration and have started to form aggregates (CMC, Table II). After the CMC, due to the interactions of the surfactant molecules that reduce the mobility of these molecules in the solution, the diffusion coefficient declines.

Through the light scattering technique it was not possible to observe a significant variation in the CMC values (Table II), except for copolymers R₁ and L₂. Nevertheless, the values obtained agreed with those obtained by fluorescence. To obtain more precise CMC values, a larger number of solutions should be used at concentrations near the maximum observed in the curves of the diffusion coefficient in function of

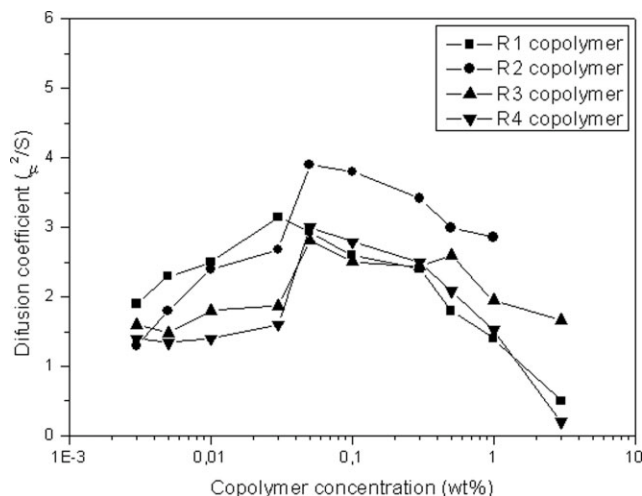


Figure 8 Diffusion coefficient as a function of aqueous solutions of branched PEO-PPO block copolymers.

the surfactant concentration. Still, the diffusion coefficient values obtained can provide information on the formation of molecular aggregates.

It can be observed that linear copolymer L₂, which has the highest EO/PO ratio, had the highest CMC value (Table II) and the highest diffusion coefficient (Figs. 7 and 8). This behavior indicates that the molecules of the copolymer with a linear and adjacent structure (L₂) are packed better at the water–air interface, increasing the formation of micelles. The increase in the diffusion coefficient can be attributed to the formation of smaller micelles at the concentrations evaluated, because their linear and adjacent structure provides better organization of the surfactant molecules in the molecular aggregates.

The diffusion coefficient values observed for the other linear copolymers (L₁ and L₃) confirm the behavior found previously by tensiometry and fluorescence. Copolymer L₁ has higher diffusion coefficient values than L₃. This can be attributed to the adjacent structure of copolymer L₁, which promotes the formation of micelles with more organized molecular structures, causing the CMC value of L₁ to be higher than that of L₃.

An analysis of the diffusion coefficients obtained for the branched copolymers initially shows the same behavior as for the linear copolymers: those with adjacent structures (R₁ and R₂) have higher numbers. However, starting at the CMC, the solubility of the copolymers starts to govern, and copolymer R₂, which is more soluble, has the highest diffusion coefficient values, and copolymer R₁, which is less soluble (lower EO/PO ratio, Table I), has the lowest diffusion coefficient values. In this case, the lower quantity of EO present in the chains favors the interaction among the surfactant molecules, quickly increasing the size of the molecular aggregates in solution.

In the case of copolymers R₃ and R₄, the branched and alternating structures promote the formation of larger and less organized molecular aggregates. Still, although the EO/PO ratio of copolymer R₄ is higher than that of R₁, the diffusion coefficient values are similar for both.

CONCLUSIONS

Measurement of the CMC of branched polyoxide-based copolymers can be done by tensiometry, fluorescence, and dynamic light scattering. The results agree although these techniques evaluate different points of the solution (the surface through tensiometry and the inside of the solution through the other two).

In the case of linear copolymers, the results obtained by tensiometry can be misleading because the better packing of these copolymers at the surface

of the aqueous solution retards their saturation, causing higher CMC values to be obtained.

More precise CMC values of polymer solutions are obtained through the fluorescence technique, based on the I₁/I₃ ratio of pyrene than by tensiometry.

Furthermore, the solubility of copolymers is affected along with their behavior in aqueous solution, depending on the position of their hydrophilic (EO and OH) and hydrophobic groups (PO and the hydrocarbon chain). All the techniques used in this study allowed evaluating this change of behavior.

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