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Investigation of Self-Assembly and Micelle Polarity for a Wide Range of Ethylene Oxide–Propylene Oxide–Ethylene Oxide Block Copolymers in Water

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Critical micelle concentrations (cmc) were determined for aqueous solutions of 15 EO–PO–EO (EO = ethylene oxide, PO = propylene oxide) block copolymers by using three different techniques: spectral changes of an iodine/iodide mixture, methyl yellow solubilization, and surface tension measurements. Two polymers showed no sign of micelle formation up to phase separation: one reverse (PO–EO–PO) and the other with low EO/PO ratio. The obtained cmc's were consistent for the different techniques employed and allowed the determination of the ΔG values associated with the micellization. These values were analyzed in terms of the EO and PO contributions, confirming the leading role of the hydrophobic PO units and revealing a small, but favorable, contribution of the hydrophilic EO chains, in contrast to the usual behavior of small nonionic surfactants. The polarity of the micelle solubilization sites was determined using the solvatochromic dye Eri30, revealing environments similar to those observed for micelles of hydrocarbon surfactants. These findings, allied to the thermodynamic similarity between the micellization and the phase separation processes for the copolymers and PPO, support the view that the micellization is accompanied by a large dehydration of the PO units.

Introduction

The EO–PO–EO (EO = ethylene oxide, PO = propylene oxide) block copolymers, commercially known as Pluronic, Plurionics, or Synperonics, have been the subject of a wide variety of recent publications. This could be attributed to their importance in practical applications as detergents, emulsifiers, defoaming agents, dispersants, or vehicles in pharmaceutical formulations.¹ Despite their long-time use, many aspects of their solution behavior remain unclear, stimulating a large number of studies recently reported in the literature. Among some of the topics studied so far, one could cite their aggregation in aqueous and water/organic solvents mixtures,^{2,3} the determination of their phase diagrams,^{4,5} their adsorption onto solid surfaces, a very important topic related to drug delivery,^{6,7} and the formation of aqueous biphasic systems for bioseparations.⁸

The specific issue of copolymer aggregation has been the subject of many investigations, both theoretical^{9,10} and experimental. In a recent paper, Holland and co-workers¹¹ discussed the origins for the large discrepancy among reported cmc's for these polymers. They have used a fluorescent probe to analyze the aggregation process and

have found that this process occurs in a sequence of steps, being able to identify up to four different regions as the polymer concentration was increased. They have proposed the labels "aggregation concentration range", to describe the onset of observed spectral shifts, and "limiting aggregation concentration", ascribed to the saturation point. According to their attribution, the latter would correspond to the classical critical micelle concentration determined for smaller surfactants. As general conclusions, they verified a cmc decrease as the PO block was increased, as the hydrophobic–hydrophilic balance decreased, and as the temperature was increased.

Hatton's group has also published a series of papers on this issue.^{12,13} They have used surface tension measurements and dye solubilization techniques to determine the Pluronic cmc's, reporting a good agreement between both techniques. In a comprehensive investigation, dealing with 12 copolymers, they have determined the thermodynamic functions, ΔG , ΔH , and ΔS , associated with this micellization. The enthalpies were calculated from the temperature variation of the cmc (actually, from the determined cmc–critical micellization temperatures), allowing the determination of entropy values. They have thoroughly discussed an observed transition in the surface tension versus concentration curve, occurring before the micellization region, which was attributed to rearrangements of the polymer molecules at the water–air interface at the saturation point. Their results have shown that this is an entropically driven process, associated with an increase in enthalpy. Moreover, the central role of the PO units in the micellization was confirmed. The cmc dependence with the size of the EO moieties and with temperature was observed to follow the trend verified for C₁₂EO₈ surfactants.

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Another series of related studies are the calorimetric investigations reported by Beezer and co-workers.^{14,15} They have applied high-sensitivity DSC to the investigation of the temperature-driven aggregation in dilute Pluronic solutions. Such studies allowed the determination of the enthalpy changes for the micellization of 27 copolymers,¹⁵ as well as their critical micellization temperatures. The analysis of these data in terms of the polymer composition established the prevailing contribution of the PO groups, both to the enthalpy changes and to the cmc. This contribution was interpreted as a consequence of the dehydration of the hydrophobic PO units associated with the micelle formation. It was also verified that the phase separation observed for pure PPO solutions follows a similar trend, confirming this hypothesis. Moreover, other thermodynamic functions were derived from these data, allowing the determination of the changes in entropy and also establishing the leading role of entropy over the endothermic enthalpic contribution.

A similar approach, reported by Leharne and co-workers,^{16,17} led to the development of a model to fit scanning microcalorimetric data for the phase separation process in PPO solutions¹⁶ and, more recently, to the aggregation of Pluronics in water.¹⁷ This model allowed the corroboration of aggregation processes occurring prior to phase separation. As micellization is concerned, average aggregation numbers and the thermodynamic functions (ΔG , ΔH , and ΔS) were determined.

One point that remains unclear is about the state of aggregation of these polymers. There is some tension as to whether this association leads to well-defined assemblies (similar to normal micelles) which remain constant over a certain concentration and/or temperature range, or to aggregates which vary continually as these conditions change. Some literature reports address this point, based mainly on results from scattering and diffusion experiments. Wanka et al. performed light and small-angle neutron scattering measurements⁴ observing spherical micelles for F127 and L64 whose size remained constant until the phase transition to hexagonal phases. This was also observed in diffusion experiments reported by Malmsten and Lindman⁵ for F127 micelles from 30 to 70 °C. Using the same technique, Fleischer¹⁸ verified that P85 micelles size is independent of temperature and concentration from 1 to 10% and from their critical micelle temperatures until close to their cloud points, where larger aggregates appear. Similarly, Wanka et al.⁴ reported that for P123 these observed aggregates increased with increasing temperature. In a series of small-angle scattering experiments (SAXS and SANS), Chu and co-workers^{2,19} verified, for some of these copolymers, the occurrence of spherical micelles above the cmc which tend to aggregate at higher concentrations to form more organized structures. In addition, Nivaggioli and co-workers²⁰ reported that the hydrodynamic radii of P104 micelles do not vary from 30 to 45 °C. From these publications, one may infer

Table 1. Nominal Composition of the Studied Polymers¹

polymer	NEO	NPO	$M/(g\ mol^{-1})$
L31	2×1	18	1100
L35	2×11	17	1900
F38	2×44	17	4800
L42	2×4	24	1650
L62	2×5	34	2400
L64	2×13	31	2900
F68	2×76	30	8350
F77	2×52	35	6600
F87	2×61	41	7700
F88	2×107	42	11800
P94	2×21	49	4600
P103	2×17	62	4950
P105	2×37	58	6500
F108	2×127	50	14000
F127	2×95	64	12000
L121	2×5	71	4400
25R2	14	2×22	3100

that there is the occurrence of well-defined micelles over, at least, a certain range of concentrations and/or temperatures, followed by their increase until the formation of larger aggregates or mesophases, leading, in some cases, to the polymer phase separation. In this paper, we will use the word "micelle" for these well defined assemblies and 'aggregate' for those leading to phase separation.

Despite these very comprehensive studies, we believe that this quite complex self-assembly process is not fully understood yet. This, allied to the increasing number of related reports focused on other solution properties of the Pluronics, has prompted us to perform the investigations reported here. These deal with the examination of the micelle formation process for 17 of these copolymers, including a wide range of EO contents, from 10 to 80%, and of molecular weights, from 1.1 to 14.8 kg mol⁻¹. The micellization was followed by use of three methods, and the associated Gibbs energies were analyzed in terms of the polymer compositions. In addition, the polarity of the polymer micelles was investigated by using the solvatochromic dye E_T30.

Experimental Section

Materials. The block copolymers were donated by ICI Surfactants, Cleveland, U.K., and were used without further treatment. Their nominal compositions are shown in Table 1. The polymers with molecular weights larger than 2 kg mol⁻¹ were analyzed by GPC and presented only one elution peak, using either toluene or THF as eluents. The only exception was F127, which presented two peaks, possibly due to the diblock copolymer. Water used throughout was deionized and was of Milli-Q quality.

All the polymer solutions were left, at least, 24 h to equilibrate at 298 K before measuring, to avoid aging effects.²¹

The nonionic surfactants Renex 100 and 1000 were a gift from Oxiteno, São Paulo, Brazil, and used as received.

The other chemicals used, iodine (Roth, NY), KI (Merck, St. Louis, MO), methyl yellow (Profile Testing Laboratories, NJ), and sodium tetraborate (Vetec, Rio de Janeiro, Brazil), were of the best grade available and used as received. The dye E_T30 was a gift from Prof. C. Reichardt, Marburg, Germany.

cmc Determination. All the cmc measurements were performed at 298 K. For the experiments using the iodine/iodide mixture, a stock solution containing respectively 6.4×10^{-4} and 2.0×10^{-3} mol L⁻¹ was prepared. A 1 mL aliquot of this solution was diluted to 5 mL with a polymer solution. The absorbances were measured in a HP 8452 diode array spectrophotometer, with a Peltier temperature-controlled sample holder. The cmc determinations were made using the absorbance at 360 nm.²²

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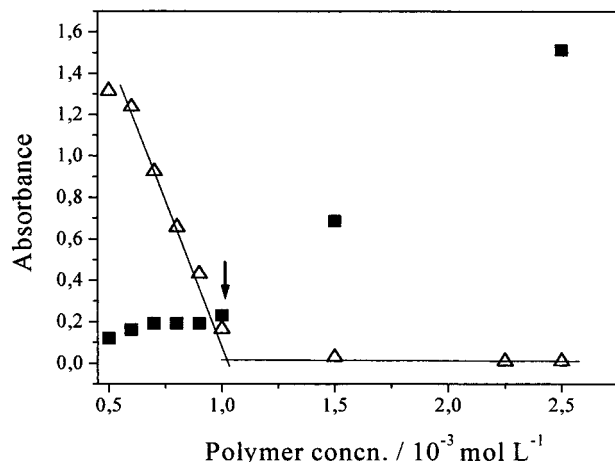


Figure 1. Determination of the cmc for P94 (Δ) by using the I_2/I^- mixture and (\blacksquare) through the methyl yellow solubilization technique. The arrow indicates the ascribed cmc.

The methyl yellow solubilization experiments were performed by adding a small excess of solid dye to polymer solutions. These solutions were sonicated for 20 min and allowed to equilibrate, at least, 2 h in a temperature-controlled water bath. The solutions were filtered through a $0.2\ \mu\text{m}$ filter prior to measurements. The cmc determinations were made using the absorbance at 444 nm.

The surface tension measurements were performed by using an automatic Sigma 701 tensiometer, from KSV, Helsinki, Finland. The experiments were done by the Du Nouy ring method in a temperature-controlled holder, connected to a Braun water bath.

The solvatochromic dye was first dissolved in methanol. An aliquot of $150\ \mu\text{L}$ was diluted with a buffered polymer solution up to 5 mL. The final borate buffer concentration was $25\ \text{mmol L}^{-1}$, its pH = 9.0, and the final dye concentration was $1 \times 10^{-4}\ \text{mol L}^{-1}$.

Results and Discussion

cmc Measurements. Considering the previous observations that different techniques could lead to conflicting cmc values,^{11,13} three different methods were employed for the determination of the polymers' cmc's.

The first method was based on changes caused by these polymers on the absorption spectra of a solution containing a mixture of iodine and iodide. This method has been already applied to the analytical determination of similar copolymers²² and to the study of the temperature-driven aggregation for some of these polymers.^{23,24} Below cmc, the absorption spectra are similar to aqueous I_2/I^- mixtures. As the polymer concentration passes the cmc, the peaks at 300 and 250 nm, ascribed to the species I_3^- , start decreasing until almost disappearing. It is assumed^{23,24} that the equilibrium of triiodide formation is displaced toward iodine and iodide as micelles are formed, as a consequence of a larger solubilization of the more hydrophobic iodine by the micelle hydrophobic sites. Therefore, polymer self-assembly leads to an abrupt absorbance decrease, allowing the cmc determination, as shown in Figure 1.

To assess the reliability of this technique, cmc determinations were carried out for two ethoxylated nonylphenols, Renex 100 and 1000, possessing respectively 10 and 100 EO units. Renex 1000 presented the same behavior observed for the copolymers, as can be seen in Figure 2,

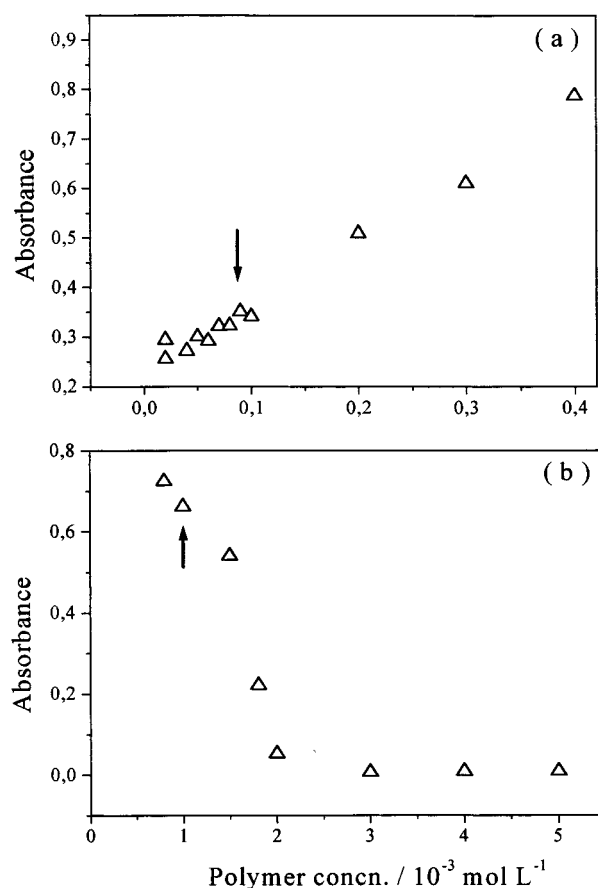


Figure 2. Spectral changes of the I_2/I^- mixture in the presence of increasing concentrations of (a) Renex 100 and (b) Renex 1000. The arrows indicate the literature cmc values for Renex 100 and Renex 1000.²²

leading to a cmc value in agreement with the literature.²⁵ For Renex 100, however, no spectral change was observed, only a continuous absorbance increase over a broad range of concentrations around the literature cmc (Figure 2). This discrepancy suggests an inadequacy of this method to probe micelle formation for surfactants with small EO moieties. This hypothesis was confirmed by the examination of copolymers with smaller EO contents (between 10 and 30%), revealing the same behavior observed for Renex 100. Such findings point to an important role for the probe interaction with the surfactant EO units which should be sensitive to a critical chain size. The continuous absorbance increase is a sign of some kind of interaction, but without the sudden absorbance decrease observed upon the micellization as with the other copolymers. An investigation of the possible aggregation of PEO in aqueous solution²⁶ produced curves similar to those observed for the block copolymers, confirming the sensitivity of this technique to such processes involving large EO chains.

For copolymers with low EO content (less than 40%), and some of the others, for validation, a second method was employed. These experiments were based on the solubilization of an insoluble dye, methyl yellow. Dye solubilization techniques require the use of small probes in order to reduce their interference on the micelle formation equilibrium. A similar dye, orange OT, was recently used in the cmc determination in solutions of

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Table 2. Free Energies of Micellization ($\Delta_{\text{mic}}G$) and Critical Micelle Concentrations (cmc) Measured for the Block Copolymers

polymer	$\Delta_{\text{mic}}G/(\text{kJ mol}^{-1})$	cmc/(mol L ⁻¹)
L31	-9.7	2.0×10^{-2}
L35	-10.8	1.3×10^{-2}
F38	-9.6	2.1×10^{-2}
L42	-12.3	7.0×10^{-3}
L62	-12.2	7.4×10^{-3}
L64	-11.7	8.8×10^{-3}
F68	-16.3	1.4×10^{-3}
F77	-15.2	2.2×10^{-3}
F87	-15.2	2.2×10^{-3}
F88	-19.0	4.6×10^{-4}
P94	-17.1	1.0×10^{-3}
P103	-17.9	7.4×10^{-4}
P105	-17.7	8.0×10^{-4}
F108	-18.8	5.1×10^{-4}
F127	-17.7	8.0×10^{-4}

some facial amphiphiles.²⁷ Due to the surfactant structures, such micelles could be easily disturbed by the use of larger probes and orange OT was found to produce reliable cmc values. In agreement with that observation, the cmc values determined with methyl yellow were essentially the same as those produced by using the I₂/I⁻ mixture, as shown in Figure 1. The cmc's for Renex 1000 and Renex 100 were also determined by this method, leading to the literature values.²⁵ The same agreement was found between the cmc values determined for copolymers with higher EO content (F108, P94, and F127). These experiments confirmed that copolymers with low EO contents self-assemble similarly to the others. The determined cmc values for 15 copolymers are shown in Table 2.

Surface tension measurements were also performed for detecting the cmc of 4 polymers (F108, L64, L31, and F88). Although this method does not involve the use of probes, it relies on the assessment of changes at the water/air interface, assuming this as a picture of processes occurring in the bulk solution. This has caused some misleading attributions of cmc, as discussed by Holland et al.¹¹ and Alexandridis et al.¹² Nevertheless, using Alexandridis' attribution of cmc as the second break in the surface tension vs polymer concentration curve, we found cmc values that confirmed the ones determined by the two other techniques (the results for F108 are shown in Figure 3).

Thermodynamics of Micellization. The changes in Gibbs energy associated with the micellization process, $\Delta_{\text{mic}}G$, were calculated from the determined cmc's through (2)

$$\Delta_{\text{mic}}G = RT \ln \text{cmc} \quad (1)$$

and the obtained values are shown in Table 2. These data can be analyzed by considering the individual contributions of the EO and PO blocks within the 15 polymers studied. This evaluation was performed through a linear multivariate regression analysis producing the following relationship:

$$\Delta_{\text{mic}}G/\text{kJ}\cdot\text{mol}^{-1} = -7.68 - 0.0160\text{NEO} - 0.150\text{NPO} \quad (2)$$

$$n = 15; \quad r = 0.930; \quad s = 1.36; \quad F = 36.9$$

where NEO and NPO represent the number of EO and PO units.

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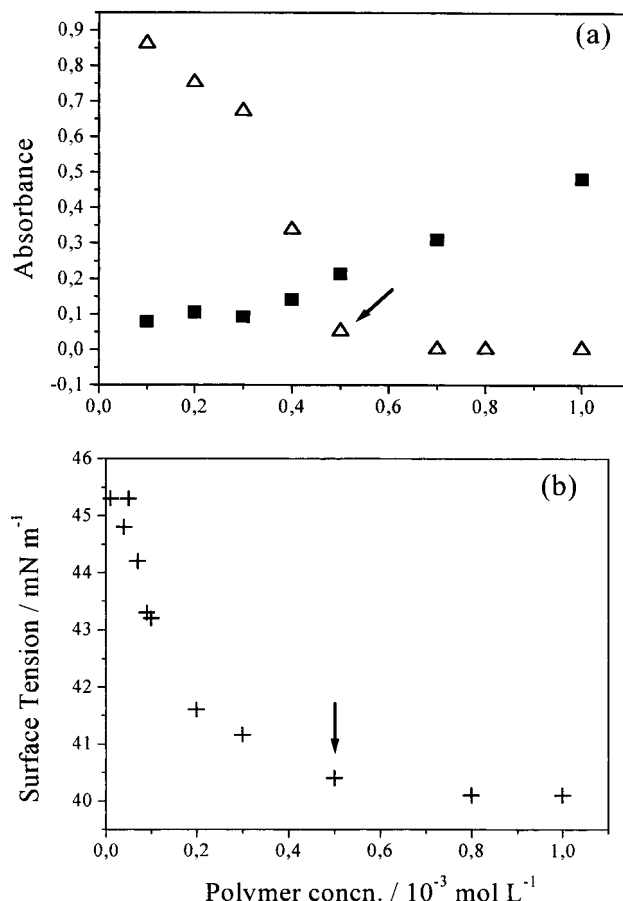


Figure 3. cmc determination for the copolymer F108: (a) (Δ) using the I₂/I⁻ mixture, and (\blacksquare) through the methyl yellow solubilization technique; (b) through surface tension measurements. The arrows indicate the ascribed cmc value.

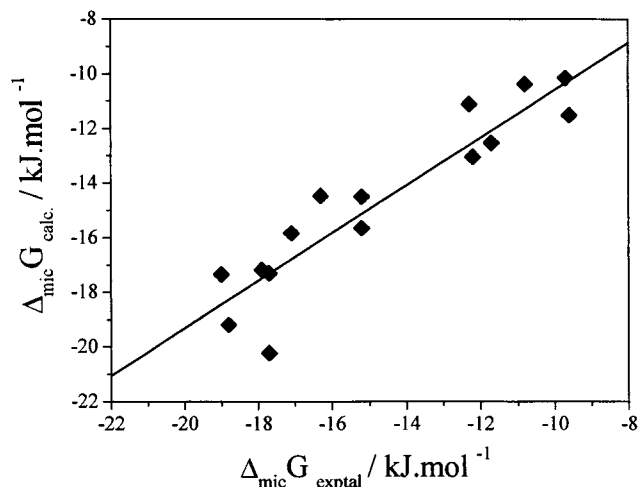


Figure 4. Analysis of the experimental $\Delta_{\text{mic}}G$ values in relation to the ones calculated by eq 2.

The adequacy of this approach is confirmed by the analysis of the predicted values, $\Delta_{\text{mic}}G_{\text{calc}}$, against the experimental ones, $\Delta_{\text{mic}}G_{\text{exptl}}$, as shown in Figure 4. The only outlier is F127, which should contain some impurities, as detected by GPC analysis.

This relationship points out that both EO and PO units present a favorable contribution to the association process, although the EO one is very close to the uncertainty limit. Despite its almost negligible contribution, this behavior is distinct from the one observed for normal nonionic surfactants,²⁸ where the increase of the EO chain leads

to an increase of the cmc. Thus, the configuration entropy contribution from the increased number of monomer units seems to counterbalance the solubility increase due to the increase of the EO hydrophilic moiety.

Alexandridis et al.¹³ have observed that, within a series of copolymers with the same PO size, the increase of the EO chain leads to a small cmc increase. However, when analyzing their whole set of data in a similar linear multivariate regression, the obtained equation is (the intercept value cannot be compared with the one of eq 2 due to their use of molar fraction units to express cmc)

$$\Delta G/\text{kJ}\cdot\text{mol}^{-1} = -25.5 - 0.0180\text{NEO} + 0.0220\text{NPO} \quad (3)$$

$$n = 12; \quad r = 0.948; \quad s = 0.566; \quad F = 39.8$$

According to this equation, the EO contribution to the micellization process is favorable, whereas, surprisingly, the PO contribution is opposite. The latter observation contrasts with their analysis for a series of copolymers with the same EO segment and increasing number of PO units, where a favorable PO contribution to the micellization process was verified. They have also noticed that, within a series with the same EO/PO ratio, the cmc decreases with an increase of the polymer molecular weight. This allowed the development of empirical equations relating the polymer cmc (or ΔG for micellization) to the polymer molecular weight and to the overall number of monomer units (NEO + NPO).^{13,29} Such a finding supports the view that larger polymers associate at lower concentrations, even if the increase in size is due to the EO chains.

Other systematic efforts have been devoted to the analysis of the thermodynamic functions for the micellization of these block copolymers in terms of the contributions of the EO and PO moieties. Beezer and co-workers have performed a comprehensive evaluation of the thermodynamics of the temperature-driven aggregation process.^{14,15} The analysis of the determined enthalpies of micellization,¹⁵ $\Delta_{\text{mic}}H$, leads to the following relationship:

$$\Delta_{\text{mic}}H/\text{kJ}\cdot\text{mol}^{-1} = -9.39 - 1.167\text{NEO} + 5.85\text{NPO} \quad (4)$$

$$n = 27; \quad r = 0.894; \quad s = 48.2; \quad F = 42.9$$

In this case, the EO and PO groups have opposite contributions to the association process, the first exothermic and the latter endothermic (which is the prevailing one). A similar picture is obtained by the analysis of the enthalpies reported by Alexandridis et al.,¹³ producing the equation

$$\Delta H/\text{kJ}\cdot\text{mol}^{-1} = 117.6 - 0.187\text{NEO} + 3.25\text{NPO} \quad (5)$$

$$n = 12; \quad r = 0.844; \quad s = 34.7; \quad F = 11.10$$

This behavior has been interpreted in terms of the different roles played by both moieties in the micellization process. The PO units are dehydrated during the association process, leading to increased PO-PO interactions, in a way similar to that in the temperature-driven phase separation that occurs in aqueous PPO solutions (also an endothermic process). The EO units, though,

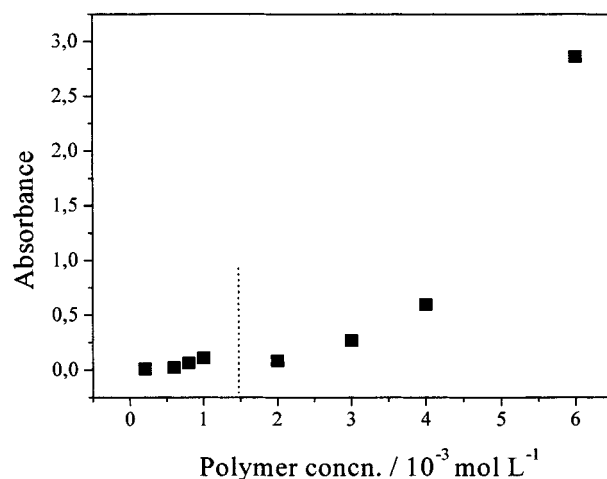


Figure 5. Absorbance due to the solubilization of methyl yellow as the concentration of the reverse copolymer 25R2 is increased. The dashed line represents the beginning of turbidity.

remain strongly hydrated, forming the micelle corona which is responsible for keeping the polymer in solution.

The model developed by Leharne and co-workers^{16,17} also confirms the driving role of the PO moiety, as pointed out by the analysis of their calculated van't Hoff enthalpies and also based on the interpretation of the negative values measured for the heat capacity changes upon association. Their calculated Gibbs energies for micellization, however, are smaller than those reported here and in the literature.¹³ Although their data were determined at temperatures ranging from 302 to 341 K, this difference cannot be accounted for by an estimated correction of ΔG based on the reported enthalpies of micellization. The trend shown by their values is, nevertheless, consistent with the observations of other studies, including this one. The discrepancies related to the absolute ΔG values might have arisen from the model used to derive those data.

In this study, two copolymers, L121 and 25R2, however, do not present signs of micelle formation when analyzed through both spectroscopic methods. The distinct feature of L121 is its small EO content and high PO content and size, although the EO molecular weight in L121 is larger than that in some of the other polymers. The polymer 25R2 possesses an inverse block structure, PO-EO-PO, where the middle block is hydrophilic. When the concentration of these polymers was increased, the only changes in the spectra of the I₂/I⁻ mixture and signs of methyl yellow solubilization occurred after the solution became turbid (Figure 5), indicating the presence of larger polymer aggregates as a result of the beginning of phase separation. The observation regarding 25R2 confirms previous studies which also verified that a similar reverse copolymer 25R4 does not form micelles in aqueous solutions.¹³ For another reverse copolymer with a larger EO chain, 25R8, a complex aggregation pattern was also reported,³⁰ indicating the occurrence of a micellar network connected through the hydrophobic PO chains.

For L31 (at 2×10^{-1} mol L⁻¹) and P103 (at 4×10^{-3} mol L⁻¹), phase separation was also observed, but at concentrations higher than the ascribed cmc (respectively 2×10^{-2} and 7.4×10^{-4} mol L⁻¹). Another phase transition, associated with a large viscosity increase, was observed at higher concentrations of F108, F88, and F38, copolymers with large EO contents. Interestingly, Alexandridis et al.¹³ observed that, at higher temperatures, the solution

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behavior of more concentrated (>5%) solutions of F68, F88, and F108 deviated from the general trend observed for the other polymers. They have also proposed that such deviations might arise from the formation of more organized structures. Both processes, phase separation and formation of mesophases, represent a small part of the complex phase diagram of these solutions, which has been the focus of extensive studies.^{4,5,31} From our results on the dilute region, a general picture could be proposed. Copolymers with high EO content form well-defined micelles over a certain concentration range (with cmc's ranging from ca. 1% to 10%) and, at higher concentrations and/or temperatures, arrange themselves into more organized structures, including gels. The copolymers with EO contents smaller than 50% form micelles, in a process that is thermodynamically consistent with the one observed for the polymers with higher EO content, obeying the same general relationship between enthalpies and Gibbs energies of micellization and polymer composition (eqs 2 and 3). At higher temperatures or concentrations, these polymer solutions present phase separation (cloud points). For one copolymer with 10% of EO it was not possible to distinguish between micelle formation and phase separation. The enthalpy changes associated with the phase separation process seem to conform to those measured for their micellization,¹⁷ indicating that they are governed by a related process, possibly the removal of the hydrophobic PO units from the aqueous environment, with this micelle formation being a preliminary step toward the ultimate phase separation.

Polarity of the Micelle Solubilization Sites. The proposed picture for the copolymer micelle comprises a hydrophobic interior, composed mainly of the PO units, and a hydrated corona formed by the EO moieties.^{2,3} Investigations by Nivaggioli et al.²⁰ using the ratio of pyrene emission bands verified the apolar nature of the micelle core. Their results indicate that the micelle interior is more hydrophilic than pure PPO and may, therefore, contain some EO units, but very little water. Similar conclusions were derived from partitioning studies for a homologous series of alkyl *p*-hydroxybenzoates into F127 micelles.³² The hydrophobic contribution, ΔG_H , to the solute partitioning was estimated and compared to similar data obtained for other biphasic systems (water/organic solvents and water/micelles or liposomes). According to this procedure, the more hydrophobic the environment, the more negative ΔG_H . The inspection of these data revealed that F127 micelles provide solubilization sites similar to those observed for SDS and CTAB micelles.

We have presently used the solvatochromic dye E_T30 to assess the polarity of the micelle solubilization sites for a series of Pluronics. This dye is one of the most established polarity probes³³ and has already been used to investigate micelles and liposomes.³⁴ The E_T30 solvatochromic band shifts from a maximum at 453 nm in aqueous environments to 810 nm in diphenyl ether.³³ This absorption band is attributed to a charge-transfer process from phenoxide oxygen. Therefore, at low pH (usually smaller than 9), the protonation of this oxygen leads to the disappearance of the solvatochromic properties. For this reason, these polarity measurements were conducted

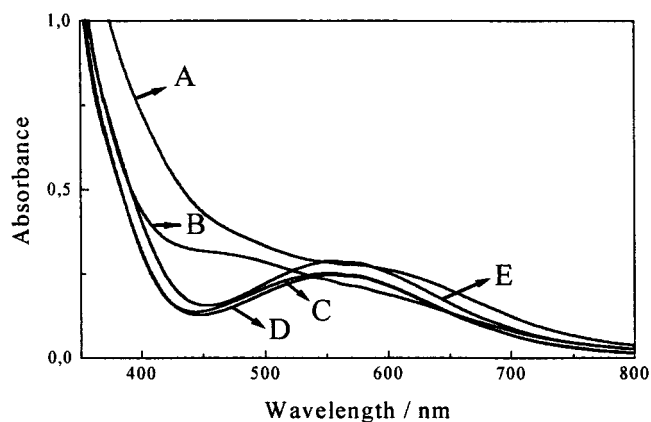


Figure 6. Absorption spectra for the solvatochromic dye E_T30 in P105 solutions at increasing polymer concentrations: (A) 4×10^{-5} , (B) 5×10^{-4} , (C) 5×10^{-3} , (D) 3×10^{-2} , and (E) 6×10^{-2} mol L⁻¹. The determined cmc for P105 is 8×10^{-4} mol L⁻¹.

Table 3. Maximum Absorption Wavelengths of E_T30 in Surfactant Solutions

surfactant	λ_{\max}/nm	surfactant	λ_{\max}/nm
L31	486	P105	554
L42	534	F108	548
F35	532	F127	546
L62	538	Renex 100	554
F38	530	Renex 1000	542
L64	546	C ₁₂ EO ₈	542 ^a
F68	512	CTAB	534 ^a
F77	534	DTAB	532 ^a
F87	550	CPC	533 ^a
F88	536	DMPC	545 ^a
P94	552	DPPC	517 ^a
P103	560		

^a Data from ref 32: CTAB and DTAB = cetyl- and dodecyltrimethylammonium bromide; CPC = cetylpyridinium chloride; DMPC and DPPC = dimyristoyl- and dipalmitoylphosphatidylcholines.

in a 25 mmol dm⁻³ borate buffer at pH 9.0. Due to the low salt concentration, it is reasonable to assume that the obtained values would be the same for pure aqueous polymer solutions. As the polymer concentration was increased, the dye spectra changed, as shown in Figure 6, in the same region of the previously determined cmc. The measured absorption maxima are shown in Table 3, along with literature values for other similar systems.

The determined λ_{\max} can be grouped in to three classes: for most of the copolymers, these values range from 536 to 560 nm; for F38 and F68, the values are between 512 and 530 nm; and for L31, the obtained maximum is at 486 nm. For comparison, the values measured for nonionic and cationic micelles and liposomes are within 530–540 nm. These values are close to the ones measured for ethanol (550 nm) and methanol (515 nm).³³

Therefore, the majority of the Pluronics studied provide solubilization sites which are very similar to the ones observed for low molecular weight surfactants. The interesting feature is that, for these surfactants, the micelle interior is composed mainly of hydrocarbon chains. For the Pluronics, the more polar PO units (in comparison to alkanes) are shown to compose an environment bearing similar polarity and, probably, similar water contents. This large dehydration of the PO units would support the thermodynamic findings that the micellization resembles the phase separation process in Pluronic or PPO solutions. For the second group of copolymers, the measurements were made at high polymer concentrations and these solutions presented high viscosity. The use of high

(31) See, for instance: Alexandridis, P.; Zhou, D.; Khan, A. *Langmuir* **1996**, *12*, 2690. Mortensen, K.; Pedersen, J. S. *Macromolecules* **1993**, *26*, 805. Yu, G.-E.; Deng, Y.; Dalton, S.; Wang, Q.-G.; Attwood, D.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2537.

(32) Loh, W.; Beezer, A. E.; Mitchell, J. C. *Langmuir* **1994**, *10*, 3431.

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(34) Drummond, C. J.; Grieser, F.; Healy, T. *Faraday Discuss. Chem. Soc.* **1986**, *81*, 95.

polymer concentrations is necessary to ensure complete dye solubilization and, hence, that the observed values reflect only one environment. Such a high viscosity indicates the existence of more ordered phases than the micellar one. These mesophases would be less polar than the micelles, or this difference might be attributed to a different dye solubilization site, perhaps closer to the micelle surface and more exposed to water. The value obtained for L31 was determined in a region very close to the cloud point, although without signs of turbidity. As discussed before, the aggregation process leading to phase separation passes by intermediate phases and this determined value might be ascribed to one of these structures.

In summary, this paper described a comprehensive study of micelle formation by a wide range of EO-PO-EO block copolymers in water. The determined cmc values were corroborated by the agreement among three different techniques. The linear multivariate analysis of the Gibbs energies of micellization in terms of the polymer composition supported the leading role of the hydrophobic PO

units in driving the micellization, also showing a small, but favorable, contribution of the EO units. For two copolymers, L121 and the reverse 25R2, no sign of micelle formation was detected before the onset of phase separation. The polarity of the micelle solubilization sites, as determined by the solvatochromic dye E_T30, is similar to that observed for other micelles and for ethanol. These results reinforce the current view that this micellization is accompanied by a dehydration of the PO units, whereas the EO chains remain strongly hydrated, forming the micelle corona.

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