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Evaluation of the Physical-Chemical Properties of Poly(ethylene oxide)-*block*-Poly(propylene oxide) by Different Characterization Techniques

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Summary: A surfactant's efficiency for a given application is dependent on its chemical structure and physical-chemical properties in solution, including surfactant solubility as a function of concentration and temperature as well as adsorption and aggregation behavior. This review work describes the main physical-chemical properties ascertained by means of various characterization techniques, which can be used to study nonionic surfactants based on poly(ethylene oxide)-block-poly(propylene oxide) (PEO-PPO). Among these, some are widely used and others are relatively new for this type of application.

Keywords: block copolymers, phase diagrams, surfactants, surfaces

Introduction

Surfactants are amphiphilic substances, that is, their chemical structure has two regions with different polarities: one polar and the other nonpolar. The nonpolar part of the molecule has little affinity for the water molecules in aqueous media and is called the hydrophobic part of the surfactant, while the polar part has a strong affinity for water molecules because of ion-dipole and dipole-dipole interactions, and is thus called the hydrophilic part.[1,2]

The polar part of surfactants is very important because it determines the solubility in water the surfactant classification, either an ionic (anionic, cationic and amphoteric), nonionic or biological surfactant.[2]

Nonionic surfactants are the largest and fastest-increasing group of surfactants.[3] The most important development in the field of these surfactants was the discovery that gradual variation in hydrophobicity can be obtained with the use of poly (ethylene oxide)-block-poly(propylene oxide), where the functionality depends on the initiator.[4] The poly(ethylene oxide) (PEO) segment is soluble in water at ambient temperature while the poly(propylene oxide) (PPO) segment, although having a similar structure to PEO, is not soluble in water at temperatures above 15 °C, thus constituting the hydrophobic part of the surfactant.[5]

The most often used and studied commercial poly(ethylene oxide)-block-poly (propylene oxide) products are Pluronic® polyals (BASF) and Synperonic® polyals (ICI). These compounds have a range of bifunctional structures, where the hydrophobic part (PO) is at least 15% of the compound's weight and the hydrophilic part (EO) is 20% to 85%. These copolymers are very stable, and because they are nonionic, they do not react with some cations normally found in water. The composition of the copolymers can be varied to meet the specific needs for emulsification, dispersion and detergents, thereby enabling applications in the lubricant, pesticide, detergent, food, cosmetic, pharmaceutical and oil industries.[4]

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In addition, a series of PEO-PPO block copolymers with different structures are being investigated for our research group.[6–18] Among these are branched and monofunctional copolymers, coupled at one end with hydrocarbon chains. These structures are shown in Table 1.

Furthermore, block copolymers with different positioning of the hydrophilic (EO and OH) and hydrophobic (PO and hydrocarbon chain) groups were also evaluated and it has been observed that this structural alteration causes significant changes in the physical-chemical properties of the surfactant in aqueous solutions.[15,16,18]

The aim of this work is to review the studies developed mainly for our research group in the evaluation of physical-chemical properties of poly(ethylene oxide)-block-poly(propylene oxide) in aqueous solutions by means of different characterization techniques.

Physical-chemical properties

The presence of two distinct parts of a single surfactant molecule is responsible for the adsorption capacity at the water-air or oil-water interface and on the surface of solids. It also results in the self-association of these molecules, causing them to form aggregates in aqueous solutions. The study of the association and adsorption of nonionic surfactants in aqueous solutions can be used to establish a useful structure-property relationship in these aqueous systems. As an example, we have obtained a correlation between the structure and composition of PEO-PPO block copolymers having different structures and their properties in aqueous solutions while also determining the efficiency of the copolymers in destabilizing petroleum emulsions.[16,18]

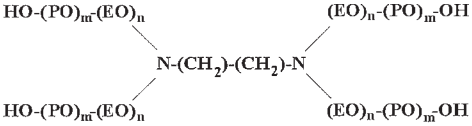
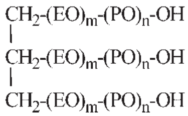
Moreover, because the surfactant chains have regions with different solubilities, it is important to study the solubility of copolymer surfactants.

Therefore, in the following sections we summarize the physical-chemical properties of solubility, formation of molecular aggregates and adsorption at the liquid-gas and liquid-liquid interfaces.

Solubility of nonionic surfactants in aqueous solutions

Specifically, the solubility of nonionic surfactants based on PEO-PPO block

Table 1.
Structures of PEO-PPO block copolymers

Copolymers	Structures
Monofunctional	$CH_3(EO)_x$-$(PO)_y$-OH $C_4(EO)_x$-$(PO)_y$-OH $C_{12}(EO)_x$-$(PO)_y$-OH
Bifunctional	HO-$(EO)_n$-$(PO)_m$-$(EO)_n$-OH
Branched	  $\begin{array}{l}CH_2\text{-}(EO)_m\text{-}(PO)_n\text{-}OH\\ \vert\\ CH_2\text{-}(EO)_m\text{-}(PO)_n\text{-}OH\\ \vert\\ CH_2\text{-}(EO)_m\text{-}(PO)_n\text{-}OH\end{array}$

copolymers depends on the hydration of the ethoxylated and propoxylated (glycol) groups of the molecule. These surfactants in aqueous solutions show phase separation with increasing temperature. The temperature at which this occurs is called the cloud point or temperature.[2,19,20] Three types of models are proposed to explain the mechanism of this behavior. The first model shows that at low temperatures the water forms an ordered structure around the ethylene oxide chain, and at higher temperatures this structure is broken.[21] The second model proposes that hydrogen bonds form between the water and oxygen molecules of the EO, which are destroyed as the temperature increases.[22] The third model demonstrates a change in the conformational structure of the EO chain as a function of temperature. At low temperatures, a conformation soluble in water with a high dipole moment is observed, while at higher temperatures other conformations with lower or no dipole moment and low solubility are energetically favored.[23]

Formation of molecular aggregates

Surfactants are soluble in water below a certain temperature and/or concentration. At low concentrations, the surfactant molecules are solubilized in the bulk of the solution in the form of unimers (that is, surfactant molecules not associates under the form of micelles) and also adsorbed at the water-air interface. At this interface, the hydrophobic part of the molecule tends to be oriented toward the air, while the hydrophilic part remains immersed in the water. This situation is energetically more favorable than the complete dissolution of either of the two phases. At higher concentrations, the saturation of the water-air interface is attained upon the formation of a monolayer, with the formation of molecular aggregates observed in the bulk of the solution.[24] These aggregates are known as micelles and essentially include two types of groups: those that do not mix well with the solvent and strongly attract, producing a stable compact form, and those that are very soluble, and for that reason tend to be externally exposed, producing soluble particles or aggregates.[25]

Micelles of PEO-PPO block copolymers have been studied in order to understand their formation and structures. The parameters that characterize the micelles are: the *concentration* at which they start to form; the *fraction* of copolymer molecules in micellar form; the *size* of the micelles and the *aggregation number* (average number of unimers in the micelles). While PEO-PPO surfactants all have relatively low molar masses, they form different types of aggregates based on variations in the molar mass, block types, solvent and temperature.[17,26–33]

The surfactant concentration above which micelles form is called the critical micelle concentration (CMC).[34] It has also been observed that micelle formation (micellization) can be induced by rising temperature, leading to another measure, the critical micelle temperature (CMT). In the particular case of PEO-PPO block copolymers, this phenomenon has been attributed to the dehydration of the copolymer's oxypropylene groups, which is theorized to induce the formation of molecular aggregates.[34]

Adsorption at the liquid-gas and liquid-liquid interfaces

Another important property of nonionic surfactants based on PEO-PPO block copolymers is their adsorption at the water-air interface.

Liquids and solids have surface tension due to the cohesive energy among the molecules. The molecules located in the interior of a liquid are, on average, subject to equal attractive forces in all directions. For example, water molecules in the bulk of a solution have hydrogen bonds, while those situated, for example, at the liquid-air interface are subjected to unbalanced attractive forces. This results in an excess of energy, the so-called surface tension, compared to the bulk of the liquid.[35,36]

As discussed already, surfactant molecules in aqueous solutions orient themselves to maintain the hydrophilic groups in the aqueous medium and the hydrophobic groups at the water-air interface. The tendency of surfactant molecules to accumulate at an interface, taking the place of water molecules, further reduces the surface tension of the solution. This decrease occurs because the intermolecular forces of attraction between water molecules and a non-polar group are weaker than the interactions among water molecules themselves.[36]

Characterization of aqueous solutions of PEO-PPO block copolymers

The properties of aqueous solutions of PEO-PPO block copolymers can be studied using various physical methods.[21] The classic techniques to study micellar systems utilize measures of macroscopic properties (such as surface tension and viscosity) or thermodynamic properties, determined by differential scanning calorimetry. Spectroscopic and light-scattering techniques can also be employed to study these properties in aqueous solutions.[37]

The same techniques are utilized to determine the CMC and CMT values, size and shape of the micelles, aggregation number, micellization enthalpy, adsorption and phase separation in aqueous solutions.

Temperature versus concentration phase diagrams

One of the simplest techniques to determine the solubility of nonionic surfactants is visual observation of the solution and plotting of temperature versus concentration phase diagrams. The values of the cloud point temperature for each sample concentration are obtained using a test tube immersed in a beaker containing water heated on a hot plate, and equipped with a thermometer in the test tube to measure the temperature. Duplicate solutions are used for each point and two measurements for each solution. The cloud point is determined by the average between the measure at which the first indication of clouding occurs and the temperature at which it disappears. The figures obtained for a single system have a maximum error of 2 °C.

A phase diagram constructed for aqueous solutions of monofunctional diblock copolymers, coupled at one end of their chains with linear and saturated hydrocarbons containing twelve carbon atoms (C_{12}-PEO-PPO-OH and C_{12}-PPO-PEO-OH) is shown in Figure 1. The curves delimit the phase separation of each copolymer solution: at the temperatures above the curve the copolymer solution has two phases and below the curve it has only one.[6,10]

It can be seen that for a given copolymers in the concentration range analyzed (0.1–10 wt%), the cloud point nearly constant. This profile of the curve can be attributed to the type of block structure of these copolymers, which because they are built of hydrocarbon chains have a more accentuated hydrophobic characteristic. A comparison of the results obtained for these copolymers shows that, as expected, the one with the highest EO/PO ratio (most hydrophilic), has the highest cloud points, and the other two copolymers have different cloud points, even though they have similar EO/PO ratios. The C_{12}-$(EO)_6$-$(PO)_5$-OH copolymer, which has hydrophilic (EO and OH) and hydrophobic (C_{12} and PO) groups in alternating positions, has higher cloud points than C_{12}-$(PO)_4$-$(EO)_5$-OH, whose hydrophilic/hydrophobic groups are in adjacent positions. This suggests that a copolymer's architecture has a strong influence on its solubility in water. To conclude, this method allows the determination of differences in solubility to characterize the different properties of surfactants in aqueous solution as a function of their composition and nanoscopic organization.[6,10]

Surface tension

To study the adsorption of PEO-PPO block copolymers at the water-air interface and determine the CMC values, surface tension tests can be conducted as a function of the copolymer's concentration in aqueous solutions.

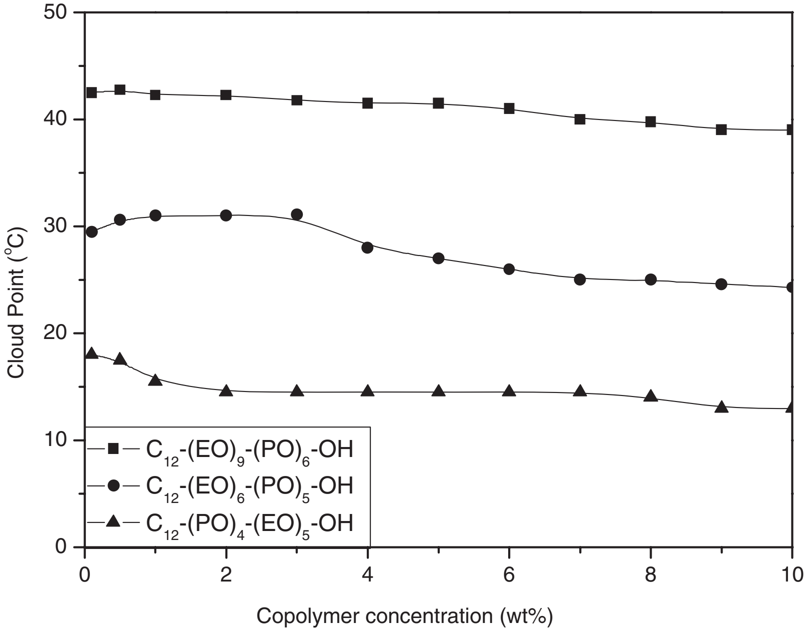


Figure 1.
Temperature versus concentration phase diagrams of PEO-PPO monofunctional diblock copolymers in aqueous solution.

There are various experimental methods of determining the surface tension values. The four leading ones are the ring, plate, contact angle and drop methods. Each method is based on a different technique and provides much other specific information. The ring method, based on force measurements, is one of the most widely used due to its universality, precision and simplicity.[38]

In general, the curves of surface tension as a function of concentration contain a discontinuity. The behavior of the first segment shows that the surface tension decreases as the surfactant concentration increases, representing its gradual adsorption at the surface. The second segment is usually a horizontal line, where the surface tension remains constant while the concentration continues to increase. At this stage, adsorption at the surface is no longer observed. The extension of these two segments is the midpoint of the discontinuity and is related to the start of aggregation of the surfactant in solution. The concentration where this point is observed corresponds to the critical micelle concentration (CMC).[39–41] Figure 2 shows a typical graph of the surface tension variation of aqueous solutions of PEO-PPO branched diblock copolymers as a function of their concentrations. At constant temperature, the surface tension of these solution decreases with increasing concentration of the surfactant until an almost constant low value is reached and the corresponding concentration is CMC. The surfactants decrease the surface tension of the water from 72 mN/m to values of 30–40 mN/m.

The results show that the copolymer with an alternating structure, that is, with alternating hydrophilic (EO and OH) and hydrophobic (R and PO) segments, does not have a defined CMC when evaluated at a concentration of 3wt%. For the copolymer that has adjacent hydrophilic/hydrophobic segments, the curve presents a well-defined intersection point in the region of the CMC. This behavior can be attributed to the fact that this type of molecular structure (adjacent segments) is more

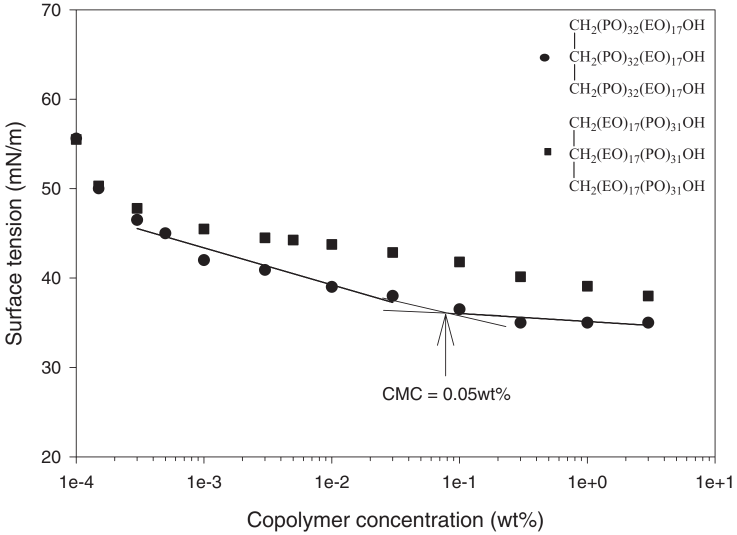


Figure 2.
Variation of the surface tension of aqueous solutions of PEO-PPO branched diblock copolymers with the concentration at 30 °C.

conducive for molecular association, as suggested by a model obtained in our previous publications, based on concordant phase separation and surface tension results.[6,18]

The measurement of surface tension γ enables determination of the mass of surfactant adsorbed at the surface Γ_a through the Gibbs adsorption isotherm, shown in Equation 1:[39,40]

$$\Gamma_a = -\frac{1}{RT}\left(\frac{\partial \ln \gamma}{\partial \ln c_2}\right)_T \qquad (1)$$

where Γ_a is the surface concentration (adsorption), c_2 is the concentration of the surfactant, T is the temperature and R is the universal gas constant.

The area A occupied by a surfactant molecule at the water-air interface can be calculated by Equation 2:[39,40]

$$A = \frac{1}{\Gamma_a N_a} \qquad (2)$$

where N_a is Avogadro's contant.

According to Equation 1, the surface tension of a solution decreases with increasing concentration of a surfactant and reflects the adsorption of solute molecules at the water-air interface. Equation 2 shows that a larger surface area of a surfactant molecule results in a lower surface tension of this solution.[39]

Viscometry

Viscosity can be defined as a fluid's resistance to flow. Within the limits of Newton's law the shear stress of a laminar flow goes linear with the velocity gradient.[42] This law applies to all gases and the majority of liquids with low molar masses over a wide range of velocity gradient. Polymer solutions at low concentrations behave as Newtonian fluids.

Measurement of the viscosity of polymer solutions, besides being of practical interest, supplies information for molecular characterization of polymers. The viscosity of macromolecular solutions is influenced by the testing conditions, namely by the temperature and shear velocity used to obtain the measurements. Besides this, a series of factors inherent to the characteristics of the molecule itself, such as its size, architecture, conformation, volume occupied in solution, molar mass, polydispersity, concentration and flexibility of the chain, can also alter the viscosity of a solution.[43]

The terms normally used to express the viscosity of polymers are relative viscosity (η_{rel}), specific viscosity (η_{sp}) and reduced viscosity (η_{red}). These parameters are defined by the mathematical expressions presented, respectively, in Equation 3–5:[42]

$$\eta_{\mathrm{rel}} = \eta_{\mathrm{sol}}/\eta_{\mathrm{solv}} \tag{3}$$

$$\eta_{\mathrm{sp}} = \eta_{\mathrm{rel}} - 1 \tag{4}$$

$$\eta_{\mathrm{red}} = \eta_{\mathrm{sp}}/\mathrm{c} \tag{5}$$

where, η_{sol} = absolute viscosity of the solution (Pa s);

η_{solv} = absolute viscosity of the solvent (Pa s).

The temperature-dependence of the relative viscosity of polymer solutions is attributed mainly to two origins: (1) an increase in Brownian motion with increasing temperature and (2) a reduced capacity for intermolecular interaction at higher temperatures. The polymer concentration also influences aggregation of the macromolecules in solution. Thus viscosity increases quickly with the concentration of the polymer due to the intermolecular interactions and formation of entanglements.[43]

The absolute viscosities can be measured using a rheometer equipment, which the basic principle consists in shearing a fluid between two concentric cylinders. One of cylinders rotates at constant velocity, while the other remains in the stationary state. Some others geometries are available, besides concentric cylinders. The dates obtained by this equipment are the shear tension (τ) and shear rate ($\dot{\gamma}$), which are transformed in the absolute viscosity ($\eta = \tau/\dot{\gamma}$).[42]

By plotting the specific viscosity as a function of concentration or temperature and observing the change in the slope of the line, the CMC and CMT values can be obtained by viscosity measurements, from change in slope of the line obtained on the graph of specific viscosity as a function of concentration or temperature, respectively. Besides this, information on the size, shape and interactions of molecular aggregates in aqueous solutions can be obtained using this technique.[10,43–46]

The shape and volume of the micelles of surfactants in solution are analyzed by means of the Guth-Simha equation (Equation 6) and by plotting a specific volume graph, obtained from Equation 7, as a function of the surfactant's concentration:[43]

$$\eta_{\mathrm{rel}} = 1 + 2,5\phi + 14,1\phi^2 \tag{6}$$

$$V = \phi/c \tag{7}$$

Here η_{rel} is the relative viscosity, ϕ is the volumetric fraction occupied by the particles, c is the concentration of the surfactant solution expressed in g/dl and V is the surfactant's effective specific volume, including the hydrated water.

Figure 3 shows the graphs obtained for PEO-PPO monofunctional diblock copolymers, where it can be seen that for the copolymer coupled with a smaller hydrocarbon chain (C_4), the specific volume, V, remains practically constant between 2 and 8 g/dL. Similar results obtained by another authors[47] suggest that this behavior is typical of spherically shaped micelles. Regarding copolymers coupled with C_{12}, the copolymer C_{12}-$(EO)_9$-$(PO)_6$-OH presented the same behavior in all temperatures studied, except at 30 °C. In this temperature and at this concentration range studied, the volume of copolymer C_{12}-$(EO)_6$-$(PO)_5$-OH was not constant. A cause for this behavior may be that the micelles were not in spherical form since 30 °C is near the cloud point of this polymer.

In Figure 4 we demonstrated the temperature dependence of reduced viscosity for a monofunctional PEO-PPO copolymer at different concentrations in water. The measures were taken at concentrations above the CMC, from relatively low temperatures up to temperatures around the cloud point (cloud point at 1 wt% = 30 °C). We observe that the reduced viscosity η_{red} decreases with the rising temperature up to 25 °C. Afterward the viscosity increases considerably with rising temperature. This

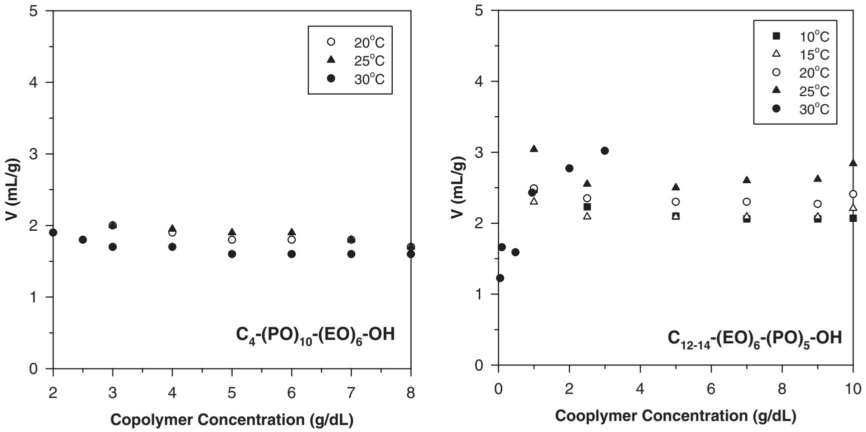


Figure 3.
Graph of effective specific volume as a function of concentration obtained for PEO-PPO monofunctional diblock copolymers, at different temperatures.

effect can be related to the intermicellar interactions.

The intrinsic viscosity [η] and the Huggins constant K_H also can be analyzed as a function of the temperature of aqueous solutions of PEO-PPO block copolymers. The intrinsic viscosity is related to the hydrodynamic volume of the molecules or molecular aggregates in solution, and K_H reflects the intermolecular interaction among the micelles of the copolymers. Using values from the plots of reduced viscosity η_{red} as a function of concentration (for example Figure 4), the intrinsic

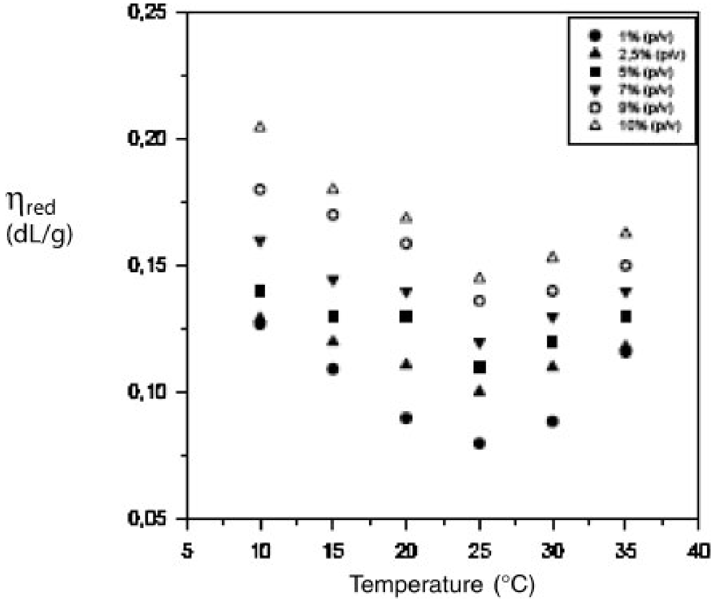


Figure 4.
Graph of reduced viscosity as a function of the temperature obtained for PEO-PPO monofunctional diblock copolymer at different concentrations in water.

Table 2.
Reduced viscosity values as a function of the concentration, at 25, 30 and 35 °C

Copolymer	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
			[η] (dL/g)			
C_{12}-$(EO)_6$-$(PO)_5$-OH	0.065	0.052	0.053	0.050	0.040	–
C_{12}-$(EO)_9$-$(PO)_6$-OH	0.082	0.079	0.080	0.068	0.062	–
			K_H			
C_{12}-$(EO)_6$-$(PO)_5$-OH	1.0	2.3	3.2	5.1	15.6	–
C_{12}-$(EO)_9$-$(PO)_6$-OH	1.8	1.6	1.5	1.9	2.5	–

viscosity and K_H values are calculated using Equation 8:[48,49]

$$\eta_{red} = [\eta] + [\eta]K_HC \qquad (8)$$

As shown in the literature,[50] a value of $K_H < 0.5$ is expected for molecules that do not interact, and higher values for the processes of micellization and phase separation.

Using the method just described, we report in Table 2 values of C_{12} coupled copolymers at 25, 30 and 35 °C. At low temperatures (10–20 °C), intrinsic viscosity and K_H values for the copolymer C_{12}-$(EO)_9$-$(PO)_6$-OH are constant indicating that no significant changes in the micelle size and shape are occurring. Above 20 °C, the intrinsic viscosity decreases, suggesting a more compact arrangement of the micelles as the temperature increases. Others[50] have attributed this compaction to the intermolecular interactions. For the copolymer C_{12}-$(EO)_6$-$(PO)_5$-OH the intrinsic viscosity begins falling off at the first increase in temperature from 10 to 15 °C. This reduction is likely due to the gradual aggregation of the unimers for the formation of the micelles, which we observed when were analyzed the reduced viscosity as a function of temperature (Figure 4). The results obtained for the K_H values confirm this behavior of the copolymer C_{12}-$(EO)_6$-$(PO)_5$-OH. Them K_H values increase as the temperature goes up, indicating the presence of interactions in the micelles. At a temperature near the cloud point of this copolymer (30 °C), the value of K_H becomes much higher.

Calorimetry

The calorimetric technique is used to characterize aqueous solutions of surfactants by two equipments: differential scanning calorimeter (DSC) and microcalorimeter.

Calorimetry is useful for determining the values of CMT, micellization enthalpy and phase separation of an aqueous solution of a nonionic surfactant.[12,33,51–53]

The micellization process is analyzed thermodynamically based on two theories. The phase separation theory considers micelles at the CMC as new phase, while the mass action theory holds that the micelles and non-aggregated unimers are in equilibrium. Both theories describe formation of micelles in terms of classic thermodynamics, and despite the apparent conceptual difference, ultimately provide the same result when applied to surfactants with high aggregation numbers.

The micellization process can be described by Equation 9:[2]

$$\mathrm{NS} \Leftrightarrow M_N \qquad (9)$$

where S represents a unimer and M_N represents a micelle with an aggregation number N.

Applying the law of mass action, which assumes a balance between unimers and a range of micellar types with aggregation number n, the equilibrium constant K is defined by Equation 10:

$$\mathrm{K} = [\mathrm{M}]/[\mathrm{S}]^{\mathrm{N}} \qquad (10)$$

If C_s and C_N represent the unimer and micelle concentration, respectively, then:

$$\begin{aligned} -\Delta G^\circ &= RT\ln K \\ &= RT\ln C_M - nRT\ln C_s \qquad (11) \end{aligned}$$

where R is the universal gas constant and T is the absolute temperature. The standard Gibbs free energy, ΔG°, per unimer is given by:

$$-\Delta G^\circ = (RT/N)\ln C_M - RT\ln C_s \qquad (12)$$

In the micellization process, N is very large (>100) and the equation's first term can be disregarded. Hence, the variation in the Gibbs free energy ΔG° to transfer 1 mol of surfactant to the micellar phase (energy of micellization), in the absence of electrostatic interactions (nonionic surfactants), is[2]

$$\Delta G^\circ = RT\ln C_s \qquad (13)$$

The micellization enthalpy ΔH° along with the micellization entropy per mol of surfactant ΔS° can be obtained from Equation 14:[24]

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (14)$$

In a study utilizing aqueous solutions of Pluronic® polyols, the values of ΔG°, ΔH° and ΔS° (utilizing Equations 13 and 14) were obtained by plotting a graph of the ΔG° values as a function of temperature. These values were calculated in the CMC at different temperatures. As expected, values of ΔG° are negative, since the thermodynamically stable micelles are formed spontaneously. The micellization enthalpy (ΔH°) is positive, indicating that the transfer of the copolymers in solution to the micellar form occurs by an endothermic process. However the entropic contribution (ΔS°) is positive and larger than the enthalpic contribution, thus favoring the micellization of these copolymers.[54] As showed by Tandford,[55] the entropic contribution positive is due to the hydrophobic effect caused by the change in the arrangement of the water molecules.

In our study, the endothermic enthalpy of micellization was confirmed by DSC analysis of an aqueous solution of a monofunctional PEO-PPO block copolymer (Figure 5). We observed the phase separation of this copolymer in aqueous solution on heating the solution, whose initial temperature (30 °C) was that of the cloud point (as determined by a phase diagram for this copolymer). The second exothermic peak upon cooling indicates the micelle formation process, which is attributed to the hydration of the PO groups. The enthalpy of the micellization and the phase separation were positive.[12]

Adding to the thermodynamic quantities obtained by DSC, the increased sensitivity of microcalorimetry allows us to observe the thermodynamic changes associated with the formation and growth of micelles and crystalline structures in the aqueous solutions of nonionic surfactants. These structures are mainly formed from micelle-micelle interactions at high concentrations and intermediate temperatures.[56]

Spectroscopic Analysis

Molecular absorption spectrophotometry

Molecules that are insoluble in a given solvent can be solubilized by the presence of an appropriate surfactant in this chemical environment. The solubilization, in general, is attributed to the micelles, which have the characteristic of lodging the insoluble molecules with in the medium.[39,57]

The location of the solubilized molecules in the micelles varies: nonpolar molecules in an aqueous solution are solubilized inside the nonpolar center of the micelles, while polar molecules sit parallel in the polar tails with the surfactant molecules, oriented toward the aqueous medium. Some organic materials (such as aromatic dyes) will be preferentially solubilized in a layer of PEO chains around a hydrocarbon core of the micelles of a nonionic surfactant, since the PEO chains are soluble in polar solvents. The solubilization phenomenon requires the presence of micelles and can never occur in solutions where surfactants exist only in the form of unimers. Solubilization of an insoluble compound can therefore be used as a method to determine the CMC and CMT.[39]

Molecular absorption spectrophotometry, also known as colorimetry, is based on the method of solubilization of a hydrophobic dye inside the micelles formed in aqueous surfactant solutions.[56] The intensity of absorption by the dye can be

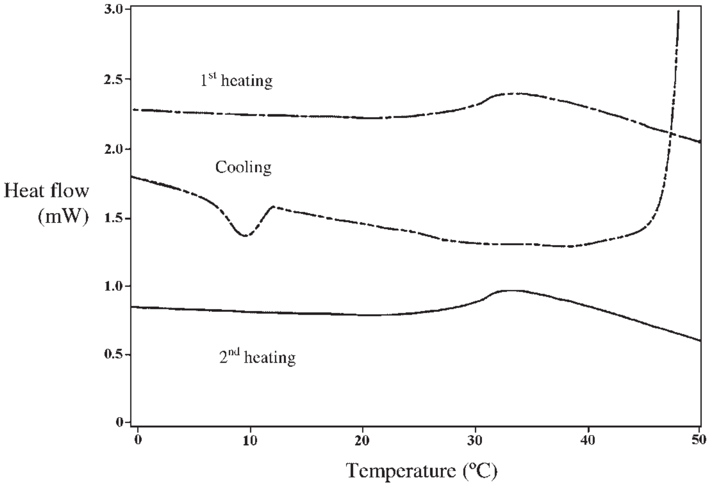


Figure 5.
DSC curves of aqueous solution of C_{12}-$(EO)_6$-$(PO)_5$-OH copolymer at 10% w/v.

measured with an ultraviolet-visible (UV-Vis) spectrometer or a colorimeter.[8,44,58] At temperatures or concentrations where the surfactants are still not free in aqueous solution, there is no absorption of the dye due to its hydrophobic character. Once the PEO-PPO block copolymers have formed micelles (at higher temperatures or concentrations), the dye is solubilized inside these micelles producing a different and characteristic absorption spectrum. A plot of dye absorption intensity (at the wavelength where the dye's absorption is maximum) versus temperature (at a constant concentration, as in Figure 6) can be used to identify the CMT, which appears an inflection point in the curve.[56] Similarly, the CMC values can be identified by plotting instead the dye absorption intensity versus concentration, at a constant temperature.[58,59]

Fluorescence

The fluorescent emissions occur in some compounds when photons are released during the relaxation of excited electrons. Typically a molecule absorbs light of a particular wavelength, exciting an electron, and then emits a photon of longer wavelength due to the electron relaxation process. Others mechanisms exist, such as chemical reactions and internal conversions, by which molecules lose their excitation energy. These competitive routes reduce the emission of light, a phenomenon known as quenching.[60]

The fluorescence technique using pyrene has been an important method of studying aqueous solutions of PEO-PPO block copolymers, because the pyrene has well resolved emission and excitation spectra, due to its high quantum emission yield. Besides this, the fact that the emission spectrum is sensitive to the polarity of the medium where the pyrene is found makes this method very useful to study the micellization of copolymers in aqueous solutions.[32,33,61–63]

The fluorescence spectrum of polynuclear aromatic compounds, such as pyrene, varies as a function of concentration and of polarity of the suspension medium. At low concentrations ($\sim 10^{-5}$ M), the spectrum of the unimer of pyrene has five narrow bands in the region of 350–420 nm, however the greater the medium's polarity, the greater will be the reduction of the I_1/I_3 ratio (the ratio between the intensity of band 1 and that of band 3, numbered from lower to higher wavelength). At concentrations above 10^{-5} M, a wide band is also observed at higher wavelengths ($\sim$460 nm). This

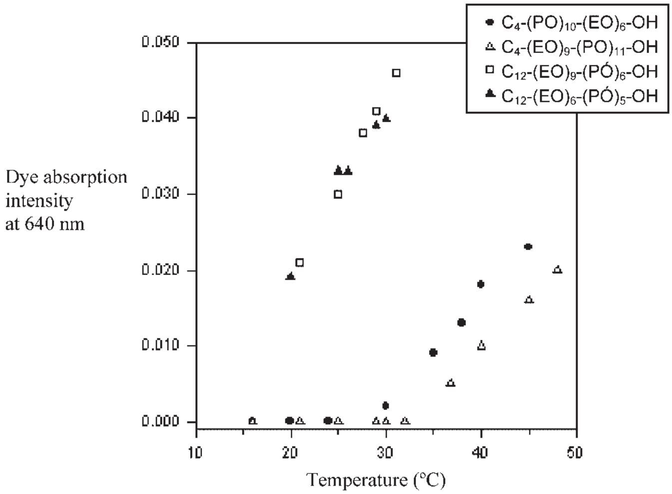


Figure 6.
Dye absorption intensity in function of the temperature of the aqueous solution of PEO-PPO block copolymers, at a constant concentration.

band is attributed to the pyrene excimer, which is a reversible complex formed of an excited molecule and a molecule in the ground state. This formation is also sensitive to the concentration because it involves the interaction between these two states of pyrene molecules.[63,64]

The fluorescence method to determine the CMT and CMC values utilizes the changes of the pyrene spectrum that occur along with the changing polarity of the copolymer suspension as it is heated or the copolymer concentration increased. To determine the CMT values, a graph is plotted of the I_1/I_3 ratio as a function of the temperature. When micelles are not present, the I_1/I_3 ratio is high, since the pyrene molecules are in a predominantly polar environment. However, this ratio is lower in copolymer solutions than in pure water, indicating a less polar environment, even before the formation of micelles. As the temperature rises, I_1/I_3 decreases, meaning that the environment around the pyrene molecules has become less polar. This indicates the start of micelle formation and the CMT values are obtained from the curve's inflection.[54]

The CMC values were determined for two branched PEO-PPO block copolymers by plotting the graphs of I_1/I_3 and also of I_E/I_M as a function of the copolymer concentration (Figure 7 and 8, respectively). I_E is the intensity of the excimer (at 460 nm) and I_M is the intensity of the monomer (measured at 183 nm, which corresponds to the third vibrational band).

The CMC values obtained by the two methods are not in agreement, as observed in the Figure 7 and 8. This behavior can be attributed to the lower intensity at a wavelength of 460 nm observed for the alternating copolymer, which exhibits a small excimer formation, as evidenced by Figure 8. As already proposed based on the results obtained from phase separation and surface tension measures, the copolymers with adjacent structure self-associate and form micelles easier than the copolymers with alternating structure.[6,18]

Besides this, in the method using the I_E/I_M ratio, the excimer formation depends on the number of micelles formed and also on the number of pyrene molecules captured by these micelles, while the other method (based on I_1/I_3 ratio) depends only on the formation of these micelles. Thus, the I_E/I_M method can cause greater errors in determining the CMC values. By comparing the value of CMC of adjacent branched

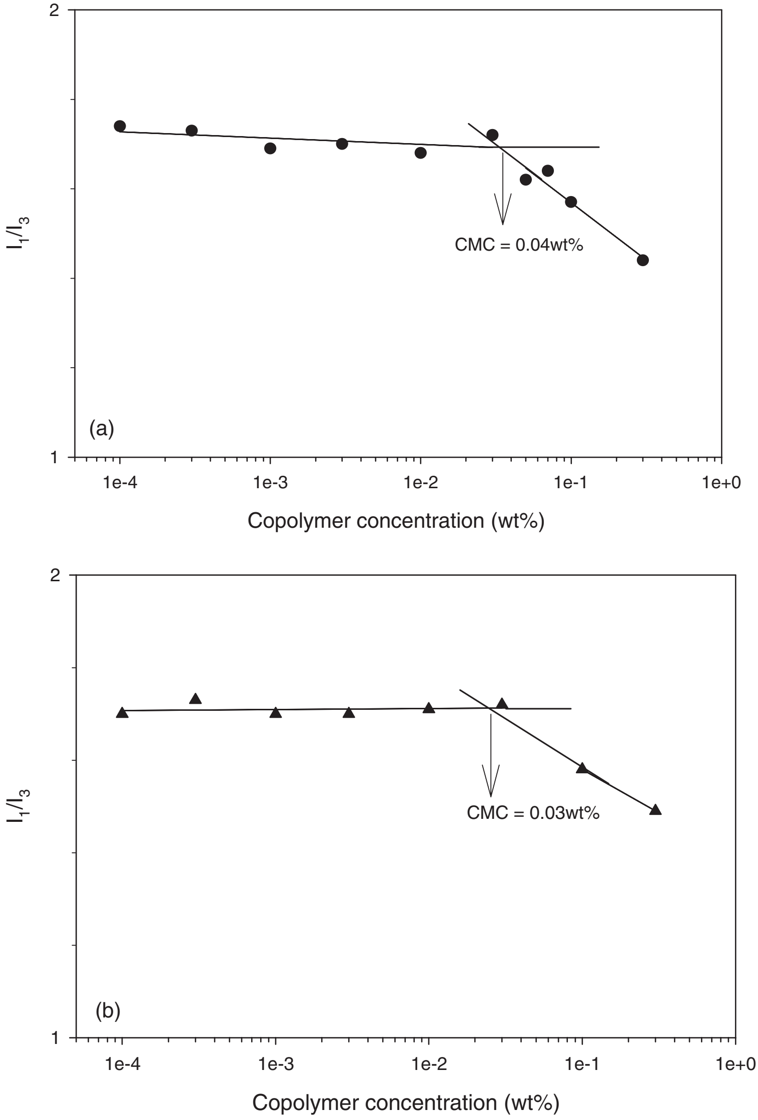


Figure 7.

I_1/I_3 ratio of pyrene versus branched copolymer concentrations in aqueous solution. (a) with adjacent structure; (b) with alternating structure.

copolymer obtained by surface tension (Figure 2 – CMC = 0.05 wt%) with its CMC value obtained by I_1/I_3 method (0.04wt%), we confirm that they are close but quite different from the CMC value obtained by I_E/I_M method (0.005 wt%).

Nuclear magnetic resonance

The nuclear magnetic resonance (NMR) technique is widely used to study the interactions that can occur in polymer solutions.[13,65–67] This technique enables determining the composition of PEO-PPO block copolymers and the CMC and CMT values of these surfactants in solution, by observing the chemical shifts of the groups that undergo alterations when the molecules pass from unimeric to micellar form. Because the NMR chemical shift of different functional groups changes based on the

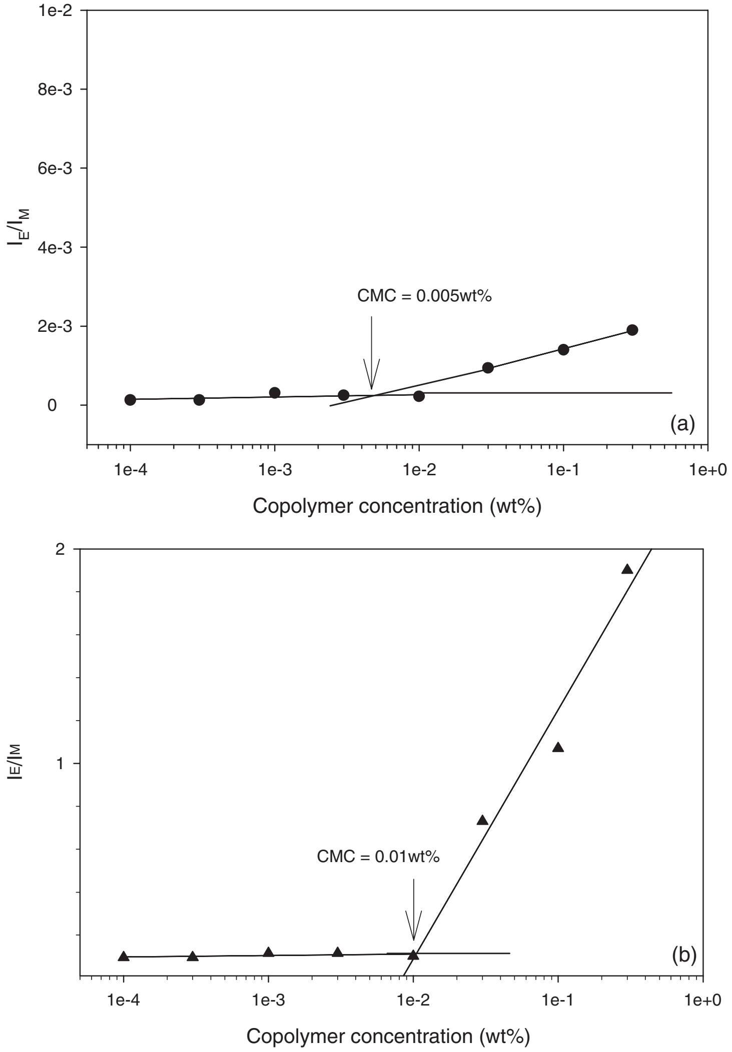


Figure 8.
I_E/I_M ratio of pyrene versus branched copolymer concentrations in aqueous solution. (a) with adjacent structure; (b) with alternating structure.

chemical environment, quantification of the changes can be used efficiently to detect interactions among the dissolved molecules.[13,65–67]

The micellization process of PEO-PPO copolymers as a function of temperature can be studied specifically by nuclear magnetic resonance of hydrogen (^{1}H-NMR). By ^{1}H-NMR signals corresponding to the CH_2 and CH units of the copolymer chains are analyzed. At low temperatures, narrow peaks are observed related to the CH_2-CH units of the PPO chains, which partly overlap the signals of the CH_2 units of the PEO chains. These narrow peaks indicate that the copolymer chains are in the form of unimers, so the chains' segments move freely in the aqueous solution. As the temperature increases, the spectra do not vary until the CMT is reached ($\sim$23 °C). At this temperature, the signals related to the PO groups change drastically, with the narrow peaks giving way to broader signals, and signals also begin to appear at lower frequencies. This behavior can be attributed to the loss of mobility of the PPO chains after the micellization process, since these chains remain located inside the micelles formed. The signals related to the EO groups do not vary with increasing temperature, confirming that these groups are located on the outside part of the micelles, where the chemical environment remains unchanged.[51]

Some models have been described in the literature for determining the CMC of a surfactant system using information from NMR.[68] The pseudophase model considers the concentration of the unimer surfactant C_{uni} after micellization as a constant, thus the chemical shift observed will be the weighted average of the shifts related to unimers and micelles:[68]

$$\delta_{obs} = (C_{uni}/C_t)\delta_{uni} + [(C_t - C_{uni})/C_t]\delta_{mi} \qquad (15)$$

where δ_{obs} represents the chemical shift observed of the proton of the CH_3 group of the surfactant's hydrocarbon chain, δ_{uni} represents the chemical shift of this group in unimeric form, that is, at a concentration below the CMC, and δ_{mi} represents the corresponding chemical shift to the micellar form, C_t is the total concentration of the surfactant in solution and C_{uni} is its concentration in unimeric form.

Above the CMC, the concentration of the non-aggregated surfactant, C_{uni}, remains constant and equal to the CMC, so that Equation 15 can be written as:

$$\delta_{obs} = \delta_{mi} - (CMC/C_t)\delta_{mi} - \delta_{uni} \qquad (16)$$

The surfactant's CMC can then be obtained by the angular coefficient of the graph of δ_{obs} versus 1/C. A study using monofunctional diblock copolymers showed that the CMC values obtained by this method are in close agreement with those obtained by surface tension and calorimetry.[6,13]

Alternatively, the single-step model allows calculating the aggregation number N of the micelles of surfactants.[68] This model assumes there is a reduction in the value of C_{uni} after micellization and is based on the mass action theory, where the unimers and micelles are in equilibrium. The total concentration of the surfactant is $C_t = C_{uni} + NC_{mi}$ and δ_{obs} is given by:[68]

$$\delta_{obs} = (C_{uni}\delta_{uni} + NC_{mi}\delta_{mi})/C_t \qquad (17)$$

Considering $\delta_{uni} = 0$

$$\begin{aligned} C_{mi} &= C_t\delta_{obs}/N\delta_{mi} \text{ and} \\ C_{uni} &= C_t(\delta_{mi} - \delta_{obs})\delta_{mi} \end{aligned} \qquad (18 \text{ and } 19)$$

By the mass action theory, Equations 18 and 19 can be written as:

$$\begin{aligned} &\log(C_t\delta_{obs})N \log[C_t(\delta_{mi} - \delta_{obs})] \\ &\quad + \log K + \log N \\ &\quad - (N - 1)\log \delta_{mi} \end{aligned} \qquad (20)$$

Linear adjustment permits the aggregation number to be obtained by the angular coefficient of the line $\text{Log}(C_t\delta_{obs})$ versus $\log[C_t(\delta_{mi} - \delta_{obs})]$.[13] The limitation of this model's application is that it must be applied to colloidal system with large particles.[68]

The study the micellization process of PEO-PPO block copolymers has also been done by measuring spin-lattice (T_1) and spin-spin (T_2) relaxation time. The graphs of T_1 and T_2 of the metallic protons of the PPO as a function of temperature present an abrupt change, which have been related to the TMC value.[69]

Adsorption in the Fourier transform infrared (FTIR) region

Spectroscopy in the infrared region with Fourier transform, with the assistance of the attenuated total reflectance (ATR) method,[70–72] can be used to characterize only the surface of a solid or liquid film. According to methods already developed,[73,74] it is possible to obtain spectra that characterize the physical-chemical nature of the surface without interference from the composition and structure of the interior of the sample. The IR radiation penetrates to a depth of around 0.3–3.0 μm, therefore, ATR-FTIR is only suited to characterize a surface layer of a specimen on a molecular level but not for the bulk material. Nevertheless, it is useful, for instance, to characterize the migration or diffusion of additives in the surface region, or to determine whether the surface of a mixture of materials is composed of a greater quantity of one of the constituents compared to its presence in the bulk of the mixture.

The ATR technique is based on the phenomenon of total reflection of radiation beam at the interface of materials with different refraction indices. The beam is aimed at the interface between the sample and crystal (with the incident angle slightly greater than the critical angle, to have total reflection), penetrates and is reflected at the surface of the sample. Part of its energy is absorbed (attenuated radiation) and can be detected. The penetration depth is of the same order as the radiation wavelength and is a function of the total refraction index of the crystal, the sample and the incident radiation angle (Equation 21). For liquids, cylindrical internal reflectance (CIR) and multiple internal reflectance (MIR) techniques can be used.[75]

$$d_p = \frac{\lambda_c}{\sqrt{2\pi[\sin^2\theta - (\eta_s/\eta_c)^2]}} \qquad (21)$$

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

In the CIR technique, the radiation penetrates and travels through a cylindrical crystal (for example, ZnSe) by 10 cylindrical internal reflections at a 45° angle. The solution is placed in a Pyrex tube that surrounds the reflection cylinder and the radiation, in circulating within it, penetrates the first layers of the solution, by which the spectrum can be obtained. This technique permits analyzing the surface of aqueous solutions, emulsions and fluids, among others.

In the MIR technique, the radiation zigzags through a crystal, reflecting on one of its sides, for example, four times, and the other five times, at an incidence angle of 30, 45 or 60°. On reaching the crystal's surface, the radiation penetrates the sample, reflects, returns to the crystal and so on successively. The depth of the radiation's penetration in the sample varies according to the radiation incidence angle. The same occurs with the number of reflections inside the crystal, which can vary from 9 to 90 reflections. This technique permits analyzing greases, papers, tissues, plastic coverings, liquids and opaque plastics.[75]

The performance of FTIR spectrometers enables many new applications to characterize solid-liquid interfaces, particularly in kinetic studies. The reflection-absorption and ATR techniques have been widely used for wet interfaces, and even for the water-air interface.[73,74]

We have used this technique to study the adsorption at the liquid-solid interface of PEO-PPO block copolymers in aqueous solutions. The FTIR analysis was conducted using the CIR technique with a zinc selenide (ZnSe) crystal that is insoluble in water and has a high refraction index. The results showed that it is possible to determine the behavior of aqueous solutions of PEO-PPO copolymers at the liquid-solid interface in aqueous solutions and also to evaluate the influence of the presence of additives in aqueous copolymer solutions.[14]

Light scattering technique

Light scattering is a phenomenon that occurs any time electromagnetic radiation falls on a material. Among the light scattering techniques, Dynamic (DLS) and Static (SLS) Light Scattering have been used to study surfactant systems. In such technique, the electrical field component of this radiation induces the formation of an oscillating electric dipole moment within the material that is of the same frequency and phase as the incident radiation. This oscillating dipole, in turn, emits radiation in all directions.

These techniques can furnish information about the size, shape and interaction of particles due to the fact that the intensity, polarization and angular distribution of light scattered by a colloidal dispersion depends on the size and shape of the particles that caused the scattering, the interactions among the particles and the difference between the refraction indices of the particles and the dispersing medium.[76] This technique is generally divided into dynamic light scattering and static light scattering.

During the dynamic light scattering experiment the exponential decay of the correlation intensity, originated by the Brownian movement of the micelles, is measured. The decay of the correlation depends on the diffusivity of the molecules, according to Equation 22:[48]

$$\Gamma = Dq^2 \tag{22}$$

where Γ = relaxation or constant of correlation; D = coefficient of effective translational diffusion and q = scattered light vector.

The diffusion coefficient depends on the temperature, concentration and type of copolymer and viscosity of the solvent. The hydrodynamic radius of the micelles (R_h) is obtained from the value of D through the Einstein-Stokes equation:

$$R_h = \frac{kT}{6\pi\eta D} \tag{23}$$

where k = Boltzmann constant; T = absolute temperature and η = viscosity of the solvent.

By means of the light scattering technique, it is possible to plot the Zimm graph. This involves measuring the intensity of the light scattered for various angles and concentrations, obtaining a graph of Kc/R_θ as a function of [sin(θ/2) + Kc], where:[48,77]

$$K = \frac{\left[2\pi^2 n_0^2 \left(\frac{dn}{dc}\right)^2\right]}{N\lambda^4} \tag{24}$$

$$R_\theta = \frac{i}{I_0} * \frac{r^2}{(1+\cos^2\theta)} \tag{25}$$

c = concentration of the solute (g/cm^3);

n_0 = refraction index of the solvent at the wavelength used in the experiment;

dn/dc = increment in the specific refraction index of the solute;

N = Avogadro's constant;

λ = wavelength of the light used in scattering;

θ = angle at which the scattered light is measured;

i = intensity of the scattered radiation;

I_0 = intensity of the incident radiation;

r = distance from the photodetector to the sample;

K = an arbitrary constant.

The Zimm graph by extrapolation provides the zero concentration and zero angle, Equation 26:

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2A_2c \tag{26}$$

The intercept of a plot of the left-hand side of Equation 26 versus the concentration ($c \rightarrow 0$ and $\theta \rightarrow 0$) gives access to the weight average of the molar mass of the dissolved polymer and to its average radius of gyration, respectively. The slope yields the second virial coefficient, A_2 that is correlated with the Flory-Huggins-Staverman polymer-solvent interaction parameter indicating how much the scattering of the solution deviated from the ideal.

Others have used the dynamic and static light scattering techniques to study aqueous solutions of PEO-PPO copolymers.[25,28,48,76,77]

We have generated plots of D as a function of aqueous mono-functional copolymer solution concentrations, at 25, 30 and 35 °C. Table 3 gives the values of the determined hydrodynamic radii. It can be observed that the PEO-PPO block copolymers coupled to C_4 have higher hydrodynamic radii than PEO-PPO block copolymers coupled to C_{12}. This behavior is attributed to the fact that copolymers coupled to C_4 are more soluble than copolymers coupled to C_{12}.[6] A comparison of the results of the copolymer coupled with C_{12} solution, at the same temperature, shows that the C_{12}-(EO)$_9$-(PO)$_6$-OH copolymer (with the highest EO/PO ratio) has the lowest hydrodynamic radius. This behavior indicates that the EO/PO ratio influences the R_h value, in other words, the higher the EO/PO ratio is, the lower the R_h value will be. However, C_4-(EO)$_4$- (PO)$_{11}$-OH copolymer, which contains hydrophilic (EO and

Table 3.
R_h of the micelles of the PEO-PPO copolymers

Copolymer	R_h (at 25 °C) (nm)	R_h (at 30 °C) (nm)	R_h (at 35 °C) (nm)
C_4-$(EO)_4$-$(PO)_{11}$-OH	16	19	25
C_4-$(PO)_{10}$-$(EO)_6$-OH	18	21	–
C_{12-14}-$(EO)_6$-$(PO)_5$-OH	5	4	–
C_{12-14}-$(EO)_9$-$(PO)_6$-OH	2	2	2

OH) and hydrophobic (C_{12} and PO) segments in alternate positions, has a lower R_h value than C_4-$(PO)_{10}$- $(EO)_6$-OH copolymer, in which the hydrophilic/hydrophobic segments are in adjacent positions, in spite of the former having a lower EO/PO ratio.

Others have also used the dynamic light scattering technique to determine the R_h values of the micelles of Pluronics® polyols.[28] It was observed that the values of R_h are independent of the temperature. However, another study showed that the molar mass of the micelles (determined by static light scattering) increases linearly with increasing temperature, while the R_h of the micelles remains practically constant.[25]

For highly diluted solutions, the intensity of the scattering is directly proportional to the weight average aggregate number of the micelles, <Nw>.[78] A large increase in the scattered light intensity, then, indicates an increase in <Nw>. Besides this, the graph of the scattered light intensity as a function of temperature can provide the CMT value of the copolymer, which is measured as the intensity starts to vary.[33]

Conclusions

By the studying of the physical-chemical properties of nonionic surfactants based on PEO-PPO block copolymers can establish a useful structure-property relationship for their use in specified applications and systems. For this purpose, various characterization techniques are available. The phase separation or cloud point can be determined by simple visual observation and by calorimetric techniques. The CMC and CMT values can be observed by various techniques including tensiometry, viscosimetry, colorimetry, nuclear magnetic resonance (NMR), fluorescence and static light scattering. Moreover, the results obtained from these different techniques are in good agreement. Tensiometry also supplies information about the adsorption of molecules at the liquid-air interface, while FTIR can provide information about the adsorption at the liquid-solid interface. The static light scattering technique can be utilized also to determine the weighted mean molar mass (M_w), according to the virial coefficient (A_2) and aggregation number (N), while the dynamic light scattering technique provides information on the hydrodynamic radius of the micelles, distribution of the particle size in terms of R_h and also the fraction in weight of unimers and micelles. Another application of NMR technique is determination of the aggregation number, along with identification of the chemical environment where the molecules are located. Finally, viscometry can also be used to determine the hydrodynamic volume of the particles as well as the shape of the micelles formed.

The advantage of having various techniques available to study the question is to be able to count on different mean values of the property under consideration, depending on its availability and the parameter of interest. Besides this, it is possible to compare the results obtained, since some techniques evaluate surfactants in the bulk of the aqueous solution, while others evaluate their interfacial action, which can cause different results in the parameters determined.

[1] W. E. Duck, in: "*Encyclopedia of Polymer Science and Technology*," H. F. Mark, N. G. Gaylord, N. M. Bikales, Eds., Interscience Publishers, New York **1986**, *v. 5*, p. 801.
[2] T. F. Tadros, in: "*Encyclopedia of Physical Science and Technology*," R. A. Meyers, Ed., Academic Press Inc. Orlando **1987**, *v. 10*, p. 462.
[3] M. J. Schick, in: "*Nonionic Surfactants*", M. J. Schick, F. M. Fowkes, Eds., Marcel Dekker, Inc., New York **1966**, *v.. 1*, p. 1.
[4] I. R. Schmolka, in: "*Nonionic Surfactants*", M. J. Schick, F. M. Fowkes, Eds., Marcel Dekker, Inc. New York **1966**, *v. 1*, p. 300.
[5] F. E. Bailey, J. V. Koleske, in: "*Nonionic Surfactants*", M. J. Schick, F. M. Fowkes, Eds., Marcel Dekker, Inc. New York **1966**, *v. 2*, p. 794.
[6] C. R. E. Mansur, C. M. F. Oliveira, G. González, E. F. Lucas, *J. Appl. Polym. Sci.* **1997**, *66*, 1767.
[7] C. R. E. Mansur, C. M. F. Oliveira, G. González, E. F. Lucas, "Behavior of hydrotrope/surfactants mixtures in aqueous solutions by calorimetric, surface tension and viscometric measurements". Second International Symposium on Colloid Chemistry in Oil Production-ISCOP'97, September 1997, Rio de Janeiro, RJ, Brazil.
[8] C. R. E. Mansur, L. S. Spinelli, C. M. F. Oliveira, G. González, E. F. Lucas, *J. Appl. Polym. Sci.* **1998**, *69*(2), 2459.
[9] C. R. E. Mansur, L. S. Spinelli, G. González, E. F. Lucas, "Micelar behavior of poly(ethylene oxide-b-propylene oxide) copolymers in aqueous solutions by viscometric and light scattering analyses". 6th Latin American and 4rd Ibero American Polymer Symposium 1998, October **1998**, Viña del Mar, Chile.
[10] C. R. E. Mansur, L. S. Spinelli, G. González, E. F. Lucas, *Colloids and Surfaces – A* **1999**, *149*, 291.
[11] C. R. E. Mansur, L. S. Spinelli, G. González, E. F. Lucas, "Caracterização de sistemas tensoativos de PEO-PPO: tensiometria, colorimetria, viscosimetria, DLS, DSC e FTIR". 5º Congresso Brasileiro de Polímeros, November 1999, Aguas de Lindóia, SP, Brazil.
[12] C. R. E. Mansur, G. González, E. F. Lucas, *Polímeros-Ciência e Tecnologia* **1999**, IX, n° 2- abr/jun, 45.
[13] C. R. E. Mansur, C. R. N. Pacheco, G. González, E. F. Lucas, *Revista Química Nova* **2001**, n°1, 47.
[14] C. R. E. Mansur, M. R. Benzi, E. F. Lucas, *J. Apl. Polym. Sci.* **2001**, *82*(7), 1668.
[15] C. R. E. Mansur, G. González, E. F. Lucas, *Polymer Degradation and Stability* **2003**, *80*(3), 579–587.
[16] C. R. E. Mansur, S. P. Barboza, G. González, E. F. Lucas, *Journal of Colloid and Interface Science* **2004**, *271*(1), 232–240.
[17] C. R. E. Mansur, R. V. Pires, G. González, E. F. Lucas, *Langmuir* **2005**, *21*, 2696–2703.
[18] C. R. E. Mansur, F. C. Lechuga, A. C. Mauro, G. González, E. F. Lucas, *Journal of Applied Polymer Science* in press, 04/2007.
[19] S. Saeki, N. Kuwahara, M. Nakata, M. Kanenko, *Polymer* **1976**, *17*, 685.
[20] W. D. Hergeth, I. Alig, J. Lange, J. R. Lochmann, T. Scherzer, S. Wartewig, *Makromol Chem., Macromol. Symp.* **1991**, *52*, 289.
[21] R. Kjellander, E. Florin, *J. Chem. Soc. Faraday Trans.* **1981**, *77*, 2053.
[22] R. E. Goldstein, *J. Chem. Phys.* **1984**, *80*, 5340.
[23] G. J. Karlström, *J. Chem. Phys.* **1985**, *89*, 4962.
[24] R. J. Hunter, "*Foundations of Colloid Science*", Clarendon Press, Oxford **1986**.
[25] K. Mortensen, J. S. Pedersen, *Macromolecules* **1993**, *26*, 805.
[26] W. Brown, K. Schillen, M. Almgren, S. Hvidt, *P. Bahadur, J. Phys. Chem.* **1991**, *95*, 1850.
[27] P. Linse, M. Malmsten, *Macromolecules* **1992**, *25*, 5434.
[28] M. Malmsten, B. Lindman, *Macromolecules* **1992**, *25*, 5446.
[29] P. N. Hurter, J. M. H. M. Scheutjens, T. A. Hatton, *Macromolecules* **1993**, *26*, 5030.
[30] P. N. Hurter, J. M. H. M. Scheutjens, T. A. Hatton, *Macromolecules* **1993**, *26*, 5592.
[31] B. Chu, *Langmuir* **1995**, *11*, 414.
[32] T. Nivaggioli, P. Alexandridis, T. A. Hatton, *Langmuir* **1995**, *11*, 730.
[33] P. Alexandridis, T. Nivaggioli, T. A. Hatton, *Langmuir* **1995**, *11*, 1468.
[34] B. Chu, Z. Zhou, in: "*Nonionic Surfactants*", M. J. Schick, F. M. Fowkes, Eds., Marcel Dekker, Inc. New York **1987**.
[35] D. J. Shaw, "*Introdução à química dos colóides e de superfícies", traduced by J.H. Maar*, Edgar Blucher Ltda, São Paulo **1975**.
[36] K. Tsujii, "*Surface activity. Principles, phenomena and applications*", Academic Press, Inc., New York **1998**.
[37] B. Chu, Z. Zhou, in: "*Nonionic surfactants*", V. M. Nace, Ed.; Marcel Dekker, Inc. New York **1996**, p. 67.
[38] GmbH. Krüss Wissenschaftliche Laborgerate. "Digital-Tensiometer K10 for the automatic measurement of interfacial and surface tensions of liquids", Borsteler Chaussee, 85–99a, D-2000 Hamburg 61, **1980**.
[39] J. Óscik, "*Adsorption*", John Wiley & Sons, New York **1982**.
[40] W. J. Moore, "*Physical Chemistry*", Prentice-Hall, Inc., New Jersey **1972**.
[41] L. T. Okano, *Master Dissertation*, USP, Brazil **1993**.
[42] W. J. Freeman, in: "*Encyclopedia of Polymer Science and Engineering*", H. M. Mark, N. M. Bikales, C. G. Overberger, G. Menges, Eds., John Wiley & Sons, New York **1985**, v. 3.
[43] F. R. Eirich, "*Rheology-theory and application*", Academic Press, Inc., **1956**, *v. 1* p. 573.

[44] M. Malmstem, B. Lindman, *Macromolecules* **1993**, *26*, 1282.

[45] G. Wu, Z. Zhou, B. Chu, *Macromolecules* **1993**, *26*, 2117.

[46] K. Pandya, P. Bahadur, T. N. Nagar, A. Bahadur, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1993**, *70*, 219.

[47] Y. Saitõ, T. Satõ, *J. Phys. Chem.* **1985**, *89*, 2110.

[48] F. W. Billmeyer, "*Textbook of Polymer Science*", John Wiley & Sons, New York **1984**, p. 198.

[49] W. Brown, K. Schillén, S. Hvidt, *J. Phys. Chem.* **1992**, *96*, 6038.

[50] L. Melleur, A. Hardy, F. Quirion, *Langmuir* **1996**, *12*, 4697.

[51] G. Wanka, H. Hoffmann, W. Ulbricht, *Macromolecules* **1994**, *27*, 4145.

[52] G. E. Yu, Y. Deng, S. Dalton, Q. G. Wang, D. Attwood, C. Price, C. Booth, *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 2537.

[53] P. Alexandridis, J. F. Holzwarth, *Langmuir* **1997**, *13*, 6074.

[54] P. Alexandridis, J. F. Holzwarth, T. A. Hatton, *Macromolecules* **1994**, *27*, 2414.

[55] C. Tanford, *PNAS USA* **1979**, *76*, 4175.

[56] B. Michels, G. Waton, R. Zana, *Colloids and Surfaces* **2001**, *183*, 55.

[57] R. Nagarajan, K. Ganesh, *Macromolecules* **1989**, *22*, 4312.

[58] P. Alexandridis, J. F. Holzwarth, T. A. Hatton, *Macromolecules* **1994**, *27*, 2414.

[59] P. N. Hurter, T. A. Hatton, *Langmuir* **1992**, *8*, 1291.

[60] F. MacRitchie, "*Chemistry at Interfaces*", Academic Press, Inc., New York **1990**.

[61] K. Schillén, W. Brown, C. Konak, *Macromolecules* **1993**, *26*, 3611.

[62] K. Schillén, W. Brown, R. M. Johnsen, *Macromolecules* **1994**, *27*, 4825.

[63] M. Bohorquez, C. Koch, T. Trygstad, N. Pandit, *J. Colloid and Interface Sci.* **1999**, *216*, 34.

[64] D. I. Schuster, in: "*Encyclopedia of Physical Science and Technology*", R. A. Meyers, Ed., Academic Press, Inc., Orlando **1987**, p. 386.

[65] A. P. Mikhalkin, *Colloid J.* **1994**, *56*(3): 336.

[66] C. M. F. Oliveira, E. F. Lucas, *Polymer Bulletin* **1990**, *24*, 363.

[67] R. M. Silverstein, C. G. Bassler, T. C. Morril, "*Spectrometric Identification of Organic Compounds*", 3rd ed. John Wiley & Sons, Inc., New York **1974**, p. 159.

[68] C. Chachaty, *Progress in NMR Spectroscopy* **1987**, *19*, 183.

[69] F. Cau, S. Lacelle, *Macromolecules* **1996**, *29*, 170.

[70] N. J. Harrick, "*International Reflection Spectroscopy*", Wiley Interscience, New York **1967**.

[71] R. J. Jakobsen, in: "*Application of FT-IR to Surface Studies in Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems*", J. R. Ferraro, L. J. Basile, Eds., Academic Press, New York **1979**, *v. 2*, p. 165.

[72] R. E. Pepper, R. J. Samuels, in: "*Characterizationof. Oriented. Surfacesin. Polymer. Characterization*". C. D. Craver, T. Provder, Eds., American Chemical Society, Washington-DC **1990**, p. 315.

[73] I. Kossler, in: "*Encyclopedia of Polymer Science and Technology*", H. F. Mark, N. G. Gaylord, N. M. Bikales, Eds., Interscience Publishers, New York **1966**, *v. 7*, p. 486.

[74] H. A. Wilis, V. J. Zichy, in: "*Polymer Surfaces*", D. T. Clark, W. J. Feast, Eds., John Wiley & Sons, New York **1978**, p. 287.

[75] W. A. Bueno, "*Manual de Espectroscopia Vibracional*", MacGraw-Hill, Ltda, São Paulo **1990**, p. 456.

[76] M. Kerker, "*The Scattering of Light and Other Eletromagnetic Radiation*", Academic Press, Inc., New York **1969**.

[77] P. Linder, T. Zemb, "*Neutron, X-Ray and Light Scattering: Introduction to Investigate Tool for Colloidal and Polymeric Systems*", North-Holland Elsevier Science Publishers, Amsterdam **1991**, p. 301.

[78] K. Mortensen, W. Brown, *Macromolecules* **1993**, *26*, 4128.