

Phase Behavior of Aqueous Systems Containing Block Copolymers of Poly(ethylene oxide) and Poly(propylene oxide)

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ABSTRACT: Phase behavior of aqueous systems containing block copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) was evaluated by building up temperature-concentration phase diagrams. We have studied bifunctional triblock copolymers (HO-PEO-PPO-PEO-OH) and monofunctional diblock copolymers (R-PEO-PPO-OH and R-PPO-PEO-OH, where R length is linear C₄ and C₁₂₋₁₄). The cloud points of the polymer solutions depended on EO/PO ratio, polarity, R length and position of the hydrophilic and hydrophobic segments along the molecule. Such factors influence on the solutions behavior was also analyzed in terms of critical micelle concentration (CMC), which was obtained from surface tension vs. concentration plots. Salts (NaCl and KCl) added into the polymer solutions change the solvent polarity decreasing the cloud points. On the other hand, the cloud points of the polymer solutions increased as a hydrotrope (sodium *p*-toluenesulfonate) was added. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1767–1772, 1997

Key words: aqueous systems; block copolymers; poly(ethylene oxide); poly(propylene oxide)

INTRODUCTION

The major development in the field of nonionic surfactants has been the discovery that the gradual variation of hydrophobicity can be brought about by the use of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) block copolymers. The functionality of these block copolymers depends on the initial starting material. Countless combinations and variations in composition of these polyoxides block copolymers are possible.¹ Although PPO and PEO have a similar structure, the former is not water soluble under usual conditions, and it is the hydrophobic portion of the sur-

factant.² The widely known series of commercial products, PLURONIC polyols, made by propylene oxide and ethylene oxide are very stable and do not react with some cations in aqueous solutions because they do not ionize under such conditions. By depending on their composition, they are used as detergents, emulsifiers, dispersion, and so on, in the lubricant, detergent, food, cosmetic, drugs, and oil industries.^{1,3}

The phase behavior of PEO–PPO surfactant aqueous solutions is very important because these compounds present phase separation at increasing temperature. The temperature in which this phase separation occurs is known as cloud point.⁴ Several studies have been done to explain the mechanism of solubilization and to establish the behavior of PEO in aqueous solution. Saeki et al.⁵ have determined the upper and lower critical so-

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lution temperatures in PEO aqueous solutions. Kjellander and Florin⁶ have proposed a first model in which, at low temperatures, water forms an ordered structure around the ethylene oxide (EO) chain, and such structure is broken down at higher temperatures. In a second model, hydrogen bonds between water and EO–oxygen molecules, which are destroyed at increasing temperature, have been proposed.⁷ The third model demonstrated occurrence of a conformational structure variation of the EO chain as a function of temperature. At low temperatures the EO chain is in a polar conformation that interacts with water, and at higher temperatures the system entropy favors the less polar structures that do not interact with water.⁸

EO–PO block copolymers have been studied dissolved into several polar solvents and, at increasing temperature, phase separation does not occur, except in water and formamide. It has been observed that added salt decreased the cloud points of the aqueous solutions.⁹ On the other hand, ionic surfactant added to the aqueous solution of nonionic surfactant increases the cloud points.¹⁰ Some investigations have demonstrated phase separation at increasing temperature for EO–PO block copolymers dissolved in small and polar molecules; and the higher polarity difference between polymer and solvent, the easier the cloud point observation.¹¹ Such study confirms both second and third models, which have been proposed to explain EO behavior in aqueous solution.

Another important research has been done to describe PEO–PPO copolymers solution behavior related to the formation of aggregates, known as micelles, which occur in solution before the cloud point. These micelles are considered spheres composed of a central core of dense PPO and an outer corona of hydrated EO units.¹² The critical micelle concentration (CMC) is the concentration in which the micelles start forming. Surface tension measurements as a function of surfactant solution concentration in solution is an usual method to determine CMC.¹³

The purpose of this work is to verify the phase behavior of EO–PO block copolymer aqueous solutions as a function of copolymer structure and composition by building up temperature vs. concentration phase diagrams. The copolymers behavior was also analyzed through CMC values, which were obtained from surface tension vs. concentration plots. The influence of salts and hy-

drotropes on copolymer aqueous solution behavior was also evaluated.

EXPERIMENTAL

Materials

Bifunctional triblock copolymers of ethylene oxide (EO) and propylene oxide (PO) (HO-PEO-PPO-PEO-OH) and monofunctional diblock copolymers of EO-PO (R-PEO-PPO-OH and R-PPO-PEO-OH, R length = linear C₄) were obtained from Grupo Ultra-Divisão Química. Monofunctional diblock copolymers of EO–PO (R-PEO-PPO-OH and R-PPO-PEO-OH, R length = linear C_{12–14}) were obtained from Henkel S.A. Indústrias Químicas.

Salts (NaCl and KCl) and sodium *p*-toluenesulfonate (NaPTS) were obtained from Reagen-Ind. Quim. and COEMA S.A., respectively.

Copolymers Characterization

Copolymers characterization data are summarized in Table I.

Phase Diagrams

The cloud point measurements were done in an electrically thermostated bath with two determinations for each double sample. The cloud point was taken from the average of the temperatures where the last visible sign of clouds disappeared upon cooling and the first visible sign of clouds appeared upon heating.

The temperature vs. concentration phase diagrams of each copolymer solution were built up using the following concentrations: (1) for aqueous solutions: the copolymer concentrations were 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 wt %; (2) for aqueous solutions containing salt: the copolymer concentration was constant and equal to 1 wt %. The salt concentrations were 1.0, 2.5, 5.0, and 10.0 wt %; (3) for aqueous solutions containing sodium *p*-toluenesulfonate (NaPTS): the copolymer concentration was constant and equal to 1 wt %. NaPTS concentrations were 0.13, 0.25, 0.50, 0.75, 1.05, 1.47, and 2.10 molar.

Critical Micelle Concentration (CMC)

The surface tension measurements were performed on a Krüss K-10 digital tensiometer, at

Table I Characterization of Block Copolymers of Poly(ethylene oxide) and Poly(propylene oxide)¹⁴

Copolymer Structure	\bar{M}_n^a	\bar{M}_w/\bar{M}_n^b	Monomer Repeat Units ^c		EO/PO Ratio	O/C ^d Ratio
			EO	PO		
HO-(EO) ₂ -(PO) ₂₂ -(EO) ₂ -OH	1460	1.44	4	22	0.18	0.38
HO-(EO) ₈ -(PO) ₂₈ -(EO) ₇ -OH	2290	1.58	15	28	0.54	0.40
C ₄ -(EO) ₄ -(PO) ₁₁ -OH	920	1.24	4	11	0.36	0.36
C ₄ -(PO) ₁₀ -(EO) ₆ -OH	900	1.23	6	10	0.60	0.37
C ₁₂₋₁₄ -(PO) ₄ -(EO) ₅ -OH	600	1.15	5	4	1.25	0.29
C ₁₂₋₁₄ -(EO) ₆ -(PO) ₅ -OH	720	1.15	6	5	1.20	0.30
C ₁₂₋₁₄ -(EO) ₉ -(PO) ₆ -OH	910	1.19	9	6	1.50	0.33

^a Determined by vapor pressure osmometry (VPO).

^b Determined by gel permeation chromatograph (GPC).

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

^d O/C means oxygen/carbon atoms ratio.

30°C. For each copolymer solution, a surface tension (mM/m) vs. concentration (wt %) plot was built at a range of 3–0.0001 wt % to determining CMC values.

RESULTS AND DISCUSSION

Phase Diagrams of the Copolymer Aqueous Solution

The phase diagrams of the copolymers aqueous solutions are shown in Figure 1. At the tempera-

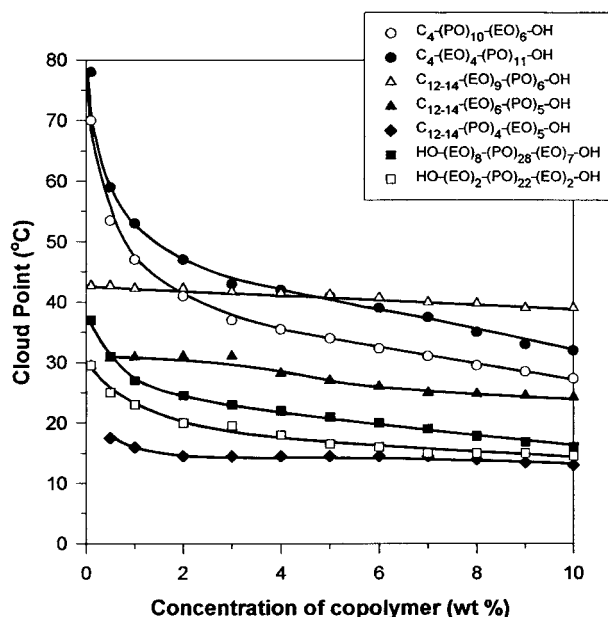


Figure 1 Phase diagrams of ethylene oxide and propylene oxide block copolymer aqueous solutions.

tures above each curve the copolymer solution presents two phases, and below, only one phase.

By comparing the results obtained for both bifunctional triblock copolymers, it can be observed that HO-(EO)₂-(PO)₂₂-(EO)₂-OH presents lower cloud points than HO-(EO)₈-(PO)₂₈-(EO)₇-OH due to the former having a lower EO/PO ratio (Table I); this means less hydrophilic character.

By comparing the results obtained for the monofunctional (R length = C₄) diblock copolymers, it is observed that both present a similar curve outline, as shown in Figure 1. At increasing the copolymer concentration, the cloud points decrease until becoming almost constant, starting from ~ 3 wt %. C₄-(EO)₄-(PO)₁₁-OH presents higher cloud points than C₄-(PO)₁₀-(EO)₆-OH, in spite of the former having a lower EO/PO ratio (Table I). It can probably be due to the position of the hydrophilic (EO and OH) and hydrophobic (R and PO) segments in these copolymers.

A different curve behavior can be seen for the monofunctional (R length = C₁₂₋₁₄) diblock copolymer solutions, which present cloud points seemingly constant, over the concentration range (0.1–10 wt %) analyzed. This curve outline can be attributed to R length (= C₁₂₋₁₄) of these copolymers providing a more hydrophobic character. By comparing the copolymer (R length = C₁₂₋₁₄) solution curves, as expected, C₁₂₋₁₄-(EO)₉-(PO)₆-OH (the highest EO/PO ratio) presents the highest cloud points. The other two copolymer solutions present different cloud points despite both having a similar EO/PO ratio. C₁₂₋₁₄-(EO)₆-(PO)₅-OH, which contains hydrophilic/hydrophobic segments in alternate position, presents

Table II Critical Micelle Concentration (CMC) Values for EO-PO Block Copolymers Calculated by Surface Tension Measurements as a Function of Copolymer Concentration in Aqueous Solutions

Copolymer	EO/PO Ratio	CMC (wt %)
$C_4-(PO)_{10}-(EO)_6-OH$	0.60	1.4
$C_4-(EO)_4-(PO)_{11}-OH$	0.36	3.9
$C_{12-14}-(PO)_4-(EO)_5-OH$	1.25	0.001
$C_{12-14}-(EO)_6-(PO)_5-OH$	1.20	0.003
$C_{12-14}-(EO)_9-(PO)_6-OH$	1.50	0.007

higher cloud points than $C_{12-14}-(PO)_4-(EO)_5-OH$, in which the hydrophilic/hydrophobic segments are in an adjacent position. The same behavior was observed in the monofunctional (R length = C_4) block copolymer solutions, suggesting that the copolymer structure plays an important role in its water solubility.

Critical Micelle Concentration

To study the CMC influence on the phase behavior of EO-PO block copolymers, surface tension measurements as a function of copolymer aqueous solution concentration were performed. In general, surface tension vs. concentration plots present a discontinuity in the slope. The first portion of the curve (at lower concentration) is related to the surfactant adsorption at the interface, and the second portion of the curve (at higher concentration), in general, is a parallel straight line to the concentration axis and indicates that in this step adsorption does not take place. The extension of both portions leads to the discontinuity average, which is related to the copolymer aggregation in solution, i.e., CMC.¹⁵

Table II shows CMC values obtained from the discontinuity of surface tension vs. concentration plots.

The results show that the copolymers (R length = C_{12-14}) present much lower CMC values than those found in the copolymers (R length = C_4). This can be attributed to the hydrophobic segment length.

By comparing the CMC values results (Table II) with the phase diagrams (Fig. 1), it is observed that the copolymers (R length = C_4) solutions present CMC values close to the concentration where the phase diagram slope changes. It suggests that this slope changing is related to the

molecular aggregation. On the other hand, the CMC values of the copolymers (R length = C_{12-14}) solutions are below the concentration range analyzed (0.1–10 wt %), which explains the seemingly constant values of the phase diagrams curves for these copolymers. It was not possible to confirm the slope changing of the phase diagrams related to CMC due to experimental limitations.

By analyzing CMC results (Table II) for the copolymers (R length = C_{12-14}) solutions, $C_{12-14}-(EO)_9-(PO)_6-OH$ presents the higher CMC because of its highest EO/PO ratio. On the other hand, $C_{12-14}-(EO)_6-(PO)_5-OH$ presents higher CMC values than $C_{12-14}-(PO)_4-(EO)_5-OH$, even though their EO/PO ratios are similar. The copolymer in which hydrophilic (EO and OH)/hydrophobic (R and PO) segments are alternated, presents higher CMC values. The same behavior is observed for the copolymers (R length = C_4) where $C_4-(PO)_{10}-(EO)_6-OH$, adjacent hydrophilic/hydrophobic segments, presents lower CMC values than $C_4-(EO)_4-(PO)_{11}-OH$, alternate hydrophilic/hydrophobic segments, in spite of the former having a higher EO/PO ratio. Such behavior can be attributed to the ease molecular association induced by the structure for the copolymer in which the hydrophilic/hydrophobic segments are adjacent, as the proposed model shows in Figure 2.

Phase Diagram of Polymer Aqueous Solutions Containing Salt

Some information related to molecule interactions can be obtained from studying the electrolytes influence on the phase diagrams of polymer aqueous

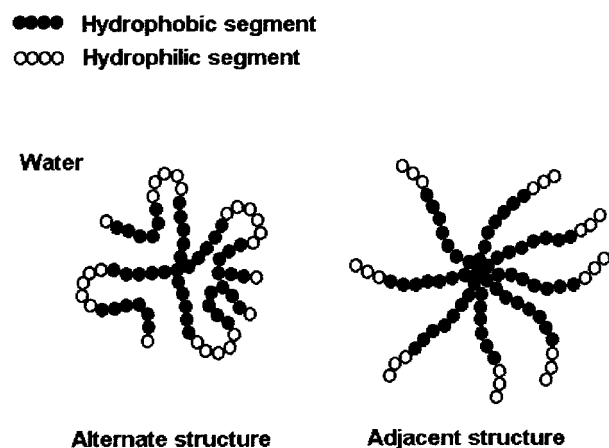


Figure 2 Schematic representation for both adjacent and alternate hydrophilic/hydrophobic segment structures of the copolymers in aqueous solution.

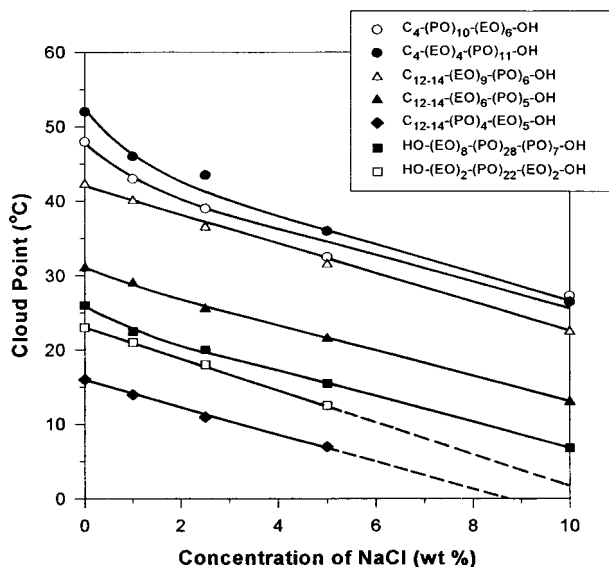
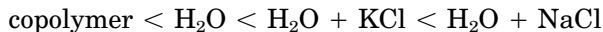


Figure 3 Phase diagrams of EO-PO block copolymer aqueous solutions as a function of NaCl concentration.

solution. Figure 3 shows the phase diagrams of copolymer aqueous solutions (1 wt %) cloud points as a function of NaCl concentration. All copolymer solutions exhibit similar curves outlined over the salt concentration range (0–10 wt %) analyzed. The electrolyte provides a decrease of the solution cloud points due to the increase of the polarity difference between solvent and copolymer, because the interaction between electrolyte and water increases the solvent polarity. The cloud points for HO-(EO)₂-(PO)₂₂-(EO)₂-OH and C₁₂₋₁₄-(PO)₄-(EO)₅-OH above 4°C are not observed, at 10 wt % NaCl concentration.

The phase diagrams of C₄-(PO)₁₀-(EO)₆-OH and HO-(EO)₈-(PO)₂₈-(EO)₇-OH aqueous solutions containing NaCl and KCl are shown in Figure 4. The cloud points of polymer aqueous solution containing NaCl are lower than those that contain KCl, because NaCl increases the solvent polarity to higher values than KCl does. This means that the higher polarity difference between solvent and polymer, the lower polymer solubility in such solvent. Increasing the polarity:



The extensive self-association of water by hydrogen bonds at and below room temperature weakens its solvent power. Ions can salt the surfactant in or out.¹⁶ Ions that tighten the structure of water and enhance its self-association salt the surfactant out, lowering its cloud point.

Phase Diagrams of Polymer Aqueous Solutions Containing a Hydrotrope

Sodium *p*-toluenesulfonate (NaPTS) is known to act as a hydrotrope in aqueous systems. Hydrotropes or hydrotropic agents are organic compounds that enhance in the aqueous solubility of poorly soluble organic compounds. At present, it seems clear that hydrotropy differs from micellar solubilization and from the salting-in effect promoted by some inorganic salts. However, the molecular mechanism of hydrotropic solubilization has not yet been explained.¹⁷ Figure 5 shows the cloud points of polymer solutions (1 wt %) as a function of NaPTS concentration. Hydrotropy effect is observed for all copolymers solutions, cloud points increase as increasing NaPTS concentration, but the curve behavior depends on the copolymer solution analyzed. The bifunctional copolymers (similar structures) exhibit similar curves outline and both are more sensitive to the added NaPTS only at higher concentrations. On the other hand, C₁₂₋₁₄-(EO)₉-(PO)₆-OH and C₁₂₋₁₄-(EO)₆-(PO)₅-OH (similar curve outlines), are sensitive to small amounts of NaPTS, and then trending to seemingly constant cloud points. The different behavior between two copolymers sets suggests that the molecular mechanism of hydrotropic solubilization depends also on the solute.

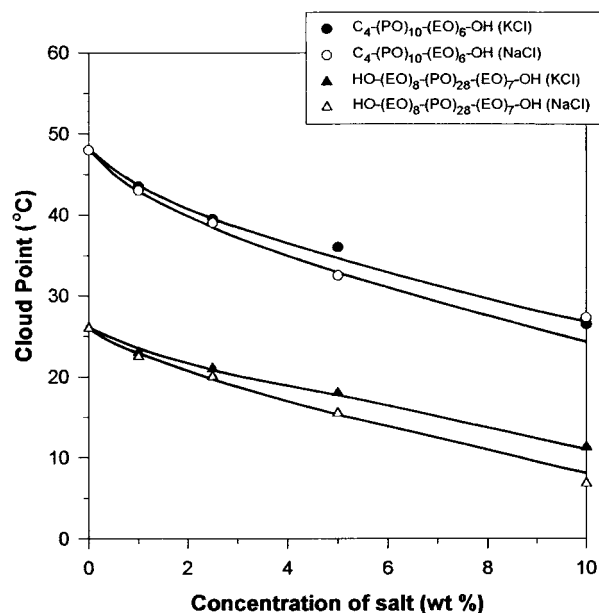


Figure 4 Phase diagrams of C₄-(PO)₁₀-(EO)₆-OH and HO-(EO)₈-(PO)₂₈-(EO)₇-OH aqueous solutions (1 wt %) as a function of electrolyte (NaCl and KCl) concentrations.

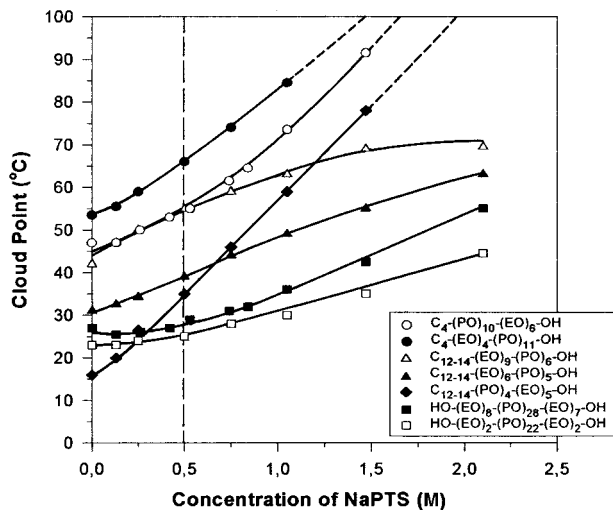


Figure 5 Phase diagrams of EO-PO block copolymer aqueous solutions (1 wt %) as a function of sodium *p*-toluenesulfonate (NaPTS) concentration.

An unusual effect is observed for $C_{12-14}-(PO)_4-(EO)_5-OH$, which shows large cloud point changing as a function of NaPTS concentration, even below the NaPTS association concentration ($\sim 0.5M$, at $30^\circ C$). This copolymer has an adjacent hydrophilic/hydrophobic segment structure that is not very water soluble, and it is more sensitive to the effects provided by NaPTS. The same unusual effect is observed for $C_4-(EO)_4-(PO)_{11}-OH$ and $C_4-(PO)_{10}-(EO)_6-OH$; which are made up of long PPO hydrophobic segments counterbalancing the short R length = C_4 . The similar behavior of the curves, in spite of these copolymers structures being different, can be conferred by the short R length = C_4 , which does not markedly contribute to the solubility difference as a function of the polymer structure in the systems containing NaPTS.

The unusual behavior of the last three copolymer solutions can likely be attributed to a hy-

drotrope molecule incorporation close to the core of the copolymer micelle forming a mixed micelle. This mixed micelle would be more stable due to the ionic stabilization, which would be helping the steric one.

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