

Behavior of Mixtures of Nonionic Polyoxide-Based Surfactants and Their Application in the Destabilization of Oil Emulsions

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ABSTRACT: During the petroleum dehydration process, it is necessary to use chemical demulsifiers to break the water–oil emulsions that are formed during oil extraction. The majority of the products used are formulations containing nonionic surfactants based on poly(ethylene oxide–propylene oxide) (PEO–PPO) block copolymers with different ethylene oxide/propylene oxide molar ratios. In this work, PEO–PPO block copolymers of different structures were used. The physical–chemical properties of aqueous PEO–PPO solutions and their mixtures were analyzed, along with their effectiveness as water–oil emulsion destabilizing agents. The results showed that all the PEO–PPO copolymers could reduce the interfacial tension between water and oil. Nevertheless, the most efficient water–oil emulsion demulsification was achieved by the PEO–PPO

branched copolymer, whose structure presented hydrophilic segments [poly(ethylene oxide) and OH] side by side at the free end of the molecule. This copolymer also exhibited the highest water solubility. Such behavior could be attributed to its structure, which promoted better interaction with the water droplets dispersed in the water–oil emulsion. The performance of the surfactant mixtures appeared to be related to their capacity to reduce the water–oil interfacial tension. The addition of a surfactant at a concentration of roughly 30% without demulsifying action does not compromise the action of a well-performing surfactant. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2947–2954, 2007

Key word: solution properties; block copolymers; interfaces

INTRODUCTION

The demulsification process is of great importance in the oil industry because the occurrence of emulsions is a natural phenomenon of oil extraction from reservoirs containing systems of oil, water, and gas. It is necessary to separate these components. The gas so recovered can be attractive economically, and the water must be removed because it has a high salt content and forms emulsions with viscosities greater than that of the dehydrated oil. This behavior affects the sizing of the pumping system and the transfer and tankage of petroleum and also generates prob-

lems of encrustation and corrosion in oil pipelines carrying the outflow.¹

In the oil dehydration process, the use of demulsifying products is essential to coalesce the emulsions formed in the field. All agents that prevent or break down emulsions have some tendency to be adsorbed at the interfaces. It is this tendency that permits them to displace the natural emulsifiers of the oil and thus destabilize the emulsions or prevent their formation.^{2,3}

Because of the great importance of breaking down emulsions, there are many chemical demulsifiers available for this purpose, but the selection of one of them for a determined emulsion requires a complete chemical and physical characterization of both the emulsion and demulsifier.^{4,5}

The choice of a demulsifier is difficult because its performance can be affected by various factors, including the type of oil, the presence and wettability of solids, the viscosity of the oil, and the size distribution of the dispersed water phase.⁵

The demulsifiers used in the primary processing of petroleum are in most cases surfactants based on block copolymers of poly(ethylene oxide–

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propylene oxide) (PEO–PPO) with different ethylene oxide (EO)/propylene oxide (PO) molar ratios. A surfactant's efficiency in a determined application is intimately related to its chemical structure and physical–chemical properties in solution. An evaluation of the solubility in aqueous nonionic surfactant solutions is important because these surfactants can present phase separation with increasing temperature.^{6,7}

In many oil-recovery processes, mixtures of surfactants are used instead of pure surfactants. This occurs not only because of the high demand for pure surfactants but also because a mixture can have better properties. In general, a surfactant mixture brings a synergy; that is, the characteristic properties of these mixtures are superior to those of the individual components. This synergy can be attributed to the behavior of a nonideal mixture in the aggregates, which results in critical micellar concentrations and interfacial tensions substantially lower than would be expected from the properties of the pure surfactants.⁸

The objective of this work was to evaluate the behavior of aqueous nonionic surfactant solutions based on PEO–PPO block copolymers with respect to their properties in aqueous solutions and their performance in destabilizing oil/water emulsions in the oil industry. For this purpose, we used different types of copolymers with branched and linear structures.

EXPERIMENTAL

Materials

Dow Química, Ltd. (São Paulo, SP, Brazil), supplied the linear and branched polyols that were employed in this work as PEO–PPO block copolymers.

Methods

The molecular weights and EO/PO ratios of the PEO–PPO block copolymers were determined with ¹H-NMR and size exclusion chromatography (SEC), respectively, as described in previous works.^{7,9}

The measurements of the cloud points and interfacial tension of the aqueous block copolymer solutions and the aqueous copolymer mixture solutions, as a function of the copolymer concentration, were also performed as described in previous works.^{9,10}

The performance of the PEO–PPO copolymers and copolymer mixtures was evaluated with water–oil gravitational separation tests or bottle tests with the as-prepared emulsion. The test and emulsion preparation were described in a previous publication.⁷

RESULTS AND DISCUSSION

Chemical characterization of the PEO–PPO block copolymers

Table I shows the PEO–PPO copolymer characterization. The branched and linear copolymers are called R and L, respectively. The R copolymers have similar molecular weights; in particular, R₂ and R₃ have the same EO/PO ratio but different positions of the poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) segments in the molecule. The L copolymers present similar molecular weights, which are also similar to the molecular weight of one branch of the R copolymers. Besides this, each pair (L₁–L₃ and L₂–L₄) has the same EO/PO ratio and different positions of the PEO and PPO segments. Such a molecule family allows an evaluation of the influence of the linearity, EO/PO ratio, and PEO–PPO positions on a surfactant solution's behavior.

Physical–chemical characterization of the PEO–PPO block copolymers

In this section, we discuss the results obtained from the physical–chemical characterization of the nonionic surfactant solutions and their mixtures with respect to the solubility and interfacial tension.

Phase diagrams (solubility)

The cloud point is the temperature below which a single phase of a molecular solution exists. Above the cloud point, a nonionic surfactant loses its solubility in water, presenting clouding of the system (two phases). Above this temperature, some or all of the functions of surfactants suffer degradation. Thus, the cloud point can be used to limit the choice of a nonionic surfactant for certain applications.¹¹

It is believed that the solubility of a nonionic surfactant in water is related to the hydration of the oxyethylene groups. The hydration of the ether oxygen by hydrogen bonding results in the bonding of at least two water molecules per EO unit. This hydration increases with the lengthening of the PEO chain. However, extremely long PEO chains can increase the formation of aggregates and can result in dehydration.¹¹

Phase diagrams of aqueous solutions of the PEO–PPO block copolymers. The phase diagrams of aqueous solutions of monofunctional diblock PEO–PPO copolymers and their linear and branched structures are shown in Figure 1.

The results show that as a copolymer's concentration in the solution increases, the cloud point diminishes until a certain concentration, beyond which the cloud point no longer varies significantly.

TABLE I
Characterization Data of the PEO-PPO Block Copolymers

Copolymer	M_n^a	M_w^a	M_w/M_n^a	EO/PO ratio ^b	Copolymer structure
R ₁	6800	7100	1.04	0.32	$\begin{array}{c} \text{CH}_2(\text{PO})_{31}(\text{EO})_{10}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{31}(\text{EO})_{10}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{31}(\text{EO})_{10}\text{OH} \end{array}$
R ₂	7900	8200	1.03	0.53	$\begin{array}{c} \text{CH}_2(\text{PO})_{32}(\text{EO})_{17}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{32}(\text{EO})_{17}\text{OH} \\ \\ \text{CH}_2(\text{PO})_{32}(\text{EO})_{17}\text{OH} \end{array}$
R ₃	7800	8000	1.02	0.54	$\begin{array}{c} \text{CH}_2(\text{EO})_{17}(\text{PO})_{31}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{17}(\text{PO})_{31}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{17}(\text{PO})_{31}\text{OH} \end{array}$
R ₄	9100	9400	1.03	0.47	$\begin{array}{c} \text{CH}_2(\text{EO})_{18}(\text{PO})_{38}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{18}(\text{PO})_{38}\text{OH} \\ \\ \text{CH}_2(\text{EO})_{18}(\text{PO})_{38}\text{OH} \end{array}$
L ₁	2900	3300	1.14	0.36	$\text{CH}_3-(\text{PO})_{39}-(\text{EO})_{14}-\text{OH}$
L ₂	3300	3700	1.13	0.56	$\text{CH}_3-(\text{PO})_{39}-(\text{EO})_{22}-\text{OH}$
L ₃	2600	2700	1.05	0.38	$\text{CH}_3-(\text{EO})_{13}-(\text{PO})_{34}-\text{OH}$
L ₄	3300	3400	1.05	0.56	$\text{CH}_3-(\text{EO})_{22}-(\text{PO})_{39}-\text{OH}$

^a By SEC.

^b By ¹H-NMR. M_w = weight-average molecular weight; M_n = number-average molecular weight.

Among the branched copolymers, copolymer R₂ is the most soluble in an aqueous solution, even though its EO/PO ratio and molar mass are similar to those of copolymer R₃ (Table I). In this case, these samples could have been expected to show similar solubilities. However, the chemical structure of copolymer R₂, with the hydrophilic segments (PEO and OH) in an adjacent and more external position in the molecules, facilitates interactions with the water molecules.^{9,12}

The position of the EO group in the molecule gives a copolymer greater or lesser hydration. When the EO groups are in the molecule's center, these groups are packed very near one another, and their agglomeration results in a less hydrated molecule in comparison with molecules whose EO groups are at their ends. For small molecules, this steric effect on the hydration can be disregarded.¹¹

Therefore, copolymers with adjacent structures are more hydrophilic than those with alternating structures when we analyze copolymers of the same chemical composition.

The type of behavior can be confirmed by a comparison of solutions of copolymers R₁ and R₄. Copolymer R₄, although it has a higher EO/PO ratio than copolymer R₁, is less soluble because of the differences in the architecture. In this case, copolymer R₄ has a slightly higher molar mass than copolymer R₁, but this difference is not sufficient to cause the observed reduction in the solubility. This can be proved by the observation of the cloud-point ranges presented in Figure 1(a,b): despite the molar mass differences between the linear and branched copolymers, the cloud points lie within a very similar temperature range.

A comparison of the results obtained for the copolymers with linear structures shows, as expected, that the one with the lowest EO/PO ratio (copolymer L₁) presents the lowest cloud points, whereas copolymers L₂ and L₄ have different cloud points, even though their EO/PO ratios and molar masses are similar. This behavior confirms what has just been observed for branched copolymers: the adjacent structure of copolymer L₂ favors its higher solubility

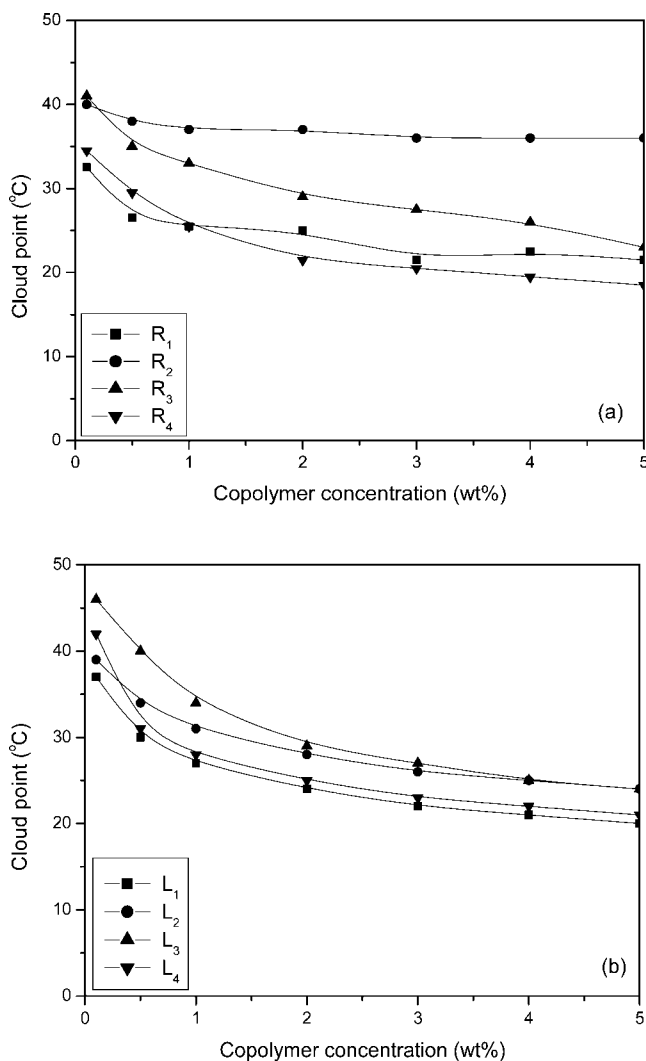


Figure 1 Phase diagrams of aqueous solutions of PEO-PPO block copolymers: (a) branched and (b) linear.

in aqueous solutions. An analysis of the solubility of aqueous solutions of copolymers L_1 and L_3 shows that despite the alternating structure of copolymer L_3 , its solubility is higher than that of L_1 (a copolymer with an adjacent structure). In this case, the effect of the higher EO/PO ratio presented by copolymer L_3 , associated with its lower molar mass, prevails over the effect of its architecture on its behavior in solution.

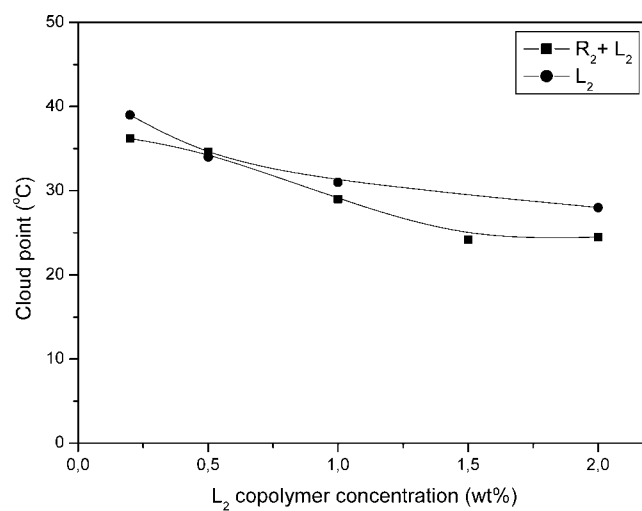
Phase diagrams of aqueous solutions of the copolymer mixtures. To carry out solubility tests of aqueous solutions of the mixtures of the PEO-PPO block copolymers, we selected only copolymers R_2 , L_2 , and L_4 . The choice of branched copolymer R_2 was due to its greater solubility. We chose linear copolymers L_2 and L_4 because they have different architectures but similar molar masses and EO/PO ratios. Because the cloud-point differences between L_2 - L_4 and L_3 - L_1 are similar, we could also have chosen the L_1 - L_3 pair

because they also have different architectures but similar molar masses and EO/PO ratios.

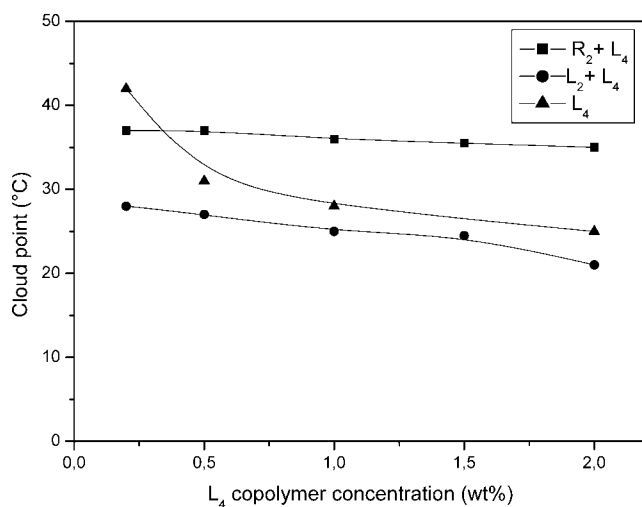
We measured the cloud points of the binary mixtures as a function of the concentration of one of the copolymers, whereas the other's concentration was kept constant at 1 wt %.

The phase diagrams of aqueous solutions of the mixtures of the monofunctional PEO-PPO copolymers are shown in Figure 2.

The results presented by the mixtures containing copolymer R_2 show that the presence of copolymer L_4 did not cause a significant variation in the solubility of an aqueous solution of copolymer R_2 . On the other hand, the presence of copolymer L_2 significantly diminished the solubility of copolymer R_2



(a)



(b)

Figure 2 Phase diagrams of aqueous solutions of PEO-PPO block copolymer mixtures as a function of (a) the copolymer L_2 concentration and (b) the copolymer L_4 concentration.

TABLE II
Cloud Points of the Copolymers and Their Mixtures

Mixture	Cloud point of the copolymer at 2 wt % (°C)			Difference between the cloud points of the pure copolymers at 2 wt % (°C)	Cloud point of the copolymer mixtures at 2 wt % (°C) ^a
	R ₂	L ₂	L ₄		
R ₂ -L ₄	37	—	25	12	36
R ₂ -L ₂	37	29	—	8	29
L ₂ -L ₄	—	29	25	4	25

^a Obtained from the cloud-point curves as a function of the copolymer concentration at 1 wt% because the other component was present at a fixed concentration (also 1 wt %).

[Fig. 2(b)]. This behavior can be associated with the solubility of aqueous solutions of copolymers L₂ and L₄. Copolymer L₂, which is more soluble in water [Fig. 1(b)] than L₄, causes an increase in the dissolved quantity in the solution and, consequently, a decrease in the number of free solvent molecules for the solubilization of copolymer R₂. Besides this, the solubility of copolymer L₂ is also altered: at a concentration of 1 wt %, its cloud point is 31°C [Fig. 1(b)], a figure that goes down to around 25°C in the R₂-L₂ mixture.

For the mixture of copolymers L₂ and L₄ [Fig. 2(b)], there was a small reduction in the solubility of L₂ with an increased concentration of L₄. This fact can also be attributed to the low solubility of copolymer L₄ in an aqueous solution.

Unlike the behavior of the R₂-L₄ mixture, the L₂-L₄ and R₂-L₂ mixtures were less soluble than the pure copolymers. There appears to be an influence of the solubility differences between the copolymers. Table II presents the cloud-point temperatures for each of the pure copolymers at 2 wt %, the cloud-point differences for each mixture (based on the cloud-point values of the pure components at 2 wt %), and the cloud points of the mixtures taken from the curves of Figure 1 at 1 wt % (because the other copolymer is also present at 1 wt %, making a total concentration of 2 wt % in the mixtures). The data in the table show that the B₂ mixture has the greatest solubility difference among the components of the mixture (12°C), and the least soluble component does not compete for the water molecules with the most soluble one. The result is a cloud point similar to that of the pure copolymer B₂. In the L₂-L₄ and R₂-L₂ mixtures, which have smaller cloud-point differences between the components of each mixture, the components compete for the water molecules, with the cloud point of the least soluble compound prevailing. That is, the differences observed between the L₂-L₄ mixture and pure L₂ curves and between the curves of R₂-L₂ and pure L₂ are basically the fruit of the different concentrations of the solutions.

Analysis of the water-oil interfacial tension

The behavior of a demulsifier in an emulsion, particularly its distribution between two phases (e.g., water and oil), is related to the interfacial activity of the chemical products used.

The reduction in the interfacial tension depends directly on the substitution of the solvent molecules at the interface by the surfactant molecules. When the surfactant molecules replace the water and oil molecules of the original interface, the interaction of this interface is now between the surfactant's hydrophilic groups and the water molecules on one side of the interface and between the surfactant's hydrophobic groups and the oil molecules on the other side. The tension on the interface is significantly reduced by the adsorption of the surfactant molecules because these interactions are stronger than the original ones between the oil and water molecules.¹³ *Interfacial tension between oil and aqueous PEO-PPO block copolymer solutions.* Table III shows the interfacial tension values obtained between oil and aqueous solutions containing the PEO-PPO copolymers at a concentration of 100 ppm. To carry out the measurements, we chose two branched copolymers (B₂ and B₄) and two linear ones (L₂ and L₄), with each group

TABLE III
Interfacial Tension Between Oil and Aqueous Copolymer Solutions

Copolymer (100 ppm)	Interfacial tension (±0.5 mN/m)
Blank	18.0 ^a
R ₂	5.5
R ₄	6.5
L ₂	10.5
L ₄	13.5
R ₂ -L ₂ ^b	5.0
R ₂ -L ₄ ^b	6.5
L ₂ -L ₄ ^b	10.0

^a Between oil and water.

^b The concentration of each copolymer in the mixture was 100 ppm; the total concentration of the copolymer in the mixture was 200 ppm.

having a copolymer with adjacent hydrophilic and hydrophobic segments and another in which these segments were in alternating positions. All the copolymers, when added in the aqueous phase, reduced the interfacial tension values of the water–oil system, and this indicated their ability to displace the natural surfactants present in the oil. Copolymer B₂ caused the greatest reduction in the interfacial tension values, followed by B₄. This efficiency may be associated with the branched structure of these copolymers, in which the EO and PO groups are better distributed in their chains, thus facilitating their dispersion between the phases of the water–oil emulsion. Besides this, the greater efficiency observed for copolymer R₂ is associated with its greater solubility in water (Fig. 1). The literature shows that the best breakers of water-in-oil emulsions (demulsifiers) are those with higher HLB, that is, those that are more soluble in water.¹⁴

An analysis of the results obtained for the different copolymer families shows that copolymers that have structures with the EO and PO groups in an adjacent position have slightly smaller interfacial tension values than those with alternating structures. This is due to the different positions of the copolymers at the interface, as shown in a previous work investigating the superficial tensions of aqueous PEO–PPO copolymer solutions.¹² Adjacent copolymers have greater packing facility at the interface, minimizing the contact between the water and oil molecules and thus causing a greater reduction in the interfacial tension, whereas alternating copolymers tend to position themselves at the interface with a more horizontally extended conformation, permitting more contact between the water and oil molecules.

Interfacial tension between oil and aqueous solutions of the copolymer mixtures. Table III also shows the interfacial tension values between oil and aqueous solu-

tions containing the copolymer mixtures. The concentration of each polymer in the mixture was 100 ppm, so the total solution concentration was 200 ppm.

The results for the mixtures containing copolymer R₂ show that the presence of copolymer L₄ reduced the interfacial activity of R₂, with the mixture having a higher interfacial tension than pure R₂. On the other hand, the presence of copolymer L₂ did not change the interfacial tension of R₂. This behavior may be associated with the positioning of the hydrophilic and hydrophobic groups. The mixture of copolymers R₂ and L₂ may have favored the packing of these two structures at the interface, if this interface had both types of molecules. From the results obtained, it is not possible to state that copolymer L₂ is also present at the interface or whether preferential adsorption of copolymer R₂ occurs. Copolymer L₄ (alternating structure) does not permit such good packing, reducing the interfacial activity. In this case, because of the small difference between the interfacial tension values of pure R₂ (5.5 mN/m) and the R₂–L₄ mixture (6.5 mN/m), there could have been preferential adsorption of the R₂ molecules at the interface.

The interfacial tension value obtained for the L₂–L₄ mixture is equal to that for pure L₂. The preferential adsorption of the adjacent structure at the interface also prevails here.

Evaluation of the performance of the PEO–PPO block copolymers and their mixtures

We evaluated the performance of the PEO–PPO block copolymers in the destabilization of water-in-oil emulsions by a bottle test⁷ to attain a product offering good efficiency.

We used the PEO–PPO block copolymers that presented less solubility in water (samples R₂, R₄, L₂, and L₄), as shown in the phase diagram of Figure 1.

TABLE IV
Performance of the Gravitational Separation of a Synthetic Emulsion by PEO–PPO Block Copolymers in Water

Time (min)	EF_{WO} (vol %)						
	R ₂				R ₄ (100 ppm) ^a	L ₂ (100 ppm) ^a	L ₄ (100 ppm) ^a
	50 ppm ^a	100 ppm ^a	150 ppm ^a	200 ppm ^a			
5	0	0	0	0	0	0	0
10	0	32	30	70	0	0	0
15	0	64	70	82	0	0	0
20	22	67	71	84	0	0	0
25	36	68	73	84	0	0	0
35	46	71	73	85	0	0	0
45	50	72	73	86	0	0	0
55	52	73	75	86	0	0	0
65	52	74	76	86	0	0	0
75	52	75	76	86	0	1	0

^a The final copolymer concentration in the synthetic emulsion.

TABLE V
Performance of the Gravitational Separation of a Synthetic Emulsion by PEO-PPO Block Copolymer Mixtures in Water

Time (min)	EF_{AO} (% v/v)		
	R ₂ -L ₂ ^a	R ₂ -L ₄ ^a	L ₂ -L ₄ ^a
5	0	0	0
10	56	22	0
15	66	58	0
20	67	66	0
25	67	67	1
35	69	69	1
45	71	70	2
55	71	70	2
65	71	70	3
75	71	70	5

^a The ratio of the copolymers in the mixture was 1 : 1. The total copolymer concentration in the mixture after addition in the synthetic emulsion was 200 ppm.

We calculated the efficiency of each formulation as follows:

$$EF_{WO} = (VW_S/VW_T) \times 100 \quad (1)$$

where EF_{WO} is the water-oil gravitational separation efficiency (vol %), VW_S is the volume of water separated during the test (mL), and VW_T is the total volume of water present inside the pipe (mL).

We prepared formulations by dissolving the copolymers in water at a concentration of 40 wt %. We then evaluated the formulations containing copolymer R₂ in concentrations ranging from 50 to 200 ppm of the active material of the product in the water-oil emulsion, at increments of 50 ppm, to determine the optimal concentration of this copolymer in the demulsifying process. We assessed the other copolymers only at a concentration of 100

ppm, except for copolymer L₂, which we also evaluated at 150 ppm, with no difference in the results obtained. These results are shown in Table IV.

Only copolymer R₂ led to gravitational separation of the water in oil in all the formulations, although all of them reduced the interfacial tension between the water and oil, as shown in Table III. We attribute this behavior to the position of the EO group (in an external adjacent position) in the chains of copolymer R₂, which could be increasing its interaction with the water droplets dispersed in the water-oil emulsion, a factor responsible for this copolymer's better efficiency. Besides this, the efficiency of the branched copolymer can be associated with its structure, in which the EO and PO groups are more distributed in its chains, thus facilitating its dispersion between the phases of the water-oil emulsion.

On the other hand, branched copolymer R₄ did not promote the gravitational separation of the water in oil, even though it also has the EO and PO groups distributed in its chains. This behavior is probably associated with the position of these groups, which occur alternately, thus causing this copolymer to be less soluble in water, as already observed in the phase diagram in Figure 1, and consequently causing a weaker interaction of this copolymer with the dispersed water droplets.

The results obtained for the other copolymers can be associated with their low specificities to act as destabilizers of emulsions, that is, the difficulty of these compounds in displacing the natural emulsifiers of the oil at the interface of the water droplets.

The demulsification efficiency was related to the concentration of copolymer R₂ in the aqueous solution prepared; that is, for the concentration range evaluated, the higher the concentration was, the better the performance was. Below 200 ppm of the active material of the additive in the emulsion, the

TABLE VI
Performance of the Gravitational Separation of a Synthetic A/O Emulsion by PEO-PPO Block Copolymer Mixtures (R₂-L₂) in Water

Time (min)	EF_{WO} (vol %)					
	3 : 1 R ₂ /L ₂ (vol %)		1 : 1 R ₂ /L ₂ (vol %)		1 : 3 R ₂ /L ₂ (vol %)	
	100 ppm ^a	200 ppm ^a	100 ppm ^a	200 ppm ^a	100 ppm ^a	200 ppm ^a
5	0	0	0	0	0	0
10	56	31	48	56	0	24
15	69	80	54	66	0	52
20	71	80	67	67	0	60
25	73	82	68	67	0	62
35	74	82	70	69	0	65
45	75	84	71	71	0	66
55	76	84	71	71	0	67
65	76	84	72	71	1	68
75	76	84	72	71	1	68

^a The total copolymer concentration in the mixture after addition in the synthetic emulsion.

system probably did not have sufficient molecules to attain the desired performance.

We also ran gravitational separation tests with aqueous formulations containing binary mixtures of copolymers R_2 , L_2 , and L_4 at a total concentration of 40% (p/v). The final concentration of the copolymers in the emulsion was 200 ppm. A comparison of the results presented by the mixtures containing copolymer R_2 (Table V) with those obtained with pure copolymer R_2 (at a concentration of 200 ppm; see Table IV) shows that the presence of copolymers L_2 and L_4 degraded the formulation's performance. On the other hand, the presence of these copolymers (L_2 and L_4) in the mixture did not significantly change the performance of copolymer R_2 at a concentration of 100 ppm (Table VI), with the performance of copolymer R_2 in the mixture being a bit below that of its pure form. This behavior can be associated with the values of the interfacial tension between the water and oil for mixtures R_2 - L_2 and R_2 - L_4 (Table III), which showed a preferential adsorption of copolymer B_2 at the water-oil interface. The L_2 - L_4 mixture showed a slightly better performance than that of pure copolymers L_2 and L_4 in the aqueous formulations (Table IV), probably because of the increased concentration of the active material (from 100 to 200 ppm). The performance of the mixture was nearer to that of pure copolymer L_2 , and this result is also in line with the interfacial tension obtained for the L_2 - L_4 mixture, which was similar to that of pure copolymer L_2 (Table III).

We evaluated other mixtures of copolymers R_2 and L_2 in separating the water-oil emulsion. In these mixtures, we varied the proportion by volume between copolymers R_2 and L_2 (3 : 1, 1 : 1, and 1 : 3) and the total copolymer concentration in the mixture after addition in the synthetic emulsion (100 and 200 ppm). The results, presented in Table VI, show that for the R_2/L_2 copolymer ratio of 1 : 1, the lower concentration of 100 ppm produced a result similar to that of the 200 ppm concentration. With a R_2/L_2 ratio of 3 : 1, there was no significant variation in performance in comparison with the performance of pure R_2 at either 100 or 200 ppm (Table IV). This result indicates that the substitution of roughly 30% of copolymer R_2 in the formulation prepared with copolymer L_2 does not significantly alter this formulation's performance in separating the water-oil emulsion. On the other hand, a greater quantity of copolymer L_2 in the formulation (R_2/L_2 ratio of 1 : 3) significantly worsened the final performance in breaking the emulsion, especially at the 100 ppm concentration, at which the efficiency of the separation process was practically nil.

CONCLUSIONS

The solubility in water of the branched copolymer diminished when it was mixed with a linear copolymer with an adjacent structure, whereas the addition of a linear copolymer with an alternating structure did not significantly influence the solubility of the branched copolymer. On the other hand, the linear copolymer with an alternating structure reduced the interfacial activity of the branched copolymer, whereas that with an adjacent structure did not have any influence.

The best demulsifier system was an aqueous solution of the branched copolymer that was most soluble in water.

The efficiency of the separation process of the water-oil emulsions was practically the same when the pure branched copolymer and a 3 : 1 mixture of the branched polymer with the adjacent-structure linear copolymer were used. This means that a significant quantity of a lower cost component can be added to the active demulsifying material without lowering the performance of the water-oil separation process.

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