Joao Batista Ramalho[1,2], Natalie Ramos[2] and Elizabete Lucas[2]

THE INFLUENCE OF SOME INTERFACIAL PROPERTIES OF PEO-b-PPO COPOLYMERS ON DEWATERING OF WATER-IN-OIL ASPHALTENE MODEL EMULSIONS

[1] Petrobras Research Center (CENPES), Cidade Universitaria, Rio de Janeiro, Brazil
[2] Institute of Macromolecules, Federal University of Rio de Janeiro, Brazil
jramalho@petrobras.com.br, naty.a.ramos@gmail.com, elucas@ima.ufrj.br

Abstract. Three different macromolecular structures of poly(ethylene oxide-b-propylene oxide) copolymers, used in formulations of commercial demulsifiers for breaking water-in-crude oil emulsions, were investigated. The interfacial activity (a), the lower interfacial tension (g_m), the critical micelle concentration (CMC), the interfacial concentration (Γ) and the molecular area (A) adsorbed at the interface of the surfactant solutions were evaluated. These results were correlated to surfactant performance in coalescing three different asphaltene model emulsions. The PEO-b-PPO commercial demulsifiers, that were capable to dewater asphaltene model emulsions, exhibited interfacial activity to the oil-water interface, reduced the interfacial tension to low values, reached the CMC at low concentration and presented low molecular area adsorbed at the interface.

Key words: crude oil, dewatering, demulsifier, polyoxides, asphaltenes, interfacial tension.

1. Introduction

The reasons to form stable water-in-crude-oil emulsion during the petroleum production are: (i) the two liquid phases (water and oil) are immiscible; (ii) the flow shearing through the column and production pipelines, promotes the dispersion of the water phase into the oil phase in the shape of droplet and (iii) the natural emulsifiers existing in a petroleum composition deposit on the water droplet surface and create a physical barrier (film) that prevents the coalescence between the water droplets [1]. The most polar fraction of the petroleum, well known as asphaltenes, plays an important role in the process of formation and stabilization of the water-in crude-oil emulsion [2].

Demulsifier is a surface-active chemical used to destabilize water-in-crude-oil emulsions and the commercial demulsifier formulations have one or more surfactant agents (demulsifier base) dissolved in organic solvents, such as toluene, xylene and ethanol. The poly(ethylene oxide-b-propylene oxide) (PEO-b-PPO) copolymer derivatives are the demulsifier bases mostly used in preparing commercial formulations [3]. The poly(ethylene oxide) block (EO) provides the hydrophilic characteristics to the nonionic surfactant and the poly(propylene oxide) block (PO) gives the lipophilic characteristics to the molecule [4].

Kim *et al.* [5] demonstrated that the commercial demulsifiers present a good performance (fast coalescence) when maintaining a low dynamic interfacial tension during the film drainage. Later, Kim and Wasan [6] established the demulsifier that presents the high degree of static and dynamic interfacial activity, the low interfacial shear viscosity, the low film dilational modulus and the high adsorption rate exhibits a high demulsification performance. Ese *et al.* [7] observed that the demulsifier restricts the formation of the asphaltene film at the oil-water interface due to the more extensive adsorption of the demulsifier molecule. Djuve *et al.* [8] concluded that the activity and the structure of the demulsifier also play an important role in the demulsification process. Sun *et al.* [9] showed that the demulsifiers which have a branch structure present better performance than the linear one because smaller vacancies are let on the oil-water interface, which makes difficult for the surface active crude-oil fractions to be inserted again at the interface. Zhang *et al.* [10] observed that the better performance was achieved by the demulsifier with a lower interfacial molecular area. Later, Zhang and other co-workers [11] observed that a high-branched demulsifier molecule is more efficient in breaking water-in-crude oil emulsions.

2. Experimental

2.1. Materials

The following materials were used: three commercial demulsifier bases, supplied by Dow Quimica from Brasil; toluene P.A., from Tedia Company, USA; *n*-heptane P.A., from Vetec Quimica Fina Ltda, Brazil; sodium chloride P.A, from Vetec Quimica Fina Ltda, Brazil; three asphaltenes extracted from three different crude oils from Brazilian fields. Three commercial demulsifier bases are poly(ethylene oxide-b-propylene oxide) copolymer (PEO-b-PPO), which present different molecular structure. Three demulsifier bases were labeled as D1, D2 and D3, respectively for linear, star and branched structures. Fig. 1 illustrates the molecular structure of each demulsifier base and Table 1 shows some of their characteristics. Table 2 exhibits the main characteristics of three crude oils.

2.2. Extraction of Asphaltenes

The asphaltenes were extracted from three crude oils following the standard test method IP 143/01 [12]. 25 mL of the crude oil was added to one liter of *n*-heptane, shaken and let in repose over night. The asphaltene precipitate was separated by filtration and exhausted by washing with *n*-heptane at room temperature. The precipitated asphaltene was dried at 333 K in an oven, over night. The asphaltenes extracted from crude oil 1, crude oil 2 and crude oil 3 were labeled as A1, A2 and A3, respectively.

2.3. Interfacial Tension Measures

The interfacial tension measurements were carried out using a digital tensiometer K10ST, from KRUSS, at temperature of 298 K, by using the Du Nouy method.
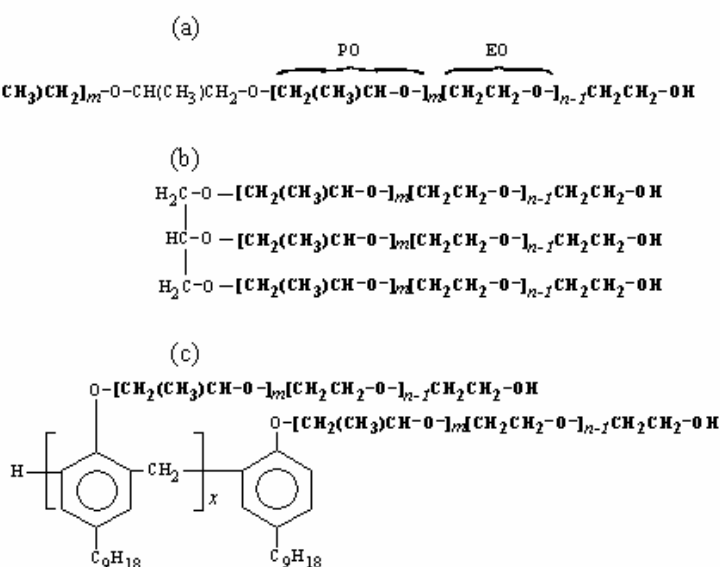

Fig. 1. Molecular structure of the commercial demulsifier bases: (a) linear, (b) star and (c) branched

Table 1

Characteristics of commercial demulsifier bases

Characteristics	D1	D2	D2
Molecular configuration	Linear	Star	Branched
Molar mass from Gel Permeation Chromatography	2340	4420	4510
Ethylene oxide content from ^{13}C RMN (mol %)	28	33	30

Table 2

Main characteristics of crude oils

Characteristics	Crude oil 1	Crude oil 2	Crude oil 3
API degree (ASTM D4052)	28.3	23.9	19.0
Saturates (w/w %)	58.4	47.1	40.5
Aromatics (w/w %)	26.2	29.3	30.8
Resins (w/w %)	14.6	22.3	26.2
Asphaltenes (w/w %)	0.79	1.3	2.5
Molar mass of the asphaltenes (by Gel Permeation Chromatography)	4430	5350	6400

The oil phases were formed by a commercial demulsifier base dissolved in toluene, at concentrations between 1 ppm and 50 ppm. The aqueous phase was a solution of 50 g NaCl/l of distillated water. The interfacial tensions were quantified for 15 min after putting the oil and water phases in contact. The software Grapher version 2.0, from Golden Software Inc., was used to build graphics, which correlate natural log concentration *versus* interfacial tension.

2.4. Preparation of Water-in-Oil Asphaltene Model Emulsions

The model emulsions were synthesized having 30 % of water. The oil phase consisted of 0.025 % of asphaltenes A1, A2 or A3 in the mixture of toluene (T) and *n*-heptane (H) in volumetric ratio of 2:5. The asphaltenes were dissolved in toluene before adding *n*-heptane. The solution of 50 g NaCL/l in distilled water was the aqueous phase. 30 ml of the aqueous phase and 70 ml of the oil phase were sheared together in a Polytron PT 3100 homogenizer, from Kinematic, at 8000 rpm for one minute.

2.5. Dewatering of Water-in-Oil Asphaltene Model Emulsions

The performance of commercial demulsifier bases in dewatering the water-in-oil asphaltene model emulsions was evaluated by a bottle-test. The commercial demulsifier base was added to 100 ml of the synthetic model emulsion, at the concentration of 50 ppm by weight of the active material; the emulsion was shaken by hand for one minute and the water separation was observed during 20 min. Each demulsifier base was added to the model emulsion from solutions having 50 % by weight of the demulsifier in toluene.

3. Results and Discussion

3.1. Commercial Demulsifier Base Chemical Characteristics

As shown in Table 1, three PEO-b-PPO commercial demulsifier bases were well selected from the experimental study because they have similar hydrophilic block content (% EO) and, consequently, similar lypophilic block content (% PO), however their structure and molar mass are quite different.

3.2. Interfacial Properties

The effect of the demulsifier concentration (*Ln C*) on the reduction of the interfacial tension (γ) of the synthetic oil-water interface at 298 K is showed in Figs. 2, 3 and 4, respectively for the demulsifiers D1, D2 and

D3. All curves presented similar expected behavior for surfactants. First, a linear decreasing in the interfacial tension is observed with increasing the demulsifier concentration, which means that the adsorption of the demulsifier molecule at the oil-water interface is in accordance with the Gibbs adsorption isotherm. The interfacial activity was available by the rate of the interfacial tension decreasing to the increasing in the natural log of the demulsifier concentration (Eq. 1), and it was got from the angular coefficient of the linear curves in *g–Ln C* plot.

$$a = -dg/d\,Ln\,C \qquad (1)$$

where: *a* is the interfacial activity, N/m; *g* is the interfacial tension, N/m; and *C* is the demulsifier concentration, mol/kg.

From a certain concentration, the interfacial tension value became constant. It was assumed that the saturation of the demulsifier molecule at the interface was reached and micellization took place, by the self-aggregation of demulsifier molecules. The *CMC* value was got by the intersection of two segments prolongation in *g–Ln C* plot.

The demulsifier base D1 with the linear structure presented an interfacial activity value (0.003764 N/m) a little lower than the demulsifier base D2 with a star structure (0.003094 N/m), and the demulsifier base D3 with a branched structure presented the higher interfacial activity (0.007792 N/m). Complementarily, the branched structure reached the lowest interfacial tension value (0.0005 N/m) at the stabilization plateau, followed by the star structure (0.0085 N/m) and then by the linear one (0.0108 N/m). In addition, the branched structure had the lowest *CMC* value (13 ppm), and the star structure presented a *CMC* value (16 ppm) higher than the linear structure (14 ppm).

The interfacial concentration of the commercial demulsifier base adsorbed at the interface was determined applying the Gibbs isotherm equation (Eq. 2):

$$\Gamma = -1/RT \cdot dg/dLn\,C \qquad (2)$$

where Γ is the concentration of the species adsorbed at the interface, mol/ml; *R* is a constant (8.3141 J/K·mol); *T* is the assay temperature (298 K) and *dg/Ln C* is the interfacial activity, N/m.

The molecular area occupied by one demulsifier molecule adsorbed at the interface was estimated by Eq. 3.

$$A = 1/N_a\Gamma \qquad (3)$$

where *A* is a molecular area of the adsorbed species, Å^2; and N_a is Avogadro's number (6.02·10^{23} mol^{-1}).

Table 3 shows the results of interfacial properties of three commercial demulsifier bases. The commercial demulsifier base D1 (linear structure) presented a little higher value of the molecular concentration adsorbed at the oil-water interface (1.43·10^{-6} mol/ml) than the commercial demulsifier base D2 (1.18·10^{-6} mol/ml) with the star structure. Consequently, the molecule of the linear demulsifier base D1 exhibited the lower value of the area adsorbed at the interface (116 Å^2) than the area occupied by the molecule from the star structure D2 at the interface
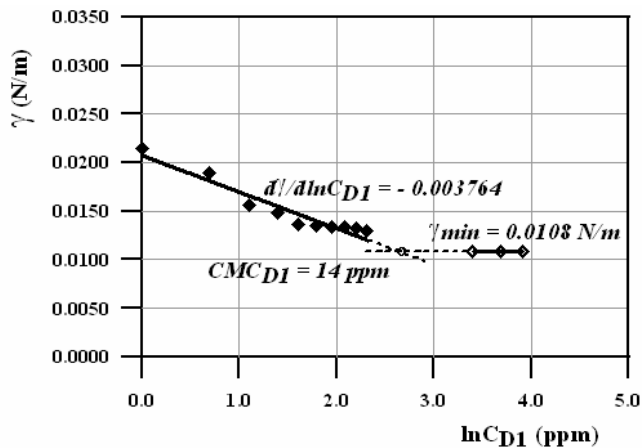
Fig. 2. Interfacial tension as function of *Ln C* for the commercial demulsifier base D1
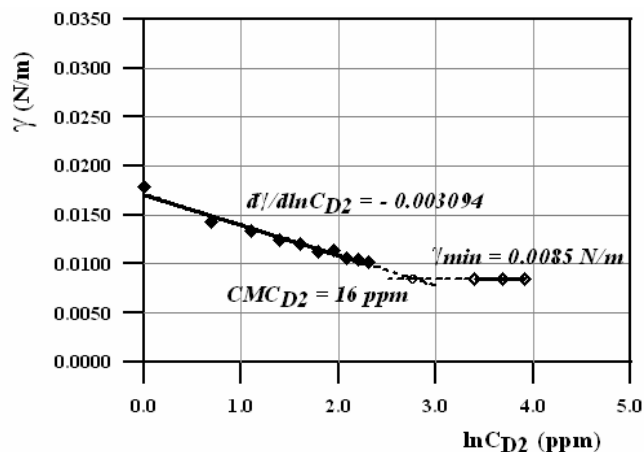

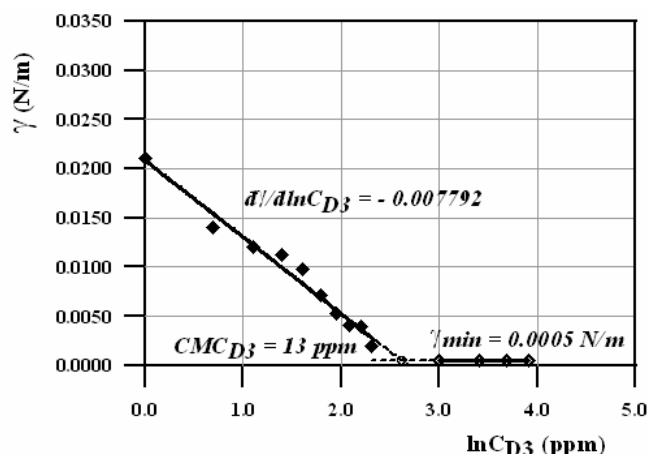**Fig. 3.** Interfacial tension as function of *Ln C* for the commercial demulsifier base D2

Fig. 4. Interfacial tension as function of *Ln C* for the commercial demulsifier base D3

(141 $Å^2$). But, the commercial demulsifier base with the branched structure presented the highest value of the molecular concentration adsorbed at the interface ($2.96·10^{-6}$ mol/ml) and the lowest value of the occupied area by each molecule at the interface (56 $Å^2$). The magnitude of the results is in accordance with the results obtained by Paulis and Sharma [13].

Table 3

Interfacial properties of three different commercial demulsifier bases

Demulsifier base	Molecular structure	Γ, mol/ml	A, Å ^{2}
D1	Linear	$1.43·10^{-6}$	116
D2	Star	$1.18·10^{-6}$	141
D3	Branched	$2.96·10^{-6}$	56

3.3. Asphaltene Model Emulsion Dewatering

Figure 5 illustrates the water droplet coalescence rate for three model emulsions containing the asphaltenes extracted from three different crude oils (Table 2) dispersed in the oil phase. The model emulsions were maintained stable without adding the demulsifier base and dewatering took place only after the commercial demulsifier base was added to the synthetic emulsion. The dewatering rate increased with the increase of time after the demulsifier base was added. Each commercial demulsifier base presented similar performance in dewatering three different asphaltene model emulsions. The branched structure promoted the separation of 93.3 % of water in five minutes ($t_{93.3\%} = 5$ min). The separation of 93.3 % of water happened in 10 min after adding the demulsifier star structure ($t_{93.3\%} = 10$ min). The separation of 93.3 % of water was reached after 20 min of adding the linear structure ($t_{93.3\%} = 20$ min).

The results correlation is better in Table 4. Both PEO-b-PPO demulsifier bases were capable to dewater the water-in-oil asphaltene emulsions and it was observed that they presented interfacial activity to the oil-water interface, reduced substantially the interfacial tension, reached the *CMC* at a very low concentration and presented very low values of the area occupied by the molecule at the interface. The branched structure (D3) of the poly(ethylene oxide-b-propylene oxide) copolymer commercial base demulsifier had a better performance in dewatering of three water-in-oil asphaltene model oil emulsions than the star structure (D2) and the linear one (D1), which means that the coalescence of the water droplets was faster when the demulsifier base having branched molecular structure was added to the asphaltene model emulsions, followed by the star and linear structures ($t_{93.3\%}$D3 < $t_{93.3\%}$D2 < $t_{93.3\%}$D1). On the other hand, the branched structure demulsifier base presented the highest interfacial activity (*a*), which means
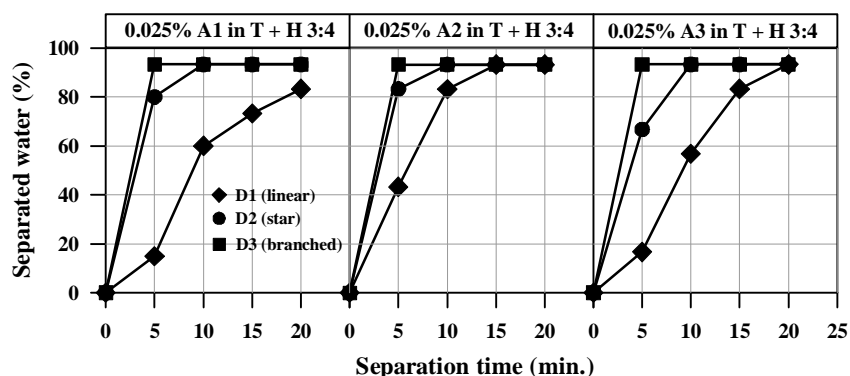
Fig. 5. Effect of commercial demulsifier bases, with different molecular structures, on the dehydration rate of water-in-oil model emulsion

Table 4

Correlation of experimental results

Demulsifier base	Molecular structure	$t_{93.3\%}$, min	a, N/m	g_m, N/m	CMC, ppm	Γ, mol/ml	A, Å^2
D1	Linear	20	0.003764	0.0108	14	$1.43 \cdot 10^{-6}$	116
D2	Star	10	0.003094	0.0085	16	$1.18 \cdot 10^{-6}$	141
D3B	Branched	5	0.007792	0.0005	13	$2.96 \cdot 10^{-6}$	56

that the branched structure has the higher adsorption ability to the oil-water interface than the other two structures. In addition, this branched demulsifier base reached the lowest value of the interfacial tension (g_m). The branched structure also reached the lowest value of the *CMC* in the oil phase, which suggests less affinity to the oil phase than the star and the linear structures. It must be highlighted that the branched structure brought up the highest interfacial concentration (Å) and, consequently, the lowest molecular area (*A*) adsorbed at the oil-water interface. Although the star demulsifier base had presented a better demulsification performance than the linear demulsifier, the star structure exhibited a little lower interfacial activity than the linear structure. Besides the interfacial concentration adsorbed at the interface and the area occupied by a star macromolecule at the interface were a little higher, but the star structure reduced the interfacial tension to the lower value and reached the *CMC* at lower concentration. These results are in accordance with previous works [7-11].

4. Conclusions

The results show that each PEO-b-PPO commercial demulsifier bases presented similar performance in dewatering of three different asphaltene model emulsions and these demulsifier bases exhibited an interfacial activity to the oil-water interface, reduced substantially the interfacial tension, reached the *CMC* at a very low concentration and presented low area occupied by the macromolecule at the interface. The best demulsification performance was reached for the demulsifier with branched molecular structure, followed by the star and the linear ones. The branched structure exhibited the higher interfacial activity, reached the lower interfacial tension at the interface, got the *CMC* value at the lower concentration, the amount of macromolecules adsorbed at the interface was higher and, consequently, the macromolecules presented the lower area occupied at the interface.

Acknowledgments

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ВПЛИВ МІЖФАЗНИХ ВЛАСТИВОСТЕЙ PEO-b-PPO КОПОЛІМЕРІВ НА ЗНЕВОДНЕННЯ АСФАЛЬТЕНОВИХ МОДЕЛЬНИХ ЕМУЛЬСІЙ ВОДА-НАФТА

Анотація*. Досліджено три різних макромолекулярних структури полі(оксид етилену-b-оксид пропілену) кополімерів, які входять до складу промислових деемульгаторів для руйнування емульсій вода-сира нафта. Визначені такі величини, як активність на поверхні розділу, нижній міжфазний натяг, критичну концентрацію міцели (СМС), міжфазну концентрацію і площі, які займають адсорбовані молекули на розділі фаз. Отримані результати встановлюють співвідношення між поверхнево-активними властивостями трьох різних асфальтенових модельних емульсій. Показано, що промислові деемульгатори PEO-b-PPO, здатні зневоднювати такі емульсії, виявляють активність на поверхні розділу вода-нафта, знижують міжповерхневий натяг, досягають СМС при малих концентраціях і малій площі, яку займають молекули на поверхні розділу фаз.*

Ключові слова*: сира нафта, зневоднення, деемуль-гатор, поліоксиди, асфальтени, міжфазний натяг.*