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Assessment of polymeric flocculants in oily water systems

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Abstract Oil-in-water emulsions are usually formed during oil production and treatment. Before being discarded, such dispersions should be treated. In order to improve the oil–water separation process using physical processes (decantation, flotation, centrifugation, etc.) the particle size of the disperse phase should be increased. This may be achieved through flocculation, which consists in the agglomeration of various particles or drops, using, as flocculating agents, high molecular weight hydrophilic macromolecules. A few studies have been carried out on the flocculation of finely divided oil drops in brine with the aid of generally ionic polyelectrolytes. This work shows the results obtained using nonionic polymers as flocculants. Commercial samples of poly(ethylene oxide-*b*-propylene oxide) and poly(vinyl alcohol) were evaluated through flocculation–flotation tests as well as the drop size distribution. The performance of such additives as flocculants for oil–water dispersions is related to their structure, composition, molecular weight and hydrophilic–lipophilic balance. The composition of the produced water is also an important parameter when choosing the features of the flocculant additive.

Keywords Emulsions · Flocculation · Oily water · Polyoxides · Poly(vinyl alcohol)

Introduction

During the last few decades, the oil industry has devoted special attention to offshore production activities, where the recovery products are often accompanied by the production of formation water from the petroleum reservoir, this causing the generation of huge volumes of oily water to be discarded to the sea. Such oily water, named produced water, generally contains a high amount of salt and includes a complex mixture of organic and inorganic compounds, the composition of which varies with the life span of the petroleum field, the volume of produced water tending to increase with field aging [1]. Generally, the constituents of produced water include dissolved minerals from the producing formation, dissolved and dispersed oily constituents, chemicals employed during the production process, solids including corrosion products, bacteria and asphaltenes, as well as dissolved gases, including CO_2 and H_2S [1].

In order to secure the quality standard of the produced water to be discarded, the National Environment Council (CONAMA, Brazil) established that the maximum acceptable total oil and grease (TOG) content for discarded produced water should be lower than or equal to 20 mg/L [2]. The treatment of oily-residuum-containing waters in the petroleum production or other industrial activity steps is rendered difficult mainly when the oil concentrations are low, since the shearing caused by pumps, valves and other equipment present in the producing process may admix phases and create stable emulsions [3]. The reduced size of the dispersed oil drops present in the oily water generated during the petroleum production process is the main problem to be circumvented during the treatment of such a residuum.

The most viable approach to obtain the effective removal of such oil is the size increase of such dispersed drops and further separation using physical methods (decantation, centrifugation, membrane filtration, flotation, etc.). The aggregation process of such oil droplets may be rendered viable by using substances having affinity for both phases, thus promoting interaction among the dispersed oil drops by working as a link between them. Such a process is known as flocculation and the substances cited as promoting such a phenomenon are known as flocculating agents [4, 5, 6, 7, 8]. Specifically in the case of the oily water treatment from the oil industry, the process involved is the destabilization of the generated emulsion, i.e., the system flocculation, followed by the coalescence of the drops to form a macroscopic oil phase. Basically, the flocculation process of dispersions consists in the agglomeration of dispersed-phase particles caused by a polymeric flocculating agent that makes possible the formation of larger aggregates. The knowledge of the mechanism through which the flocculation of a system occurs is very useful for the success of phase separation [6, 7, 8]. The flocculation mechanisms already known from the literature are bridge flocculation, charge neutralization flocculation, polymer exclusion flocculation and asymmetrical flocculation [8]. The bridge formation mechanism is considered as a consequence of the adsorption of individual moieties of the polymer flocculant molecules on the surface of more than one particle. The particles linked by formed bridges entail individually compacted aggregates, prone to sediment or to be easily removed by filtration. An optimum concentration of flocculating agent has already been experimentally confirmed, and the flocculation process may be turned into stabilization by the variation of the polymer concentration, as shown in Fig. 1 [7, 8]. The flocculation process through charge neutralization involves the use of polymeric flocculating agents with charges opposite to the particle charge. Since the oil drops have generally negative electrical charges, the most commonly used flocculating agents are cationic polyelectrolytes. Such polyelectrolytes induce flocculation by means of the neutralization of the particle surface charges [9, 10]. Oil drops and air bubbles present, in general, a negative surface in aqueous media. In electrolyte solutions this fact is ascribed to the preferential adsorption of anions at the oil–water interface. In the case of solutions containing petroleum or crude oil components a negative surface charge due to the presence of oil polar fractions that are predominantly negative species is also observed.

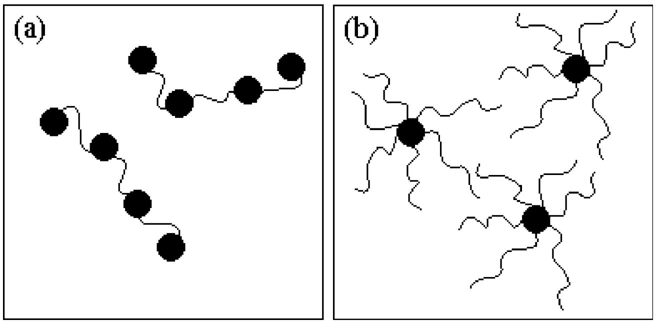


Fig. 1a, b Effect of polymer concentration in the flocculation process. **a** Particle or drop flocculation through bridge formation, at low polymer concentration. **b** Sterical stabilization of particles or drops at high polymer concentrations

The presence of free polymers in the emulsified system may induce the aggregation of colloidal particles. Such a process is called flocculation by polymer exclusion. The exclusion of the polymer chains among the particles renders possible the formation of essentially pure “solvent microreservoirs” in the zones between particles. Therefore, in a “good solvent”, a closer approximation of particles is favored [8, 11]. In complex systems containing more than one kind of dispersed particle, improvements in the flocculation process have been observed when using the asymmetric flocculation process, where the adsorption of polymeric materials to one kind of particle allows it to be adsorbed to other particles for entropy reasons [8, 12]. Aiming at the optimization of separation processes through the increase in the size of the drops present in the dispersed phase, we aim to assess in this work the efficacy of a series of commercial polymers of varied degrees of hydrophobicity as flocculating agents of oil-in-water emulsions.

Experimental

Materials

Polyoxide and poly(vinyl alcohol) (PVA) polymers were supplied by BASF Brazil and Air Products, respectively.

Characterization of commercial polymer samples

The viscometry technique was used to assess the molecular weight of the PVA- and poly(ethylene oxide) (PEO)-based polymers. By means of viscometry measurements carried out with a Contraves low-shear LS40 rheometer, it was possible to determine the intrinsic viscosity and therefore the molecular weight of PVA (PVA 1, PVA 2, PVA 3 and PVA 4) as well as those of PEO (PEO 1, PEO 2 and PEO 3) samples. The shearing range employed was from 40 to 100 s^{-1} and the temperatures were 30 and 35 °C for the PVA and PEO samples, respectively. The intrinsic viscosity was assessed from the extrapolation to zero concentration of the straight line obtained by mathematically adjusting the experimental points of the curve of reduced viscosity as a function of the polymer solutions in an aqueous medium (with the concentration varying from 0.1 to 0.5% w/v). From the assessment of the intrinsic viscosity, by applying the Mark–Houwink–Sakurada [13] equation it was possible to calculate the average viscometric molecular weight. For PVA, the k and a values were 42.8 mL/g and 0.64, respectively, at 30 °C. For PEO polymers the k and a values were 48.8 mL/g and 0.66, respectively, at 35 °C.

The vapor pressure osmometry technique was used to assess the molecular weight of polyoxide-based copolymers [PEO–PPO 1, PEO–PPO 2 and PEO–PPO 3, where PPO is poly(propylene oxide)]. The equipment employed in the analyses was a WESCAN model 233 vapor pressure osmometer. The solvent used to prepare the solutions (standard and polymeric) was toluene. The temperature in the chamber was 88 °C and the thermistor current was 20 mA. The K value was obtained from the assessment of the standard sample (spectrophotometric grade benzyl).

^{1}H NMR was used to assess the degree of hydrolysis of the PVA-based polymers as well as the ethylene oxide (EO)-to-propylene oxide (PO) ratio of the polyoxide-based copolymers. A Gemini 300 (Varian) spectrometer was employed in the analysis. In order to assess the EO-to-PO ratio of the polyoxide copolymers, polymer samples were solubilized in deuterated water (D_2O) at ambient temperature. The calculations for the establishment of the EO-to-PO ratio were as described in the literature [14]. The degree of hydrolysis was assessed using the relationship $[H_\alpha(O)]/[H_\alpha(A)+H_\alpha(O)]$, where $[H_\alpha(O)]$ is the area of the vinyl alcohol α-hydrogen nuclei, while $[H_\alpha(A)]$ is the area of the vinyl acetate α-hydrogen nuclei. PVA samples were analyzed in the concentration of 10% w/v in dimethyl sulfoxide-d_6) in tubes of 5 mm outer diameter. The frequency used was 300 MHz and the temperature was 60 °C.

Preparation of synthetic emulsions

In order to reproduce the marine environment, brine having a salt concentration of 55,000 ppm (250 g/L sodium chloride and 25 g/L calcium chloride) was prepared. By means of a Turrax PT 3100 blender, at a rotation speed of 13,000 rpm, an oil aliquot (approximately 0.8 mL/1 L brine) was slowly added (addition period of about 9 min) using a long-neck syringe. At the end of the oil addition, the rotation was immediately increased to 15,000 rpm and kept as such for 15 min. The freshly prepared oily water was admixed to a further amount of brine (1.5 times the amount used in the beginning of the preparation). This system was then submitted to a 5,000-rpm agitation for 5 min. For the experiments, it is necessary to prepare fresh oily water and it is very difficult to control the initial TOG values. So, we have expressed the results in terms of the efficiency in oil removal (percentage).

Flocculation tests in an induced-air flotation cell

The freshly prepared synthetic emulsion (2.5 L) was transferred to the reservoir of the flotation cell. For assessing the oil-in-water content (blank test, without the addition of any flocculant), one aliquot of approximately 60 mL of the emulsion was collected. Then, the system was agitated (9,000 rpm) and the solution of polymeric flocculating agent was added, several kinds of flocculants and varied concentrations being used. After 1 min, the system was submitted to air-induced flotation, for 1 min, at a flow rate of 110 L/h. After a 30-min rest, 800 mL of the emulsion was drained from the bottom of the flotation reservoir and immediately thereafter an aliquot of approximately 60 mL was collected for assessing the oil-in-water content.

Measurement of the size distribution of the emulsion droplets

The emulsions prepared were characterized by the size distribution of the emulsified droplets, using a Malvern Instruments Mastersizer X light scattering apparatus.

Measurement of the TOG content of the emulsions

The TOG content present in the aliquots collected before and after the flocculation–flotation process was assessed with the aid of a HORIBA-model OCMA-350. The samples collected were submitted to a previous extraction process. An addition funnel and S-316 solvent (supplied by HORIBA) were used. The overall volume of the sample collected was noted for further use in the calculations of the TOG value. The principle of the technique for determining the content of oil and grease in emulsions is based on IR detection of the amplitude of C–C and C–H bonds present in a sample, making a correlation with the amount of solvent used and providing the sample oil concentration in parts per million.

Results and discussion

Characterization of the commercial polymers

Commercial polymers were selected as a function of their structural and functional features, suitable for use as flocculating agents of oil-in-water emulsions. Those polymers were characterized by the molecular weight and on a case-by-case basis, the degree of hydrolysis and the EO-to-PO ratio. The characterization results are listed in Table 1. The results indicate that the chosen samples, within the same family, have similar structures and varied molecular weights, thus allowing the evaluation of the influence of the molecular weight on the flocculation–flotation processes. The PVA-based polymers were selected within the same range of the degree of hydrolysis (87–89%). The option for the partially hydrolyzed PVA samples stems from the fact that they show efficient adherence to hydrophobic surfaces; this leads to better oil droplet–polymer interaction (bridge flocculation) [15]. The polyoxide-based copolymers have similar molecular weights and varied EO-to-PO ratios, thus making it possible to investigate the influence of this parameter on the flocculation–flotation processes.

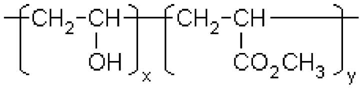
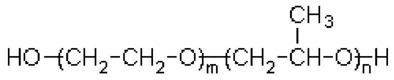
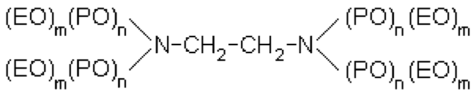
Flocculation-flotation tests

Aiming at standardizing the flocculation–flotation tests, instead of oily water produced in an oil field, where the composition and kind of emulsion may vary according to the origin, we used an emulsion of oil in synthetic water brine. The performance of the flocculating agents was obtained from the relationship between the initial TOG content in the synthetic emulsion and the final TOG content measured after the addition of the flocculating agent and subsequent flotation process. The results for the initial TOG, the final TOG and the percentage of oil removal efficiency [(initial TOG−final TOG)×100/initial TOG] are listed in Table 2. The differences observed for the initial TOG values do not have a significant impact on the results. The effect of the kind of polymer was studied for 2, 5 and 10 ppm concentrations. For each concentration, the flocculating agent presenting the best performance was identified, i.e., that

Table 2 Evaluation of the polymer efficiency in oil removal, for three distinct additive concentrations

Product	Concentration (ppm)	Initial TOG (ppm)	Final TOG (ppm)	Efficiency in oil removal (%)
PVA 13	2	192.0	38.0	80.0
PEO 12		173.0	40.0	77.0
PEO–PPO 11		74.5	32.5	56.5
PEO–PPO 12		116.2	16.5	86.0
PEO–PPO 13		78.9	30.4	61.5
PVA 13	5	98.6	8.0	92.0
PVA 14		97.0	7.7	92.0
PEO 12		200.0	76.0	62.0
PEO–PPO 11		92.4	16.9	81.7
PEO–PPO 12		69.2	14.6	79.0
PEO–PPO 13		99.0	34.0	66.0
PVA 11	10	42.0	38.0	9.5
PVA 12		42.0	17.0	59.5
PVA 13		158.0	39.0	75.0
PEO 11		197.0	135	31.5
PEO 12		158.0	102	35.5
PEO 13		175.0	68.0	61.0
PEO–PPO 11		102.1	57.7	43.5
PEO–PPO 12		70.6	8.7	87.7
PEO–PPO 13		69.7	15.0	78.5

Table 1 Characterization data of the commercial polymers

Polymer	Chemical Structure	Molecular Weight	Hydrolysis Degree (%)	EO/PO ratio (%w/w)
PEO 11	$HO\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$	$4.8x10^6$ [(a)]	-	-
PEO 12		$5.2x10^6$ [(a)]	-	-
PEO 13		$6.5x10^6$ [(a)]	-	-
PVA 11	 $-[CH_2\text{-}CH(OH)]_x-[CH_2\text{-}CH(CO_2CH_3)]_y-$	40,050 [(a)]	88.0 [(c)]	-
PVA 12		21,000 [(a)]	86.7 [(c)]	-
PVA 13		260,000 [(a)]	87.9 [(c)]	-
PVA 14		67,000 [(a)]	87.8 [(c)]	-
PEO-PPO 11	 $HO\text{-}(CH_2\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_n\text{-}H$	7,200 [(b)]	-	3.5 [(c)]
PEO-PPO 12		7,400 [(b)]	-	6.2 [(c)]
PEO-PPO 13		20,500 [(b)]	-	8.6 [(c)]

[(a)] Assessed by Viscometry
[(b)] Assessed by Vapor Pressure Osmometry
[(c)] Assessed by Hydrogen Nuclear Magnetic Resonance

having the highest capacity for oil removal from the synthetic emulsion. Such a study is of great practical importance since it may be used as a valuable tool for selecting the kind of flocculating agent to be employed, so as to assess the product having the best performance at a certain concentration.

The results in Table 2 indicate that among the flocculating agents tested, when a concentration of 2 ppm was added, the best performing product was PEO–PPO 12, while PEO–PPO 11 exhibited the worst performance. In spite of the fact that both products belong to the same copolymer family, having high hydrophilic character and similar molecular weights, at this low additive concentration the higher percentage of EO present in the structure of the PEO–PPO 12 copolymer (EO-to-PO ratio of 6.2) may be suggested as a paramount factor for its better performance, as compared with PEO–PPO 11 (EO-to-PO ratio of 3.5). The relatively more hydrophilic character exhibited by PEO–PPO 12 provides for higher mobility throughout the dispersing medium, making easier its interaction with a larger number of drops dispersed in the system. In structural terms, these two additives are very similar, with their basic difference lying in their hydrophilic features consequent to the higher or lower number of EO groups of their chains.

However, it is interesting to point out that at 5 ppm concentration, the performance of PEO–PPO 11 was slightly superior to that of PEO–PPO 12. Such behavior may be interpreted on the basis that at this concentration the main effect arises from the higher molecular weight of the hydrophobic chain (PPO) present in the PEO–PPO 11 structure, which could provide a greater polymer/oil drop interaction, as compared with the PEO–PPO 12 structure, which has a lower molecular weight hydrophobic chain. At the 5 ppm concentration, PEO 12 had the worst performance. Although we do not have experimental evidence, it is possible to suggest that such behavior is due to the fact that the high molecular weight of PEO 12 favors the phenomenon of redispersion as its concentration in the system is increased.

Owing to its high hydrophilic character, which conveys to it better mobility in the system, associated with a better polymer–oil drop interaction (as a function of the hydrophobic portion of the PPO moiety), once more PEO–PPO 12 had the best performance in the tests using 10 ppm flocculating agent.

Upon verifying the influence of the molecular weight on the efficiency of oil removal, it is possible to observe, for the 10 ppm concentration, that the structure and hydrophilic character of the products are the two main factors. However, by separately scrutinizing each compound family (particularly those of high molecular weight PVA and of PEO), it may be observed that the increased efficiency in oil removal is intimately related to the increased molecular weight of the flocculating agent. Such a molecular weight effect is not observed for the PEO–PPO copolymer family, since the products employed have varied compositions and structures. By comparing PEO–PPO 13 and PEO–PPO 11, we can see a better performance of PEO–PPO 13 relative to PEO–PPO 11 caused by different structures in the two molecules, which may influence the interaction mechanism in the oil–water system. In this case, the effect of the molecular weight is neglected, since at 5 ppm concentration, the efficiency of PEO–PPO 13 is lower than that of the PEO–PPO 11 and PEO–PPO 12 samples.

Generally, flocculating agents of varied structures have different performances as a function of the concentration, which may present an optimum value. This characterizes the existence of an optimum efficiency concentration. Below the optimum concentration, there are not enough molecules to displace the natural stabilizers of the emulsion. On the other hand, above the optimum concentration, the additive molecules fill in the oil–water interface, providing the sterical stabilization of the emulsion (Fig. 1b). The optimum concentration is achieved when the interface contains enough additive molecules to provide the bridge formation of the polymer among the droplets (Fig. 1a).

In order to identify the optimum working concentration of the products, some data from Table 2 were plotted in graphs of percentage efficiency in the oil removal as a function of the flocculant concentration (Fig. 2). From the study of Fig. 2 it may be observed that PEO–PPO 12 should be considered as the more efficient flocculating agent, since it shows reasonable performance (approximately 85% efficiency in oil removal) at a lower concentration (2 ppm). However, the best performance was reached by PVA 13 (approximately 90%) at a relatively higher concentration

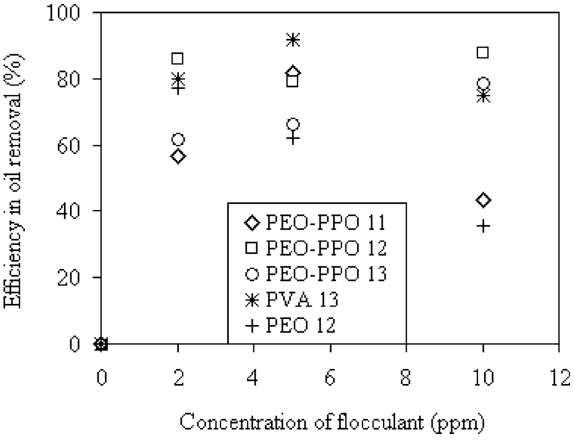


Fig. 2 Evaluation of the efficiency in oil removal (%) as a function of the variation in the added flocculating agent concentration

(5 ppm). In practical terms, the choice of one kind of agent should take into account the cost-to-benefit ratio.

It may be further observed that in general terms the optimum performance concentration of an additive is closely related to its molecular weight. The optimum concentration of PEO 12 (molecular weight 5.2×10^6) is around 2 ppm, while the optimum concentration for PVA 13 (molecular weight 2.6×10^5) is around 5 ppm. This is a feature of the flocculation process by bridge formation, where, at high polymer concentrations, in spite of having higher flocculation, there is a sterical stabilization of the dispersion; such stabilization being attained at lower concentrations for higher molecular weight polymers [16]. Particularly in the case of the PEO–PPO 13 product, the efficiency in oil removal gradually increases with concentration, this being explained by the fact that the optimum concentration range for this polymer is higher than that of other polymers, it having not attained, for the concentration range tested, the sterical stabilization of the dispersion caused by the excess of flocculating agent present in the medium. This behavior is associated with the relatively low molecular weight of the PEO–PPO moieties, caused by their starlike structure.

Distribution of the droplet sizes of the emulsions

The performance of the flocculating agents employed in the flocculation–flotation tests was evaluated from the capacity of each product to increase the aggregate size (flocculation process). In this way the associated flotation process is favored, thus directly boosting the process of oil removal from the synthetic emulsions.

At first, the droplet size distribution of the synthetic emulsions, prepared from an oil of density 0.8945 g/cm^3 was assessed at different times, keeping the samples homogenized after being prepared. The average size of the emulsified oil drops was in the range 12–15 μm. Also, it can be noticed that the emulsion stability varied with time, shifting the distribution range towards larger sizes as a function of the increased flocculation of the dispersed lower droplets (Fig. 3).

Associated with flocculation (Fig. 4), an improved flotation process was noticed consequent to the addition of polymeric flocculating agents. In view of the occurrence of the separation of part of the oil (flotation), the drop diameters of the resulting emulsion are smaller. This effect is coherent with the reduction in TOG content observed in the flocculation–flotation study carried out using an induced-air flotation cell.

The most common shape of the particle size distribution curves shows a peak, being conceptualized as a normal distribution. However, there are some systems where the size distribution has two or more peaks, being conceptualized, respectively, as bimodal or multimodal distributions. In the systems studied in the present work, most curves had bimodal behavior. In this way, as the statistical parameter $D(V,0.5)$ is related to the average diameter, i.e., divides the distribution exactly in half, this parameter is not suitable for comparatively drawing an actual quantitative analysis. Since in the case of the oil-in-water emulsions the spherical shape is a suitable model for representing the geometrical profile at which the oil drops are dispersed in the aqueous medium, statistical parameters $D(4,3)$ and $D(3,2)$ are more suitable to quantitatively evaluate the variation in the dimension of the dispersed aggregates. This is because such parameters are, respectively, related to the average volumetric diameter and the surface area average diameter, considering that the representative sphere has the same volume and surface area of the sample particles [17]. The results obtained in the study of the size distribution of dispersed drops are listed in Table 3. It can be noticed that the best performing polymers exhibited higher values of the particle size distribution.

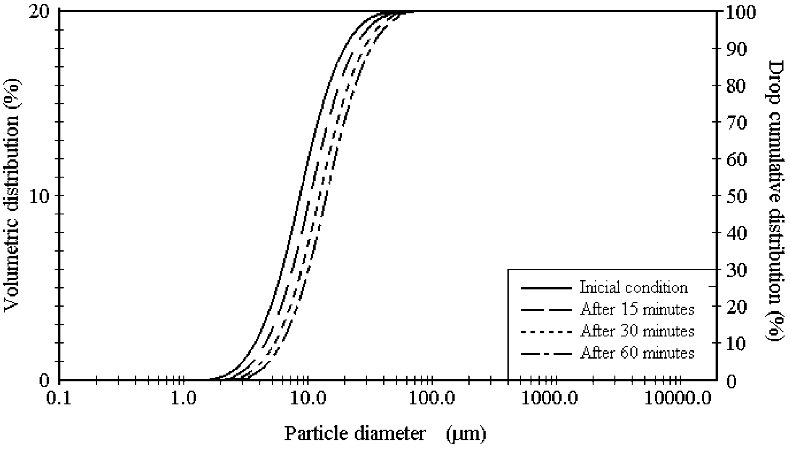


Fig. 3 Drop size distribution of an emulsified system in the absence of a polymeric flocculating agent

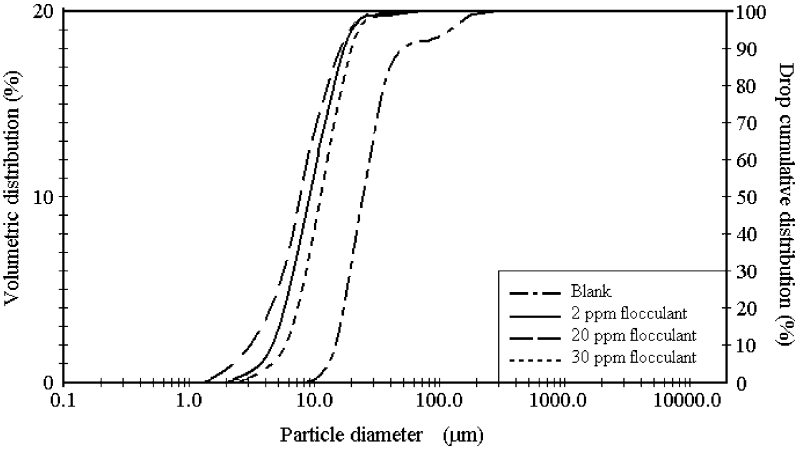


Fig. 4 Effect of the resulting emulsion on the drop size distribution after the flotation process with the addition of a polymeric flocculating agent

Table 3 Average values obtained in the study of the particle or droplet size distribution

Polymers	Average values of the particle/droplet size distribution (μm)	
	D(4,3)	*D*(3,2)
Blank	12.60	3.55
PVA 11	15.81	4.89
PVA 12	16.30	5.08
PVA 13	23.69	7.82
PVA 14	24.01	8.50
PEO 11	18.03	6.40
PEO 12	16.96	5.84
PEO 13	15.50	4.69
PEO–PPO 11	19.63	5.90
PEO–PPO 12	19.48	6.43
PEO–PPO 13	18.69	6.17

Conclusions

For additives of the poly(EO-*b*-PO) kind, the molecule having stronger hydrophilic character has better performance in view of its higher mobility in the dispersing medium. Actually, for copolymer-based additives, the chemical structure and the hydrophilic–lipophilic balance are the two factors that more strongly influence the performance as a flocculating agent. However, for homopolymer (PVA and PEO)-based additives, there is a close relationship between molecular weight and performance; the additive efficiency rises with the increase in molecular weight. The choice of the additive in terms of structure, composition, molecular weight and hydrophilic–lipophilic balance will depend on the composition and concentration of the oily water to be treated, with lower contents of oil in water requiring more hydrophilic additives. Each product, in each system, requires an optimum dosage range, where its flocculating properties are improved because the additive molecules provide the bridge formation of polymer among the droplets. Below the optimum concentration, there are not enough molecules to displace the natural stabilizers of the emulsion. On the other hand, above the optimum concentration, the additive molecules fill in the oil–water interface, providing the sterical stabilization of the emulsion. Better performing additives provide higher values of the particle size distribution to the systems. The synthetic oily water is not able to reproduce the behavior of produced oily waters, but the results obtained through its study add to the understanding of the influence of structure, composition and molecular weight on the flocculation mechanism.

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